



NETWORK STRUCTURE OF BINARY AND
TERNARY GLASSES
BASED ON ADDITIVITY RULE

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1. INTRODUCTION

Among various components of oxide glasses, B_2O_3 , SiO_2 , P_2O_5 and GeO_2 can construct frameworks of glass structure, being called network forming (NWF) oxide. Corresponding cations, B^{3+} , Si^{4+} , P^{5+} and Ge^{4+} are called NWF cations. In Table 1 the four NWF cations are compared with each other in their properties such as electronegativity x and order of ionicity of the bonds with oxygen atoms [1-5]. One can estimate the degree of ionicity of each NWF cation-O bond from x values which have been obtained by Hinze and Jaffe [1], assuming that NWF atoms as well as oxygen have electron cloud lobes of tetrahedral symmetry due to sp^3 hybridization. The electronegativity of Ge is estimated to be similar to that of Si from Pauling's data, although it has not been reported by Hinze and Jaffe [1]. The more ionic is the NWF cation-oxygen

Table 1. Characteristics of B, Si, P and Ge.

	B	Si	P	Ge
Electronic config.	(He) $2s^2 2p^1$	(Ne) $3s^2 3p^2$	(Ne) $3s^2 3p^3$	(Ar) $4s^2 4p^2$
Electro-negativity, $X_M^{[1]}$	$3Tr^3:1.93$ $4T^3:1.81$	$4T^4:2.25$	$4T^5:2.79$	$4T^4: ?$
$X_O - X_M$	4.1	3.68	3.14	?
Order of ionicity	$P-O < Si-O \approx Ge-O < B-O$			
p-d π [2] p-d π [3-5]	m nul	nul w	nul w,m	nul tr.
Oxygen co-ordination number	3,4	4,6	4	4,5,6
Hybridization: Tr: sp^2 , T: sp^3 $X_O = 5.93$ ($2T^1.2T^2$)				

bond, the more easily the NWF cation changes their oxygen coordination number CN. B and Ge atoms are 3- and 4-fold coordinated by oxygens in boron and germanium oxides, while an addition of an alkali oxide changes BO_3 to BO_4 [7] and GeO_4 to GeO_6 [8]. An Si-O bond is less ionic and Si atoms take CN=6 under restricted conditions, namely, under very high pressure and in SiP_2O_7 crystal stable at atmospheric pressure [9]. A P-O bond has a highly covalent character due to a p-d π -interaction between 2p orbitals of O and 3d of P. P atoms are bonded to four oxygens like Si atoms, though they form a P=O double bond with one of the four oxygens. When trivalent cations such as B, Al and Fe are coexistent, however, the P=O bond is converted to a single bond by forming $\text{O}_3\text{X-O-PO}_3$ type bonding (X=B, Al, Fe) with a four-coordinated X, where P and X atoms bear respectively a unit positive and negative charge. Such behavior of P is visualized in AlPO_4 and BPO_4 crystals [9].

Structures and properties of glasses change on addition of network modifying (NWM) oxides such as R_2O and MO to these NWF oxides. Such changes will be more complex in glasses containing many NWF oxides than in the single NWF oxide glasses because the network former affect with each other. No systematic studies have been conducted yet on effects of the coexistence of the NWF oxides except for the borosilicate systems. The present study has been made to investigate thoroughly the composite effects of the NWF oxides and to clarify the nature of the effects in terms of the glass constitution.

Essential principles utilized in this study are (1) additivity in extensive quantities and (2) a packing of voids as the model of glass structure.

The former principle "additivity" assumes that an extensive quantity such as volume, enthalpy, entropy, free energy, and internal energy is represented by a linear combination of the products of a factor assigned to a component unit with the fraction of the unit. In other words, an extensive quantity of glass is assumed to be estimated from the composition of glass. This principle is verified by the fact that relations between a number of properties of glasses and their composition can be approximated by linear equations as the first order approximation. In order to apply this principle, it is very important to properly select the atomic groups as the component units for a particular quantity. For instance, bond energies of Si-O and O-R bonds are of significance for description of enthalpy, but they may be of no significance for molar volume.

The latter principle "a packing of void" has seldom been paid any attention to. Most of the theories on glass structures so far proposed have described only the configurations of certain units like SiO_4 and BO_3 , bond lengths, bond angles, etc. In this study the void in glass structure is treated as one of the major constituents of glass. On regarding a glass as a random packing of voids enclosed by the network skeleton and evaluating their size and distribution in the actual glasses, one can elucidate the knowledges on the configurations of the constituent atomic

units. Furthermore, comparison of the size of the voids with that of NWM cations gives insight into the composition dependence of the properties of the glasses as well as the behavior of the cations in a series of glasses. The structural models proposed in the past have described the glasses as the mixture of tetrahedra enclosed by plane surfaces, hence they cannot express exact sizes and shapes of the voids.

The information on glass structure for series of glasses can be divided into the following two parts.

(a) information on the bulk glass

(b) information on the local structure in the first or at most second nearest neighbors of an atom in the glass.

Since X-ray and neutron diffractometry do not give decisive information on glass structure, the studies like the present one are very important in order to elucidate local information (b) such as atomic arrangements and character of a specific bonding out of bulk information (a) in terms of some plausible models or reasonable assumptions. Inversely, one can explain changes of bulk properties such as volume and elasticity from local information. In the present study a number of properties have been measured as functions of glass composition. Among them, density, molar volume, elastic constant and thermochemical quantities are related to bulk information (a), and optical absorption and IR spectra to local information (b).

In the present study, molar volume, elastic properties and thermochemical quantities have been measured for the glasses

in a number of binary and ternary systems as functions of the composition. On the basis of the experimental results, the constitutions of the glasses have been discussed by proposing some structural models.

Chapter 1 concerns the molar volume and elastic properties of alkali silicate glasses. A cristobalite type cage structure model of glass is derived from the dependences of the molar volume of the crystals and glasses. The model visualizes the distribution of the voids and the configurations of atomic units in the glass structure. The bulk modulus vs. volume relation is also discussed on the basis of alkali ions occupying the voids.

Chapters 2 and 3 describe the structures of alkali borate and germanate glasses which exhibit boron oxide and germanium oxide anomalies, respectively, where a coordination change of B and Ge atoms is involved. First, the arrangements and fractions of RBO_4 and GeO_6 units, which are denoted as N_4 and N_6 , respectively, are studied. Then, referring to the results on the crystals, the correlations between the fractions N_4 and N_6 and the composition dependences of elastic constants and molar volume of glass are clarified.

Chapter 4 presents the measurements of molar volumes, elastic constants and optical absorption spectra of Ni^{2+} ions for alkali borosilicate glasses. A role of the alkali oxide in forming non-bridging oxygen and the difference in the structure between alkali borate and borosilicate glasses are shown. Size of the voids associated with BO_4 units is compared

with that of the alkali ions. The effects of alkali ions filling the voids upon the elastic constants are also discussed. Furthermore, the boron oxide anomaly is interpreted in terms of the concept of thermochemical stability.

Chapter 5 describes the network structure of alkali germanosilicate glasses based on the measured molar volumes and elastic constants. The difference in the structure between the borosilicate and germanosilicate glasses is inferred. Partition of the alkali oxide to silica and germania is also investigated in relation to the alkali species and mixing ratio $r = \text{SiO}_2/\text{GeO}_2$.

Chapter 6 presents the network structure of alkali borophosphate glasses on the basis of their molar volumes, elastic constants and IR spectra. Behavior of P and B atoms is considered in terms of P=O double bond and N_4 of B atoms. A structural model is proposed.

Chapter 7 describes evaluation of the size of the voids in high-cristobalite type network structures and comparison of the size of the voids with that of alkali ions. The network structures of borate, silicate, borosilicate and germania containing glasses will be characterized by the size of the voids.

Chapters 8 and 9 are concerned with thermochemical discussions on the constitutions of the glasses in the systems $\text{R}_2\text{O}-\text{P}_2\text{O}_5$, $\text{MO}-\text{P}_2\text{O}_5$ and $\text{MO}-\text{SiO}_2$ on the basis of heats of solution vs. composition relations assuming additivity rule. Bond energies of P-O and O-M bonds are obtained in RPO_3 , $\text{M}(\text{PO}_3)_2$ and MSi_2O_5 glasses from the calculated heats of

formation data. The bond characteristics such as ionicity and degree of polarization of oxygen atoms are compared for O-R, O-M and NWF cation-oxygen bonds.

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Chapter 1

NETWORK STRUCTURE OF ALKALI SILICATE GLASSES

Majority of commercial glasses consist of silicate systems, which are modified by adding a minor amount of B_2O_3 , P_2O_5 and rarely GeO_2 and a number of network modifying (NWM) oxides. As a first order approximation, however, one can regard the multicomponent glasses as mixtures of several binary glasses with a network forming (NWF) oxide. Any deviation of properties and structure of mixed NWF oxide glasses from the additivity rule may be regarded as a mixing effect. In order to investigate the mixing effect, it is necessary first to find correlations between the structures and properties of simple binary glasses. Therefore, the constitutions of glasses in the system R_2O-SiO_2 will be studied by measuring molar volume, elastic constant and thermochemical properties.

Addition of an R_2O to SiO_2 , a representative of NWF oxides, creates non-bridging bonds, modifying $SiO_{4/2}$ units to $ROSiO_{3/2}$ units without changing a coordination number (CN) of Si atoms. Such behavior of SiO_2 is in sharp contrast with that of B_2O_3 , P_2O_5 and GeO_2 since the glasses containing the last three oxides may exhibit somewhat complicated property vs. composition relations due to the change in CN of B and Ge atoms and the presence of $P=O$ double bonds for P_2O_5 . In this chapter, it is intended to derive a cage structure model of the alkali silicate glasses and to discuss the properties of

voids present in the network, in order to obtain a fundamental concept of the structure of glasses.

1.1 A cage structure model

The molar volumes of the glasses in the range $0 \leq R_2O \leq 33.3 \text{ mol\%}$ are investigated in terms of additivity rule, assuming that two atomic units $\text{SiO}_{4/2}$ and $\text{ROSiO}_{3/2}$ are the component units of the glasses in the range $0 \leq R_2O \leq 33.3 \text{ mol\%}$. The calculated molar volumes of the glasses due to the additivity rule are compared with the measured ones. Assuming that the two units are replaced by the spheres with the same volumes as the partial molar volumes of the units, the two kinds of spheres are randomly packed and the packing densities are measured in order to study whether the random packing model can approximate the composition dependence of the molar volume of the glasses. Moreover, on the basis of cristobalite type cage structure model for SiO_2 and alkali silicate glasses, a distribution of voids in the glasses is discussed and the atomic arrangements near the non-bridging bonds will be proposed.

1.1.1 Experimental procedures and results

Table 1.1 shows density and elastic constants of the alkali silicate glasses. The density data are expressed in g/cm^3 : $1 \text{ g/cm}^3 = 10^3 \text{ kg/m}^3$. Density of most glasses can be seen

Table 1.1. Density and elastic constants of the alkali silicate glasses.

R_2O mol%	density (g/cm^3)	v_l (km/s)	v_s (km/s)	E (GPa)	G (GPa)	K (GPa)
Li_2O-SiO_2						
20.0	2.286	5.909	3.664	72.90	30.69	38.90
22.5	2.294	5.936	3.669	73.55	30.88	39.66
25.0	2.305	5.925	3.603	72.21	29.92	41.02
27.5	2.315	6.038	3.638	74.46	30.64	43.55
30.0	2.319	6.019	3.584	73.00	29.79	44.30
32.0	2.341	6.106	3.621	75.42	30.69	46.35
33.3	2.343	6.096	3.644	76.04	31.11	45.59
Na_2O-SiO_2						
16.67	2.362	5.295	3.173	58.02	23.78	34.52
18.0	2.365	5.345	3.256	60.42	25.07	34.13
20.0	2.397	5.263	3.184	58.87	24.30	33.99
22.5	2.405	5.288	3.151	58.49	23.88	35.41
27.5	2.452	5.281	3.009	55.93	22.20	38.73
30.0	2.465	5.276	3.017	56.40	22.43	38.69
33.3	2.485	5.269	3.037	57.36	22.92	38.43
K_2O-SiO_2						
18.0	2.363	4.958	2.889	49.03	19.72	31.79
20.0	2.373	4.867	2.846	47.67	19.22	30.58
22.5	2.411	4.810	2.758	46.04	18.34	31.33
25.0	2.416	4.783	2.672	43.92	17.25	32.27
Cs_2O-SiO_2						
16.67	3.104	4.014	2.252	39.99	15.74	29.03
20.0	3.281	3.778	2.128	37.67	14.86	27.02
25.0	3.412	3.555	1.918	32.50	12.55	26.38

in several reports [1], except that of cesium glasses. However, density of all glasses was measured in order to complement the data and to ensure consistency. The present data agreed well with the reported one, so that all of the density data including the cited one were taken into the subsequent discussions. A binary sphere packing was conducted according to a method of McGeary [2]. JIS B 1501 steel balls were employed. The ratios of diameters of the larger spheres to the smaller ones d_l/d_s were 2.33, 3.20, 4.63, 6.95, 8.93 and 11.11. The packing density data, however, necessary to

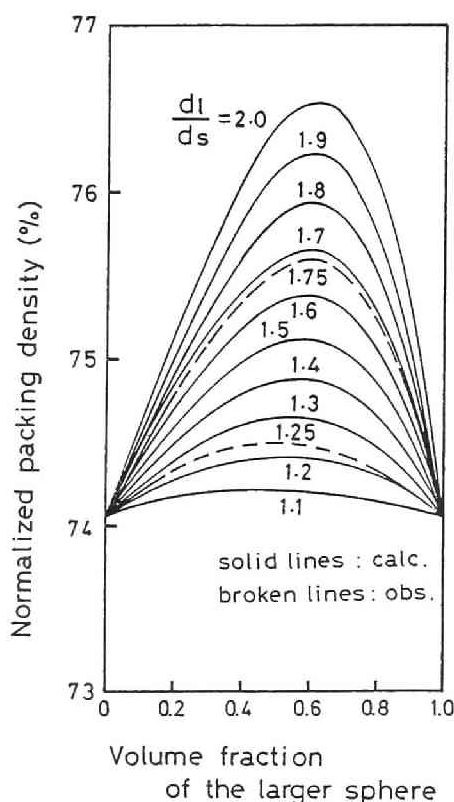


Fig. 1.1. Normalized packing density of binary systems.

calculate the molar volumes of the alkali silicate glasses were in the range $d_1/d_s < 2.0$. Fig. 1.1 represents a series of packing density data obtained by extrapolations from the range $d_1/d_s > 2$ to $d_1/d_s < 2$. The data of the random packing density of a single kind of spheres are normalized to the packing density of the closest packed spheres, that is, 74.05%. The broken lines represent the measured packing densities for $d_1/d_s = 1.75$ and 1.25 obtained by averaging those of 5 runs, where segregations prevent from a uniform mixing of the spheres. Nevertheless, the packing densities represented by the broken lines agree with the extrapolated ones represented by the solid lines for similar diameter ratios, hence it can be concluded that the data in Fig. 1.1 should stand for the following discussions.

1.1.2 Component units of the alkali silicate glasses

There have been some attempts to describe the several properties of the glasses in terms of the additivity rule, such as the struction theory by Huggins [3] and a model by Smith et al. [4] where a mixture of the structions is treated statistically. One can point out, however, a few significant shortcomings in them. A large number of structions should be necessary for describing the structure of binary alkali silicate glasses and much more structions for the glasses of more complex compositions. Irregularity of the network structure, being one of the essential characteristics of glass, cannot be represented unintentionally.

When the additivity is one of the fundamental principles for investigating the glass constitutions as in the present study, it must be noticed that one cannot uniquely determine the component units if one finds a linear relation between a property and glass composition showing the additivity. One must select the most essential and smallest atomic units as the component units which should be present actually in the glasses of relevant composition range.

In silica glass, every Si atom is bonded to neighboring Si through four bridging oxygens, while on addition of an alkali oxide an Si-O-Si bridging bond is broken, giving rise to two non-bridging bonds, Si-OR. Such changes proceed until the composition reaches $R_2O \cdot 2SiO_2$, where every Si atom has three bridging and one non-bridging bonds as confirmed in disilicate crystals [3]. This is the reason why one should consider the glasses in the range $0 \leq R_2O \leq 33.3\text{mol}\%$ as random mixtures of the two atomic units, $SiO_{4/2}$ and $ROSiO_{3/2}$. Unstatistical distribution of the alkali ions in the glasses has been proposed by "discrete ion theory". Since the random packing model is based on the statistical distribution of the two units, $SiO_{4/2}$ and $ROSiO_{3/2}$, the distribution of the alkali ions should be left untouched at the present stage. According to a similar consideration as in the range $R_2O \leq 33.3\text{mol}\%$, the glasses in the range $33.3 \leq R_2O \leq 50\text{mol}\%$ can be regarded as mixtures of $ROSiO_{3/2}$ and $(RO)_2SiO_{2/2}$ units. Thus, one should select such atomic units that have one Si atom each and are present in the glasses, before one discusses their structures based on a concept of the additivity rule.

1.1.3 Additivity of molar volumes

It has been indicated by the present author [5] that Huggins' equation [6], representing the additivity for specific volumes of glasses, is equivalent to a linear combination of the products of the mol fraction of the component oxides and their partial molar volume. Thus, it can be said that in Huggins' struction theory, the molar volume of the glasses is partitioned to non-existing component units like R_2O molecules in glasses. This might be improper as mentioned above. Therefore, it is intended to approximate the irregular network structure of alkali silicate glasses by the random packing of the two atomic units present actually in the glasses, namely $SiO_{4/2}$ and $ROSiO_{3/2}$. Let v_S and v_R the partial molar volumes of the units $SiO_{4/2}$ and $ROSiO_{3/2}$, and c the mol fraction of the alkali oxide. The volume $V(\text{cm}^3/\text{mol-Si})$ of a mixture of the two units containing 1 mol Si atoms is expressed by eq. 1.1.

$$V = v_S + 2(v_R - v_S)x, \quad (1.1)$$

where $x = c/(1-c)$. Thus, if the partial molar volumes of the units are constant, V is linearly dependent on the molar ratio $x = R_2O/SiO_2$. Eq. 1.1 can be modified to eq. 1.2.

$$(1-c)V = v_S + (2v_R - 3v_S)c, \quad (1.2)$$

where $(1-c)V$ represents the volume of the glass containing $(1-c)\text{mol } SiO_2$, i.e., the averaged molar volume V_m of the glass, whose composition is expressed as $cR_2O \cdot (1-c)SiO_2$. As far as eq. 1.1 is valid, eq. 1.2 must be also valid. Consequently, when the partial molar volumes of those

units are independent of the composition, V and V_m depend linearly upon their composition parameters, x and c , respectively.

However, as exemplified by the glasses in the system $\text{Na}_2\text{O}-\text{SiO}_2$ shown in Fig. 1.2, the plots of the measured volumes show a slight but distinct deviation from linear relation, which can be seen for all alkali silicate glass systems. Hence, the partial molar volumes assigned to the units are not constant but suffer from some modifications depending on the composition. It is only a rough approximation to assume that a glass should be taken as a mixture of some component units

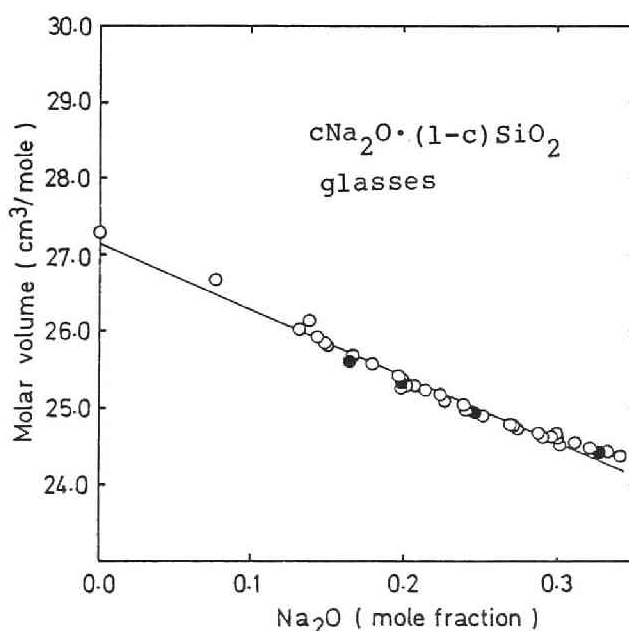


Fig. 1.2. Averaged molar volumes of the glasses $c\text{Na}_2\text{O} \cdot (1-c)\text{SiO}_2$. Those from the additivity rule are represented by the solid line. ●: this work, ○: ref. 1.

having constant volumes, though this assumption of additivity can represent well the variation of the molar volume of the glass as the first order approximation.

1.1.4 Approximation of the deviation from additivity by binary sphere packing

There are two ways for representing the deviation of the measured molar volumes from the calculated ones assuming the additivity rule.

- * The volumes of component units are adjusted intentionally so as to reproduce the measured volumes.
- * Binary random packing of the spheres representing the units is conducted to vary unintentionally the volume of the interstices of packed spheres, expecting that apparent volumes of the units and thus that of the packing (=glass) should be changed.

The latter is adopted here. Let P the packing density shown in Fig. 1.1, v the volume of a sphere with one Si atom whose packed volume is identical to the molar volume of silica glass. The volume of the other sphere is represented by kv whose packed volume is identical to that of an $R_2O \cdot 2SiO_2$ glass. The constant k ($k > 1$) represents the ratio of the molar volume of the disilicate glass to that of silica glass, being equivalent to $(d_1/d_s)^3$. Two Si atoms are present in the volume kv . Let f_1 and f_2 the volume fractions of the two spheres. The averaged molar volume V_m of the glass of the composition $cR_2O \cdot (1-c)SiO_2$ ($0 \leq c \leq 0.33$) is given by eq. 1.3.

$$V_m = (v/p) / (f_1 + 3f_2/k), \quad (1.3)$$

where $f_1 + f_2 = 1$. The parameters v and k are determined so that eq. 1.3 should give V_m of the two terminal glasses, $R_2O \cdot 2SiO_2$ and SiO_2 when $(f_1, f_2) = (0, 1)$ and $(1, 0)$, respectively. The parameter k being so adjusted, one could implicitly make a correction for taking two $ROSiO_{3/2}$ units as one sphere. The value of p corresponding to the fraction f and ratio k is interpolated in Fig. 1.1, then, V_m can be calculated due to eq. 1.3. Thus obtained V_m has been plotted in Fig. 1.3 as a function of c (R_2O mol fraction). It is clearly seen that the sphere packing model can reproduce V_m - c curves very well for any alkali species.

1.1.5 A cage structure model of each unit and void in the network

The internal structure of the two component units is studied in detail. The volumes V of the alkali silicate glasses containing 1 mol SiO_2 , whose compositions are expressed as $xR_2O \cdot SiO_2$ (later denoted simply as the molar volume), have been calculated from the V_m data in Fig. 1.3 and plotted in Fig. 1.4 (a) as a function of x . Fig. 1.4 (b) represents the molar volumes of several alkali silicate crystals, obtained from the lattice parameters in Table 1.2 [7]. It is clear that the equation of additivity (eq. 1.1) can approximate the molar volumes of the glasses and crystals very well. Owing to eq. 1.1, the extrapolation of the volumes of the glasses in each alkali silicate system to 0 in x gives

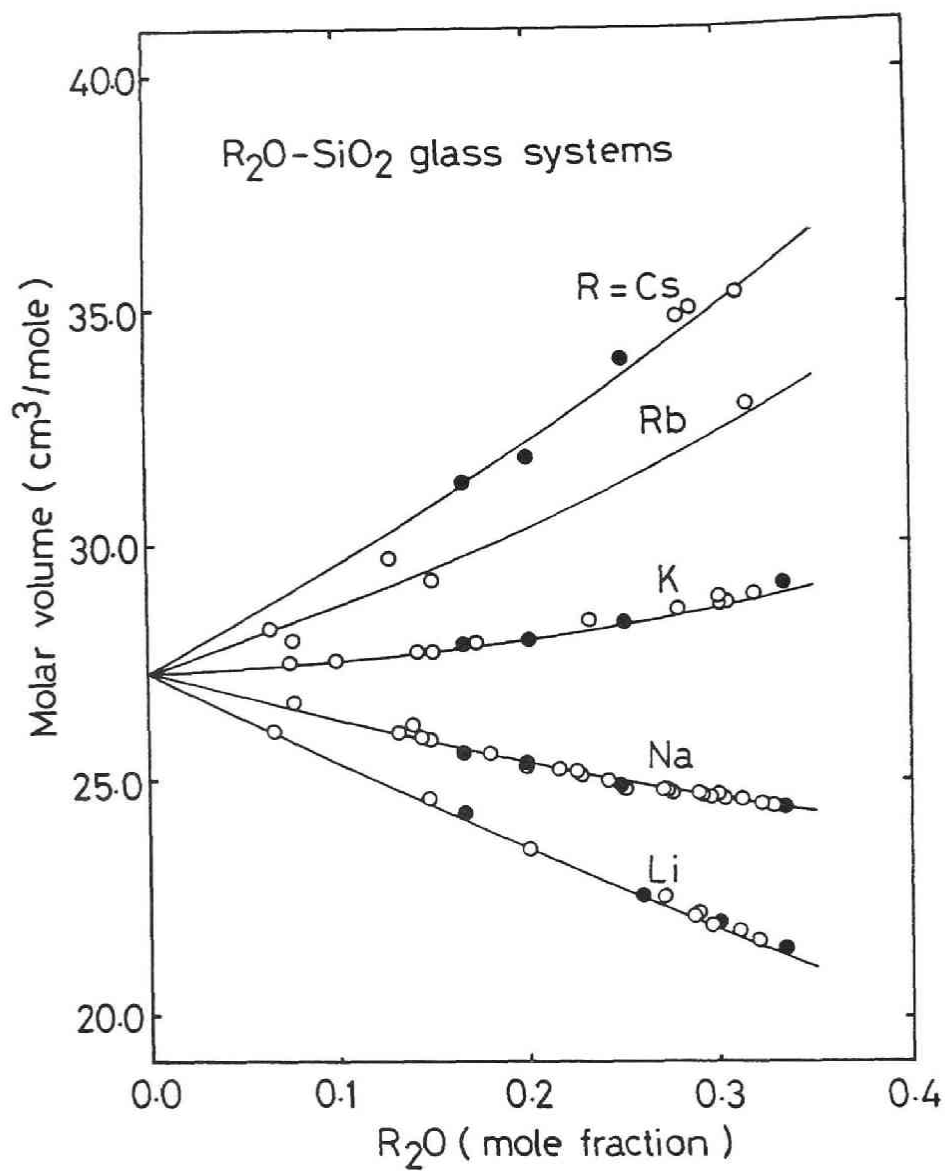


Fig. 1.3. Averaged molar volumes of the glasses $cR_2O \cdot (1-c)SiO_2$. The solid curves represent those from binary sphere packing model. o: this work, o: ref. 1.

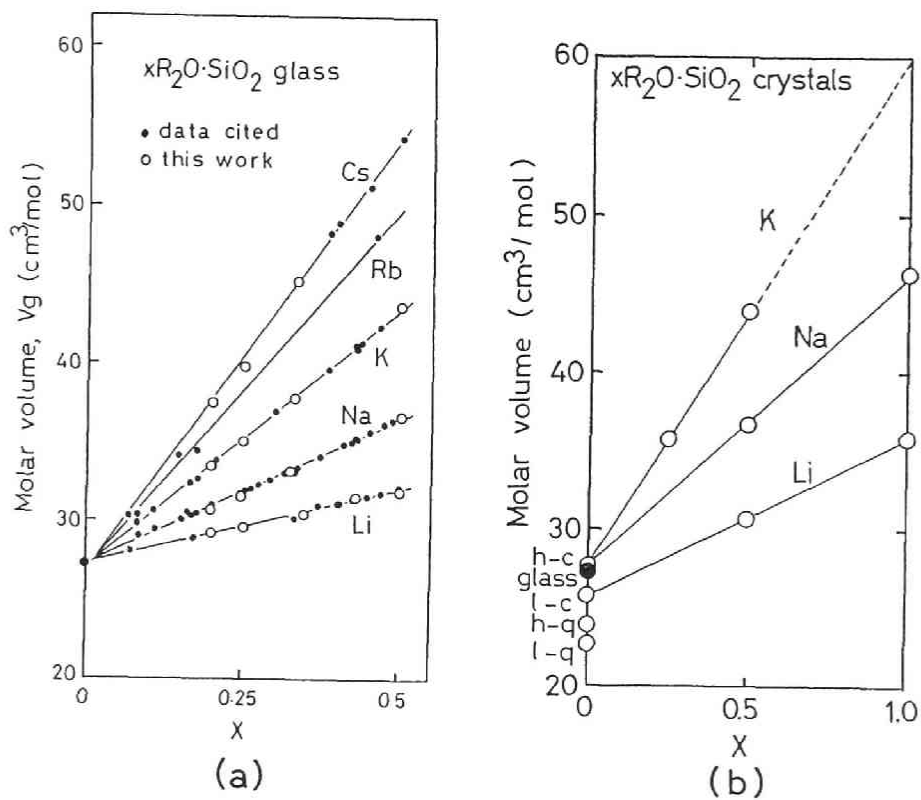


Fig. 1.4. The molar volumes of the alkali silicate (a) glasses (o: this work, •: ref. 1) and (b) crystals (ref. 7).

Table 1.2. Lattice constants of the alkali silicate crystals
(ref. 7).

$R_2O:SiO_2$	Lattice	Z	a/α ($10^{-1}nm$, deg)	b/β (deg)	c/γ	V (cm^3/SiO_2)
Li, 1:2	M*	4	5.82	14.66 90.0	4.79	30.8
1:1	O	4	5.43	9.41	4.66	35.8
Na, α -1:2	O	4	15.45	4.909	6.428	36.7
1:1	O	4	10.52	6.07	4.82	46.4
K, 1:4	A	1	12.32	4.943	8.369	35.8
1:2	M	24	9.72	111.19 25.26 90.0	89.69 14.24	43.9
l-q	Tri	3	4.913		5.405	22.7
h-q	H	3	5.01		5.47	23.9
l-c	Tetrg	4	4.973		6.926	25.8
h-c	C	8	7.16			27.6

* M: monoclinic, O: orthorhombic, A: triclinic,
Tri: trigonal H: hexagonal Tetrg: tetragonal,
C: cubic

the partial molar volume of the $SiO_{4/2}$ units which is almost the same as the molar volume of silica glass as indicated in Fig. 1.4 (a). The volumes extrapolated to 0 in x for the crystals exhibit the effect of alkali ion size upon the volume of Si-O-Si skeleton. The extrapolated volume for the lithium silicates with the smallest atom Li is as large as the molar volume of low-cristobalite (l-c), while that for the sodium and potassium crystals is almost identical with the molar volume of high cristobalite (h-c). However, since it is taken for granted that the structural parameters such as bond angles and bond lengths are distributed around average values, one can take the h-c structure for a network model of silica glass, because the volumes of silica glass and the two modifications of cristobalite are similar to each other.

Moreover, a stepwise and random substitution of Si-OR RO-Si non-bridging bonds for Si-O-Si bridging bonds can derive a network structure of the alkali silicate glasses similar to that of h-c. Fig. 1.5 (a) represents the network of the h-c structure as the model of silica glass, where the solid lines denote the bridging bonds. (b) is a model network of the alkali disilicate glasses in which one non-bridging bond represented by the broken line is introduced for each Si atoms. (c) and (d) show their unit cages constituting the networks (a) and (b). In subsequent paragraphs the cages are examined in detail.

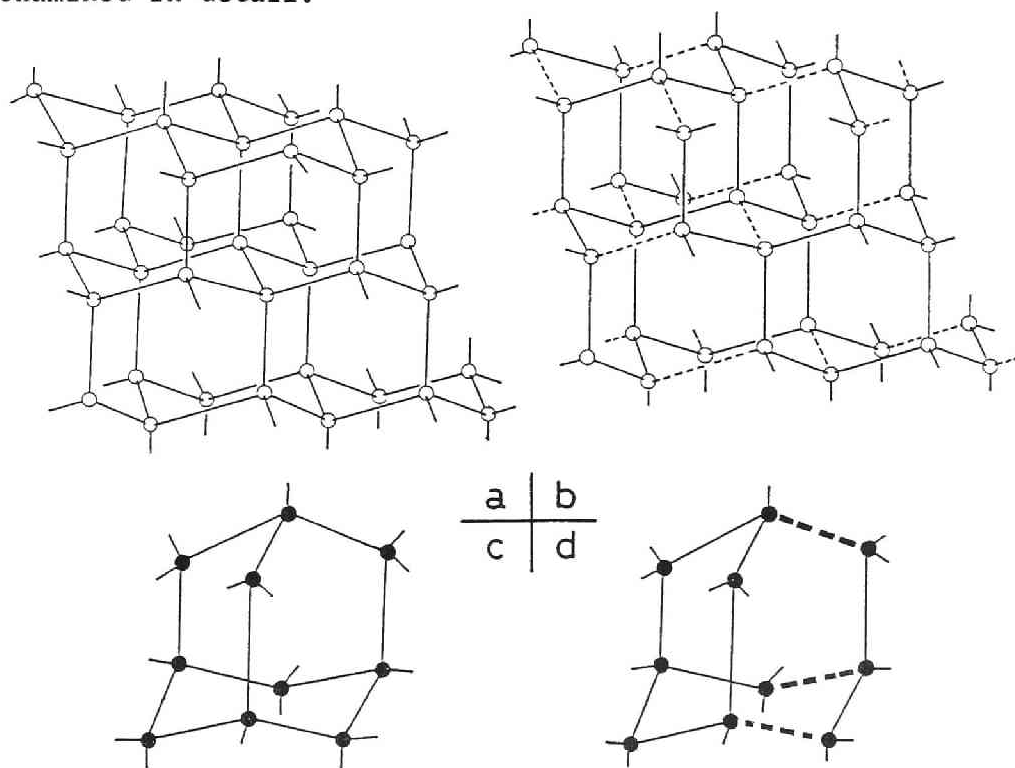


Fig. 1.5. Network model of (a) SiO_2 glass and (b) $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ glass. (c) and (d) represent their unit cages. The solid and broken lines represent Si-O-Si and Si-OR RO-Si bonds, respectively.

The structure of h-c consists of the cage $\text{Si}_{10}\text{O}_{12}$ composed of four $(\text{Si-O-Si})_6$ rings. Each Si-O-Si bridging bond is shared by 6 cages and each Si atom at the vertices by 10 cages. As a result, one of the cages is stoichiometrically equivalent to an SiO_2 molecule, that is, its volume represents that of the space occupied by one $\text{SiO}_{4/2}$ unit. Silica glass and h-c are considered similar in structure since their volumes are almost the same, being 27.3 and 27.6 cm^3/mol for the glass and h-c [6], respectively. "Doorway radii" calculated from activation energies for gas permeability [8] and shear modulus of silica glass ($G=3.12\text{GPa}$ [9]) range from 0.09 to 0.13nm depending on the gas. They agree very well with the radii of openings, 0.093 and 0.13nm of $(\text{Si-O-Si})_5$ and $(\text{Si-O-Si})_6$ rings, respectively. It was proposed [10] that silica glass consisted mostly of $(\text{Si-O-Si})_5$ rings. However, it is natural to consider a distribution in the size of the rings, and it might be plausible that an $(\text{Si-O-Si})_6$ ring is modified to an $(\text{Si-O-Si})_5$ ring with accompanying the formation of a seven membered ring, $(\text{Si-O-Si})_7$. Therefore, it can be concluded that silica glass structure is approximated by the h-c type cage structure model consisting of $(\text{Si-O-Si})_6$ rings.

On the other hand, as mentioned before, one can derive the skeleton of the $\text{R}_2\text{O}\cdot 2\text{SiO}_2$ glass composed by the disilicate unit $\text{ROSiO}_{3/2}$ shown in Fig. 1.5 (b) and (d), in which the distribution of the bridging and non-bridging bonds is represented equivalently to that in the alkali disilicate crystals [7]. The broken lines represent the non-bridging bonds Si-OR RO-Si, connecting the skeleton layers composed by

the bridging bonds. As in the $\text{SiO}_{4/2}$ units, the edges and vertices of the unit cage (d) are shared by neighboring cages and one unit cage (d) stoichiometrically corresponds to an $\text{ROSiO}_{3/2}$ unit. For example, as to the number of the alkali ions, the cage has three non-bridging bonds, Si-OR RO-Si (broken lines) with two alkali ions and each non-bridging bond is shared by 6 cages, hence one alkali ion ($3 \times 2 \times 1/6 = 1$) belongs to each cage. It should be noted, however, that the distribution of the non-bridging bonds indicated in Fig. 1.5 is valid only in the alkali disilicate crystals, and might be different in the glasses in the range $x \leq 0.5$. It is important that the volume occupied by the cage unit represents the partial molar volume of the $\text{ROSiO}_{3/2}$ unit. Naturally, the units in the glasses have the larger volume than those in the crystals. Consequently, regarding the glass in the range $0 \leq x \leq 0.5$ as mixture of the component units $\text{SiO}_{4/2}$ and $\text{ROSiO}_{3/2}$ is equivalent to regarding the volume of the glass as the sum of that of the voids enclosed by such cage skeletons. Moreover, the sphere packing model regards the glass as the packing of such spheres that represent the voids.

1.1.6 Distribution of the voids

As can be seen in Fig. 1.5 (a) and (b), 12 cages are present in the neighbor of each cage unit, sharing the edges. Four of them tetrahedrally surround the relevant cage, sharing the $(\text{Si-O-Si})_6$ rings. When every bridging bond is substituted by C-C bond, the network is the diamond lattice. One can

expect that the alkali ions occupy the inner space of these cages, i.e., the void [6,11,12]. Percolation theory [13] tells the critical percolation probability p_c for the diamond lattice is 0.425. It means that a particle can migrate from one end to the other along the sites available for it which are linked together continuously. Therefore, when the fraction of the cages corresponding to $\text{ROSiO}_{3/2}$ units exceeds p_c , namely 0.123 in $x(=x_c)$ or 17.5mol% in the R_2O content as the results of increase in the content of the alkali oxide, the cages for the disilicate units line up in contact with each other forming an alkali ion channel [14] through which the alkali ion can migrate in the glass. Exarhos et al. [15] have shown that the activation energy E for ionic conduction in glass can be approximated as

$$E = (1/2) M l^2 v^2,$$

where M , l and v denote the mass of the cation, the jump distance and the jump frequency, respectively. On neglecting other structural factors affecting the ionic conduction, the activation energy E should be larger for the glasses in the range $x < x_c$ than in the range $x > x_c$, because the alkali ion channel is not formed and continuous contact of the $\text{ROSiO}_{3/2}$ units cannot be expected due to their random distribution, resulting in longer jump distances in the range $x < x_c$. However, in the range $x > x_c$ E might be independent of the glass composition since the channel is formed. Although the measured activation energies for cationic conduction were scattered depending on the investigators, Hakim and Uhlmann [16] reported that those for the sodium, potassium and cesium

silicate glasses became constant at the range $15 < R_2O < 20$ mol% and were invariant on further addition of the alkali oxides. Such composition range coincides with the range where the percolation theory predicts the presence of the alkali ion channels. In consequence, it is concluded that the cages corresponding to $ROSiO_{3/2}$ units are randomly distributed in the alkali silicate glasses, inversely, this conclusion confirms the cage structure model of the alkali silicate glasses.

1.1.7 Configurations of atoms near the non-bridging bonds

For simplicity, in order to discuss atomic configurations near the non-bridging bonds, one can modify the structure model of the alkali disilicate glasses into the other one in which pairs of non-bridging bonds interlink the layers composed of regular hexagon of the $(Si-O-Si)_6$ ring. The structure is regarded as consisting of those hexagonal cylinders which contain two $ROSiO_{3/2}$ units when the sharing of the edges by the cylinders is taken into consideration. Then one can evaluate the Si-Si distance for the pair of non-bridging bonds corresponding to the height of the cylinder. Let h the height of the cylinder and d the length of the edge of the hexagons at the bottoms equivalent to a distance of two Si atoms adjacent to a bridging oxygen. The partial molar volume v_R of the $ROSiO_{3/2}$ unit is given by

$$v_R = (3\sqrt{3}/4) d^2 h N_A \quad (1.4)$$

where N_A is the Avogadro's number. The value of $d=0.3087\text{nm}$ in

silica glass given by Mozzi and Warren [17] is adopted, assuming that d is independent of the alkali content and the kind of alkali species. One should make correction on v_R for some errors introduced by approximating $(\text{Si-O-Si})_6$ rings of "chair" configuration by planar hexagons and other simplifications for calculation. Here, the height h_0 of the hexagonal cylinder is obtained for silica glass according to eq. 1.4, and the difference $\Delta l = h - h_0$, indicated in Table 1.3, is assigned to the effect of alkali addition upon the Si-Si distance at the non-bridging bonds. Since $(\text{Si-O O-Si}) - (\text{Si-O-Si}) = \langle \text{O} \rangle$, the comparison of Δl with the diameter d_0 of the bridging oxygen (0.27 or 0.28 nm [11]) can indicate that d_0 in the rubidium and cesium glasses is less than Δl , hence, the two Si and O atoms may be arranged linearly in an array of four atoms like Si-O O-Si. However, since d_0 in the lithium, sodium and potassium glasses is greater than Δl , the two non-bridging oxygens are separated on either side of the Si-Si tie line.

Table 1.3. Difference in Si-Si distance at the bridging and non-bridging bond, $(\text{Si-O O-Si}) - (\text{Si-O-Si})$ (nm).

R	Li	Na	K	Rb	Cs
Δl (nm)	0.063	0.124	0.219	0.300	0.362

1.2 Elasticity measurements and bulk modulus vs. volume relations

A method of measuring the elastic constants will be described which utilizes the ultrasonic waves propagating in solid bodies. One of the elastic constants, i.e. bulk modulus K , has a specific relation to the molar volume of crystals of similar structure. Therefore, the bulk modulus vs. volume relation (K - V relation) might be applied to investigate the glass structure. The physical meaning of the K - V relations will be described in relation to the internal energy of solid.

1.2.1 Elasticity measurements

One of the pulse transmission methods [18] is employed to obtain the elastic constants, where elastic wave velocities (longitudinal and shear modes) propagating in a glass specimen are measured. Fig. 1.6 shows its block diagram [18]. Ag electrodes are developed on both surfaces of the specimen polished parallel, on which PZT transducers are fixed by phenyl salicylate. A high-power pulse generator PG-2 triggered by a system controlling pulse generator PG-1 produces high voltage pulses, which the transducer at first end converts into elastic waves. They propagate through the specimen, reach the second end and are converted into a series of electric pulses, which are displayed on channel A on the scope. PG-1 produces simultaneously a series of N pulses, displayed on channel B on the scope. The frequency f of PG-1 and the delay

time at PG-2 are adjusted so that the onset of motion of the first signals of A and B should coincide with each other and that the onset of motion of the first arriving pulse on A after propagating through the specimen should coincide with that of Nth pulse on B. Let L the length of the specimen. The travel time t of the elastic waves is given as $t = (N-1)/f$. The velocity v is then obtained by

$$v = f L (N-1).$$

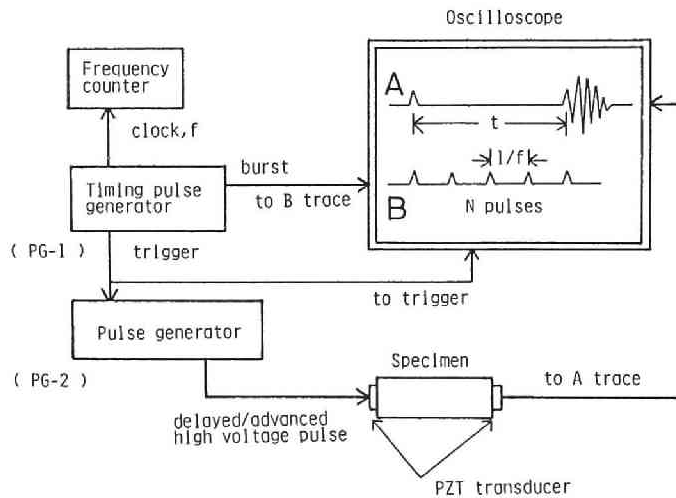


Fig. 1.6. A block diagram of the apparatus for the pulse transmission method.

The longitudinal and shear wave velocities v_l and v_s give the bulk modulus K and shear modulus G with density d obtained separately [18],

$$K = d (v_l^2 - (4/3) v_s^2), \quad G = d v_s^2.$$

Young's modulus E and Poisson's ratio σ are expressed in terms

of K and G as [19]

$$E = 9K/(3K + G), \quad \sigma = (3K - 2G)/(6K + 2G).$$

Variation of bulk modulus among the four constants is mainly discussed because bulk modulus is related to the internal energy and volume of a solid. It should be also noted that the bulk modulus obtained by the present method is that under an adiabatic condition ($S=\text{const.}$), K_s , and related to that under isothermal condition ($T=\text{const.}$), K_t , by eq. 1.5 [19].

$$K_s = K_t (1 + \alpha r T), \quad (1.5)$$

where α and r denote the volume expansion coefficient and the Grueneisen constant, respectively. For an ordinary glass α and r are respectively of the order of 10ppm and 1, so that $\alpha r T$ is about 3×10^{-3} at room temperature. Therefore, taking 1% error for the measured constants into consideration, one can virtually regard $K_s = K_t$.

1.2.2 Bulk modulus - volume relations

The bulk modulus is defined as eq. 1.6 at $T=0K$.

$$K_0 = -V_0 (dP/dV) = V_0 (d^2U/dV^2) \quad (1.6)$$

The internal energy U of ordinary ionic crystals can be represented by Born equation as a function of cation-anion distance r .

$$U = -A/r + B/r^n,$$

where A is a constant with a meaning similar to that of the Madelung constant, and B represents the repulsive potential. Since V is proportional to r^3 , eq. 1.6 is modified to eq. 1.7.

$$K_0 = (1/9) A (n-1) C V_0^{-4/3}, \quad (1.7)$$

where C is a constant related to packing state of ions in the solid. It has been known that Madelung constants of a number of crystals are in the narrow range from 1.4 to 1.60 if mean atomic volume or mean atom-pair volume is taken for the volume of the crystals as the basis of calculating the constants. Since a series of crystals of the same structure have similar values of A , n and C , the bulk modulus K_0 is a unique function of V_0 and varies in proportion to $V_0^{-4/3}$ when the cation is changed from one kind to another.

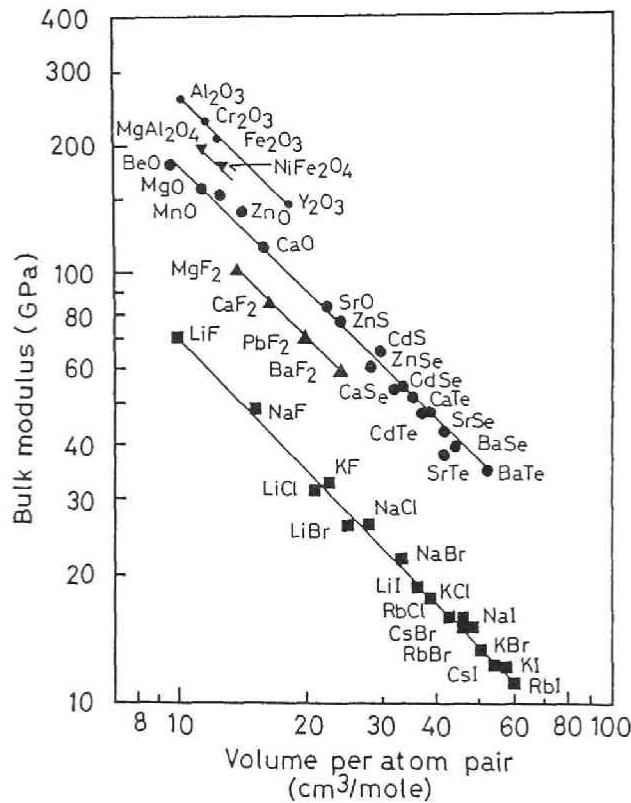


Fig. 1.7. Bulk modulus vs. mean atom-pair volume relations for several series of crystals.

Fig. 1.7 represents bulk modulus vs. mean atom-pair volume (K-V) relations for several series of crystals at room temperature. Slopes of the solid lines are -1, being almost equal to -4/3, hence eq. 1.7 is satisfied. On the other hand, if the radii of cations are sufficiently smaller than those of the anions that the cations can occupy interstitial sites in the anion packing, a higher order repulsive energy among the anions becomes the major part of the internal energy. In this case, it is known [18] that the bulk modulus is related with the volume as eq. 1.8.

$$K \propto V_0^{-4} \quad (1.8)$$

Thus, it has been shown that the bulk modulus can be correlated to the mean atom-pair volume of the solid in two ways, that is, eqs. 1.7 and 1.8. They are very important and useful for studying glass structure. That is, one can obtain a clue on the structure of a series of glasses by studying whether the K-V relation of the glasses should obey either of the equations, as the analogy of the relation for the crystals.

1.3 Elastic properties and roles of the alkali ions

On the basis of the cage structure model derived in the preceeding section, the K-V relations of the alkali silicate glasses are studied and the effect of the alkali ions on the elastic properties of the glasses is discussed in this section.

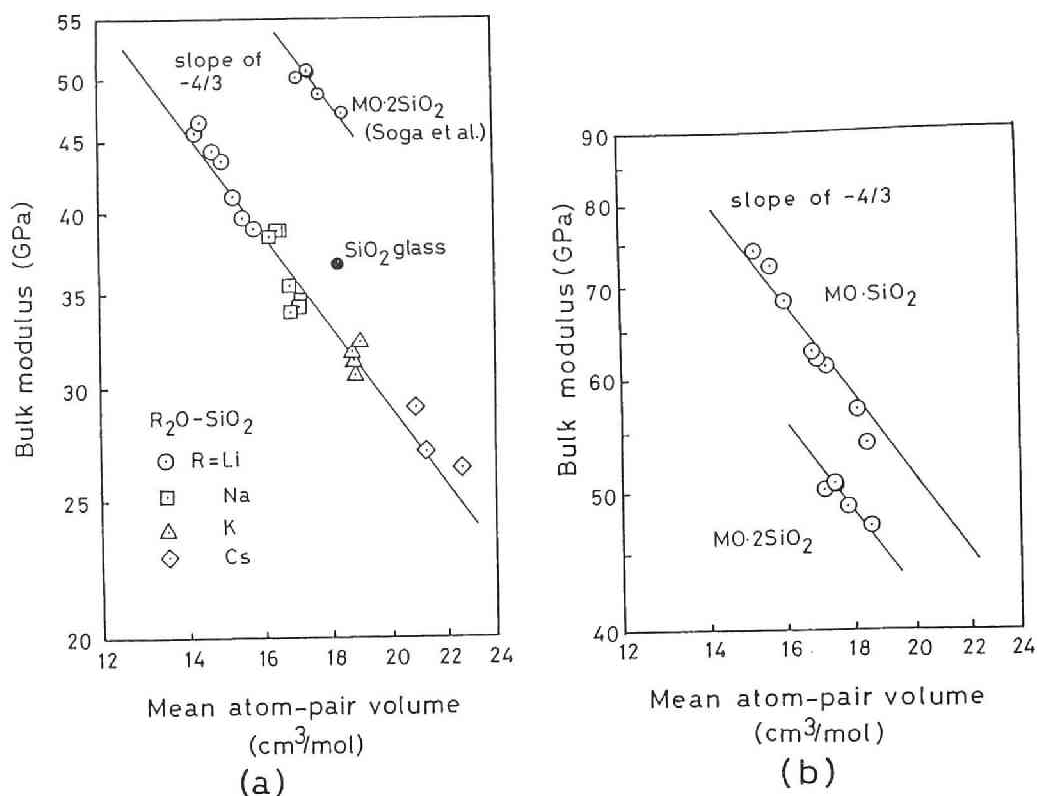


Fig. 1.8. K-V relations for (a) alkali silicate glasses (this work) and (b) alkaline earth silicate glasses (ref. 20).

1.3.1 K-V relation of the alkali silicate glasses

Fig. 1.8 (a) represents the relation between bulk modulus and mean atom-pair volume (K-V relation) for the alkali silicate glasses. The plots for all glasses are located in the neighborhood of the solid line with a slope $-4/3$. According to the theory on the K-V relation described in the previous section, the result indicates that the alkali

silicate glasses behave as if they were solid solutions, having similar structure, like a series of crystals of, say, the rock salt structure. Soga et al. [20] investigated the structures of $MO \cdot SiO_2$ and $MO \cdot 2SiO_2$ and theoretically derived the followings.

- (1) The data points for the series of $MO \cdot nSiO_2$ glasses with a molar ratio $n=MO/SiO_2$ will compose a line having slope $-4/3$ when M is substituted from one kind to another.
- (2) The plots for the glasses having different n will lie on the respective lines of slope $-4/3$.

The two items above have been confirmed experimentally [20], as indicated in Fig. 1.8 (b). On the other hand, the present author measured the elastic properties of a series of mixed alkali glasses $xNa_2O \cdot (1-x)Cs_2O \cdot 5SiO_2$ [21] and indicated the presence of a deviation from the additivity, i.e., a mixed alkali effect, in the elastic property. However, the deviation was not very significant and it could be considered that a series of alkali silicate glasses with the same molar ratio $R_2O/SiO_2=1/5$ behaved similarly as the alkaline earth silicate glasses with $n=1$ or 2 did. Therefore, Fig. 1.8(a) indicates that $KV^{4/3}=\text{const}$ is also valid for the alkali silicate glasses having different ratio of alkali oxide to silica. In Fig. 1.8 (a), the mean atom-pair volume of the potassium glasses remains roughly constant and the bulk modulus of them varies little. Therefore, one can interpret the figure as showing that the bulk modulus of the alkali silicate glasses depends upon only the mean atom-pair volume, while that of the alkaline earth silicate glasses depends upon both the volume

and the molar ratio n . Thus the alkali ions apparently play the role to determine the volume of the alkali silicate glasses.

1.3.2 Role of the alkali ions

The non-bridging bonds destroy the continuous, cross-linked structure of silica glass and may decrease the elastic constants, reducing the strength of the glass network. However, the elastic constants may increase when the alkali ions fill the voids of the oxygen cages without enlarging them as has been mentioned in the previous section. Thus, the alkali oxide may affect the elasticity of the glasses on either of the opposite directions. Therefore, in order to understand the K-V relation for the alkali silicate glasses, it is necessary first to evaluate the size of void in the cage and to see whether the cage can accommodate the ion in the voids or not by comparing the sizes of the alkali ions and void. In the cage units shown in Fig. 1.5 (a), Si-Si distance adjacent to a bridging oxygen is 0.309nm [17] and the O-O distance is 0.509nm [5,22], when the bridging oxygen is assumed to locate at the center of Si-Si tie line. Then it can be shown that the radius $r(R)$ of the maximum sphere to be accommodated in the void of the cage unit of silica glass is expressed as a function of the radius of oxygens $r(O)$ by

$$r(R) + r(O) = 0.509 / \sqrt{3}. \quad (1.9)$$

Letting $r(O) = 0.135\text{nm}$ for the oxygen of two-fold coordination [5,11], $r(R)$ is obtained as 0.156nm. Therefore, the spherical

ions with radii less than 0.156nm can be accommodated in the internal space (void) in the cage of silica glass without enlarging the cage. Table 1.4 shows the effective ionic radii of the alkali ions under several coordination numbers CN given

Table 1.4. Effective ionic radii of the alkali ions for several coordination numbers, CN (ref. 11).

Effective ionic radii (10^{-1}nm)					
CN	Li	Na	K	Rb	Cs
4	0.59	0.99			
5		1.00			
6	0.74	1.02	1.38	1.49	1.70
7		1.13	1.46	1.56	
8		1.16	1.51	1.60	
9		1.32	1.55		1.78
10			1.59		1.81
12			1.60	1.73	1.88

by Shannon and Prewitt [11]. It can be seen by comparing them with $r(\text{R})=0.156\text{nm}$ that Li^+ , Na^+ and K^+ ions can be accommodated in the voids of silica glass skeleton, whereas Rb^+ and Cs^+ ions larger than the three ones cannot be accommodated without elongating the Si-Si distance of the silica glass. It is indicated that the Si-Si distance of the cages in rubidium and cesium glasses is inclined to be lengthened in order to accommodate the cations in the voids. In addition to such tendency, the negatively charged non-bridging oxygens tend to be apart from each other as far as possible due to the repulsive force acting between them. However, they cannot occupy in the voids on both sides of the

Si-Si tie line since the bulk alkali ions already occupy those sites. Therefore, it is reasonable that a pair of non-bridging bonds Si-O^- are arranged linearly as $\text{Si-O}^- \text{ } ^-\text{O-Si}$, as can be seen from Table 1.3, in order to relax the repulsive force between the negatively charged non-bridging oxygens. In the glasses with smaller alkali ions, the non-bridging oxygens are located at the sites deviated from Si-Si tie line probably due to the structure tightening effect of the alkali ions for relaxing the repulsion between the non-bridging oxygens. Thus, the elongated Si-Si distances at the non-bridging bonds calculated in sect. 1.1.7 have been interpreted in terms of the sizes of the alkali ions and voids in the glasses by the above discussion.

In order to explain the variation of the elastic constants represented in Fig. 1.8, it should be noted that when the added alkali ions gradually fill the void of the oxygen cages in the glass networks, the bulk modulus of the glasses increases. If no effects other than that of the ions filling the voids are significant, the bulk modulus of the lithium, sodium and potassium glasses increases in proportion to V^{-4} . The bulk modulus of the rubidium and cesium glasses is likely to increase due to the effect of the cations filling the voids though the cations enlarge the cages. Formation of the non-bridging oxygens, however, reduces the strength and rigidity of the glass network. The non-bridging bonds in the rubidium and cesium glasses contribute to much less extent to the strength of the network than those in the glasses with smaller alkali ions because the structure tightening effect

cannot be expected and Si-Si distance at the non-bridging bonds is much longer than in the lithium and sodium glasses. Therefore, the larger the alkali ion is, the more markedly the glass network is weakened.

In consequence, for the alkali silicate glasses in the range $0 \leq x \leq 0.5$ ($0 \leq R_2O \leq 33.3 \text{ mol\%}$) the Si-O-Si skeletons similar to those of h-c network first determine the strength of the glasses. Then, other factors, such as the formation of the non-bridging bond, elongation of Si-O-Si bridging bond, and effects of the alkali ions filling the voids of the skeletons, should modify the elastic properties of the glasses. As a summed result of those factors, the K-V relation appears as is shown in Fig. 1.8 (a).

1.4 Summary

The composition dependence of molar volumes of the alkali silicate glasses in the range $0 \leq x \leq 0.5$ ($0 \leq R_2O \leq 33.3 \text{ mol\%}$) has been investigated on assuming $\text{SiO}_{4/2}$ and $\text{ROSiO}_{3/2}$ units as the fundamental component units. The deviations of their molar volumes calculated on the basis of additivity rule from the measured ones can be well approximated by means of random packing model of the glasses where the two atomic units are replaced by the two kinds of spheres. From the variation of the molar volumes for alkali silicate crystals and glasses as functions of composition, which is expressed as $xR_2O \cdot \text{SiO}_2$, a high-cristobalite type network model has been derived for the

glasses. The random packing model shows that a continuous channel of the alkali ions is formed at a critical composition, 0.123 in x (17.5mol% in the R_2O content) in spite of random distribution of the alkali ions in the glasses. It is also indicated that the arrangements of Si, O and R atoms at the non-bridging bonds are dependent on the size of the alkali ion and the internal space of the cages, i.e., void.

Furthermore, the plots of bulk modulus vs. mean atom-pair volume can be represented by a line of slope $-4/3$ for all alkali silicate glasses, showing that the glasses behave as a series of solid solutions irrespective of the kind and content of the alkali oxide. This result is also explained in relation to the size and site of the alkali ions according to the cage structure model.

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Chapter 2

NETWORK STRUCTURE OF ALKALI BORATE GLASSES

In this chapter, the network structure of alkali borate glasses is discussed, where a change in coordination number of B atoms is expected. At the beginning, the arrangements of structure units in the alkali borate crystals are investigated in relation to the boron oxide anomaly, based on an assumption that the arrangements of the borate units in the crystals resemble those in the glasses. Then, elastic properties of the borate glasses are studied as a function of the glass composition. The results are examined and correlated with the variation of fraction N_4 of four-coordinated boron atoms.

2.1 Arrangements and fractions of BO_3 and RBO_4 units in alkali borate crystals

The properties of alkali borate and borosilicate glasses change abruptly in the composition range $0.2 < x < 0.25$ where x represents the molar ratio $\text{R}_2\text{O}/\text{B}_2\text{O}_3$ [1], though the specific composition varies depending on the properties and the alkali species. The phenomenon, the boron oxide anomaly, has not thoroughly been clarified yet. The other abrupt change of the properties at about 0.5 in x , which can be called the second boron oxide anomaly, has been attributed to the fact that the fraction N_4 of the four-coordinated boron atoms becomes

maximum near 0.5 in x [2,3]. However, the reason why N_4 cannot continue increasing in the range $x > 0.5$ has not been explained.

In order to approach the anomalies, it seems important to know the arrangements of the $\text{BO}_{3/2}$, $\text{RBO}_{4/2}$ and $\text{ROBO}_{2/2}$ units (later denoted as B_3 , B_4 and B_R units, respectively) in the glasses, that is, to know the kinds and numbers of the units in the first neighbor of the relevant unit. The thermochemical stability of the borate unit is dependent on the nearest neighbor units which govern the orbital energy [4] of the oxygens bridging them. Although it is very difficult to know every detail of the glass constitution, some of the borate groups found in the borate crystals, such as boroxol and diborate groups, are proposed to be present in the borate and borosilicate glasses [1], suggesting the similarity of the arrangements of the B_3 and B_4 units in the glasses to those in the crystals to some extent. Therefore, it is useful in the interpretation of the boron oxide anomalies in the glasses to study the arrangements of those units in the alkali borate crystals.

2.1.1 Constitutions of the alkali borate crystals

Figure 2.1 shows the arrangements of the B_3 , B_4 and B_R units in several crystals [5] found in the phase diagrams of the systems $\text{R}_2\text{O}-\text{B}_2\text{O}_3$ [6]. Their molar ratios $\text{R}_2\text{O}:\text{B}_2\text{O}_3$ are 1:9(crystal I), 1:5(J), 1:4(K), 1:3.8(K'), 1:3(L), 1:2(M) and 1:1(N). B_2O_3 crystal is represented by H. Crystals J, L and M are built by the borate groups known as a pentaborate group, a

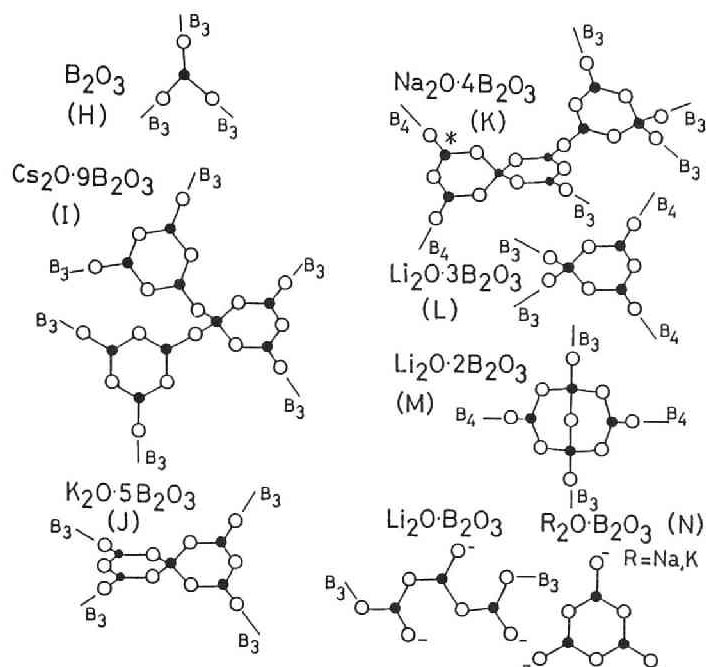


Fig. 2.1. The arrangements of the borate units in the alkali borate crystals. $\bullet$: B, $\circ$: O.

triborate group and a diborate group, respectively. A triborate group and a pentaborate group are connected to be a tetraborate group which constructs the network of sodium tetraborate crystal K. The procedure to know the arrangements of the borate units is shown for crystal K as the example in the following. In Fig. 2.1 the asterisked B_3 unit shares an extra-annular oxygen with a B_4 unit which is a member of the triborate part belonging to the other tetraborate group. The B_3 unit, thus, is bonded with one B_3 unit and two B_4 units. Consequently, the B_3 unit is represented as $B_3(B_3, 2B_4)$ in

order to indicate the kinds and numbers of the units in the neighborhood. Therefore, crystal K is built of $B_3(2B_3, B_4)$, $B_3(B_3, 2B_4)$ and $B_4(4B_3)$ units, whose fractions are 0.5, 0.25 and 0.25, respectively. In the same way, the arrangements of the borate units are examined for all crystals H through N. It has been found that, besides B_R unit in crystal N, four kinds of B_3 units such as $B_3(3B_3)$, $B_3(2B_3, B_4)$, $B_3(B_3, 2B_4)$ and $B_3(3B_4)$ and two kinds of B_4 units such as $B_4(4B_3)$ and $B_4(3B_3, B_4)$ construct the alkali borate crystals H through M. Their fractions are plotted in Fig. 2.2 as a function of x . The ordinates OP and $N'N$ represent the total fractions of the three- and four-coordinated boron atoms, N_3 and N_4 , respectively. N_3 decreases along the segment of line PR in the

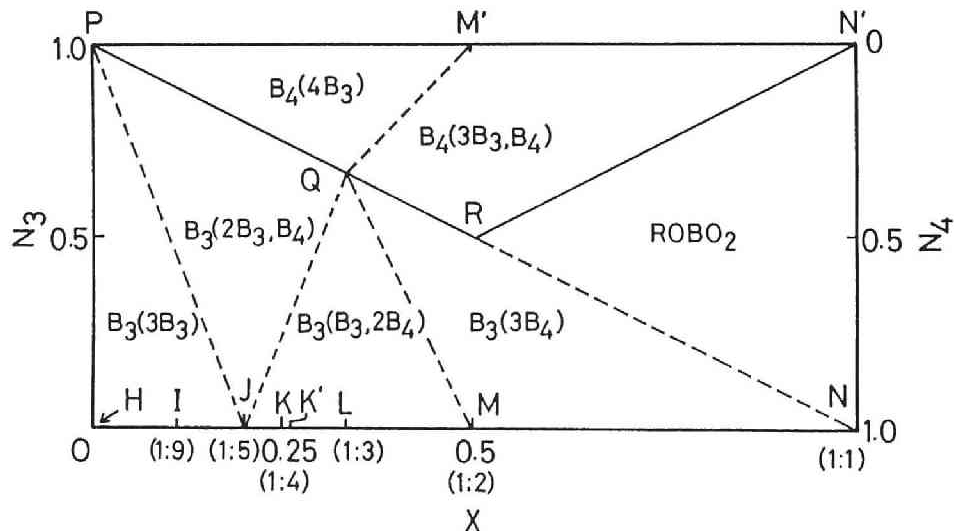


Fig. 2.2. The fractions of the B_3 and B_4 units in crystals H through N, plotted as a function of $x = R_2O/B_2O_3$.

range $x < 0.5$, and increases along RN' in the range $x > 0.5$ due to the decomposition of the B_4 units to the B_R units:



In the figure crystal K' represents $K_2O \cdot 3.8B_2O_3$ [7]. Potassium diborate [8] and high-temperature modification of sodium triborate [9] have the same borate units as lithium diborate M and lithium triborate L, e.g., $B_4(3B_3, B_4)$ and $B_4(4B_3)$, respectively, though they are constructed by the different borate groups from those constructing the lithium crystals. However, sodium diborate [10], having B_R units, and low-temperature modification of sodium triborate [11] are different in the arrangements of the borate units from the lithium crystals L and M, respectively. The behavior of the last two sodium crystals cannot be represented in Fig. 2.2 nor be explained at present.

Furthermore, N_4 of the alkali borate crystals is plotted in Fig. 2.3 along with that of the alkali borate glasses [1,12]. Here, crystal G represents sodium diborate having $N_4 = 3/8$. Therefore, N_4 of the lithium and potassium crystals varies along the segments of lines HM and MN, and that of the sodium crystals along HL, LG and GN. The broken lines LM, LG and GN indicate the presence of the crystals of unknown structure in the phase diagrams such as $Li_2O \cdot 5B_2O_3$, $2Na_2O \cdot 5B_2O_3$ and $2Na_2O \cdot 3B_2O_3$. N_4 of the alkali borate glasses in the range $x < 0.5$ varies along the segment of line HM, while it decreases very slowly with x in the range $x > 0.5$ and becomes null at 2.5 in x [12]. Such difference in the variation of N_4 between the crystals and glasses indicates the difference in

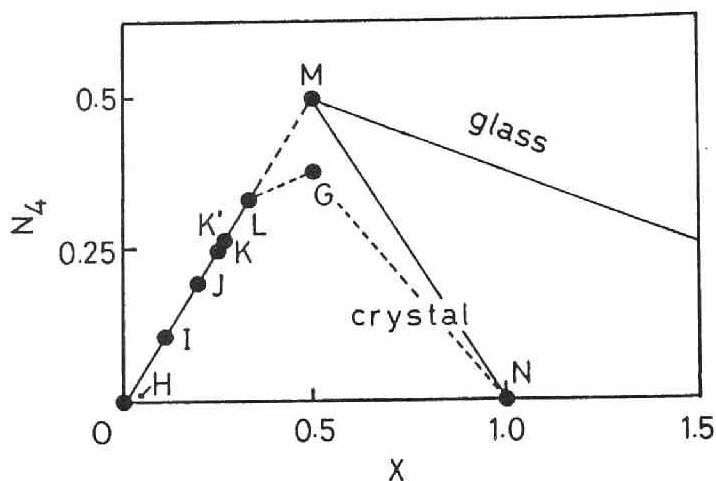


Fig. 2.3. Variation of N_4 of the alkali borate crystals (H through N) and glasses.

their constitutions in the range $x > 0.5$.

2.1.2 Discussion

It has been found that the arrangements of the borate units and N_4 vs. x relation of the sodium crystals are different from those of the lithium and potassium crystals. Such behavior of the sodium crystals will be discussed later when more knowledges are available, and the discussion here is focused on the lithium and potassium crystals.

The following two tendencies can be found from Fig. 2.2 in the lithium and potassium crystals in the range $0 < x < 0.5$.

- (1) The number n of B_4 units in the first neighbor of a B_3 or a B_4 unit increases gradually with x ; for example, $B_4(4B_3)$ ($n=0$, in crystals I, J, K, K' and L) to $B_4(3B_3, B_4)$ ($n=1$,

in crystal M).

- (2) The fraction of each B_3 and B_4 unit, e.g., $B_3(3B_4)$ and $B_4(4B_3)$, becomes maximum in one of the crystals, in which the unit is the single constituent B_3 or B_4 unit. For example, the fraction of the $B_4(3B_3, B_4)$ unit is maximum in crystal M and no B_4 units other than $B_4(3B_3, B_4)$ cannot be found in the crystal.

Therefore, when it is assumed that the change of the B_3 units to the B_4 units continuously occurs instead of formation of the B_R units in the range $x > 0.5$ as in the range $x < 0.5$, three kinds of hypothetical B_4 units, namely, $B_4(2B_3, 2B_4)$, $B_4(B_3, 3B_4)$ and $B_4(4B_4)$ with $n=2, 3$ and 4 will appear one after another. Moreover, the tendencies can be interpreted as showing that a B_4-B_4 bond is obliged to be formed when N_4 exceeds some threshold value. Since none of those B_4 units with $n \geq 2$ are present actually, the B_4 units are unstable and are decomposed immediately to the B_R units. Thus, it can be suggested that a B_4-B_4 bond is less stable than a B_3-B_4 bond and that a $B_4-B_4-B_4$ bond is much less stable. Consequently, the energy of the borate units defined as, e.g., a sum of the bond energies with the neighboring units decreases in the order of increasing number of the B_4 units bonded to them. It has therefore been shown that the second boron oxide anomaly at 0.5 in x can conclusively be explained in terms of thermochemical stabilities of a series of borate units.

On the other hand, the first boron oxide anomaly has been found in the range of x from 0.2 to 0.25 . The crystals with $x > 0.2$ exhibit such particular constitutions that the crystals

have no $B_3(3B_3)$ units and every B_3 unit is bonded to one or more B_4 units. Recently Shelby [15] reported that glass transition and deformation temperatures T_g and T_d of the alkali borate glasses became maximum near 27mol% in the R_2O content. This might suggest that a similar change of network proceeds and the same borate units appear in the glasses as found in the crystals. In crystal L with $x=0.33$ (25mol% R_2O) every B_3 unit is bonded to two B_4 units. This fact indicates that the structure changes from a two dimensional and planar one to a three dimensional network one. Although no one can assure that the arrangements of the borate units in the glasses are the same as in the crystals, it is very interesting to note, for understanding the structure of the alkali borate glasses, that the fractions of particular borate units become maximum in the crystals which appear in the ranges of the first and second boron oxide anomaly, that is, from 0.2 to 0.25 and 0.5 in x , respectively, and 0.33 in x , an intermediate composition.

2.2 Elastic properties of sodium borate glasses and their structural model

In this section, based on the measured elastic constants of the sodium borate glasses, it is intended to investigate whether a particular change in the elasticity is observed in the glasses at the compositions, namely from 0.2 to 0.25, 0.33 and 0.5 in x , where characteristic arrangements of the borate

units have been found in the crystals in the previous section. Moreover, correlation between the elastic constants and N_4 of the glasses is discussed from their composition dependence. It is also intended to investigate the glass constitutions based on the bulk modulus vs. mean atom-pair volume relation.

Table 2.1. Elastic properties of the glasses in the systems $y\text{Na}_2\text{O} \cdot (1-y)\text{B}_2\text{O}_3$ and $0.05\text{MgO} \cdot y\text{Na}_2\text{O} \cdot (0.95-y)\text{B}_2\text{O}_3$.

$\text{MgO}+\text{Na}_2\text{O}/\text{B}_2\text{O}_3$	density (g/cm^3)	V_l (km/s)	V_s (km/s)	E (GPa)	G (GPa)	K (GPa)
$y\text{Na}_2\text{O} \cdot (1-y)\text{B}_2\text{O}_3$						
0.1	2.015	4.310	2.378	29.20	11.40	22.24
0.15	2.079	4.687	2.575	35.33	13.79	27.29
0.2	2.130	4.928	2.703	39.99	15.56	30.98
0.25	2.178	5.109	2.816	44.28	17.27	33.82
0.3	2.227	5.250	2.897	47.84	18.67	36.47
0.35	2.225	5.451	3.030	52.15	20.43	38.88
0.4	2.318	5.553	3.113	57.09	22.46	41.53
0.45	2.345	5.636	3.152	59.29	23.30	43.42
0.5	2.367	5.661	3.176	60.66	23.88	44.02
$0.05\text{MgO} \cdot y\text{Na}_2\text{O} \cdot (0.95-y)\text{B}_2\text{O}_3$						
0.11	1.982	4.340	2.417	29.53	11.58	21.90
0.18	2.074	4.788	2.675	37.78	14.84	27.76
0.25	2.166	5.114	2.849	44.84	17.58	33.21
0.33	2.245	5.433	3.027	52.45	20.57	38.84
0.43	2.290	5.548	3.130	56.83	22.44	40.57
0.54	2.364	5.698	3.165	60.47	23.68	45.18
0.62	2.365	5.624	3.119	58.80	23.01	44.13

2.2.1 Experimental procedures and results

The compositions of prepared glasses were $y\text{Na}_2\text{O} \cdot (1-y)\text{B}_2\text{O}_3$ ($0 < y \leq 0.33$). Reagent grade Na_2CO_3 and B_2O_3 were mixed and placed in a Pt crucible in an electric furnace. The melts were kept for 1 hr at temperatures ranging from 900 to 1000°C

depending on the composition. In order to enlarge the glass formation region, 0.05mol MgO were substituted for 0.05 mol B_2O_3 and the composition of the glasses were expressed as $0.05MgO \cdot yNa_2O \cdot (0.95-y)B_2O_3$ ($0 < y \leq 0.33$). The sodium magnesium borate glasses were prepared in the similar way. Density and elastic constants of each glass were measured using an annealed specimen. The results are shown in Table 2.1.

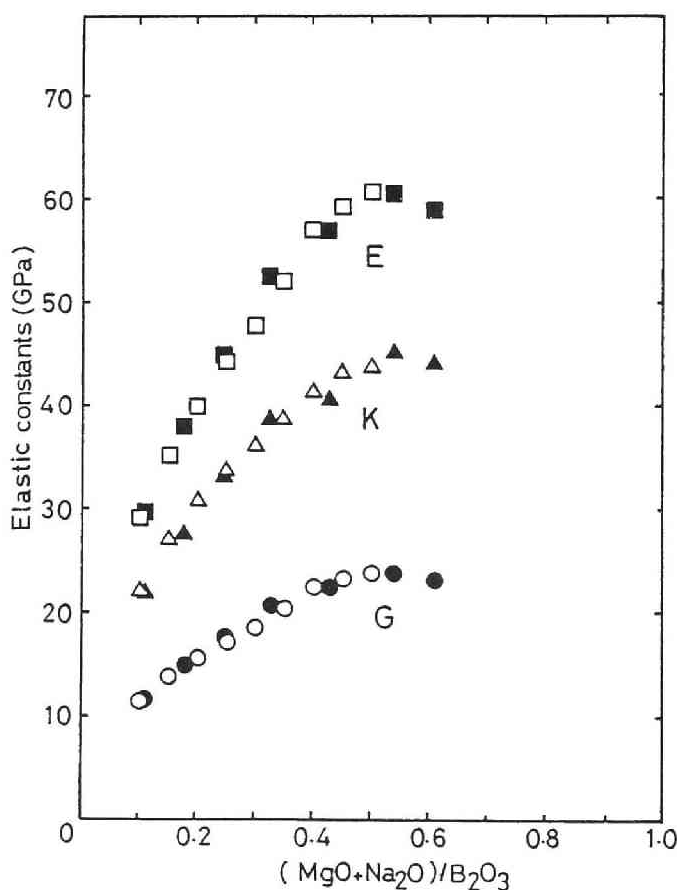


Fig. 2.4. The elastic constants of the glasses in the systems $Na_2O-B_2O_3$ (open marks) and $Na_2O-MgO-B_2O_3$ (filled marks).

2.2.2 Relation between the elastic constants and N_4

In Fig. 2.4 the elastic constants, namely, Young's modulus E , bulk modulus K and shear modulus G , of the glasses in both systems have been plotted as a function of the molar ratio $(\text{MgO}+\text{Na}_2\text{O})/\text{B}_2\text{O}_3$ (denoted as x). For the sodium borate glasses the abscissa is equivalent to the molar ratio $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$. It is clear that the elastic constants of the glasses in both systems increase smoothly with x in a concave curve in the range $x \leq 0.5$, without exhibiting any anomalous changes in the neighbor of 0.2 in x where the first boron oxide anomaly has been found for some properties. Since N_4 of the alkali borate glasses increases linearly with x in the range $x \leq 0.5$ [1], changing the glass structure to more rigid one, one can expect a close correlation between the increase in the elastic constants and that in N_4 . In order to confirm the presence of such correlation, the variation of the elastic constants of the MgO containing glasses is to be examined in the range $x > 0.5$. It can be seen in Fig. 2.4 that the elastic constants become maximum near 0.5 in x and are likely to decrease with further increase in x . Therefore, the presence of the second boron oxide anomaly is confirmed in the elastic property of the sodium borate glasses but not that of the first one. Fig. 2.5 shows a variation of N_4 for the sodium magnesium borate glasses by Kim and Bray [16], plotted as a function of x . Their compositions are equivalent to those of the present study. The cited N_4 values have been indicated by the filled circles and agree very well with N_4 values represented by the

solid line representing that the added NWM oxides are all consumed for changing the three-coordinated boron atoms to four-coordinated ones. However, measured N_4 data deviate from the solid line in the range $x > 0.5$ and indicate formations of the non-bridging oxygens. Thus, both the elastic constants and N_4 become maximum at 0.5 in x . It can therefore be concluded that the elastic constants can indicate the glass composition corresponding to the maximum N_4 and the formation of the non-bridging oxygens. Furthermore, one can suppose that the conclusion derived for the sodium borate glasses should be also valid in all other alkali borate glasses, because the dependence of N_4 on the glass composition is the same in all of the alkali borate glass systems [13].

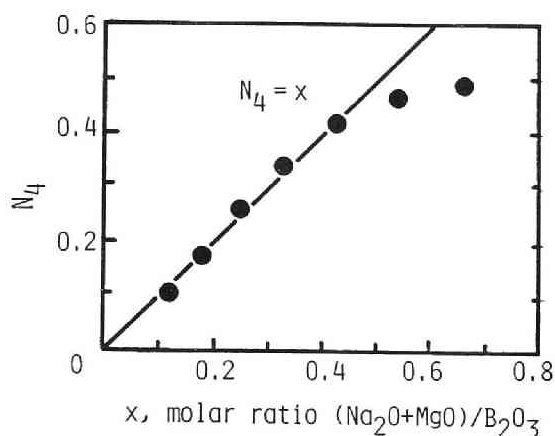


Fig. 2.5. Variation of N_4 of the glasses in the system $\text{Na}_2\text{O}-\text{MgO}-\text{B}_2\text{O}_3$. Data cited: ref. 16.

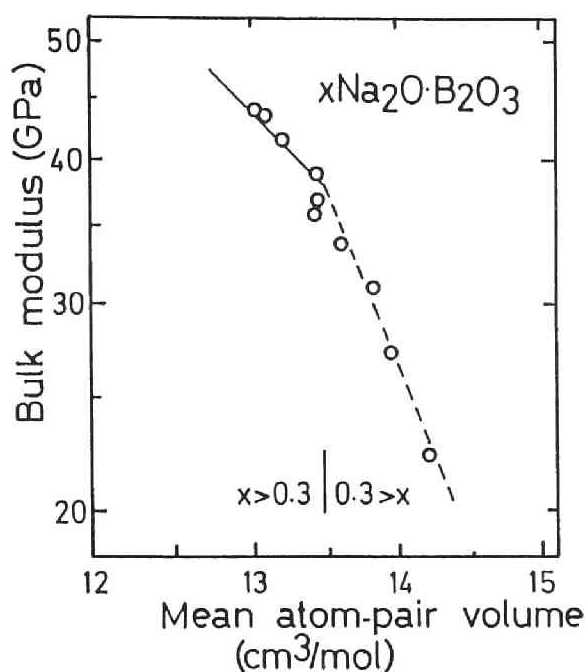


Fig. 2.6. K-V relation of the sodium borate glasses.

2.2.3 Relations between bulk modulus and mean atom-pair volume

In Fig. 2.6 the bulk moduli of the sodium borate glasses have been plotted in a log-log scale as a function of the mean atom-pair volume (K-V relation). It is seen that the data points lie on two segments of lines, showing a bending near 0.3 in x . The broken and solid line approximate the data points for the lower alkali content, $x<0.3$, and those in the higher content, $x>0.3$, respectively. Though the addition of an Na_2O molecule changes two BO_3 units to two NaBO_4 ones at any composition in the range $x\leq 0.5$ according to the N_4

measurements [13], the presence of the bending at 0.3 in x shows that the structural change other than found near 0.5 in x takes place there. The slope of the solid line is -4 in the range $x > 0.3$, and the increase in the bulk modulus can be attributed to an effect of the sodium ions filling the voids in the glasses according to the theory of the K-V relation. On the other hand, the broken line is inclined more steeply than the solid line. Thus the network of the glasses in the range $x < 0.3$ is considered to be strengthened substantially than that of B_2O_3 glass because a three dimensional linking is being prevailed in the structure due to an increase in the amount of four-coordinated boron atoms. Such a change in the glass structure significantly affects the elasticity. Moreover, the particular arrangements of the borate units like those in crystal L are supposedly formed in the glasses with the composition corresponding to the bending. If one could assume the composition of the bending to be 0.33 in x , it must be noted, as has been pointed out previously, that every BO_3 unit is bonded to two RBO_4 units and no BO_3 units other than $B_3(B_3, 2B_4)$ ones are present in the borate crystal L with $x = 0.33$. Although the total amount of four- and three-coordinated boron atoms has been studied extensively in boron oxide containing glasses, no informations have been obtained on the arrangements of the borate units: how many BO_3 and RBO_4 units are bonded to the individual borate unit. There are no ways other than to suppose their arrangements in the glasses. However, due to N_4 vs. x relation in Fig. 2.3, the "particular arrangements of the borate units" might be

attained in the glasses as in the crystals and every B_3 unit has three B_4 units in the neighborhood. If the presence of such arrangements are taken for granted in the glasses, it could be derived that the strength and rigidity of the network structure of alkali borate glasses become "saturated" at about 0.3 in x . That is, the variation of the structure from two dimensional to three dimensional one may proceed in the glasses where the planar borate groups are interlinked by the B_4 units. After that composition, 0.3 in x , the effect of alkali ions filling the voids in the glass becomes predominant since the strength of the glass skeleton has already been saturated, and the bulk modulus increases in proportion to $v^{-4/3}$.

2.3 Summary

Based on an assumption that the arrangements of the borate units in the glasses, that is, the kind and number of BO_3 and RBO_4 units in the first neighbor of a relevant B_3 or B_4 unit, are similar to those in the crystals, the arrangements of the borate units are studied in several alkali borate crystals as an aid to interpret the boron oxide anomaly. It has been shown that the fractions of $B_3(2B_3, B_4)$ units, $B_4(4B_3)$ and $B_3(B_3, 2B_4)$ units, and $B_4(3B_3, B_4)$ unit are maximum in the borate crystals with $x=0.2$, 0.33 and 0.5, respectively, where x denotes the molar ratio R_2O/B_2O_3 . The elastic constants of the glasses in the systems $Na_2O-B_2O_3$ and $Na_2O-MgO-B_2O_3$ increase smoothly with

x and become maximum at the composition corresponding to 0.5 in the molar ratio $(\text{Na}_2\text{O}+\text{MgO})/\text{B}_2\text{O}_3$, where the fraction of four-coordinated boron atoms is maximum. This shows that the first boron oxide anomaly cannot be detected near 0.2 in x but the second is observed and that the elastic constants can indicate the formation of the non-bridging oxygens. The relation of bulk modulus vs. mean atom-pair volume (K-V relation) for the sodium borate glasses can be well represented by two segments of lines, showing a bending at 0.3 in x. The slope of the line representing the plots for the glasses in the range $x > 0.3$ is found -4. Based on the variation of the fraction of the borate units such as B_3 ($2\text{B}_3, \text{B}_4$) and B_4 (4B_3) units as functions of the composition in the borate crystals, the K-V relation for the sodium borate glasses is correlated with the fact that the BO_3 units in the glasses in the range $x > 0.3$ are all bonded with two RBO_4 units or more.

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Chapter 3

NETWORK STRUCTURE OF ALKALI GERMANATE GLASSES

It is known that oxygen coordination number CN of Ge atoms changes from 4 to 6 when alkali oxides are added to GeO_2 glass [1-6]. This causes the germanate anomaly, that is, the non-linear change of properties with the alkali oxide content. However, the germanate anomaly has not thoroughly been clarified yet; the dependence of the fraction N_6 of GeO_6 units on the alkali content and maximum value of N_6 for each alkali germanate system are still open to question. As in the alkali borate glasses discussed in the preceeding sections, the non-bridging bonds Ge-OR are created when alkalis are added beyond the composition corresponding to maximum N_6 . It is expected that such structural change is accompanied by a higher increasing rate of molar volume and a decrease in elasticity with the addition of alkali oxide. Therefore, it is very useful to examine variations of the molar volume and elastic properties, in order to discuss the network structure and the arrangements of the GeO_6 units in the alkali germanate glasses.

First, the dependences of N_6 and the molar volume of the alkali germanate crystals will be described. On this basis, the variations of the molar volume and elastic constant of glasses will be discussed to derive the N_6 vs. x relation and a tentative structure model for the glasses.

3.1 Arrangements and fractions of GeO_4 and GeO_6 units in germanate crystals

3.1.1. Composition dependence of N_6 in germanate crystals

Let $R(m:n)$ represent a crystal $mR_2O \cdot n\text{GeO}_2$. The phase diagrams of the systems $R_2O\text{-GeO}_2$ ($R=\text{Li, Na and K}$) show the presence of a number of stable and metastable crystals [7]. There are some crystals with known structure other than those appearing in the phase diagrams. The fraction N_6 of GeO_6 units to the total amount of Ge atoms has been obtained for all of the crystals with known structure and plotted in Fig. 3.1 as a function of the molar ratio R_2O/GeO_2 ($=m/n=x$). The N_6 vs. x relation can be represented by several segments of lines, showing bendings at $2/9$, $1/4$ and $1/2$ in x . Consider the relation separately in the range of lower and higher alkali content. In the range of lower alkali content ($x \leq 1/4$), the N_6 vs. x relation is represented by two lines, hence the crystals can be grouped into two types; one can be denoted as 1:4-type crystals and the other as 2:9-type ones with employing the ratios $R_2O:\text{GeO}_2$ corresponding to the maximum values of N_6 . $\text{Li}(1:9)$, $\text{Li}(2:9)$ and $R(1:4)$ ($R=\text{Li, Na and K}$) are 1:4-type crystals, and $\text{K}(1:8)$ and $R(2:9)$ ($R=\text{Na and K}$) are 2:9-type ones. Here, $\text{K}(1:8)$ contains GeO_5 units with the fraction $N_5=1/4$ so that it is one of the 2:9-type crystals. Moreover, N_6 for the crystals of both types decreases to null at 1.0 in x in case a), and at 0.5 in x in case b). The composition

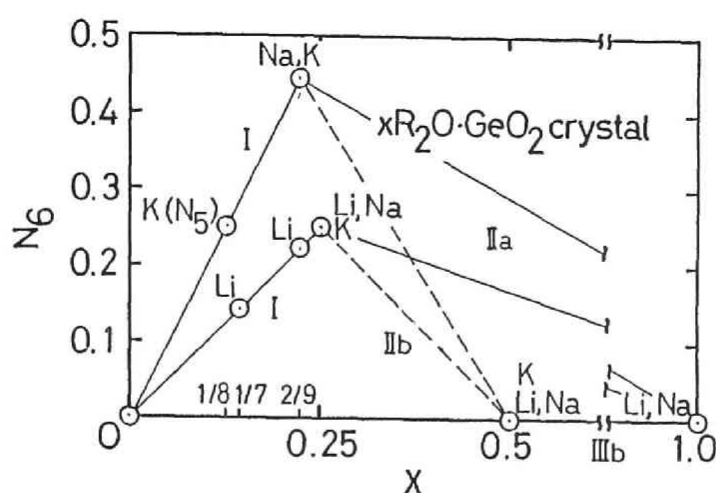


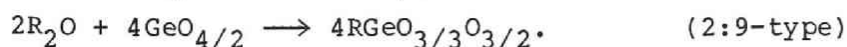
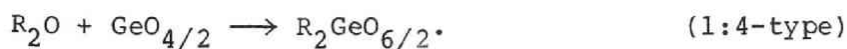
Fig. 3.1. Variation of N_6 of the alkali germanate crystals as a function of the molar ratio $x = R_2O/GeO_2$.

dependence of N_6 for respective case has been represented by the solid and broken lines in Fig. 3.1. Therefore, the whole composition range can be divided by the bendings at $2/9$, $1/4$ and $1/2$ in x into two or three ranges; I and IIa for case a), and I, IIb and IIIb for case b). Linear equation representing N_6 vs. x relation in each range has been shown in Table 3.1.

The formation reaction of the germanate units in these ranges will be described in the following paragraphs.

(1) In range I

N_6 increases with increase in x due to the following reactions,

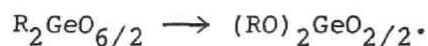


The network of the crystals consists only of the bridging

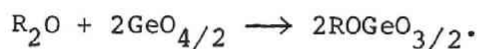
bonds in range I.

(2) In 1:4-type crystals in ranges II and III

In range IIa ($0.25 < x < 1.0$), the system is a mixture of R(1:4) and R(1:1). The GeO_6 units are decomposed according to the reaction,



Since Table 3.1 shows a rate of the decomposition to be 1/3 at addition of 1 mol R_2O , the decomposition reaction occurs at every three ordinary formation reactions of the non-bridging bond,



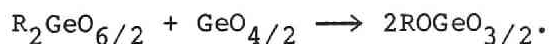
Thus created $\text{ROGeO}_{3/2}$ units will successively be decomposed to $(\text{RO})_2\text{GeO}_{2/2}$ units.

Table 3.1. N_6 vs. x relation of the alkali germanate crystals.

crystal	range I	range IIa, IIb	range IIIb
1:4 type	$N_6 = x$ $0 \leq x \leq 1/4$	a] $N_6 = -1/3(x-1)$ $1/4 \leq x \leq 1$	
		b] $N_6 = -x + 1/2$ $1/4 \leq x \leq 1/2$	$N_6 = 0$ $1/2 \leq x$
2:9 type	$N_6 = 2x$ $0 \leq x \leq 2/9$	a] $N_6 = -4/7(x-1)$ $2/9 \leq x \leq 1$	
		b] $N_6 = -4/5(2x-1)$ $2/9 \leq x \leq 1/2$	$N_6 = 0$ $1/2 \leq x$



In range IIb ($0.25 < x < 0.5$) the system is the mixture of R(1:4) and R(1:2). Then the decomposition reaction of the GeO_6 unit is



This reaction is accompanied by each ordinary formation reaction of the non-bridging bonds. That is, it is indicated that the decomposition of the GeO_6 unit occurs with consuming a $GeO_{4/2}$ one in range IIb. Thus created $ROGeO_{3/2}$ units will be changed to $(RO)_2GeO_{2/2}$ units subsequently in range IIIb ($0.5 < x < 1.0$).

(3) In 2:9-type crystals in ranges II and III

On the other hand, an R(2:9) crystal consists of the GeO_4 and $R_4Ge_4O_{10}$ groups which are composed by four $RGeO_{3/3}O_{3/2}$ units. The germanate groups are decomposed into four $ROGeO_{3/2}$ units.



The other reactions for the 2:9-type crystals are similar to those for the 1:4-type crystals in the corresponding ranges.

It is indicated that the decomposition of the GeO_6 units into $ROGeO_3$ and $(RO)_2GeO_2$ ones and the interruption of the $O_3Ge-O-GeO_3$ bridging bonds to create Ge-OR non-bridging ones take place simultaneously in ranges IIa and IIb. However, in range IIIb no GeO_6 units are left, and $ROGeO_3$ and $(RO)_2GeO_2$ will be found. Those reactions can be assumed to occur in the glasses.

The reaction of the germanate units and the variation of N_6 of the crystals are summarized followingly.

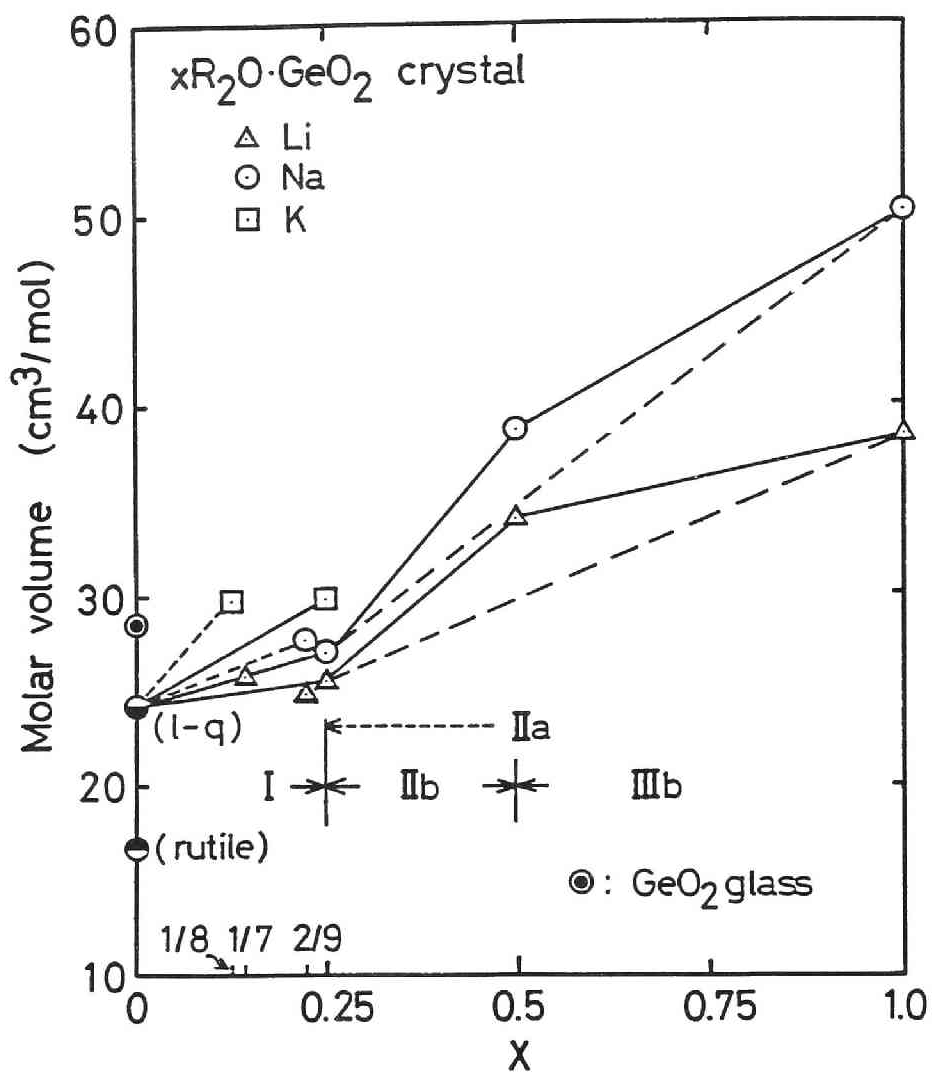


Fig. 3.2. Variation of the molar volume of the alkali germanate crystals. (l-q) and (rutile) represent low-quartz and rutile form of GeO_2 (ref. 7).

- (1) The network of the germanate crystals in range I is built only by the bridging bonds. N_6 increases with x according to either of the two equations, $N_6=x$ and $N_6=2x$, depending on crystal type, 1:4 and 2:9, respectively.
- (2) In ranges IIa and IIb the decomposition of the GeO_6 units and interruption of the bridging bonds occur simultaneously. The rate of the decrease in N_6 is smaller in range IIa than in IIb.
- (3) In case b), the GeO_6 units are thoroughly decomposed by the end of range IIb. The non-bridging bonds are created by the interruption of the bridging bonds.

3.1.2. Composition dependence of the molar volume of the germanate crystals

Fig. 3.2 represents the molar volume of the alkali germanate crystals [28], plotted as a function of x . The variation of the volume can be represented by several segments of lines, showing bendings. The solid and broken lines in range I represent the molar volume vs. x relations for the crystals of 1:4- and 2:9-type, respectively. In ranges II and III, the dependence of the molar volume on x is indicated only for the 1:4-type crystals in cases a) and b), and represented by the broken and solid lines, respectively. For 2:9-type crystals, the dependence can be represented by the lines tying $\text{Na}(2:9)\text{-Na}(1:2)$, $\text{Na}(2:9)\text{-Na}(1:1)$, etc. It is clear that the compositions corresponding to the bendings in the molar volume vs. x relation are identical with those found in

N_6 vs. x relation. Further, compare the rate of increase in the volumes, indicated by the slope of the lines, in ranges I, IIb and IIIb for 1:4-type crystals. The rate is in the order of range $I < IIIb < IIb$. From the N_6 vs. x relation this fact indicates that the rate of increase in the molar volume is dependent upon the number of the mechanisms responsible for the creation of non-bridging oxygens. That is, none are present in range I, while one and two mechanisms are effective in ranges IIIb and IIb, respectively. Therefore, the role of the alkali oxides changes at the composition corresponding to the bending. Such correlation between the composition dependences of N_6 and molar volume in the crystals will be applied to investigate the constitution of the glasses.

3.2 Elastic properties and structure of alkali germanate glasses

3.2.1 Experimental procedures and results

Reagent grade R_2CO_3 ($R=Na$ and K) and 4N-grade GeO_2 were weighed to produce 30g glass. The batches were melted in a Pt crucible placed in an electric furnace at temperatures ranging from 1000 to 1500°C, depending on the composition. The glass composition was expressed as $xR_2O \cdot GeO_2$ where x was varied from 0 to 0.6. The melts were poured into a graphite mold of 1.5x1.5x1.5cm in size to obtain quenched glass blocks. Density and elastic constants were measured for annealed samples.

Table 3.2. Densities and elastic constants of the sodium germanate glasses. Data cited: a: ref. 12, b: ref. 11, c: ref. 10, d: ref. 8, e: ref. 5.

$x\text{Na}_2\text{O} \cdot \text{GeO}_2$ x	Density g/cm^3	Elastic constants (GPa)			
		G	K	E	
0.0	3.66 a	18.10	23.87	43.33	a
0.020	(3.745)	20	29	49	b
0.031	3.80 c				
0.034	3.799 d				
0.042	(3.825)	23	30	55	b
0.053	(3.860)	20.56	30.69	50.42	a
0.058	3.87 c				
0.064	(3.890)	23	37	57	b
0.075	3.91 c				
0.087	(3.945)	27	35	63	b
0.111	4.00 c	27	39	67	b
0.111	3.972 e				
0.127	4.032 d				
0.136	(4.045)	30	39	71	b
0.143	4.05 c	26.22	42.01	65.12	a
0.163	(4.058)	29	51	74	b
0.176	4.06 c				
0.186	4.057 d				
0.190	(4.057)	27	52	70	b
0.205	4.05 c				
0.217	4.022 d				
0.220	(4.033)	29	49	73	b
0.250	4.00 c	27	50	70	b
0.250	3.977 e	26.87	44.93	67.22	a
0.282	3.95 c				
0.297	3.914 d				
0.333	(3.872)	24.67	42.11	61.91	a
0.351	(3.845)	26	43	65	b
0.370	3.82 c				
0.370	3.815 d				
0.389	(3.780)	25	42	62	b
0.414	3.684 d				
0.429	3.751 e	25	40	60	b
0.429	3.751 e	21.85	39.28	55.29	b
0.449	3.662 d				
0.504	3.574 d				
0.538	3.540 e				
0.563	3.501 d				
0.65	3.375 *				

* $0.65\text{Na}_2\text{O} \cdot \text{GeO}_2 \cdot 0.02\text{SiO}_2$

Table 3.3. Densities and elastic constants of the potassium germanate glasses. Data cited: a: ref. 9, b: this work, c: ref. 5.

$xK_2O \cdot GeO_2$ x	Density g/cm^3	Elastic constants(GPa)		
		G	K	E
0.022	3.707 a			
0.046	3.803 a			
0.064	3.842 b	21.57	35.15	53.72 b
0.071	3.842 a			
0.096	3.874 a			
0.099	3.866 b	22.40	38.03	56.17 b
0.111	3.866 c			
0.122	3.874 a			
0.124	3.881 b	23.32	40.45	58.69 b
0.149	3.872 b	22.74	42.06	57.80 b
0.176	3.849 b	22.95	40.45	57.89 b
0.176	3.841 c			
0.196	3.810 a			
0.250	3.725 b	19.98	20.39	45.19 b
0.250	3.706 c			
0.277	3.676 a			
0.333	3.595 c			
0.346	3.611 a			
0.370	3.483 a			
0.418	3.471 a			
0.429	3.360 c			
0.515	3.325 a			
0.613	3.223 a			
0.745	3.143 a			

Density data of the alkali germanate glasses have been reported by Murthy and Aguayo [8], Murthy et al. [9], Minami et al. [10] and Sakka and Kamiya [5]. The elasticity data of the sodium glasses have been reported by Shaw [11] and Hanada et al. [12], whereas no elasticity data have been given for the potassium germanate glasses. Therefore, density and elastic constants of the potassium glasses are measured. All of the data are shown in Tables 3.2 and 3.3.

3.2.2 Network structure of alkali germanate glasses

The molar volumes of alkali germanate glasses are plotted as a function of x in Fig. 3.3. A sodium glass with $x=0.65$, indicated by a filled circle, contains 0.02mol% SiO_2 . The molar volume vs. x relation for each series of glasses can be approximated by two segments of lines, showing a bending at 0.18 in x in the sodium glasses and 0.16 in x in the potassium ones. As in the crystals, the bendings divide the whole composition range into two ranges, I and II. They are $0 < x < 0.18$ (range I) and $x > 0.18$ (II) for the sodium glasses, and $0 < x < 0.16$ (I) and $x > 0.16$ (II) for the potassium ones. It should be noted that the molar volume of the sodium glasses remains constant in range I, while that of the potassium glasses increases. Moreover, it is important that the rate of increase in the molar volume is larger in range II than in range I for both glasses. Those characteristic variation of the molar volume of the glasses is extremely similar to that found for the crystals, except for the absence of the bending at 0.5 in x .

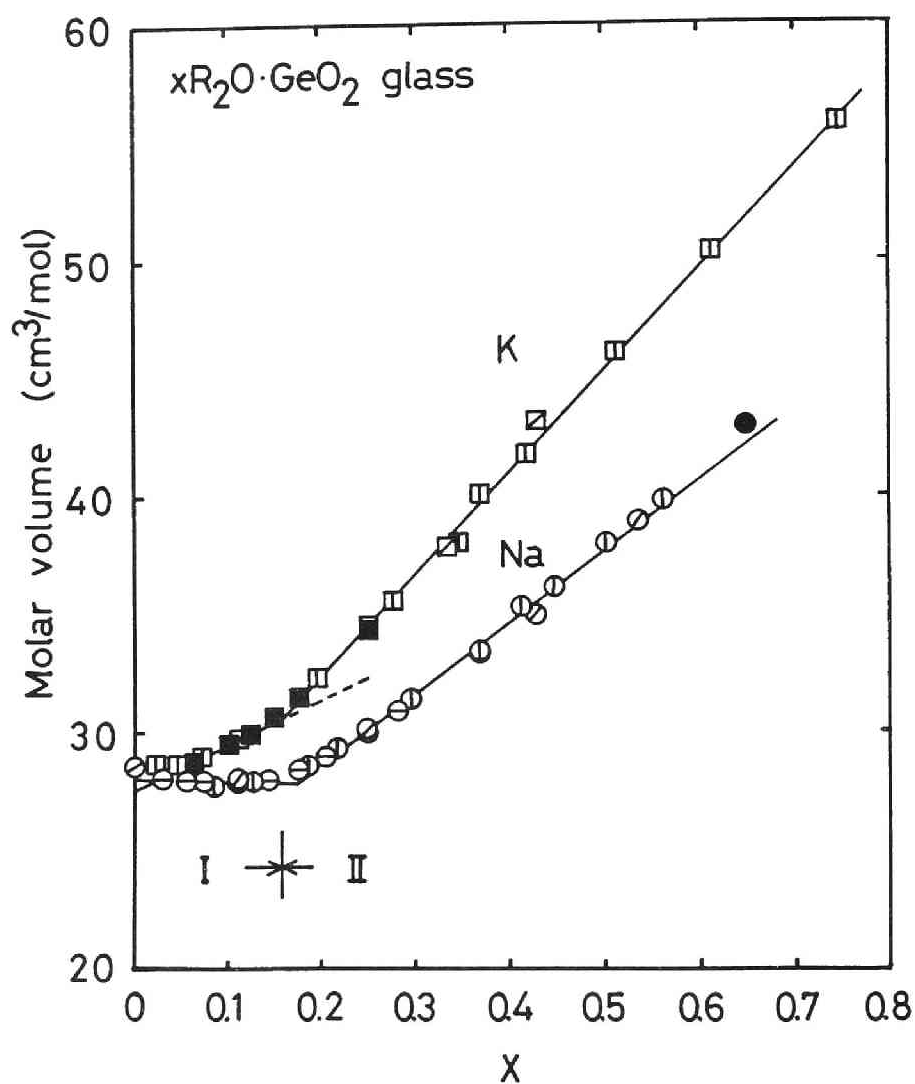


Fig. 3.3. Variation of the molar volume of the alkali germanate glasses. Data cited; $\circ, \square$: ref. 8; $\circ, \square$: ref. 10; $\circ, \square$: ref. 5; $\bullet, \blacksquare$: this work.

On the basis of the correlation between N_6 and molar volume, it is suggested that N_6 of the glasses increases in range I and decreases in range II. It is very probable that the GeO_6 units are left undecomposed to considerable extent in range II. This can be seen from the absence of any bendings in range II. This indicates that the decomposition of the GeO_6 units and formation reaction of the non-bridging bond proceed simultaneously as found in the crystals in range IIa or IIb.

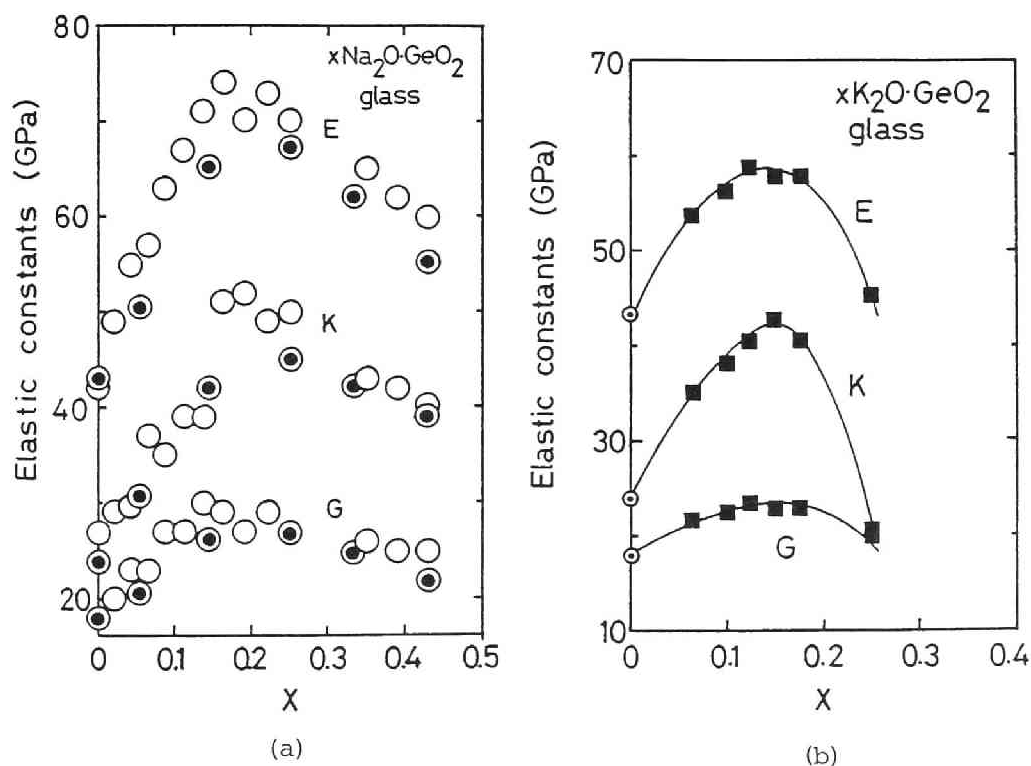


Fig. 3.4. Variation of elastic constants of the alkali germanate glasses. Data cited; O: ref. 11; $\odot$: ref. 12; $\blacksquare$: this work.

Fig. 3.4 (a) and (b) represent variation of the elastic constants, E , K and G of the sodium germanate glasses cited from [11,12] and the potassium glasses from the present study. It is clear that the elastic constants become maximum at the composition corresponding to the bending found in the molar volume vs. x relation. In the previous section (2.2), it has been confirmed in the alkali borate glasses that the elastic constants and N_4 should be maximum where the formation of the non-bridging oxygen starts. In the germanate glasses, the non-bridging oxygens will also be formed at the composition corresponding to the maximum N_6 . Thus, the dependence of the molar volume and elastic constants upon glass composition can derive that N_6 becomes maximum at 0.18 and 0.16 in x in the sodium and potassium germanate glasses, respectively. It has already been pointed out that the non-bridging oxygens are created with and without being accompanied by decomposition of the GeO_6 units. As will be described in Chap. 4, the elastic constants do not decrease remarkably in alkali borosilicate glasses when the non-bridging oxygens are formed without loss of the BO_4 units. On the other hand, the elastic constants of the alkali germanate glasses have decreased considerably after the maxima. Thus it is suggested that the non-bridging oxygens are created by the interruption of Ge-O-Ge bridging bonds and decomposition of the GeO_6 units. Moreover, the rate of decomposition in the sodium and potassium glasses is constant throughout range II, since the composition dependence of the molar volume can be approximated by the linear equation of x for each series of glasses in Fig. 3.3.

Fig. 3.5 represents the bulk modulus vs. mean atom-pair volume relation (K-V relation) for the alkali germanate glasses, where the data for the sodium borate glasses are also shown as the reference. The plots for the sodium germanate glasses in range II, indicated by the filled circles, are approximated by the broken line. The K-V relation of the sodium glasses in range I including GeO_2 glass can be well represented by the solid line of slope -4. On this basis, the structure of the sodium glasses can be derived; the arrangements of oxygens are not so much modified from those in GeO_2 glass by the formation of the GeO_6 units, and the sodium ions occupy the voids of the glass network built by GeO_4 and GeO_6 units. As the results, the following network structure might be unfavorable, such as that of $\text{Na}(2:9)$ and $\text{K}(1:8)$ crystals. In the former the GeO_4 and GeO_6 are aggregated with sharing the edges of the tetrahedra and octahedra. The structure requires modification of oxygen arrangements from those of GeO_2 glass to a greater extent. In the latter crystal the network is composed by sharing edges of the GeO_5 units. These atomic groups violate the Zachariasen's rules on glass formation. On this basis, it is suggested that N_6 in the sodium germanate glasses varies according to $N_6=x$ in range I as that in 1:4-type crystals. This agrees well with the results of Ueno et al. [6]. In Fig. 3.5 the plots for the potassium glasses cannot be approximated by the line of slope -4. It shows that the potassium ions enlarge the germanate skeleton and occupy the voids in it. However, on the analogy on the borate glasses, one might consider that potassium oxide

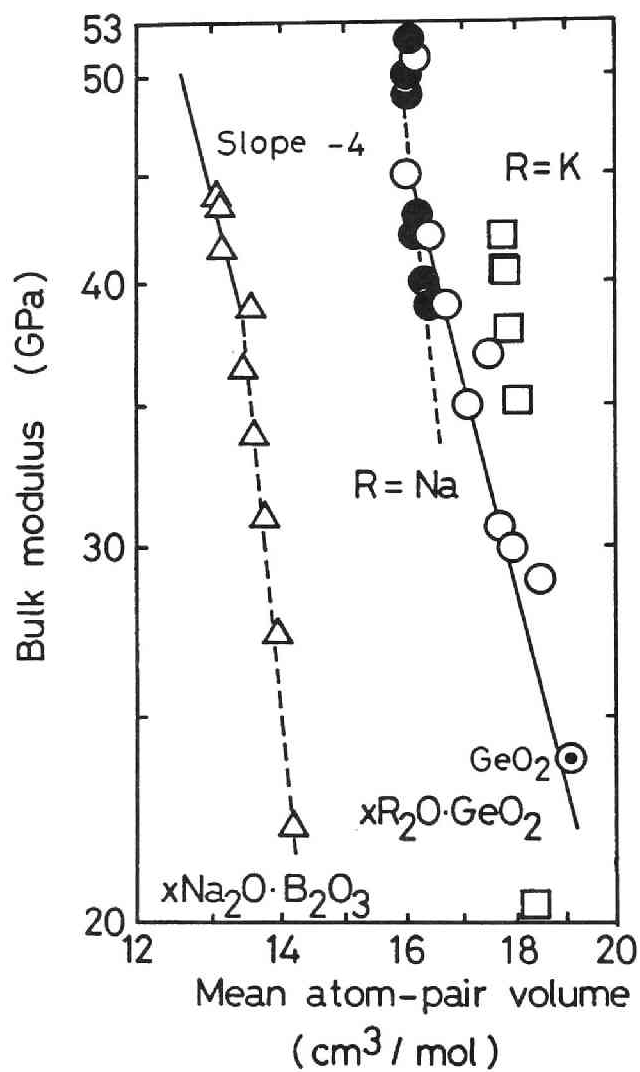


Fig. 3.5. K-V relation of the sodium ($\circ, \bullet$) and potassium ($\square$) germanate glasses. That of the sodium borate glasses (Δ) is also shown for comparison.

Table 3.4. Estimated N_6 vs. x relations in the alkali germanate glasses, assuming $N_6=0$ at 1.0 in x .

	range I	range II
Na	$N_6=x$ ($0 < x < 0.18$)	$N_6=-0.22(x-1)$ ($0.18 < x < 1$)
K	$N_6=x$ ($0 < x < 0.16$)	$N_6=-0.19(x-1)$ ($0.16 < x < 1$)

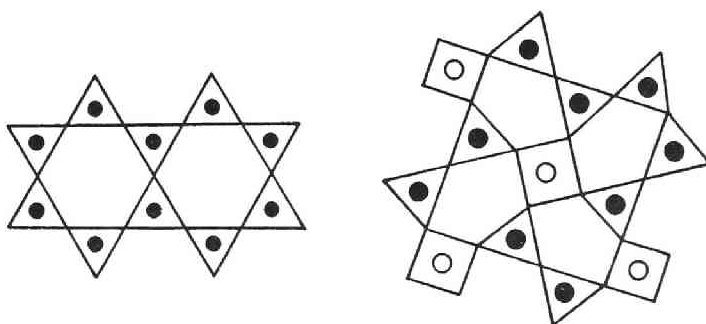


Fig. 3.6. Two dimensional model of (a) GeO_2 and (b) an alkali germanate glass in range I. The triangles and squares represent 4- and 6-coordinated Ge atoms.

plays the same role as sodium oxide. Therefore, N_6 of the sodium and potassium germanate glasses varies as that of 1:4-type crystals in range I. It can also be assumed that N_6 decreases in range II and becomes null at 1.0 in x as the crystals in case a). Consequently, N_6 vs. x relation in the glasses can be described in each range as shown in Table 3.4. Moreover, due to the previous estimation that the oxygen arrangements are not much modified from that of GeO_2 glass, a structure model can be proposed for the sodium germanate glasses where the GeO_4 units in six-membered rings of silica type are partly substituted by the GeO_6 units, giving rise to a structure like that of $\text{Li}(1:4)$ [7c]. This model might be preferred to the other one where the GeO_4 units are in three-membered rings of $[\text{Ge}_3\text{O}_9]$ type with linked by the GeO_6 units, as found in $\text{K}(1:4)$ crystal [7k]. Fig. 3.6 represents a two dimensional structure model of the alkali germanate glasses in range I. The tetrahedra represented by the triangles are rearranged from a hexagonal configuration to somewhat distorted one and the octahedra are represented by the squares. The alkali ions (not shown) are located in the open spaces.

3.3 Summary

The relations of the molar volume and the fraction N_6 of six-coordinated Ge atoms on the composition have been examined for the alkali germanate crystals. It has been shown that N_6

and molar volume of the crystal exhibit complicated dependence on the molar ratio $R_2O/GeO_2=x$. The dependence can be represented by several segments of lines showing bendings at $2/9$, $1/4$ and $1/2$ in x . The molar volume of the sodium and potassium germanate glasses has also been investigated as a function of the composition. The molar volume of the sodium glasses is independent of the alkali content in the range $x<0.18$ and increases linearly with x in the range $x>0.18$. The molar volume of the potassium glasses, however, increases gradually and linearly up to 0.16 in x , and does rapidly in the range $x>0.16$. The elastic constants of the glasses become maximum at 0.18 and 0.16 in x for the sodium and potassium glasses, respectively. On this basis the composition dependence of N_6 and the network model have been derived for the alkali germanate glasses.

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Chapter 4

NETWORK STRUCTURE OF ALKALI BOROSILICATE GLASSES

In the preceding three chapters on $R_2O-B_2O_3$, R_2O-SiO_2 and R_2O-GeO_2 glasses, it has been shown that each NWF oxide constructs a characteristic network. When two of the four NWF oxides, namely, B_2O_3 , SiO_2 , P_2O_5 and GeO_2 are present simultaneously in a glass, they will interact with each other and form new specific structures which cannot be found in the binary glasses.

In the following three chapters, the structure of glasses in the systems $R_2O-B_2O_3-SiO_2$, $R_2O-GeO_2-SiO_2$ and $R_2O-B_2O_3-P_2O_5$ will be discussed.

The network structure of the glasses in the systems $R_2O-B_2O_3-SiO_2$ ($R=Na$ and K) will be discussed in this chapter. The role of the alkali oxides and the change in CN of B atoms are stressed. The structure and property of the borosilicate glasses are characterized from those of the borate and silicate ones.

4.1 Molar volume of alkali borosilicate glasses and coordination number of B atoms

In this section, the variations of the molar volume and optical absorption spectra of Ni^{2+} ions are investigated in borate, silicate and borosilicate glasses as functions of

composition. On this basis, the behavior of the boron atoms and alkali ions will be discussed.

4.1.1. Experimental procedures and results

Compositions of the sodium and potassium borosilicate glasses prepared here were expressed as $xR_2O \cdot B_2O_3 \cdot rSiO_2$. The parameters x and r represented the molar ratios R_2O/B_2O_3 and SiO_2/B_2O_3 , respectively, where x was varied from 0.01 to 2.0 and r was 1 or 2. The series of glasses with $r=1$ were referred to as series A and those with $r=2$ as series B. Reagent grade R_2CO_3 ($R=Na$ and K), B_2O_3 and silica sand were mixed together. The batches were placed in a Pt crucible and melted in an electric furnace at temperatures ranging from 1100 to 1450°C depending on the glass composition. The homogenized melts were cast into a graphite mold of 1.5x1.5x1.5 cm in size. The sodium glasses of series B containing 0.03 mol NiO per litre of glass were also prepared.

The compositions of some glasses were located in the immiscible region in the sodium [1a] and potassium [1b] borosilicate systems, as shown in Fig. 4.1. In order to determine the temperature for annealing the glasses without causing phase separation, the deformation temperature T_d and the glass transition temperature T_g were measured for all glasses. T_d and T_g of the sodium glasses of series B were shown as the example together with the immiscible region [1a] in Fig. 4.2. Phase separation was checked by taking replicated electron micrographs of glass samples below the immiscible

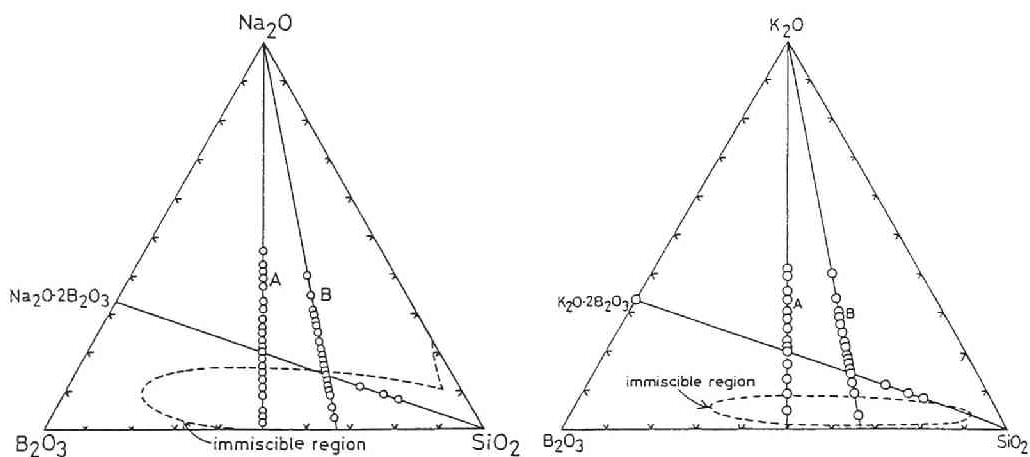


Fig. 4.1. Compositions of the alkali borosilicate glasses prepared are indicated by the open circles. The immiscible regions are enclosed by the broken lines.

region heated for about five days. No phase-separated particles could be detected except in glass in the range $x < 0.1$. Preliminary studies on phase separation [2] of $9.5\text{Na}_2\text{O} \cdot 30.5\text{B}_2\text{O}_3 \cdot 60.0\text{SiO}_2$ (wt%) glass revealed that the particles grew with time but the total volume fraction of phase separated particles remained constant. Utsumi et al. [3] reported similar results on $2\text{Li}_2\text{O} \cdot 33\text{B}_2\text{O}_3 \cdot 65\text{SiO}_2$ (wt%) glass. Therefore, the fact that no particles were detected after an elongated heat treatment could be interpreted as indicating that no phase separation would occur on heating at the temperatures indicated in Fig. 4.2. Similar results were also obtained for other series of glasses. Thus it was confirmed that all of the glasses prepared here were

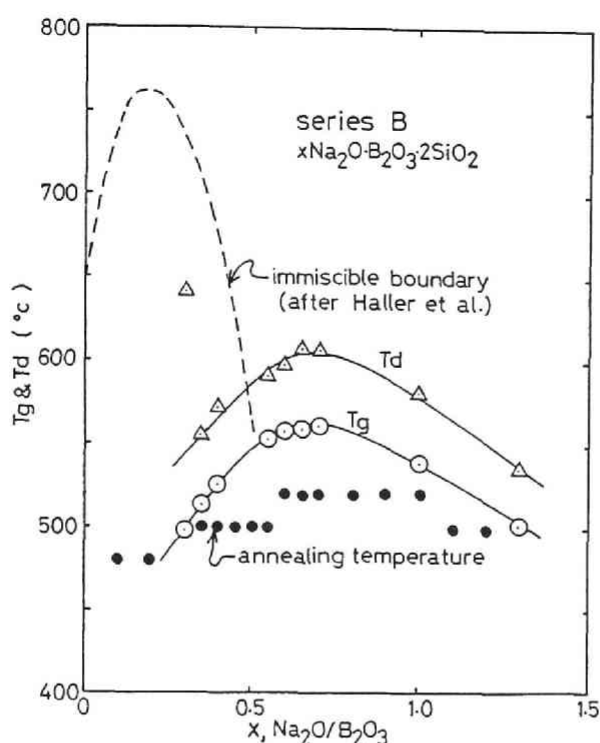


Fig. 4.2. Annealing temperature of the sodium borosilicate glasses of series B.

homogeneous. The volume of a glass containing one formula-weight of $x\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ was defined as its molar volume. The density and molar volume data of the borosilicate glasses were shown in Table 4.1.

4.1.2 Dependence of molar volume on composition

The molar volumes of the sodium and potassium borosilicate glasses of series A have been plotted in Fig. 4.3(a) as a function of the molar ratio $\text{R}_2\text{O}/\text{B}_2\text{O}_3 = x$. The plots for series B

Table 4.1. Densities and molar volumes of the alkali borosilicate glasses, $xR_2O \cdot B_2O_3 \cdot rSiO_2$.

x	d (g/cm ³)	V (cm ³ /mol)	x	d (g/cm ³)	V (cm ³ /mol)
Series A, R=Na			Series A, R=K		
0.04	2.018	65.51	0.1	2.041	68.20
0.07	2.045	65.55	0.2	2.160	68.76
0.105	2.080	65.49	0.3	2.236	70.64
0.2	2.161	65.79	0.4	2.302	72.71
0.25	2.212	65.54	0.5	2.345	73.69
0.3	2.261	65.56	0.6	2.389	77.95
0.35	2.311	65.51	0.7	2.431	80.48
0.4	2.350	65.74	0.8	2.423	84.63
0.45	2.389	65.97	1.0	2.434	91.99
0.5	2.429	66.16	1.1	2.406	91.97
0.55	2.449	66.88			
0.6	2.480	67.30			
0.7	2.499	69.26			
0.8	2.516	71.43			
0.9	2.518	73.63			
1.0	2.536	75.61			
1.2	2.561	79.71			
1.3	2.560	82.14			
1.5	2.481	88.60			
Series B, R=Na			Series B, R=K		
0.1	2.098	93.42	0.3	2.192	98.32
0.2	2.147	94.17	0.4	2.290	99.36
0.3	2.237	93.15	0.5	2.324	101.54
0.35	2.284	92.59	0.55	2.362	102.31
0.4	2.308	92.97	0.6	2.416	101.94
0.45	2.366	92.01	0.65	2.427	103.44
0.5	2.396	92.17	0.7	2.445	104.62
0.55	2.430	92.13	0.8	2.460	107.80
0.6	2.450	92.65	0.9	2.473	111.05
0.65	2.471	93.11	1.0	2.483	114.40
0.7	2.480	94.02	1.1	2.477	118.48
0.8	2.507	95.48	1.25	2.468	124.62
0.9	2.517	97.57	1.3	2.465	126.70
1.0	2.530	99.52	1.5	2.484	133.29
1.1	2.518	102.45	2.0	2.426	155.91
1.2	2.521	104.79			
1.3	2.526	107.03			
1.35	2.503	109.24			
1.62	2.526	114.89			
2.0	2.542	123.44			

are shown in Fig. 4.3(b). Dependence of the molar volume upon x can be summarized as follows.

- (1) The molar volume vs. x relations can be approximated by segments of lines, assuming the additivity.
- (2) Two bending points are found; one at 0.55 in x and the other at 0.8 in x for series A, and one at 0.6 in x and the other at 0.9 in x for series B. These values of x are almost identical in sodium and potassium glasses.

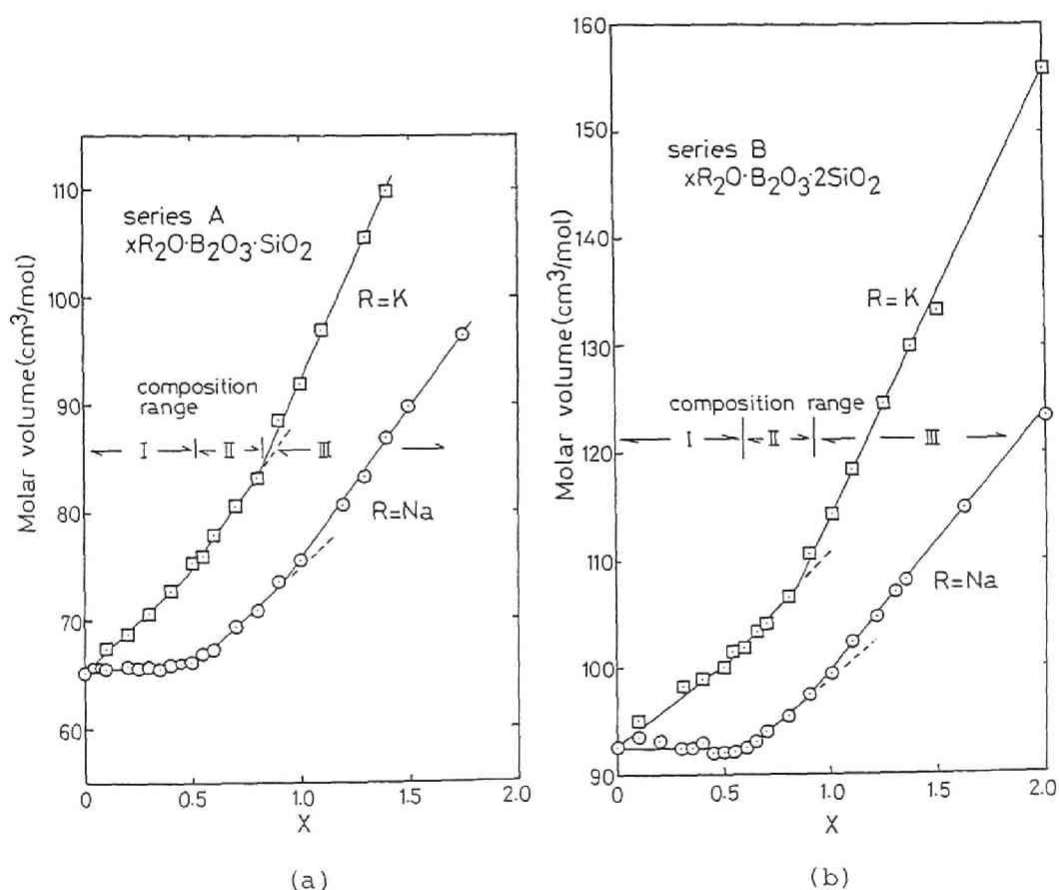


Fig. 4.3. Variation of the molar volume of the alkali borosilicate glasses. (a) series A, (b) series B.

- (3) The whole composition range is divided by those bending points into three ranges, I, II and III in the order of increasing x as indicated in the figures.
- (4) In range I the molar volumes of the sodium glasses of series A and B remain constant, being independent upon the Na_2O content.

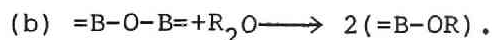
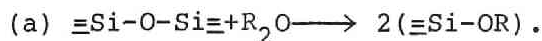
It has already been shown in alkali borate glasses in Chap. 2 that all kinds of alkali oxides act equivalently as to the change of BO_3 units to RBO_4 ones and the formation of the non-bridging oxygens (denoted as NBOs). Item (1) described above strongly suggests that potassium oxide plays the same role as sodium oxide in the alkali borosilicate glasses as well as in the alkali borate glasses. Then the following discussion might be applied to the behavior of any alkali species.

To be mentioned later, the added sodium oxide is consumed only by changing CN of the boron atoms from 3 to 4 and no NBOs are created in range I. Therefore, the fraction N_4 of four-coordinated boron atoms can be represented in the range by

$$N_4 = x. \text{ (range I)}$$

The slopes of the lines representing the molar volume vs. x relations are larger in range II than in range I. According to the the discussions on the alkali silicate glasses, creation of NBOs increases the molar volumes of the glasses. Thus, it can be said that the formation of NBOs starts at the compositions corresponding to the first bending point in each series of the borosilicate glasses. Moreover, the bendings at

0.8 in x for series A and 0.9 in x for series B in Figs. 4.3(a) and (b) can be attributed to a discontinuous increase in the rate of formation of NBOs. Another mechanism creating NBOs is present in range III in addition to that effective in range II. There are three possible mechanisms to create NBOs in the alkali borosilicate glasses.



Here the formation of RBO_4 units with an NBO, $\text{RB}(\text{O}_{3/2})-\text{OR}$, has not taken into consideration, although the possibility could not be completely ruled out. The last mechanism represents the self-decomposition of an RBO_4 unit into a $=\text{B}-\text{OR}$ unit and is estimated from N_4 data [4]. Mechanisms (b) and (c) give identical borate units. The borate and silicate units with more than one NBOs can be obtained similarly by mechanisms (a) and (b).

4.1.3 Crystal field strength Dq of Ni^{2+} ions

In order to know the kinds of unit with NBOs created in range II and III, optical absorption spectra of sodium borosilicate glasses of series B containing Ni^{2+} ions have been measured. An absorption band at the near-infrared region has been assigned to a d-d transition ${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}$ of Ni^{2+} ions in octahedral crystal field. This band directly gives the crystal field strength Dq [5]. The values of Dq have been plotted in Fig. 4.4 as a function of x . Those of the sodium

borate and silicate glasses are also plotted in the figure against the molar ratio $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$, respectively. In order to enlarge the glass formation range, 0.03 mol SiO_2 have been added to some of the sodium borate glasses which are represented by filled squares in Fig. 4.4. Almost no differences in Dq have been observed for $0.5\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ glass with and without SiO_2 , indicating that the addition of SiO_2 causes no more effects than vitrifying the sodium borate glasses with high alkali contents. Composition ranges I and II, derived from the molar volume measurements, are also indicated in Fig. 4.4.

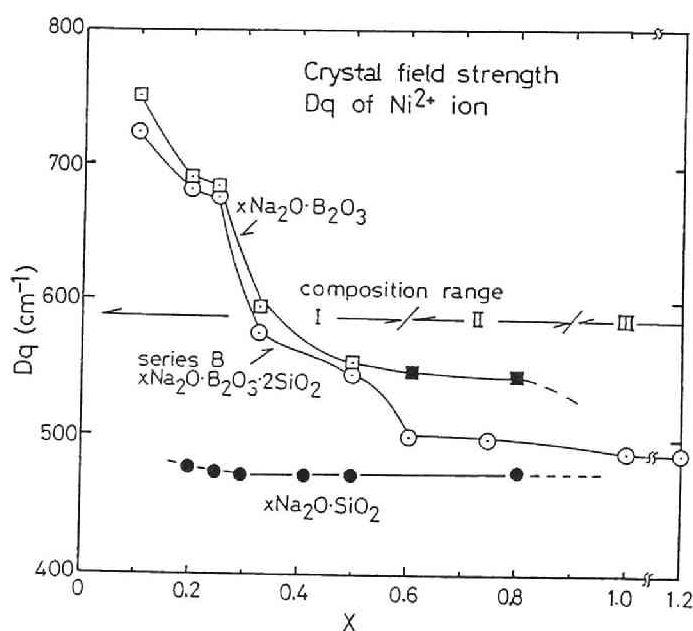


Fig. 4.4. Variation of Dq of Ni^{2+} ions in the sodium borate, borosilicate and silicate glasses.

The values of D_q for sodium borate glasses decrease with increasing x until they become constant in the composition range $x > 0.5$. Those for the borosilicate glasses decrease in a similar way in range I and exhibit an abrupt decrease at 0.6 in x to remain constant in range II. Those for the sodium silicate glasses are almost independent of the alkali contents in ranges I and II, and agree well with the results reported by Sakka and Nishiyuki [6].

On comparing the values of D_q for the borate, silicate and borosilicate glasses, it is clear that in range I the borate and borosilicate glasses exhibit nearly equal values of D_q . This fact suggests that Ni^{2+} ions change BO_3 units to BO_4 units and are present in the neighborhood of borate units such as BO_3 and BO_4 units. The negative formal charge on the BO_4 unit is neutralized by the cation. However, in range II where NBOs are created the values of D_q for the borosilicate glasses are closer to those for the sodium silicate glasses rather than for the borate glasses. This can be explained by either of the following possibilities:

- (1) No borate units with an NBO or NBOs are formed but silicate units (O_3Si-OR) in the borosilicate glasses in range II, and two of the 6 ligand oxygens around Ni^{2+} ions are NBOs of the silicate units.
- (2) Both borate and silicate units with an NBO are formed but Ni^{2+} ions have higher affinity to $Si-O^-$ than that to $B-O^-$. However, considering that Ni^{2+} ions are located near the borate units in range I, the second possibility is unlikely. It will be examined further on the basis of N_4 data [4,7-10]

whether item (1) is plausible or not.

4.1.4 N_4 vs. x relation and the role of alkali oxides

N_4 data of $x\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ glasses published so far have been plotted in Fig. 4.5 as a function of x . The data of Yun and Bray [4] are indicated by open circles and the data by others are shown by filled circles [7], filled squares [8], open triangles [9] and open squares [10]. Yun and Bray interpreted the results as showing that the decrease in N_4 starts at the composition where N_4 of the glasses deviates from that proposed by the relation, $N_4 = x$. However, there seems to be plateau stage in the N_4 vs. x plots before N_4 decreases, that is, in the range $0.6 < x < 0.9$ in the system with

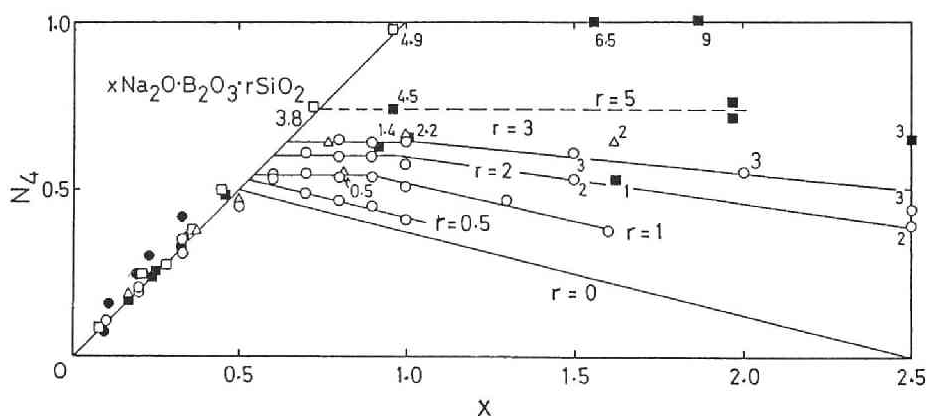


Fig. 4.5. N_4 vs. x relation in the sodium borosilicate glasses. The arabic numerals represent the molar ratio $r = \text{SiO}_2/\text{B}_2\text{O}_3$. Data cited; O:ref. 4, ●:ref. 7, ■:ref. 8, △:ref. 9, □:ref. 10.

$r=1$ and 2, and $0.7 < x < 1.0$ in that with $r=3$. Such a trend cannot be seen in the borosilicate glasses with $r=0.5$ and the borate glasses. It might suggest the difference in structure between the glasses with $r \leq 0.5$ and those with $r \geq 1$. Furthermore, the composition ranges showing constant values of N_4 are almost identical with range II for each series of glasses, A and B. The presence of those plateau stages means that NBOs are created by either of mechanisms (a) and (b) described previously. According to Yun and Bray [4] the amount of asymmetric BO_3 units ($=\text{B}-\text{OR}$ and $-\text{B}=(\text{OR})_2$) becomes significant only after x exceeds 0.8 in series A and 1.0 in series B, that is, in range III. Thus it has been indicated that in range II the silicate units with an NBO are mainly created by mechanism (a).

The role of alkali oxides in the borosilicate glasses can be summarized in Fig. 4.6. In range I the alkali oxides change BO_3 units to RBO_4 units. In range II where N_4 is independent

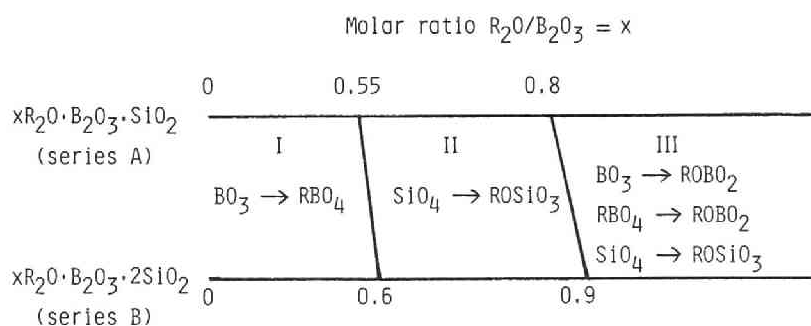


Fig. 4.6. The role of the alkali oxides in each composition range.

of x , O_3Si-OR units are formed by mechanism (a). In range III, the self-decomposition mechanism (c) takes part in the formation of NBOs as well as mechanisms (a) and (b).

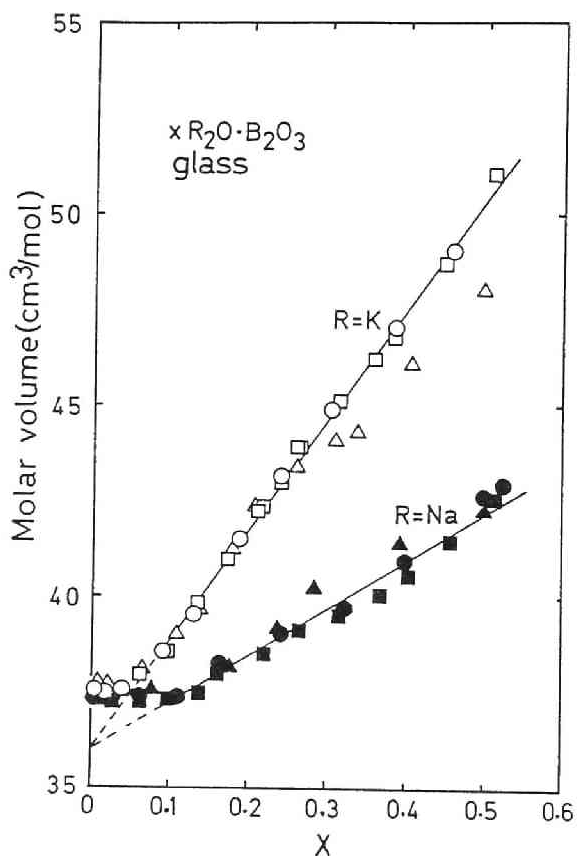


Fig. 4.7. Variation of the molar volumes of the alkali borate glasses. Data cited; $\circ, \bullet$: ref. 10, $\square, \blacksquare$: ref. 11, $\triangle, \blacktriangle$: ref. 12.

4.1.5 Molar volumes of the borate and borosilicate glasses in range I

The molar volumes of the sodium borosilicate glasses of series A and B are independent of x in range I as described previously, while those of the sodium borate glasses $x\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$, calculated from density data [11-13], increase linearly with x as indicated in Fig. 4.7. The relation between the molar volume V of the sodium borate glasses and x can be represented by eq. 4.1.

$$V = v(\text{BO}_3) + 2[v(\text{NaBO}_4) - v(\text{BO}_3)], \quad (4.1)$$

where $v(\text{BO}_3)$ and $v(\text{NaBO}_4)$ denote the partial molar volume of the BO_3 and NaBO_4 units, respectively. Although the effect of the formation of any borate groups, e.g., boroxol and triborate groups, on the partial molar volumes of the BO_3 and NaBO_4 units is not taken into consideration, eq. 4.1 seems valid as the first order approximation. Application of eq. 4.1 to the sodium borate glasses gives $v(\text{BO}_3)=18.0$ and $v(\text{NaBO}_4)=24.2 \text{ cm}^3/\text{mol}$. Assuming additivity in the molar volume and that the borate units may take the same configurations in the borosilicate glasses as in the borate glasses, the molar volumes of the glasses $0.5\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ with $r=1$ and 2 are calculated as 69.5 and $99.5 \text{ cm}^3/\text{mol}$, respectively, while the measured volumes are 65.2 and $96.8 \text{ cm}^3/\text{mol}$. The differences between the calculated and measured volumes, 3.3 and $4.3 \text{ cm}^3/\text{mol}$, respectively, can be attributed to change in the partial molar volume of the NaBO_4 unit, because the density data [14] show that the partial molar volumes of BO_3 and SiO_4

units are constant in the system $B_2O_3-SiO_2$. Some borate groups such as boroxol and triborate groups or free BO_3 and RBO_4 units may constitute a part of the borosilicate glass networks, taking different configurations from those in the borate glasses. The three dimensional network of the borosilicate glasses produces voids large enough to accommodate the sodium ions, whereas this is not likely in the sodium borate glasses. If it is not true, the molar volumes of the sodium borosilicate glasses must increase with the addition of Na_2O similarly as in the sodium borate glasses.

4.1.6 Sizes of the voids

In order to calculate the decrease in the partial volume of the $NaBO_4$ unit caused by the formation of borosilicate network, the volume of voids associated with SiO_4 and BO_4 units will be evaluated and the size of the void will be compared with the size of Na^+ and K^+ ions. Silica glass is probably constructed from $Si_{10}O_{12}$ cage skeletons like high-cristobalite, as has been discussed in Chap. 1. One of the Si-O-Si bridging bonds of the cage is shared by six cages so that the cage corresponds stoichiometrically to an SiO_2 molecule. Take 0.162 and 0.309nm the Si-O bond length and the adjacent Si-Si distance, respectively [15]. Then it can be shown that the alkali ions with ionic radius less than 0.156nm can be accommodated in the void associated with SiO_4 units without expanding the Si-O skeleton, as shown in Chap. 1. The average bond length for a BO_4 tetrahedron is 0.147nm in

several borate crystals [16]. Since the volume is proportional to third power of the bond length, a BO_4 tetrahedron may occupy a volume as large as $20.4 \text{ cm}^3/\text{mol}$ when the BO_4 units are assumed to substitute SiO_4 units in the silica glass network [16]. The largest ionic radius is 0.129nm for the alkali ion which can be accommodated in the void associated with a BO_4 unit. Shannon and Prewitt [17] have reported that the effective ionic radius of Na^+ ions is 0.116 and 0.132nm for eight- and nine-fold coordinations, respectively, and that of K^+ ions is 0.138 and 0.155nm for six- and nine-fold coordinations. It is clear that sodium ions are small enough to be accommodated in the void associated with the BO_4 units, whereas potassium ions are somewhat larger and require voids as large as those associated with the SiO_4 units. Consequently, the partial molar volume of an NaBO_4 unit in the borosilicate glass networks can be taken as $20.4 \text{ cm}^3/\text{mol}$, while that in the borate glass networks is $24.2 \text{ cm}^3/\text{mol}$. The difference between them, $3.8 \text{ cm}^3/\text{mol}$, is very close to the difference between the calculated and measured molar volumes of $0.5\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ glasses, 3.3 and $4.3\text{cm}^3/\text{mol}$ corresponding to $r=1$ and 2 , respectively.

4.1.7 A comparison of sodium and potassium glasses

Table 4.2 shows the molar volumes of borate, borosilicate and silicate glasses, obtained by the linear extrapolation in each glass system, together with the difference ΔV between the sodium and potassium glasses. Such ΔV can be attributed to the

Table 4.2. Molar volumes of the sodium and potassium borate, borosilicate and silicate glasses.

Glass	V(cm ³ /mol)		$\Delta V = V_{Na} - V_K$
	R=Na	R=K	
0.5R ₂ O·B ₂ O ₃	42.3	50.3	8.2
0.5R ₂ O·B ₂ O ₃ ·SiO ₂	66.2	74.5	8.3
0.5R ₂ O·B ₂ O ₃ ·2SiO ₂	92.5	100.0	7.5
0.5R ₂ O·SiO ₂	36.4	43.4	7.0

effect of the size of the alkali ions. It is very interesting that the difference for the borate glasses is equivalent to that for the borosilicate glasses with $r=1$. The sodium borate glass network, proposed as an aggregate of some borate groups constructed by BO_3 and BO_4 units, seems expanded to produce voids just large enough to accommodate the sodium ions but not the potassium ions. Thus in both glasses, an excess volume should be necessary over the volume of the sodium glasses to accommodate potassium ions. The difference ΔV in the molar volume of the sodium and potassium borosilicate glasses with $r=2$ is smaller than that with $r=1$ and closer to that for the alkali silicates. This may be due to the fact that the fraction of the cage-type skeletons becomes large and the excess volume due to bulk potassium ions associated with the BO_4 units is absorbed to some extent by the adjacent silica cage skeletons.

Table 4.3. Elastic properties of the alkali borosilicate glasses. (a) $x\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$.

$x\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$	density (g/cm ³)	V_l (km/s)	V_s (km/s)	E (GPa)	G (GPa)	K (GPa)

x $\text{SiO}_2/\text{B}_2\text{O}_3=1$						
0.07	2.045	4.534	2.578	34.28	13.59	23.92
0.2	2.161	5.072	2.884	45.33	17.94	31.63
0.3	2.261	5.358	3.178	56.14	22.85	34.48
0.35	2.311	5.502	3.202	58.95	23.69	38.37
0.4	2.350	5.641	3.280	62.93	25.28	41.07
0.45	2.389	5.686	3.390	67.22	27.46	40.63
0.5	2.429	5.833	3.446	71.07	28.87	44.19
0.55	2.449	5.934	3.440	72.27	28.98	47.59
0.6	2.480	6.013	3.489	75.24	30.19	49.42
0.7	2.499	6.007	3.500	76.11	30.61	49.36
0.9	2.518	5.873	3.364	71.57	28.50	48.86
1.0	2.536	5.815	3.325	70.49	28.04	48.37
1.2	2.561	5.616	3.127	63.89	25.05	47.38
1.3	2.560	5.605	3.104	63.10	24.67	47.54
x $\text{SiO}_2/\text{B}_2\text{O}_3=2$						
0.1	2.098	4.758	2.867	41.90	17.25	24.50
0.2	2.147	5.092	2.991	47.57	19.22	30.05
0.3	2.237	5.346	3.098	54.08	21.47	37.48
0.4	2.308	5.650	3.306	62.54	25.23	40.04
0.45	2.366	5.730	3.377	66.61	26.70	41.69
0.5	2.396	5.819	3.488	71.10	29.15	42.26
0.55	2.430	5.943	3.566	75.31	30.89	44.64
0.6	2.450	5.940	3.486	73.70	29.78	46.73
0.65	2.471	5.973	3.556	76.59	31.25	46.49
0.7	2.480	5.969	3.536	76.50	31.11	47.13
0.9	2.517	5.927	3.489	75.70	30.66	47.55
1.0	2.530	5.926	3.492	76.16	30.86	47.70
1.1	2.518	5.850	3.426	73.25	29.57	46.57
1.2	2.521	5.850	3.400	72.55	29.14	47.43
1.3	2.526	5.791	3.350	70.49	28.18	47.17

Table 4.3 (continued). (b) $xK_2O \cdot B_2O_3 \cdot rSiO_2$.

$xK_2O \cdot B_2O_3 \cdot rSiO_2$	density (g/cm ³)	V_l (km/s)	V_s (km/s)	E (GPa)	G (GPa)	K (GPa)
x $SiO_2/B_2O_3=1$						
0.1	2.041	4.508	2.568	33.91	13.46	22.53
0.3	2.236	5.074	2.802	44.96	17.56	34.16
0.4	2.302	5.225	2.997	51.89	20.68	35.28
0.5	2.345	5.312	3.098	55.92	22.51	36.16
0.6	2.389	5.440	3.131	58.66	23.42	39.47
0.7	2.431	5.436	3.146	60.07	24.06	39.76
0.8	2.423	5.310	3.082	57.37	23.02	37.67
1.0	2.434	5.040	2.946	52.40	21.12	33.66
1.1	2.406	4.876	2.876	49.08	19.90	30.67
x $SiO_2/B_2O_3=2$						
0.3	2.192	5.138	2.986	48.67	19.57	31.81
0.4	2.290	5.271	3.174	56.09	23.07	32.86
0.5	2.324	5.400	3.220	58.99	24.09	35.64
0.55	2.362	5.545	3.264	62.15	25.17	39.07
0.6	2.416	5.551	3.300	64.55	26.31	39.37
0.7	2.445	5.632	3.281	65.44	26.32	42.45
0.8	2.460	5.637	3.257	65.21	26.10	43.37
0.9	2.473	5.567	3.213	63.84	25.53	42.60
1.0	2.483	5.395	3.143	60.98	24.53	39.57
1.1	2.477	5.456	3.136	61.06	24.36	41.26
1.3	2.465	5.101	2.881	51.80	20.46	36.86

(c) $0.5R_2O \cdot B_2O_3 \cdot mSiO_2$.

$0.5R_2O \cdot B_2O_3 \cdot mSiO_2$	density (g/cm ³)	V_l (km/s)	V_s (km/s)	E (GPa)	G (GPa)	K (GPa)
m, R=Na						
1	2.429	5.833	3.446	71.07	28.84	44.19
2	2.396	5.819	3.488	71.10	29.15	42.19
3	2.328	5.759	3.486	68.44	28.24	39.56
4	2.315	5.711	3.515	68.37	28.60	37.37
5	2.310	5.555	3.384	63.75	26.45	36.01
6	2.302	5.752	3.541	68.98	28.87	37.68
m, R=K						
1	2.345	5.312	3.098	55.92	22.51	36.16
2	2.333	5.400	3.220	59.22	24.19	35.78
3	2.323	5.455	3.283	60.89	25.04	35.74
4	2.317	5.536	3.359	63.20	26.14	36.15
5	2.315	5.665	35.05	67.68	28.44	36.37

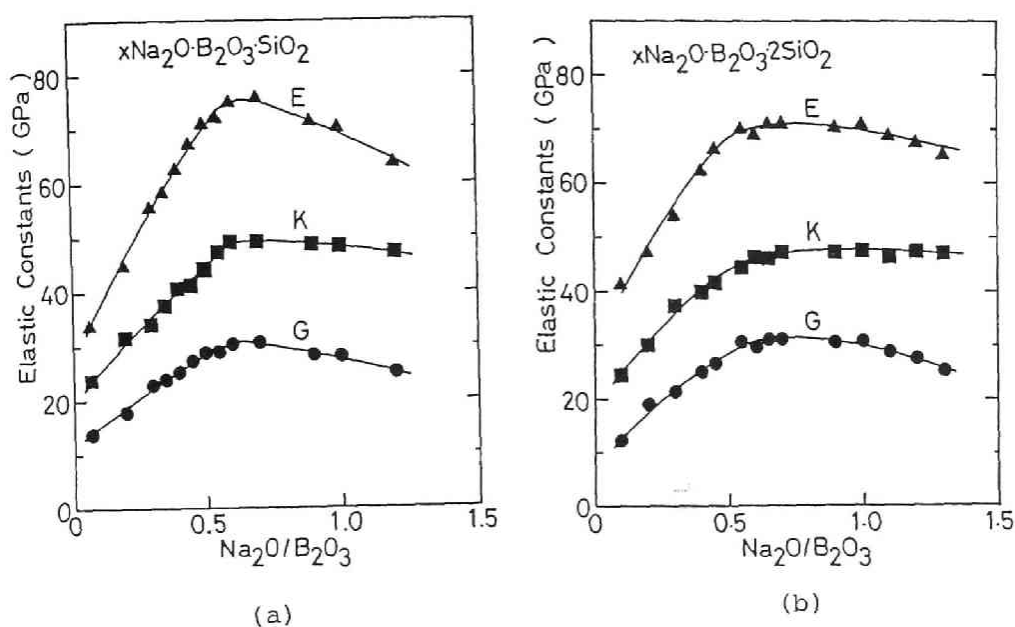


Fig. 4.8. Variation of the elastic constants of the sodium borosilicate glasses; (a) series A, (b) series B.

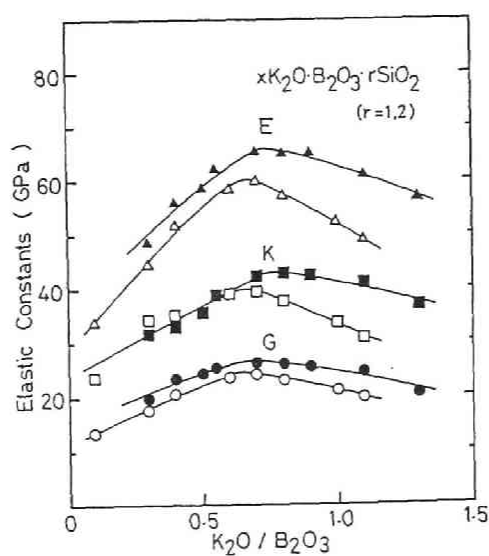


Fig. 4.9. Variation of the elastic constants of the potassium borosilicate glasses; series A (open marks), series B (filled marks).

4.2 Elastic properties of borosilicate glasses and their structure model

Characteristic properties of the borosilicate network is discussed by studying composition dependence of elastic constants and bulk modulus vs. mean atom-pair volume relation. The effect of SiO_2 content on the borosilicate structure is presented.

4.2.1 Results

The elastic properties of the alkali borosilicate glasses have been measured by the pulse transmission method described in Chapter 1. Table 4.3(a), (b) and (c) represent the elastic constants of the glasses respectively in the systems $x\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ ($r=1$ and 2), $x\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ ($r=1, 2$), and $0.5\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot m\text{SiO}_2$ ($\text{R}=\text{Na}$ and K ; $0 \leq m \leq 6$) [18]. Parameter x represents the molar ratio $\text{R}_2\text{O}/\text{B}_2\text{O}_3$ and is varied in the range $0.01 < x \leq 1.5$. Parameter r represents the molar ratio $\text{SiO}_2/\text{B}_2\text{O}_3$. The elastic constants, namely, Young's modulus, bulk modulus and shear modulus are represented by E , K and G , respectively, and v_l and v_s denote longitudinal and shear wave velocities. Fig. 4.8(a) and (b) represent the variation of the elastic constants of the sodium borosilicate glasses of series A and B, plotted as a function of x . Fig. 4.9 represents that of the potassium glasses of both series.

4.2.2 Dependence of the elastic constants on composition

Figs. 4.8 and 4.9 show that the elastic constants increase with x , become maximum and decrease on further increase in x , though those of the potassium glasses are likely to decrease slightly more rapidly than those of the sodium glasses. The composition dependence is common to all series of glasses and is the same as found in the sodium borate glasses in Chap. 2. Moreover, the compositions corresponding to the maximum elastic constants are identical with those where the molar volumes of the borosilicate glasses start increasing remarkably together with showing bending in the molar volume vs. x curve. According to the previous discussions on the borate glasses, this result verifies the N_4 vs. x relation in the borosilicate glasses represented in Figs. 4.5 and 4.6. The variation of N_4 in the potassium glasses might be similar to that of the sodium ones because of the similarity in the elastic constants vs. x curves. Thus, N_4 of the potassium glasses also becomes maximum at the compositions corresponding to the maximum elastic constants. Fig. 4.5 indicates that N_4 increases according to the relation $N_4=x$ in range I. Therefore, the value of x corresponding to the maximum elastic constants, $x_{\max}$, gives $N_{4\max}$. It is indicated previously that the value of $x_{\max}$ is almost the same in the sodium and potassium glasses due to the molar volume vs. x curves. However, the elasticity vs. x curves indicate rather different $x_{\max}$ for the sodium and potassium glasses. Fig. 4.10 shows the values of the molar ratio $R_2O/B_2O_3=x_{\max}$, equal to $N_{4\max}$,

plotted as a function of the ratio $\text{SiO}_2/\text{B}_2\text{O}_3$ ($=r$) based on the elasticity vs. x curve. The figure also shows the $N_{4\text{max}}$ vs. r relation derived from Fig. 4.5 due to NMR measurements.

The following items can be elucidated from Fig. 4.10.

- (a) In both alkali borosilicate glasses, $N_{4\text{max}}$ increases linearly with r , showing that creation of NBOs is prevented up to higher alkali content.
- (b) In the sodium glasses the values of $N_{4\text{max}}$ due to the elastic constants agree well with those due to the NMR measurements.
- (c) $N_{4\text{max}}$ for the potassium glasses is larger than that for the sodium ones with the same ratio r .

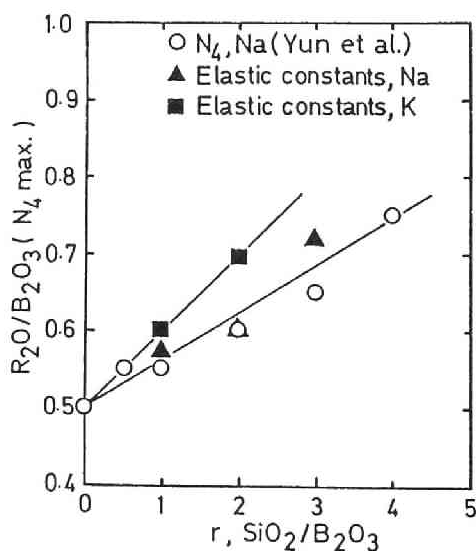


Fig. 4.10. Variation of maximum value of N_4 ($=N_{4\text{max}}$) as a function of the molar ratio $r=\text{SiO}_2/\text{B}_2\text{O}_3$.

Items (a) and (c) can be explained by assuming that an RBO_4 unit is reluctant to be bonded with the other RBO_4 one as in the borate systems. Item (c) can be interpreted as coming from that larger cages are necessary to enclose K^+ ions larger than Na^+ ions, reducing the probability of formation of $\text{RBO}_4\text{-RBO}_4$ bonds. In fact these interpretations are reasonable because the $\text{RBO}_4\text{-RBO}_4$ bond is thermochemically unstable than $\text{RBO}_4\text{-BO}_3$ one in the alkali borate crystals, as indicated elsewhere (sect. 4.3) [19,20].

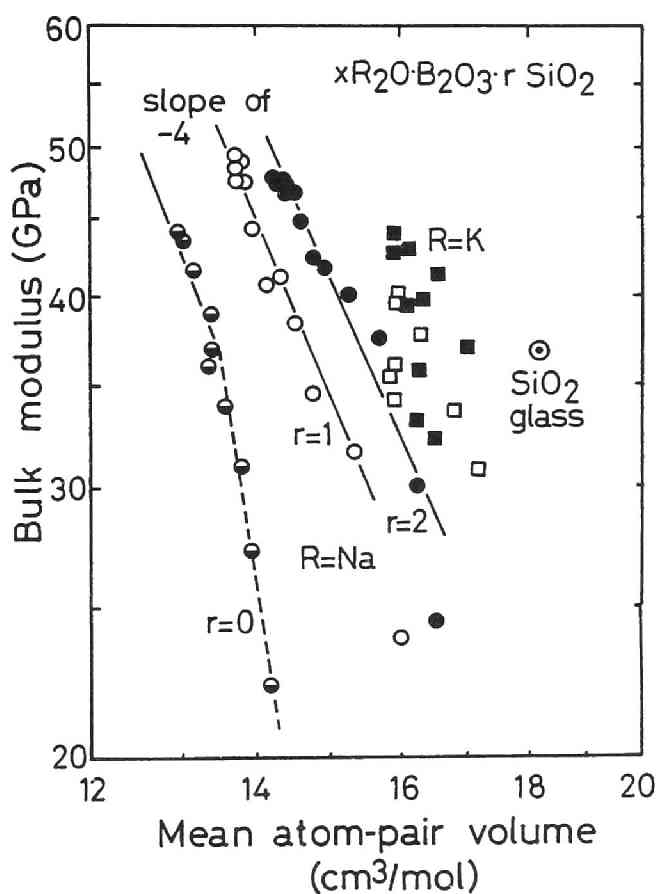


Fig. 4.11. K-V relation of the sodium (○,●,●) and potassium (□,■) borosilicate glasses.

4.2.3 Bulk modulus vs. mean atom-pair volume relation

Fig. 4.11 shows bulk modulus vs. mean atom-pair volume relation (K-V relation) in the sodium and potassium borosilicate glasses of series A and B. The K-V relation of the sodium borate glasses (Fig. 2.6) is also shown for comparison. The K-V relation of the sodium borosilicate glasses of series A and B can be well approximated by the solid lines with a slope -4. The result indicates that on addition of Na_2O to $\text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ glasses, the sodium ions occupy the voids of the oxygen cages in the vicinity of the BO_4 units without expanding the glass network. This change in structure of the sodium borosilicate glasses agrees well with that represented by Fig. 5.3(a) and (b). Furthermore, Fig. 4.11 shows that the plots for the potassium glasses cannot be approximated by the lines of slope -4. This can be attributed to the fact that K^+ ions cannot occupy the voids associated with BO_4 units without expanding the network skeletons owing to their large size.

4.2.4 Characterization of the borosilicate network structure

The sodium borosilicate glasses of series A and B are represented by respective lines. This may be caused by an effect of SiO_2 content on the glass structure. It is intended here to discuss the effect. Fig. 4.12 represents the K-V relation of the glasses of the composition $0.5\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot m\text{SiO}_2$ ($0 \leq m \leq 6$, $\text{R}=\text{Na}$ and K). Bulk modulus K of SiO_2 glass has been

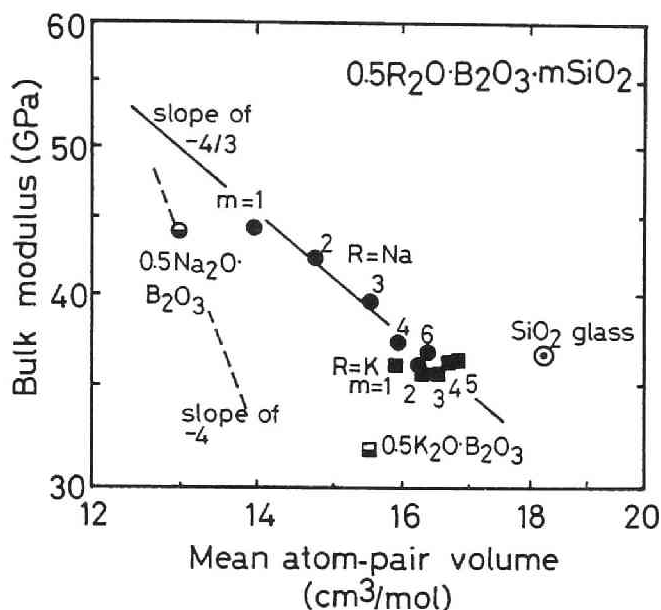


Fig. 4.12. K-V relation for the glasses $0.5R_2O \cdot B_2O_3 \cdot mSiO_2$ ($R=Na, K$; $0 \leq m \leq 6$)

cited from Bogardus [21a], and that of $0.5K_2O \cdot B_2O_3$ from Shaw and Uhlmann [21b]. The plots for the sodium glasses are located on the solid line of slope $-4/3$. This means that the glasses behave as if the two component, $0.5Na_2O \cdot B_2O_3$ and SiO_2 , in $0.5Na_2O \cdot B_2O_3 \cdot mSiO_2$ glass should be similar in structure, though the actual structures of the alkali borate and SiO_2 are different. However, the plots for the borate and silica glass are deviated from the solid line, hence the configurations of the borate and SiO_4 units are different in the borosilicate networks from those in the individual glasses.

On the other hand, the bulk modulus of the potassium

borosilicate glasses is almost independent of m and is equal to that of SiO_2 glass. The K-V relation is represented by a line parallel to the abscissa. The plots for the sodium glasses with $m=5$ and 6 are around that line. Therefore, it is suggested that the addition of Na_2O to alkali free $\text{B}_2\text{O}_3 \cdot m\text{SiO}_2$ glass modifies the network by changing CN of B atoms and that the sodium ions fill the void of the produced borosilicate glass networks. The structural modification seems to affect significantly the elasticity of the borosilicate glasses in the range $m \leq 4$, whereas it influences little in the range $m \geq 5$. This suggests that on further increase in m the plots for the sodium and potassium borosilicate glasses become nearer to that for SiO_2 glass along the line representing the plots for the potassium glasses.

Therefore, from the K-V plots in Fig. 4.12, the difference in structure of borosilicate glasses from SiO_2 and borate glasses can be obtained. That is, the borosilicate glasses with $m < 1$ have the structure like that of the borate glasses, since the plot for the sodium diborate glass does not lie on the solid line representing the plots for the sodium borosilicate glasses. The glasses with $m \geq 1$ may have characteristic structure. This verifies the absence of the plateau in N_4 vs. x relation for the glasses with the molar ratio $\text{SiO}_2/\text{B}_2\text{O}_3$ lesser than 1.0, as discussed in sects. 4.1.3 and 4.1.4. Further increase in m modifies the network to that of silica glass. In conclusion, the difference found in the networks of the borate and borosilicate glasses can be summarized as follows.

- (a) The structure of the borosilicate glasses with $m < 1$ resembles that of the borate glasses.
- (b) The structure of the glasses with $m \geq 5$ is very similar to that of SiO_2 .
- (c) The glasses in the range $1 \leq m \leq 4$ have characteristic structure of borosilicate glass.

4.3 Second boron oxide anomaly

Several properties of B_2O_3 containing glasses change abruptly near the composition corresponding to 0.5 in $x = \text{R}_2\text{O}/\text{B}_2\text{O}_3$. It has been proposed to call this phenomenon the second boron oxide anomaly and the other non-linear change found near 0.2 in x the first one. It is of particular interest to discuss thermochemically the second anomaly, because the anomaly is proposed in sections 2.1 and 4.2 to be related with the thermochemical stability of $\text{BO}_3\text{-RBO}_4$ and $\text{RBO}_4\text{-RBO}_4$ bonds.

The borate units such as BO_3 , RBO_4 and ROBO_2 units (denoted later as B_3 , RB_4 and B_R , respectively) are present in glasses or crystals containing B_2O_3 . Relative and thermochemical stabilities of these units have frequently been referred to when the boron oxide anomaly is considered. For example, Zhdanov [22] considered that formation of the RB_4 units was preferred to that of the B_R units: Abe [23] assumed that the B_3 units could not be bonded to more than one B_4 units: Beekemkamp [24] considered that $\text{RB}_4\text{-RB}_4$ bond was

absent in the glasses. The arrangements of these borate units have already been examined in Chapter 2 in several alkali borate crystals. As a result, it is postulated that a B_4-B_4 bond should be unstable than a B_4-B_3 bond. In this chapter, the thermochemical stability of the RB_4 units relative to the B_R units is presented [20] and the second boron oxide anomaly will be interpreted in terms of the stabilization energy H_{stab} .

4.3.1 Heats of formation of some alkali borate crystals

Shartsis and Capps [25] measured heats of solution of several alkali borate crystals. JANAF Thermochemical Tables [26] adopted their data and calculated the heats of formation of the borate crystals. However, judging from the composition dependence of the heats of solution by Takahashi and Yoshio [27], a few of the heats of formation data should be corrected. Detailed discussions on this item have been made elsewhere [19,20]. The recalculated data are shown in Table 4.4. Later, the heat of formation and solution of a crystal, $-\Delta H_f$ and $-\Delta H_s$, are denoted by H_f and H_s , and partial molar quantities of each borate unit are similarly denoted as h_f and h_s .

Incidentally, the thermochemical quantities are represented in the unit of kcal/mol: 1 kcal/mol=4.184 kJ/mol.

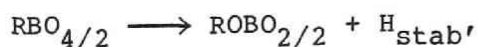
Table 4.4. Heats of formation of the alkali borate crystals (kcal/mol). Their heats of solution in 2N-HNO₃ solution are also shown.
1 kcal/mol=4.184 kJ/mol.

Crystal	$-\Delta H_f$	ref.	$-\Delta H_s$	ref.
B ₂ O ₃	304.0	26	3.6	27
Li ₂ O·2B ₂ O ₃	806.9	20	10.2	27
Li ₂ O·B ₂ O ₃	487.8	26	21.6	27
Na ₂ O·4B ₂ O ₃	1403.5	20	4.5	27
Na ₂ O·2B ₂ O ₃	782.8	20	14.6	20
K ₂ O·4B ₂ O ₃	1423.7	20	-0.4	20
K ₂ O·3.8B ₂ O ₃	1362.8	20	-1.1	20
K ₂ O·2B ₂ O ₃	799.8	20	8.2	27
K ₂ O·B ₂ O ₃	471.2	20	28.2	27

4.3.2 Stabilization energies of the RB₄ units relative to the B_R units

The molar enthalpy of a crystal is assumed to be a sum of the partial molar enthalpies of each component units. Kawazoe et al. [28] have indicated that the delocalization of the planar π -electrons of a B₃ unit is restricted by the adjacent B₄ units. This effect may change the energy of the B₃ unit. As a first order approximation, however, it is assumed that the partial molar enthalpies of the B₃ units in any crystal are equivalent to those in B₂O₃(c). The stabilization energy H_{stab} of a B₄ unit relative to the B_R unit is defined as the heat of

decomposition,



and is the difference in the partial molar heats of formation of the two units. Since the difference in the heats of solution is equivalent to that in the heats of formation, the stabilization energy is expressed as

$$H_{\text{stab}} = h_s(\text{B}_R) - h_s(\text{RB}_4) \quad (4.2)$$

For instance, lithium diborate $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3(\text{c})$ consists of two B_3 and two LiB_4 units, then

$$h_s(\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3(\text{c})) = 2h_s(\text{B}_3) + 2H_s(\text{LiB}_4).$$

Application of $h_s(\text{B}_3)=1.8$ kcal/mol and $H_s(\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3(\text{c}))=10.2$ kcal/mol gives $h_s(\text{LiB}_4)=3.3$ kcal/mol. Since $H_s(\text{LiBO}_2(\text{c}))=h_s(\text{B}_{\text{Li}})=10.8$ kcal/mol as indicated in Table 4.4, H_{stab} of the LiB_4 unit is 7.5 kcal/mol according to eq. 4.2. In this way the values of H_{stab} are obtained and shown in Table 4.5 for several crystals. It also shows the atomization energy of the

Table 4.5. Stabilization energy of RBO_4 units in some crystals relative to corresponding ROBO_2 units, and B-O bond energy of the RBO_4 units, $E(\text{B}^4-\text{O})$ (kcal/mol).

Crystal	Hstab	D(ROBO _{2/2})	D(RBO _{4/2})	E(B ⁴ -O)
$\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	7.5	534.3	541.8	135
$\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	15.0	511.2	526.2	132
$\text{K}_2\text{O} \cdot 3.8\text{B}_2\text{O}_3$	19.7	508.9	528.7	132
$\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	11.8		520.7	130

RB_4 units and B-O bond energy $E(\text{B}^4-\text{O})$.

4.3.3 H_{stab} and the boron oxide anomaly

Generally free energy must be used for discussing stability of a system. However, it has already been shown [20] that the entropy changes are substantially negligible at the formation reaction of the borate crystals from $\text{R}_2\text{O}(\text{c})$ and $\text{B}_2\text{O}_3(\text{c})$. Therefore, the partial molar heats of formation and solution of the borate units can be employed for predicting the kinds of borate units produced at the reaction between the two oxides. This indicates that H_{stab} is useful for this purpose, too.

The large positive values of H_{stab} in the range $x < 0.5$ shown in Table 4.5 indicate $h_f(\text{RB}_4) > h_f(\text{B}_R)$, and that the formation of the RB_4 unit is preferred to that of the B_R unit. Thus an increase in the fraction of the RB_4 units has been interpreted thermochemically in the range $x < 0.5$. However, the values of H_{stab} are smaller in the diborate crystals than in the tetraborate crystals, as suggested previously [19]. Therefore, the formation of the RB_4 units is getting less preferred and, contrarily, that of the B_R units becomes preferred gradually. If the B_3 units are assumed to be changed continuously to the RB_4 units in the range $x > 0.5$, the RB_4 units connected to more than one RB_4 units will appear [19]. They can be denoted as $\text{B}_4(n=2)$, $\text{B}_4(n=3)$ and $\text{B}_4(n=4)$, where n represents the number of the RB_4 units bonded to the relevant RB_4 unit. It can be indicated that there might be imaginary

crystals which would consist of B_3 and one of those imaginary B_4 units with $n=2, 3$ and 4 . Let them denoted as S , T and U depending on n . The compositions of S , T and U are 0.6 , 0.75 and 1.0 in x , respectively. Since such B_4 units are not present in the actual system, H_{stab} values of them are smaller than those of the $B_4(n=0)$ and $B_4(n=1)$ units present in tetra- and diborate crystals. If H_{stab} is assumed to be decreased linearly with n , H_{stab} of the $B_4(n=2)$ unit in S is 3.9 kcal/mol in the potassium system, where H_{stab} data are available for the B_4 units with $n=0$ and 1 in Table 4.5. In the actual borate system in the range $x > 0.5$ the diborate and metaborate crystals are mixed, while in the imaginary case the system might be mixture of the diborate and S in the range $0.5 < x < 0.6$, that of S and T in $0.6 < x < 0.75$ and that of T and U in $0.75 < x < 1.0$. In order to see the thermochemical stability of the actual and imaginary systems in the range $x > 0.5$, it is sufficient to compare H_S values of imaginary S and a mixture of diborate and metaborate (denoted as C) at 0.6 in x , because H_{stab} values of the RB_4 units in imaginary T and U might be smaller than that in S .

The difference d in H_S data of C and S containing 2.5 mol B_2O_3 is given by

$$d = 3h_S(B_4(n=2)) - 2h_S(B_4(n=1)) - h_S(B_R).$$

Application of eq. 4.2 reduces to

$$d = 2H_{stab}(B_4(n=2)) - 3H_{stab}(B_4(n=1))$$

$$d = -11.9 \text{ kcal/mol}$$

The negative value of d indicates $H_S(C) < H_S(S)$. Therefore, it has been shown that no more B_3 units can be changed to the RB_4

units in the range $x > 0.5$. This is equivalent to the fact that N_4 becomes maximum at diborate composition in the potassium system. The same conclusion might be derived for the lithium and sodium systems if H_{stab} data could be obtained for all n .

4.4 Summary

Molar volumes and optical absorption spectra of Ni^{2+} ions have been measured in alkali borosilicate glasses of the compositions $xR_2O \cdot B_2O_3 \cdot rSiO_2$ ($R=Na$ and K , $r=1$ and 2), where x ranges from 0.04 to 2.0. Behaviors of the alkali and boron atoms in the glasses have been discussed. The whole composition range can be divided into three ranges on the basis of the composition dependence of the properties. In range I the BO_3 units are changed to the RBO_4 units without creating non-bridging oxygens. In range II the non-bridging oxygens are created by a mechanism $SiO_4 \longrightarrow O_3Si-OR$, and in range III they are formed by mechanisms $BO_3 \longrightarrow O_2B-OR$, $SiO_4 \longrightarrow {}_3Si-OR$ and $RBO_4 \longrightarrow O_2B-OR$. The variation of the molar volumes in those ranges has been explained in terms of (1) the size of the alkali ions, (2) the size of the voids associated with the RBO_4 units, and (3) the creation of the non-bridging oxygens.

The elastic constants such as Young's modulus, bulk modulus and shear modulus of the borosilicate glasses have been measured. It has been indicated that the elastic constants become maximum at the molar ratio $x=R_2O/B_2O_3$ where the

fraction N_4 of four-coordinated boron atoms is maximum. From the variation of the elastic constants, the dependence of the composition corresponding to maximum N_4 on the molar ratio $r = \text{SiO}_2/\text{B}_2\text{O}_3$ has been derived, which agrees well with that from NMR measurements. The bulk modulus vs. mean atom-pair volume relation (K-V relation) has been correlated with the size of the alkali ions and voids associated with the BO_4 units. It is also correlated with the effects of the alkali ions filling the voids on the elastic constants. The K-V relation for a series of borosilicate glasses $0.5\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot m\text{SiO}_2$ ($0 \leq m \leq 6$, $\text{R} = \text{Na}$ and K) shows that the borosilicate glasses in the range $m < 1$ exhibit a character like a borate glass, those in the range $m \geq 5$ strongly resemble SiO_2 in structure, and those in the range $1 \leq m \leq 4$ have characteristic network of the borosilicate glasses.

The stabilization energies H_{stab} of the RBO_4 units relative to the ROBO_2 units, calculated by use of the heats of formation of several alkali borate crystals, can explain the presence of the second boron oxide anomaly near 0.5 in x .

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Chapter 5

NETWORK STRUCTURE OF ALKALI GERMANOSILICATE GLASSES

In this chapter, structure of germanosilicate glasses will be discussed in which the oxygen coordination of Ge atoms is expected to change from 4 to 6 and from 6 to 4, depending on the composition. It is intended to obtain the knowledges on the roles of R_2O , coordination number of Ge atoms and structure change at substitution of SiO_4 for GeO_4 units. For this purpose, the molar volume and elastic constant which give important informations on the glass networks have been measured.

5.1 Molar volume of alkali germanosilicate glasses and coordination number of Ge atoms

In this section, composition dependence of the molar volumes of alkali germanosilicate glasses is studied. It is intended to propose the variation of the fraction N_6 of six-coordinated Ge atoms and clarify the behavior of R_2O partitioned to GeO_2 and SiO_2 depending on the molar ratio SiO_2/GeO_2 .

5.1.1 Experimental procedures and results

Reagent grade R_2CO_3 ($R=Na$ and K), SiO_2 and 4N-grade GeO_2

were mixed to give about 20g glass. The compositions were expressed as $xR_2O \cdot GeO_2 \cdot rSiO_2$ ($0 < x < 1$; $R=Na, K$; $r=1/3, 1$). Parameters x and r represented the molar ratio R_2O/GeO_2 and SiO_2/GeO_2 , respectively, being in the range $0 < x < 1$ and $r=1/3$ and 1 . The volume of a glass corresponding to one formula-weight was defined as its molar volume. The batches were melted in a Pt crucible placed in an electric furnace at temperatures ranging from 1000 to 1450°C depending on the composition. The melts were cast into a graphite mold of 1.5x1.5x1.5cm in size. The quenched glass cubes were annealed for 30 min at appropriate temperature determined else. Density was measured by the Archimedes method with kerosene as the immersing liquid, from which the molar volume was calculated. The results were shown in Table 5.1(a) and (b) respectively for the sodium and potassium glasses. Fig. 5.1 shows variation of the molar volumes of the glasses, plotted as a function of x . That of the alkali germanate glasses with $r=0$, studied previously in sect. 2.3, is also shown by the segments of lines obtained by the least square method. The molar volume of $GeO_2 \cdot SiO_2$ glass has been cited from Riebling [1].

5.1.2 Composition dependence of the molar volume

The composition dependence of the molar volume of the alkali germanosilicate glasses with $r=0, 1/3$ and 1 shown in Fig. 5.1 can be summarized as follows.

- (a) The molar volume vs. x relation in each series can be well approximated by two segments of lines,

Table 5.1. Densities and molar volumes of the glasses,
 $xR_2O \cdot GeO_2 \cdot rSiO_2$. (a) $R=Na$, (b) $R=K$.

(a) $R=Na$					
	d	V		d	V
x	(g/cm ³)	(cm ³ /mol)	x	(g/cm ³)	(cm ³ /mol)
Series A, $r=1/3$			Series B, $r=1$		
0					56.2
0.07	3.476	37.10	0.07	3.037	55.65
0.10	3.544	36.91	0.10	3.066	55.73
0.12	3.594	36.74	0.12	3.106	55.41
0.15	3.642	36.77	0.15	3.132	55.55
0.18	3.65	36.86	0.18	3.159	55.66
0.20	3.666	37.37	0.20	3.178	55.72
0.23	3.663	37.91	0.22	3.199	55.74
0.25	3.658	38.30	0.25	3.212	56.09
0.28	3.656	38.83			
0.30	3.636	39.39	0.30	3.238	56.60
0.35	3.617	40.45	0.33	3.259	56.81
0.40	3.560	41.97	0.40	3.256	58.19
0.45	3.506	43.50			
0.50	3.462	44.95	0.50	3.222	60.73
0.60	3.353	48.26	0.60	3.193	63.22
0.70	3.281	51.21	0.70	3.139	66.28
			0.80	3.107	68.96
			0.9	3.066	71.90
			1.0	3.029	74.83

(b) $R=K$					
	d	V		d	V
x	(g/cm ³)	(cm ³ /mol)	x	(g/cm ³)	(cm ³ /mol)
Series A, $r=1/3$			Series B, $r=1$		
0.05	3.384	38.22			
0.10	3.489	38.42	0.10	3.975	56.62
0.15	3.530	39.37	0.15	3.113	57.44
0.20	3.533	40.60	0.20	3.152	58.22
0.25	3.499	42.35	0.25	3.158	59.60
0.30	3.440	44.44	0.30	3.160	61.06
0.40	3.333	48.69	0.40	3.120	64.86
0.50	3.210	53.49	0.50	3.065	69.09
0.70	3.047	62.54	0.70	2.966	77.75
0.90	2.985	70.15	1.00	2.869	90.23

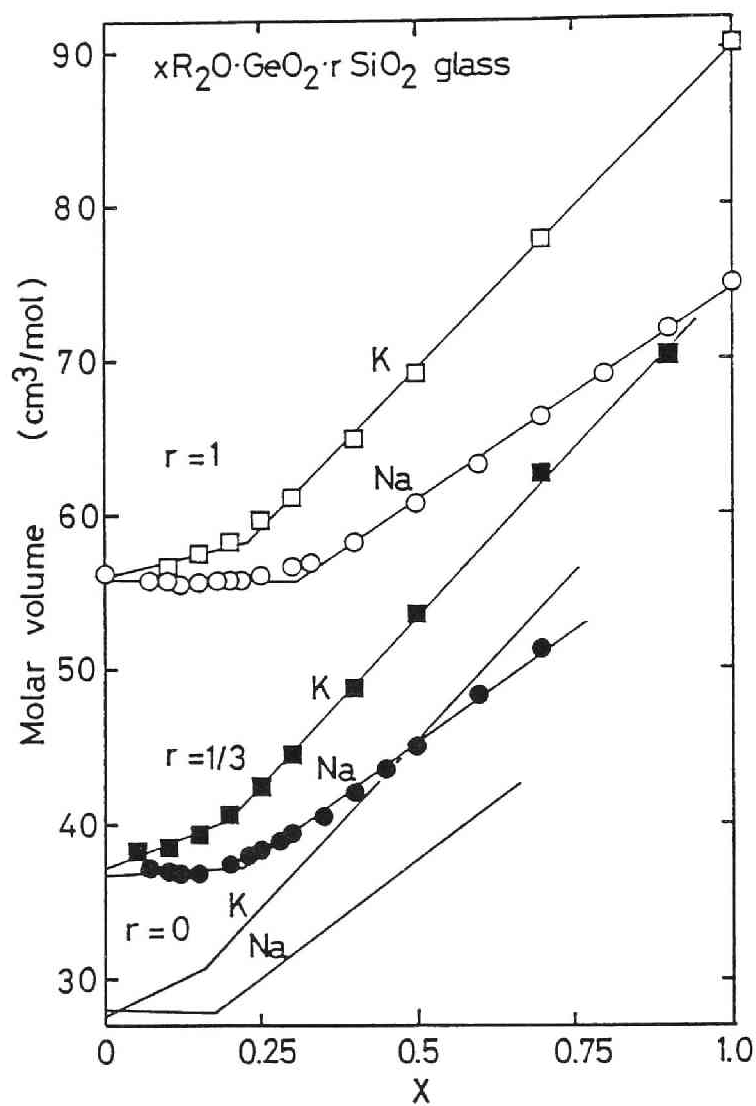


Fig. 5.1. Variation of molar volume of the alkali germanosilicate glasses, $xR_2O \cdot GeO_2 \cdot rSiO_2$ as a function of x . That of the alkali germanate glasses with $r=0$ is also indicated.

- (b) showing a bending which divides the whole composition range into two, I and II.
- (c) The linear relation indicates the presence of the additivity in the molar volume in each range.
- (d) The compositions at the bendings are dependent both on the alkali species and on the molar ratio r .
- (e) The slopes of the lines representing the rates of increase in the molar volume per each addition of R_2O are larger in range II than in range I.
- (f) The molar volumes of the sodium glasses with any r remain constant in range I.

The linear equations representing the molar volume vs. x relations are shown in Table 5.2. The behavior described in item (f) is similar to that of the sodium borosilicate glasses indicated in Chap. 4. Therefore, from the analogy of the borosilicate glasses, item (f) can be interpreted as showing that the added sodium oxide is consumed for the change of GeO_4 units to GeO_6 ones without accompanying creation of non-bridging bonds such as O_3Si-OR and O_3Ge-OR . If any non-bridging bonds were formed, the molar volumes of the sodium glasses might increase, because the creation of $ROGeO_3$ units is expected to increase the molar volumes of the glasses as the creation of the $ROSiO_3$ units increases the molar volumes of the silicate glasses. Therefore, it is suggested that the sodium ions are accommodated in the voids associated with the GeO_6 units without expanding the glass skeleton in range I as in the sodium germanate and borosilicate glasses. However, potassium ions expand the skeleton constructed by

Table 5.2. Linear relations between the molar volume and x .

r	R	Range I	Range II
0	Na	$-0.73x+28.01$ ($x<0.18$)	$30.12x+22.56$ ($0.18<x$)
	K	$19.51x+27.59$ ($x<0.16$)	$43.01x+23.86$ ($0.16<x$)
1/3	Na	$2.06x+36.71$ ($x<0.22$)	$28.70x+30.83$ ($0.22<x$)
	K	$21.80x+36.17$ ($x<0.21$)	$43.15x+31.72$ ($0.21<x$)
1	Na	$-0.38x+55.81$ ($x<0.31$)	$27.20x+47.34$ ($0.31<x$)
	K	$19.44x+54.57$ ($0.27<x$)	$41.39x+48.71$ ($0.27<x$)

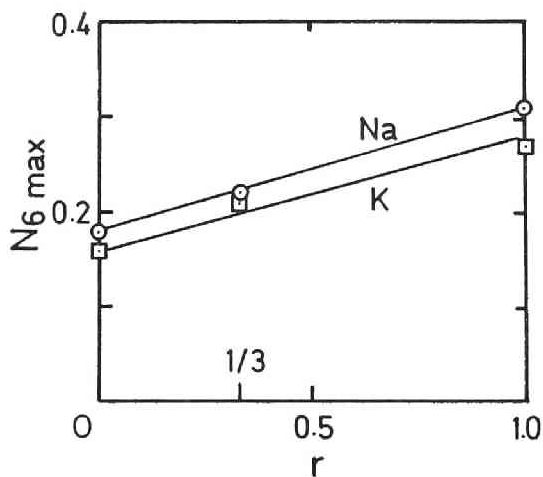


Fig. 5.2. $N_{6 \max}$ vs. r relation for the alkali germaonosilicate glasses.

GeO_4 , GeO_6 and SiO_4 , and occupy the voids in it.

5.1.3 Maximum value of N_6 and SiO_2 content

On the analogy of the borosilicate glasses, the composition at the bending in the molar volume vs. x relation for each series of glass indicates the composition of the glass giving the maximum N_6 . Such composition is obtained as that corresponding to the intersect of the two lines which represent the molar volume vs. x relations in ranges I and II. In the similar way as in sect. 2.3 it can be derived that N_6 in the germanosilicate glasses changes according to

$$N_6 = x \text{ (range I).}$$

Thus the intersect composition x_{max} directly gives the maximum value of $N_{6\text{max}}$. Fig. 5.2 represents the variation of $N_{6\text{max}}$, plotted as a function of r . It is clearly seen that $N_{6\text{max}}$ increases with increase in the molar ratio $\text{SiO}_2/\text{GeO}_2$ irrespective of the alkali species as $N_{4\text{max}}$ increases with increase in the molar ratio $\text{SiO}_2/\text{B}_2\text{O}_3$ in the borosilicate glasses. However, $N_{6\text{max}}$ of the sodium glasses is larger than that of the potassium ones, although in the borosilicates $N_{4\text{max}}$ of the potassium glasses is larger than that of the sodium ones. Furthermore, the slopes of the lines representing $N_{6\text{max}}$ vs. r relation of both alkali germanosilicate glasses are almost the same. In the borosilicates, the potassium glasses exhibit greater rate of increase in $N_{4\text{max}}$ than the sodium ones. Such difference in the composition dependence of $N_{6\text{max}}$ and $N_{4\text{max}}$ can be interpreted as indicating the

difference in structure between the borosilicate and germanosilicate glasses, although the details are uncertain at the present stage.

5.1.4 Partition of R_2O to SiO_2 and GeO_2

The additivity in the molar volume has been indicated in Fig. 5.1 in each range, I and II. Therefore, one can consider the germanosilicate glasses are composed by the two binary glasses; one is the alkali silicate glasses and the other is the alkali germanate ones. The rate of increase in the molar volume represented by the slope of the line in Fig. 5.1 is related to the amount of the $ROSiO_3$ and $ROGeO_3$ units. As in the alkali germanate glasses, the added R_2O should be thoroughly consumed by GeO_2 creating the GeO_6 units in the germanosilicate glasses in range I, because the slopes of the lines for the sodium glasses are almost null in Fig. 5.1, showing the absence of $NaOGeO_3$ and $NaOSiO_3$ units. Thus, on this basis, no alkali oxides are partitioned to SiO_2 and the partition coefficient to SiO_2 is null. In range II the alkali oxide is partitioned to each NWF oxide at a constant fraction at any compositions because linear relations are also seen in range II for the molar volume vs. x plot. When all of R_2O added is consumed by GeO_2 in the germanosilicate glasses in range II, the slopes of the lines should be the same as those of the germanate glasses, assuming additivity. However, the slopes of the silicate, germanate and germanosilicate are in the order, silicate < germanosilicate < germanate. This fact

also confirms the partition of R_2O to the two NWF oxides. Therefore, one can estimate the partition coefficients of the added R_2O to SiO_2 and GeO_2 from the slopes of the lines in ranges I and II. Here, it is assumed that the R_2O partitioned to GeO_2 in range II causes the same modifications and rearrangements of the germanate units in the germanosilicates just as it does in the alkali germanate glasses in range II. The slopes of the lines representing the molar volume vs. x relations in range II for the germanosilicate glasses have been obtained by the least square method and shown in Table 5.3.

Let k_{Si} and k_{Ge} the slopes of the binary alkali silicate and germanate glasses, and k_r that of the alkali germanosilicate glasses with the molar ratio $r=SiO_2/GeO_2$. The partition coefficients of R_2O to SiO_2 and GeO_2 are denoted respectively as C_{Si} and C_{Ge} . Then the parameters are related

Table 5.3. Rate of increase in the molar volume per addition of 1 mol R_2O (cm^3/mol^2).

	Na	K
Silicate and germanate glasses		
k_{Si}	18.55	32.88
k_{Ge}	30.12	43.01
Germanosilicate glasses		
$k_{1/3}$	28.70	43.15
k_1	27.20	41.39

with each other by the following equations.

$$k_r = C_{Si} k_{Si} + C_{Ge} k_{Ge}, \quad (5.1a)$$

$$C_{Si} + C_{Ge} = 1. \quad (5.1b)$$

Thus, the partition coefficients are obtained by

$$C_{Si} = (k_{Ge} - k_r) / (k_{Si} - k_{Ge}), \quad C_{Ge} = (k_r - k_{Ge}) / (k_{Ge} - k_{Si}). \quad (5.2)$$

The calculated partition coefficients have been shown in Table 5.4. It can be seen in the table that the fraction of R_2O partitioned to SiO_2 increases with increase in the ratio r , while that of R_2O partitioned to GeO_2 decreases with increase in r . The alkali oxides are predominantly partitioned to GeO_2 rather than SiO_2 . Moreover, the affinity of sodium oxide with SiO_2 is larger than that of potassium oxide. It is most interesting that all of potassium oxide in the glasses with $r=1/3$ are preferably partitioned to GeO_2 in range II as well as in range I. Therefore, the potassium germanosilicate glasses with $r=1/3$ can practically be regarded as mixtures of SiO_2 and binary potassium germanates.

Table 5.4. Partition coefficients of R_2O to SiO_2 and GeO_2 .

r	Na		K	
	C_{Si}	C_{Ge}	C_{Si}	C_{Ge}
range I				
1/3, 1	0	1.0	0	1.0
range II				
1/3	0.12	0.88	0	1.0
1	0.25	0.75	0.16	0.84

Table 5.5. Elastic properties of (a) sodium and (b) potassium germanosilicate glasses, $xR_2O \cdot GeO_2 \cdot rSiO_2$.

(a) R=Na						
x	d (g/cm ³)	v _l (km/s)	v _s (km/s)	K (GPa)	G (GPa)	E (GPa)
Series A, r=1/3						
0.10	3.544	4.526	2.702	38.10	25.88	63.31
0.15	3.642	4.756	2.773	45.04	28.01	69.60
0.20	3.666	4.794	2.781	46.21	28.35	70.28
0.25	3.658	4.767	2.771	47.99	28.11	70.66
0.28	3.656	4.832	2.790	47.41	28.45	71.12
0.30	3.636	4.797	2.768	46.51	27.86	69.67
0.35	3.617	4.801	2.749	46.92	27.33	68.66
0.40	3.560	4.780	2.723	46.16	26.40	66.51
0.50	3.462	4.717	2.648	44.66	24.28	61.66
Series B, r=1						
0.07	3.037	5.005	2.986	40.00	27.08	66.28
0.10	3.066	4.676	2.887	32.97	25.55	60.92
0.12	3.106	4.787	2.888	36.63	25.90	62.89
0.15	3.132	4.789	2.918	36.27	26.66	64.25
0.18	3.159	4.889	2.928	39.40	27.08	66.10
0.20	3.178	4.985	2.959	41.86	27.83	68.34
0.22	3.199	4.953	2.943	41.54	27.70	68.02
0.25	3.212	4.972	2.968	41.68	28.30	69.22
0.30	3.238	5.044	2.966	44.40	28.49	70.40
0.33	3.259	5.058	2.995	44.40	29.23	71.92
0.40	3.256	5.030	2.926	45.21	27.88	69.38
0.50	3.222	4.937	2.881	42.88	26.74	66.42
0.60	3.193	4.914	2.854	42.42	26.01	64.79
0.70	3.139	4.822	2.795	40.30	24.52	61.16
0.80	3.107	4.838	2.757	41.24	23.62	59.50
0.90	3.066	4.672	2.658	38.05	21.66	54.61
1.00	3.029	4.684	2.649	38.13	20.25	53.77

(b) R=K						
x	d (g/cm ³)	v _l (km/s)	v _s (km/s)	K (GPa)	G (GPa)	E (GPa)
Series A, r=1/3						
0.05	3.384	4.274	2.582	31.74	22.56	54.72
0.10	3.489	4.523	2.629	39.22	24.12	60.04
0.20	3.533	4.603	2.665	41.40	25.09	62.62
0.25	3.499	4.653	2.664	42.65	24.83	62.39
0.30	3.440	4.546	2.664	40.61	22.86	57.75
0.40	3.333	4.303	2.449	35.06	19.99	50.39
Series B, r=1						
0.10	3.075	4.685	2.862	33.91	25.19	60.57
0.20	3.152	4.885	2.909	39.65	26.67	65.36
0.30	3.160	4.930	2.885	41.73	26.30	65.21
0.40	3.120	4.818	2.787	40.11	24.23	60.52
0.50	3.065	4.649	2.648	37.59	31.49	54.15
0.70	2.969	4.441	2.489	34.00	18.37	46.71

5.2 Elastic properties of alkali germanosilicate glasses and their structure model

In this section the network structure and the alkali ion sites in the germanosilicate glasses will be discussed on the basis of bulk modulus vs. mean atom-pair volume relation.

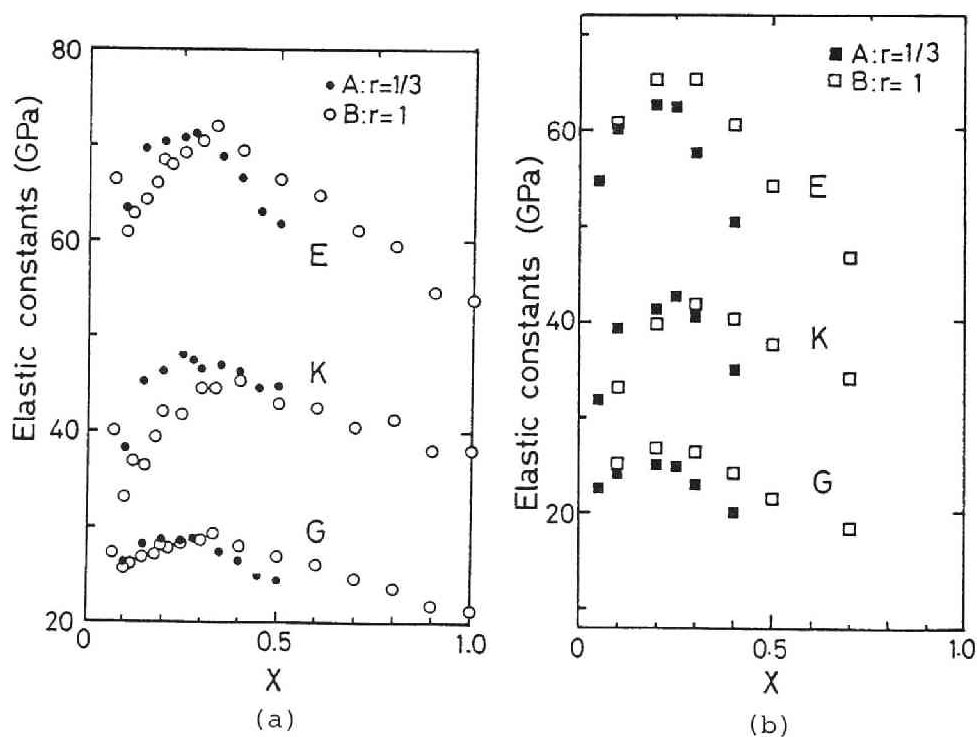


Fig. 5.3. Variation of elastic constants of (a) sodium and (b) potassium germanosilicate glasses.

5.2.1 Results

Table 5.5(a) and (b) show the measured elastic constants of the sodium and potassium germanosilicate glasses, respectively. Fig. 5.3(a) and (b) represent the variation of the elastic constants as a function of the molar ratio $x = R_2O/GeO_2$. The elastic constants become maximum at the compositions corresponding to the bending in the molar volume vs. x relation shown in Fig. 5.1. This suggests that the fraction N_6 of six-coordinated GeO_6 units becomes maximum at those compositions and that the non-bridging bonds are formed on further addition of the alkali oxide.

5.2.2 Bulk modulus vs. mean atom-pair volume relation

Fig. 5.4 shows the bulk modulus vs. mean atom-pair volume relation (K-V relation) of the alkali germanosilicate glasses. The plots for the sodium glasses including GeO_2 glass can be well approximated by a solid line of slope -4. The broken line represents those of the sodium glasses in range II where the non-bridging oxygens are present. The K-V relation of the potassium glasses is dissimilar to that of the sodium ones. On this basis, it is considered that the structure of $GeO_2 \cdot rSiO_2$ glass is modified little by creation of the Na_2GeO_6 units caused by the addition of Na_2O in range I, and that Na^+ ions are filled in the voids of the oxygen cages of the glass networks. This structure model is consistent with that derived from the molar volume vs. x relation of the sodium glasses in

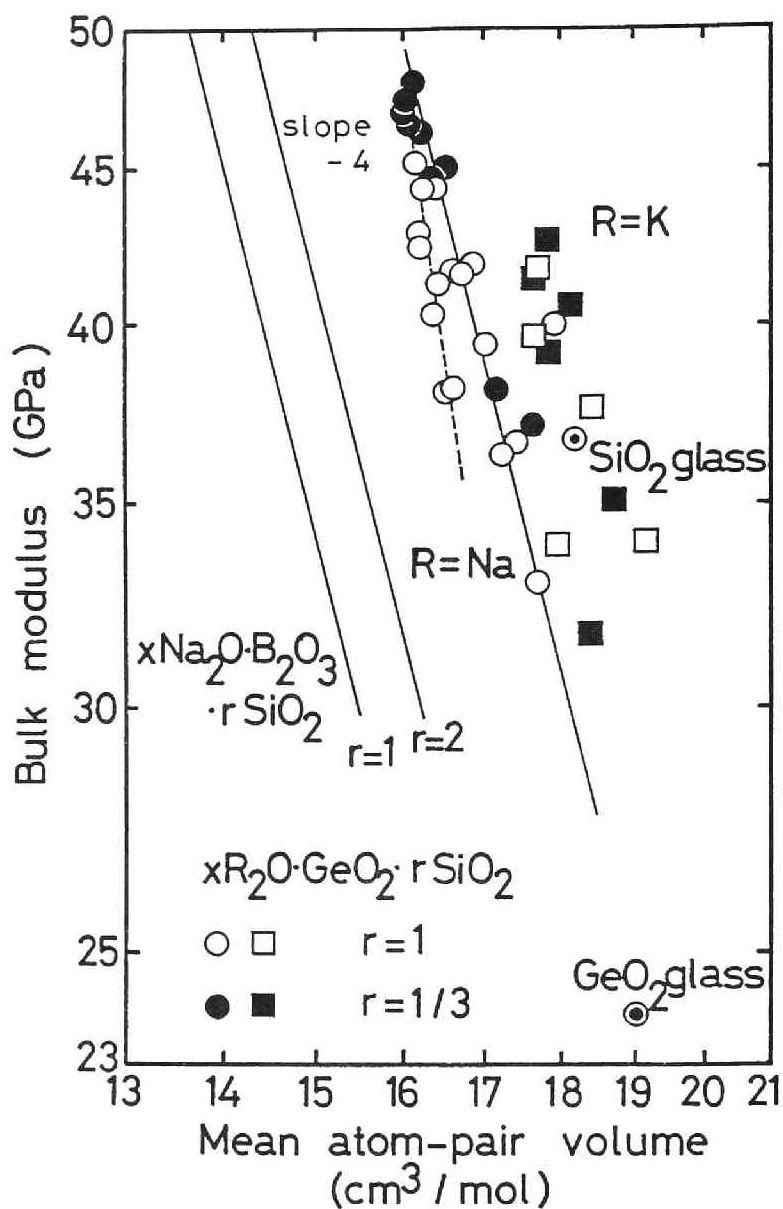


Fig. 5.4. K-V relation for sodium (O,●) and potassium (□,■) germanosilicate glasses. That of sodium borosilicate glasses is also indicated.

range I. In Fig. 5.4, the other two solid lines with the slope -4 represent the K-V relations of the sodium borosilicate glasses in range I, where added Na_2O is consumed only by changing the BO_3 units to the RBO_4 units. It is very interesting to compare the K-V relations between the borosilicate and germanosilicate glasses. The K-V relation of the former glasses is represented by two lines depending on the ratio $r=\text{SiO}_2/\text{B}_2\text{O}_3$. On the other hand, that of the latter, i.e., sodium germanosilicate glasses in range I can be approximated by single solid line, which is identical to the line for the binary sodium germanate glasses (not shown) in range I, indicated in Fig. 3.5. Further, the plots for the binary glasses in range II lie on the broken line for the germanosilicate glasses in range II indicated in Fig. 5.4. That is, the K-V relation of the sodium germanosilicate glasses can be represented by the two lines, one for range I and other for range II, which are indicated by the solid and broken lines, respectively, in Fig. 5.4. These experimental results indicate that in the GeO_2 containing glasses the GeO_4 and SiO_4 units can be substituted freely. However, since in Fig. 5.4 a line tying the K-V plots of GeO_2 and SiO_2 glass do not have the slope -4, the arrangements of the SiO_4 tetrahedra in the germanosilicate glasses are different from those in silica glass. That is, when the SiO_4 units substitute the GeO_4 ones in the alkali germanate glasses and construct the network of the germanosilicate glasses, the configuration of the GeO_4 and SiO_4 units is the same as that of the GeO_4 ones in the binary glasses.

5.3 Summary

The composition dependence of the molar volume has been studied in the alkali germanosilicate glasses of the compositions $xR_2O \cdot GeO_2 \cdot rSiO_2$ ($0 < x < 1$, $R = Na$ and K , $r = 1/3$ and 1). It has been shown that the whole composition range is divided in two ranges I and II. In range I the GeO_4 units are changed to the GeO_6 ones, and in range II the non-bridging oxygens are created by addition of R_2O . The fraction N_6 of six-coordinated Ge atoms becomes maximum at the end of range I. The maximum value, N_{6max} , in the glasses with $r = 1/3$ and 1 increases with increase in the molar ratio $r = SiO_2/GeO_2$. N_{6max} of the sodium glasses is larger than that of the potassium ones, while in the borosilicate system, N_{4max} of the potassium glasses is larger than that of the sodium glasses.

In range II, the partition coefficient of the alkali oxides to GeO_2 and SiO_2 has been obtained from the molar volume vs. x relation. It has been shown that K_2O in the glasses with $r \leq 1/3$ is preferably partitioned to GeO_2 in ranges I and II.

The elastic constants increase in range I and decrease in range II regardless to the alkali species and the molar ratio r . The bulk modulus vs. mean atom-pair volume relation of the sodium germanosilicate glasses with $r = 0$, $1/3$ and 1 can be approximated by two lines; one with slope -4 for the glasses in range I, and the other for those in range II. This observation indicates that the sites for Na^+ ions and the arrangements of the GeO_4 and GeO_6 units are similar to those

found in the binary sodium germanate glasses. The SiO_4 units substitute the GeO_4 units and have the same configuration as that of the GeO_4 units in the binary germanate glass.

Reference

- 1] R.E. Riebling, J. Am. Ceram. Soc., 51 (1968) 406-07.

Chapter 6

NETWORK STRUCTURE OF ALKALI BOROPHOSPHATE GLASSES

The structure of the glasses in the system $R_2O-B_2O_3-P_2O_5$ will be discussed in this chapter. Those glasses have two complexing factors in their constitution; one is the change in the coordination of boron atoms and the other is the presence of P=O double bonds. A silica type network composed by four-branched BO_4 and PO_4 unit as found in BPO_4 crystal [1] will be formed when B_2O_3 and P_2O_5 coexist in glass. It can be expected that the formation of such three dimensional network will increase elastic constants as in the borosilicate and germanosilicate glasses. Moreover, addition of R_2O will produce non-bridging oxygens, which might increase the specific volume of glasses. Considering these, the molar volume and the elastic constants have been measured in the pseudo-binary system $K_2O \cdot 2B_2O_3 - K_2O \cdot 2P_2O_5$. The variation of fraction of the four-coordinated boron atoms and the behavior of the P=O double bonds have been investigated in order to discuss the constitution of the glasses.

6.1 Elastic properties of alkali borophosphate glasses

6.1.1 Preparation of the glasses and chemical analysis

Among ternary alkali borophosphate systems, $R_2O-B_2O_3-P_2O_5$, the glass formation region has been reported only in the

potassium system [2], $K_2O-B_2O_3-P_2O_5$. All of the mixtures in the pseudo binary system $K_2O \cdot 2B_2O_3 - K_2O \cdot 2P_2O_5$ yield good glasses on substitution of P_2O_5 for B_2O_3 . The system thus is employed in the present study.

Reagent grade K_2CO_3 , B_2O_3 and P_2O_5 were mixed together to give about 40g glass. The batch composition of the glasses were $K_2O \cdot 2(1-x)B_2O_3 \cdot 2xP_2O_5$ ($0 \leq x \leq 1$), and the glasses with $x=0$ and 1 corresponded respectively to the binary potassium diborate and diphosphate glasses. The batches were placed in covered alumina crucibles in an electric furnace at temperatures ranging from 800 to $1000^\circ C$, depending on the composition. In the course of melting, dry O_2 gas was bubbled in the melt through a Pt pipe in order to homogenize the melt and diminish water content. After 1 hr melting, the melt was poured into a graphite mold and quenched glass block specimens of $1.5 \times 1.5 \times 1.5$ cm in size were obtained. They were annealed at appropriate temperature determined else for 30 min and were served for density and elasticity measurements. Since the glasses could not be prevented from contaminations of Al_2O_3 and H_2O , the composition of all of them was determined by chemical analysis [3]. Employed methods were ZnO substitution method for H_2O , phosphorous molybdate method for P_2O_5 , JIS R 3105-1981 for B_2O_3 and EDTA chelate titration for Al_2O_3 . Table 6.1 shows the analysed and batch composition of the glasses. No studies have been carried out on the behavior of Al atoms in the borophosphate glasses. From the analogy in the glasses of the system $CaO-B_2O_3-Al_2O_3$ reported by Bishop and Bray [4], it is assumed that Al atoms are present in the

Table 6.1. Analysed compositions of the glasses in the pseudo-binary system $K_2O \cdot 2(1-x)B_2O_3 \cdot 2xP_2O_5$.

x	r	Analysed composition(mol %)					q ^a
		K ₂ O	H ₂ O	B ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	
0	0	34.0	0.6	64.0	1.4	0	0.529
0.1 ^b							
0.125	0.114	29.1	0.6	60.0	2.4	8.0	0.421
0.25	0.251	31.5	0.5	48.0	2.9	17.1	0.470
0.333	0.325	29.4	0.9	42.6	4.2	22.8	0.443
0.375	0.291	33.6	0.5	42.0	4.7	19.2	0.518
0.5	0.458	32.4	0.6	34.1	2.2	30.7	0.492
0.625	0.621	38.0	0.7	21.2	1.5	38.5	0.633
0.666	0.693	32.1	0.7	20.0	0.6	46.6	0.489
0.75	0.716	32.6	0.8	16.5	2.4	47.7	0.501
0.875	0.846	33.7	1.1	8.9	1.1	54.8	0.543
0.95	0.886	27.0	2.0	6.6	1.5	62.9	0.408
1.0	0.968	32.5	1.1	0	2.1	64.2	0.507

a: $q = (H+K)/(B+Al+P)$, b: not analysed.

four-coordinated state as the network forming cation. It is assumed that K_2O is first combined with Al_2O_3 resulting in AlO_4 units and the rest of K_2O interacts with B_2O_3 and P_2O_5 . The molar fraction r of P_2O_5 in the total amount of the network forming oxides, that is, $r = P_2O_5 / (B_2O_3 + Al_2O_3 + P_2O_5)$, is taken as the composition parameter. Parameter r is equivalent to x if no Al_2O_3 are dissolved into the glass during melting. H_2O may play the role of a network modifying oxide as K_2O , as assumed in the binary phosphate glasses in Chap. 8. The molar ratio q of the network modifying oxides to forming ones, $q = (H_2O + K_2O) / (B_2O_3 + Al_2O_3 + P_2O_5)$, is nearly equal to 0.5 for all the glasses as indicated in Table 6.1. It confirms that the total amount of the network forming cations in one

formula-weight of the glass is 4 mol, being independent of r . Thus, the glasses with $r=0$ and 0.968 can be regarded substantially as $K_2O \cdot 2B_2O_3$ and $K_2O \cdot 2P_2O_5$ glasses. The former glass is constructed only by bridging bonds. Each P atom in the latter glass has one or two non-bridging bonds since a P=O double bond is a kind. Therefore, parameter r is related to the amount of the non-bridging bonds in the glass.

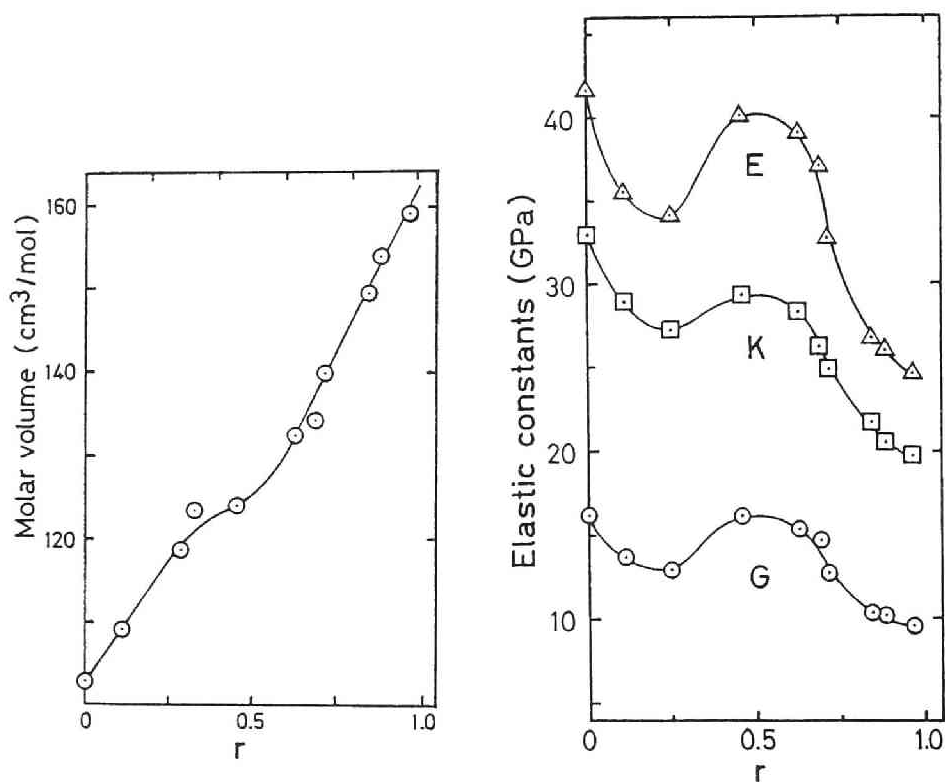
Table 6.2. Densities and elastic constants of the potassium borophosphate glasses.

x	r	d (g/cm ³)	v_l (km/s)	v_s (km/s)	G (GPa)	K (GPa)	E (GPa)
0	0	2.268	4.492	2.441	13.65	28.01	35.24
0.1		2.275	4.443	2.371	12.79	27.60	33.23
0.125	0.114	2.303	*				
0.25	0.251	2.349	4.358	2.401	13.32	26.11	34.14
0.333	0.325	2.381	*				
0.375	0.291	2.426	*				
0.5	0.458	2.466	4.562	2.563	16.11	29.58	40.91
0.625	0.621	2.470	4.446	2.495	15.38	28.32	39.06
0.666	0.693	2.459	4.317	2.443	14.69	26.24	37.14
0.75	0.716	2.442	4.141	2.288	12.78	24.83	32.73
0.875	0.845	2.404	3.846	2.073	10.33	21.78	26.76
0.95	0.886	2.394	3.770	2.054	10.10	20.55	26.04
1.0	0.968	2.375	3.698	2.004	9.54	19.77	24.65

* Not measured.

6.1.2 Results

Table 6.2 represents the density and elastic constants of the borophosphate glasses. The molar volume V of a glass is defined as $V = (4/d) \sum f M_w$, where f and M_w represent the fraction and molar weight of each oxide, and d the density.



Figs. 6.1 (left) and 6.2 (right). Molar volumes and elastic constants, plotted as a function r .

The glass with batch composition contains four network forming cations (B + P) in total in the volume V . Fig. 6.1 shows the variation of the molar volume plotted as a function of r . The molar volume increases almost linearly with r though a plateau is seen near 0.5 in r . It seems, therefore, that the amount of the non-bridging bond increases gradually in the glass and some structural change might occur near 0.5 in r . Fig. 6.2 shows the elastic constants, namely, Young's modulus E , bulk

modulus K and shear modulus G , plotted as a function of r . Although the molar volume varies rather monotonously with r , the elastic constants exhibit complicated dependence on r . They once become minimum near 0.25 in r , reach maximum near 0.5 in r and decrease remarkably in the range $r \geq 0.5$. A distinct maximum of the constants strongly suggests that two structural changes take place in glasses, which increase and decrease the elasticity.

6.2 Constitution of the borophosphate glasses and their structure model

The constitution of the potassium borophosphate glasses will be discussed in this section from the composition dependence of the molar volume and elastic constants. A structure model will be derived and the property vs. composition relations are interpreted on the basis of the model. In the course of the subsequent discussion, one can employ the molar ratio x in the batch composition to denote the composition of the glasses. This is reasonable because the molar ratio r in the analysed composition is nearly equal to x , as indicated in Table 6.1.

6.2.1 Structure units

$K_2O \cdot 2B_2O_3$ and $K_2O \cdot 2P_2O_5$ glasses are the terminal ones in the pseudo-binary system employed here. Bray and O'keefe [5]

measured the fraction N_4 of four-coordinated boron atoms in the potassium borate glasses. The measured N_4 is slightly deviated from that predicted by the equation $N_4 = K_2O/B_2O_3$, indicating the presence of non-bridging bonds. However, the deviation is negligibly small. Therefore, potassium diborate glass can substantially be regarded as being constructed by an equal amount of KBO_4 and BO_3 units which are connected by bridging oxygens. On the other hand, $K_2O \cdot 2P_2O_5$ glass can be regarded as consisting of equal amount of KPO_3 and $PO_{2.5}$ units according to the discussion in Chap. 8. The $PO_{2.5}$ units denote those found in P_2O_5 , having one $P=O$ and three bridging $P-O$ bonds. Therefore, the glasses in the pseudo-binary system may be constructed by at least four units; KBO_4 , BO_3 , KPO_3 and $PO_{2.5}$ when no more interactions are considered between B_2O_3 and P_2O_5 . The amount of the non-bridging bonds increases with increase in x , since P atoms in the two phosphate units have one or two non-bridging bonds. This causes the increase in the molar volume and decrease in the elasticity of glasses as indicated in the last three chapters. Although the increase in the molar volume can be attributed to the increase in the non-bridging bonds, the characteristic variation of the molar volume near 0.5 in x and that of elastic constants in the whole composition range cannot be explained from this basis.

Therefore, some other structural change surely occurs in the glasses which overcomes the decrease in the elasticity caused by increasing amount of the non-bridging bonds and increases it to be maximum at 0.5 in x . The increase in elasticity has been caused by the structural strengthening due

to the increase in the fraction of four- and six-coordinated B and Ge atoms as shown in the B_2O_3 or GeO_2 containing glasses. Such changes in structure take place probably in the borophosphate glasses. Moreover, N_4 has already become 0.5 in potassium diborate glass which is the maximum value attainable in the alkali borate systems as indicated in Chap. 2. Hence, the structural change should be the one that increases the amount of four-branched BO_4 units and N_4 beyond 0.5.

A preliminary IR study [6] indicated followingly. The intensity of the IR bands characteristic to a metaphosphate anion at 1270, 1090, 1000 and 890 cm^{-1} [7], found in the glass with $x=0.95$, decreased gradually with increasing B_2O_3 content. A few bands at 1170, 1090 and 935 cm^{-1} appeared in the glasses in the range $0.25 \leq x \leq 0.75$ which were characteristic bands of BPO_4 crystal of high-cristobalite structure [7]. Thus, the elasticity and IR measurements suggest formation of BO_4-PO_4 units.

6.2.2 Structure model

When B_2O_3 is substituted by P_2O_5 in $K_2O \cdot 2B_2O_3$ glass with keeping the total amount of the NWF cations constant ($=4$), the possibility of the presence of the following seven units should be considered in the glasses : four-branched KBO_4 , BO_4 and PO_4 , three branched BO_3 and $PO_{2.5}$, and two-branched $KOBO_2$ and KPO_3 . Among these, the BO_4 and PO_4 units bear formal charge of -1 and +1, respectively. Potassium ions are involved in a few units and formation reactions of these units are

competitive. Thus it is unlikely that only one of the three units, KOBO_2 , KPO_3 and KBO_4 , is preferably produced. Fig. 6.1 shows the monotonous increase in the molar volume with x in the whole composition range. Then this variation may be concerned with the phosphate units, since the content of the borate units decreases with increase in x . Further, the heat of solution of $\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5$ glass in 3N- HNO_3 aqueous solution can be given as $\Delta H_s = -30$ kcal/mol in Fig. 8.2. That of $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glass in 2N- HNO_3 solution has been reported as $\Delta H_s = -10.4$ kcal/mol [8]. The two heats of solution cannot directly be compared with each other because of difference in the solvent. However, heats of infinite dilution [9] of 2N- and 3N- HNO_3 solution are the order of 0.1 kcal/mol. Thus the heats of solution data might indicate that K_2O has preferred affinity with B_2O_3 and causes the formation of $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, due to the thermochemical discussion similar to that in section 4.5.

Then, consider the following model of the constitution of a glass $\text{K}_2\text{O} \cdot 2(1-x)\text{B}_2\text{O}_3 \cdot 2x\text{P}_2\text{O}_5$.

- (a) $2(1-x)\text{B}_2\text{O}_3$ is reacted with $(1-x)\text{K}_2\text{O}$ resulting in $2(1-x)\text{KBO}_4$ and $2(1-x)\text{BO}_3$ units as in the binary borate systems.
- (b) The rest of K_2O , i.e., $x\text{K}_2\text{O}$, is reacted with $2x\text{P}_2\text{O}_5$ creating $2x\text{KPO}_3$ and $2x\text{PO}_{2.5}$ units.
- (c) A reaction between free $2(1-x)\text{BO}_3$ and $2x\text{PO}_{2.5}$ gives $2x(\text{BO}_4 + \text{PO}_4)$ and $2(1-2x)\text{BO}_3$ in the range $x \leq 0.5$ while $2(1-x)(\text{BO}_4 + \text{PO}_4)$ and $2(2x-1)\text{PO}_{2.5}$ are formed in the range $x \geq 0.5$. The difference in the reaction products is caused

by the fact that the amount of free BO_3 is larger than that of $\text{PO}_{2.5}$ in the range $x < 0.5$, and vice versa.

Let T the total fraction of the NWF cations in four-branched units, $\text{KBO}_4 + \text{BO}_4 + \text{PO}_4$ in the 4 mol NWF cations. In the range $x \leq 0.5$, reactions (a) and (b) give $2(1-x)$ and $4x$ mol of four-branched units, indicating

$$T = (1/2) (1+x). \quad (x \leq 0.5) \quad (6.1)$$

As for the boron atoms, N_4 represents the ratio $(\text{KBO}_4 + \text{BO}_4) / (\text{BO}_3 + \text{KBO}_4 + \text{BO}_4)$, and is expressed as

$$N_4 = 1 / (2(1-x)). \quad (x \leq 0.5) \quad (6.2)$$

Consequently, it is indicated that N_4 is equivalent to the molar ratio $\text{K}_2\text{O}/\text{B}_2\text{O}_3$ in the glass. In the range $x \geq 0.5$, reaction (c) produces $2(1-x)(\text{BO}_4 + \text{PO}_4)$ and $2(2x-1)\text{PO}_{2.5}$. Then the total fraction T of the NWF cations in the four-branched units is

$$T = (3/2) (1-x), \quad (x \geq 0.5) \quad (6.3)$$

and N_4 can be represented by

$$N_4 = 1. \quad (x \geq 0.5) \quad (6.4)$$

Thus, the structure model of the borophosphate glasses described by reactions (a), (b) and (c) indicates that only the KPO_3 and $\text{PO}_{2.5}$ units have the non-bridging oxygens. The model can predict the variation of the total fraction of the NWF cations in the four-branched units which are expected to form a network like silica glass. Fig. 6.3 represents variation of T and fraction of P atoms with $\text{P}=\text{O}$ or $\text{P}-\text{O}^-$ non-bridging bonds, plotted as a function of x . It is

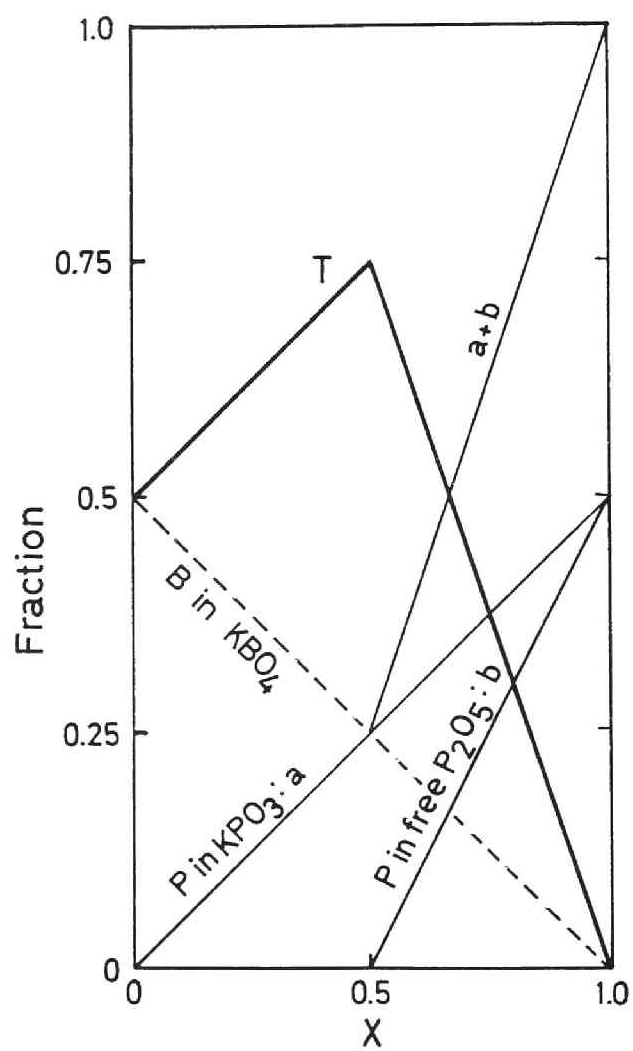


Fig. 6.3. Total fraction of four-branched units T , and the fraction of P atoms with non-bridging bonds.

indicated that T becomes maximum at 0.5 in x . This may cause the maximum elastic constants at 0.5 in r in Fig. 6.2. Therefore, the minima of the elasticity near 0.25 in r can be subsequently interpreted. The substitution of P_2O_5 for B_2O_3 increases the amount of the non-bridging oxygens, which may decrease the elastic constants. This decreasing effect is first predominant in the range $r \leq 0.25$ than increasing one caused by the increase in T . Then in the range $0.25 \leq x \leq 0.5$ the latter effect exceeds the former effect due to strengthened networks, resulting in the maximum elastic constants near 0.5 in r . In the range $r \geq 0.5$, however, the amount of non-bridging oxygens increases more rapidly because the free BO_3 units are exhausted and the formation of free $PO_{2.5}$ units starts in addition to the formation of KPO_3 units. The variations of the properties derived from the present model are consistent with the experimental results, that is, the elastic constants decrease remarkably in the range $r \geq 0.5$ in Fig. 6.2, and the rate of increase in the molar volumes in the range $r \geq 0.5$ in Fig. 6.1 becomes larger than that in the range $r \leq 0.5$.

6.2.3 Yun and Bray's NMR data

The variation of N_4 of four-coordinated boron atoms is represented as a function of x in Fig. 6.4. The solid curve represents that from the present model. Due to Yun and Bray's model [9], N_4 of the present pseudo-binary borophosphate glasses can be represented by the following equations.

$$N_4 = 1/2 + 0.31 x/(1-x), \quad (x \leq 0.5) \quad (6.1')$$

$$N_4 = 0.81.$$

$$(x \geq 0.5)$$

$$(6.4')$$

They are represented by the broken line in Fig. 6.4. It should be noted that Yun and Bray did not employ the analysed compositions for data arrangement in spite of utilizing clay crucibles for glass preparation. Considering this, N_4 vs. x curve derived here is similar in shape to the curve of Yun and Bray. The difference in the N_4 vs. x relations represented by the solid and broken curves can be attributed to the fact that the absence of the non-bridging bonds is assumed in the present model. Except this, the present model well describes the constitutions of the borophosphate glasses.

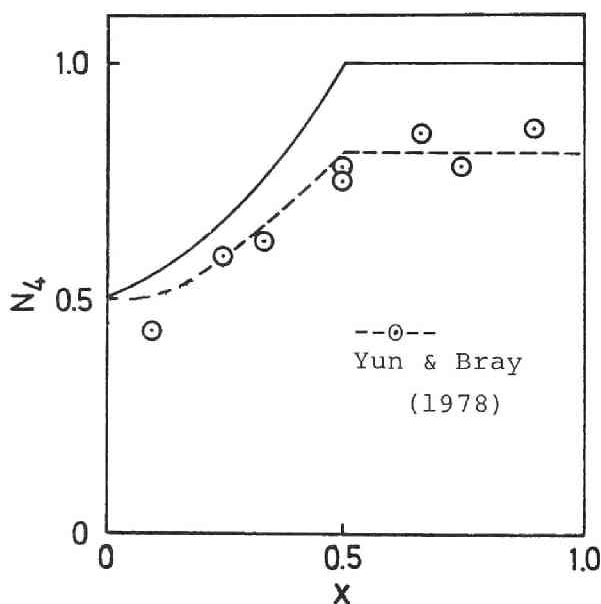


Fig. 6.4. The fraction $N_4 = \text{BO}_4 / (\text{BO}_3 + \text{BO}_4)$ due to the present model is indicated by the solid curve. The broken curve represents Yun and Bray's model (ref. 9).

6.3 Summary

The molar volumes and elastic constants of a series of potassium borophosphate glasses $K_2O \cdot 2(1-x)B_2O_3 \cdot 2xP_2O_5$ ($0 \leq x \leq 1$) have been measured. The molar volume increases monotonously with increase in x , although a plateau is seen in the molar volume vs. x relation near 0.5 in x . On the other hand, the elastic constants have exhibited complicated dependence on the composition. They first decrease, become minimum near 0.25 in x and increase up to a maximum at 0.5 in x . Further increase in x decreases the elasticity remarkably. A structure model has been proposed, where (a) K_2O first produces KBO_4 units whose amount is equal to the molar ratio K_2O/B_2O_3 as in the binary borate glasses, (b) the rest of K_2O is reacted with P_2O_5 , resulting in KPO_3 units, and (c) the free B_2O_3 and P_2O_5 are combined together to form a BO_4+PO_4 silica type network. This model can well explain the dependences of the elastic constants and molar volumes upon x . Furthermore, the variation of N_4 from the present model has been compared with that of Yun and Bray [9]. The two data show similar composition dependence; except that the latter shows a presence of a negligible amount of borate units having non-bridging oxygens. This indicate that the present model represents the constitution of the pseudo-binary borophosphate glasses very well.

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Chapter 7

VOIDS AND NETWORK MODIFIERS IN GLASS NETWORKS

When a macroscopic property is measured for several series of glasses and the results are systematically rearranged and the property of each series is compared with that of the other one in the light of a model, one can obtain knowledges of microscopic or local structures and properties of the glasses. A simple cage structure model derived from high-cristobalite (denoted as h-c) structure has been proposed successfully to interpret variations of volumetric and elastic properties of alkali silicate and borosilicate glasses [1,2]. In this Chapter, molar volume of several glasses will be discussed on the basis of 'void' present in the glasses by applying the above model to SiO_2 , GeO_2 , or some other assumed glasses. The borate glasses are different in structure from the silicate and germanate glasses that consist mainly of oxygen tetrahedra. The difference can be indicated in an enhanced way by applying the h-c type structure model.

7.1 Voids in h-c type structure

7.1.1 Void

The structures of not only simple compounds such as M_2O and MO but also multicomponent compounds can be regarded as packings of the oxygen polyhedra. For example, in alkali

aluminosilicates with stuffed silica structures, Al and Si atoms are tetrahedrally surrounded by oxygens and the alkali ions occupy the large inner space of the oxygen cages constructed by the tetrahedra. Such space occupied by network modifying (denoted as NWM) cations is called 'void' here and is distinguished from the interstitial sites in the oxygen tetrahedra or octahedra which network forming (denoted as NWF) cations can occupy. For simplicity, the size of the void will be represented by the volume of the largest sphere accommodated in it. Therefore, a glass can be regarded as consisting of the NWF cation-O skeleton and the voids. Let V_v and V_s the volumes of the void and the skeleton in the averaged volume V of an h-c type glass per one NWF cation, then

$$V = V_v + V_s. \quad (7.1)$$

Here, V_s is replaced by nV_o , where n represents the number of oxygens stoichiometrically associated with one NWF cation, e.g., $n=2$ for silica glass, and V_o is defined as the apparent volume of an oxygen. The volume V_s , and thus V_o , varies from one glass to another depending upon the composition, but one cannot estimate the exact V_o in each glass. Therefore, the volume V_o , evaluated for a reference glass, i.e., silica glass in the present study, will be applied to the other glasses to obtain the void volume V_v . Then, it is intended to clarify the effects of the various alkali ions and NWF cations on the sizes of the voids.

7.1.2 High-cristobalite structure

It should be necessary to show the reasons for taking h-c as the basis of the cage structure model in advance to calculation and discussion. The structure of h-c has been proposed, as mentioned above, to be a model structure of alkali silicate and borosilicate glasses previously [1,2]. On the other hand, Taylor and Brown, Jr.[3] have explained the RDF spectra of some feldspar glasses by assuming the distribution of the tetrahedra as in tridymite (denoted as h-t) structure. The two modifications of silica, h-c and h-t, are constructed basically by the same two kinds of oxygen layers, A and B, though their stacking sequences are different. Fig. 7.1 shows a part of ideal h-c structure. The circles represent oxygen atoms, while silicon atoms are not shown. The open circles are on the plane of the paper (layer A), the filled ones above the plane and those drawn by broken line below the plane (layers B and B'). In h-c the stacking sequence of the layers is ABA'B'A"B" in the direction of $\langle 111 \rangle$ axis, while in h-t ABAB' in the direction of c-axis. Here, ' and " indicate the layers obtained by displacing the original one in (111) or (0001) plane to some extent. Therefore, the molar volumes V_m of the two crystals should be almost the same, and practically they are; $V_m(\text{h-c})=27.6$, $V_m(\text{h-t})=27.1 \text{ cm}^3/\text{mol}$ [4]. However, h-c structure is constructed by a unit cage skeleton $\text{Si}_{10}\text{O}_{12}$ which consists of 4 $(\text{Si-O-Si})_6$ rings of chair conformation, whereas that of h-t structure is $\text{Si}_{12}\text{O}_{12}$ consisting of 3 $(\text{Si-O-Si})_6$ rings of boat conformation. Since

Si-O-Si bridging bonds are shared by the several cages, the unit cages of h-c and h-t structure correspond stoichiometrically to one and two molecules of SiO_2 , respectively. That is, the volumes of the space in these unit cages enclosed by the rings are equal to the volume of one and two molecules of SiO_2 . It has been already shown[1] that the structure of the alkali silicate glasses should be regarded as a mixture of a few atomic units, such as $\text{SiO}_{4/2}$ and $\text{ROSiO}_{3/2}$,

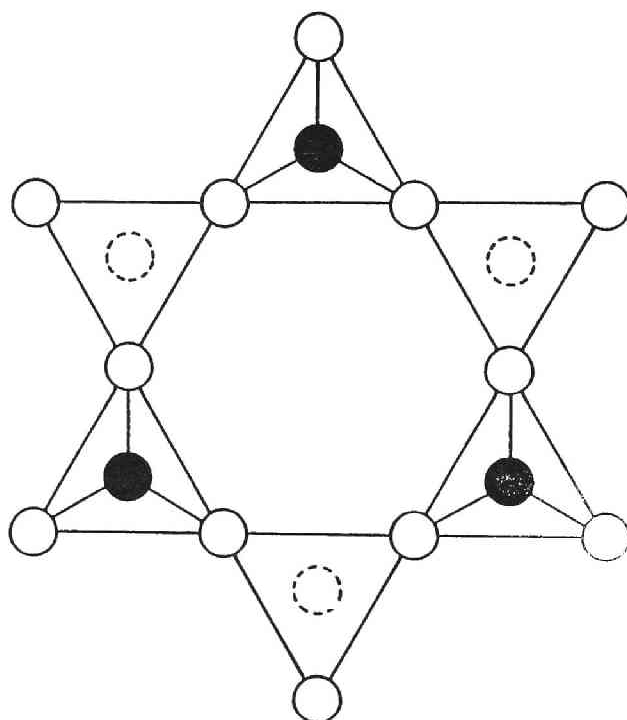


Fig. 7.1. A part of ideal high-cristobalite structure.
The circles represent oxygen atoms, forming laryes
A (●) and B, B' (○, ()). Si atoms are not shown.

which are present actually in the glasses, and it is important that one unit cage contains one Si atom. Thus, it is preferred from that view point to take h-c structure for the model of glass networks, because one Si atom corresponds to one unit cage, that is, one void in h-c. This correspondence relation is of special importance to consider the voids in the network in which BO_4^- tetrahedra and $^-\text{OSiO}_3$ tetrahedra are present with accompanying NWM cation in their neighborhood. Moreover, an $\text{Si}_{10}\text{O}_{12}$ is the single kind cage unit in h-c structure, whereas h-t structure has two kinds of voids enclosed by Si_8O_9 and $\text{Si}_{12}\text{O}_{12}$ cages, the latter being mentioned previously. This is another reason for taking h-c structure as the basis of model rather than h-t structure.

7.2 Volume data and calculation procedures

7.2.1 Volume data

Table 7.1 shows the volume data[1,5-7] for glasses and atomic units used in the following calculations. The molar volumes of $\text{R}_2\text{O} \cdot 2\text{SiO}_2$ glasses have been obtained by a linear approximation of the molar volume of $x\text{R}_2\text{O} \cdot \text{SiO}_2$ glasses vs. x relation [1]. The molar volumes of NaBO_4 and KBO_4 units in the alkali borate glasses are obtained in the similar way as in the silicates. Those of $x\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ glasses ($r=1$ and 2) [5] are extrapolated from the range $0 < x < 0.5$ to 1 in x in order to obtain the volumes of assumed glass networks $2\text{RBO}_{4/2}\text{SiO}_{4/2}$

Table 7.1. Partial molar volumes of several structure units (cm^3/mol).

Unit	Volume	Unit	Volume
SiO_2 glass a)		Alkali disilicate glasses a)	
$\text{SiO}_{4/2}$	27.3	$\text{ROSiO}_{3/2}$, R=Li	32.0
GeO_2 glass b)		Na	36.4
$\text{GeO}_{4/2}$	28.0	K	43.4
Borosilicate glasses c)		Rb	45.7
$2\text{BO}_{3/2}\text{SiO}_{4/2}$	65.7	Cs	55.2
$\text{BO}_{3/2}\text{SiO}_{4/2}$	46.8	Alkali borosilicate glasses d)	
Germanosilicate glasses b)		$2\text{RBO}_{4/2}\text{SiO}_{4/2}$, R=Na	66.2
$(\text{Ge}_{1/2}\text{Si}_{1/2})\text{O}_{4/2}$	27.9	K	82.9
$(\text{Ge}_{3/4}\text{Si}_{1/4})\text{O}_{4/2}$	27.5	$\text{RBO}_{4/2}\text{SiO}_{4/2}$, R=Na	92.1
		K	108.0

a): ref. 2, b): § 7.1, c): ref. 4, d): ref. 3.

and $\text{RBO}_{4/2}\text{SiO}_{4/2}$ in which the boron atoms are all in fourfold coordination. The volumes of $2\text{BO}_{3/2}\text{SiO}_{4/2}$ and $\text{BO}_{3/2}\text{SiO}_{4/2}$ glasses are interpolated using the data of Cousen and Turner[6], where the boron atoms are in threefold coordination.

It has been shown from the study on the glasses of the composition, $x\text{R}_2\text{O} \cdot \text{GeO}_2 \cdot r\text{SiO}_2$ (R=Na and K, $r=0, 1/3$ and 1), the molar volume of the sodium glasses remains constant with increase in x in the range of lower alkali content ($x < 0.3$). The molar volume of alkali free glasses $\text{GeO}_2 \cdot r\text{SiO}_2$ has been obtained by extrapolating that of the sodium germanosilicate glasses to 0 in x .

7.2.2 Calculation

Let 0.162 and 0.309nm Si-O bond length and neighboring Si-Si distance as in silica glass [8], and 0.135nm the radius of bridging oxygens given by Shannon and Prewitt (denoted as S&P)[9] as the radius of the two-coordinated oxygen ions. It has been already shown[1,2] that the largest sphere to be accommodated in the voids of silica glass, approximated by h-c structure, has a radius as large as 0.156nm. Thus the volume of the void $V_v = 9.6 \text{ cm}^3/\text{mol}$ is obtained due to $V_v = (4/3)\pi N_A r^3$, where $r = 0.156\text{nm}$ and N_A is the Avogadro's number.

Letting $v(\text{SiO}_{4/2})$ the volume of a cage corresponding to an $\text{SiO}_{4/2}$ unit, $v(\text{SiO}_{4/2})$ can be written as follows according to eq. (7.1).

$$v(\text{SiO}_{4/2}) = V_v + 2V_o, \quad (7.2)$$

where $2V_o$ represents the volume unavailable for accommodation of the sphere in the cage. In silica glass, $v(\text{SiO}_{4/2}) = 27.3$ and $V_v = 9.6 \text{ cm}^3/\text{mol}$ give $V_o = 8.9 \text{ cm}^3/\text{mol}$. It is natural that the size of oxygens depends on the glass composition and NWF oxide and varies from bridging oxygens to non-bridging ones. Nevertheless, the apparent volume of oxygen in silica glass, that is, $V_o = 8.9 \text{ cm}^3/\text{mol}$ will be applied as the first order approximation to all of the glasses including the alkali disilicate and borate glasses. If it is possible to evaluate a change in the size of oxygen atoms by the volume for various coordination numbers (denoted as CN), it is proper to take the radii of S&P's two- and six-coordinated oxygen atoms 0.135 and 0.140nm, respectively. The apparent volumes of close-packed

oxygens having the radii of 0.135 and 0.140nm are 8.38 and 9.35cm³/mol, respectively. A difference of about 1.0cm³/mol between the two would not affect the subsequent discussions. Moreover, Vo=8.9cm³/mol is fortuitously equal to the average value of the two. In consequence, using silica glass as the reference material, the volume of the largest sphere, i.e., the volume of the void, in any structures can be evaluated by eq. (7.3).

$$V_v = v(\text{cage}) - nV_o, \quad (7.3)$$

where $v(\text{cage})$ represents the averaged volume of a glass per one NWF cation, n the number of oxygens stoichiometrically associated with one NWF cation, and $V_o=8.9\text{cm}^3/\text{mol}$. Although the structure of alkali borate glasses may be different from h-c structure[5], the same equation is applied in order to compare the void volume with those of the other glasses.

The cage structures consisting only of the bridging bonds have been mentioned. A similar h-c type structure has been proposed[1,2] for the network constructed by disilicate units $\text{ROSiO}_{3/2}$ in which each Si has one non-bridging bond. Though the size of the bridging and non-bridging oxygens should be different, the size of the voids in the disilicate network are estimated in a similar way applying $n=2.5$.

One should evaluate the sizes of the alkali ions. Based on the effective ionic radii of S&P, R-O distances are calculated for several CN's of R. On comparison of the calculated R-O distances with those found in some silicate, borate and phosphate crystals, it has been indicated[10] that the calculated ones for R=Li, Na and K of CN=4, 6 and 7,

respectively, agree well with those in the crystals. The radii of Rb and Cs are then taken for those of CN=8 and 10, respectively.

Table 7.2 shows the volume and radius of the largest sphere to be accommodated in the voids associated with the structure units. Those of alkali ions are also indicated.

Table 7.2. The volumes of the alkali ions and the largest spheres to be accommodated in the voids associated with those structure units (cm^3/mol). Their radii (10^{-1}nm) are indicated in parentheses.

		Li	Na	K	Rb	Cs	
Voids	v(R)	0.53	2.67	8.02	10.34	14.96	Cages enclosed by
	r(R)	(0.59)	(1.02)	(1.46)	(1.60)	(1.81)	
High-cristobalite structure							
	SiO _{4/2}				9.6(1.56)		
	GeO _{4/2}				10.3(1.60)		
Unoccupied.	(Ge _{1/2} Si _{1/2})O _{4/2}				10.2(1.59)		Bridging bonds, only
	(Ge _{3/4} Si _{1/4})O _{4/2}				9.8(1.57)		
	BO _{4/2}				2.7(1.02)		
	2/3BO _{3/2} 1/3SiO _{4/2}				4.2(1.19)		
	1/2BO _{3/2} 1/2SiO _{4/2}				5.7(1.31)		
Disilicate units, RO ₂ SiO _{3/2}							
		9.8	14.3	21.2	23.6	33.1	Bridging &
		(1.57)	(1.78)	(2.03)	(2.11)	(2.36)	non-bridging bonds.
Borosilicate units							
Occupied.	(B _{2/3} Si _{1/3})O _{4/2}		4.4	8.9			
			(1.20)	(1.52)			
	(B _{1/2} Si _{1/2})O _{4/2}		5.3	9.3			Bridging bonds, only.
			(1.28)	(1.54)			
BO _{4/2} units in alkali borate glasses							
			6.6	14.6			
			(1.38)	(1.80)			

7.3 Size of the voids and alkali ions

7.3.1 Borate and borosilicate networks

It was shown previously [5] that the radius of the largest sphere in the hypothetical $\text{BO}_{4/2}$ network was 0.129nm, while Table 7.2 gives 0.102nm for it due to the present approximation. Thus the application of $V_o=8.9\text{cm}^3/\text{mol}$ to boron oxide containing glasses is indicated to bring an over-estimation of the apparent volume of oxygen. However, the following discussions are valid even if a smaller value of V_o deriving the larger V_v is applied to those glasses instead of $V_o=8.9\text{cm}^3/\text{mol}$ for silica glass. Here, hypothetical networks built by $\text{BO}_{4/2}$ and $\text{RBO}_{4/2}+\text{SiO}_{4/2}$ ($\text{R}=\text{Na}$ and K) are studied in order to see the effects of bond lengths and the sizes of the ions on the void. These networks can similarly be approximated by the h-c network but they show different void volumes depending upon the mixing ratio of B and Si and the kind of R^+ ions. On comparison of the sizes of the voids and ions, Li^+ and Na^+ ions are shown to be placed in the voids in h-c type structures built by $\text{BO}_{4/2}$ and $\text{BO}_{3/2}+\text{SiO}_{4/2}$ without expanding the cages. Actually, hypothetical sodium borosilicate networks $\text{NaBO}_{4/2}+\text{SiO}_{4/2}$ have the voids as large as the voids of the alkali free borosilicate networks ($\text{BO}_{3/2}+\text{SiO}_{4/2}$) which are larger than sodium ion. On the other hand, K^+ ions expand the borosilicate network since they are larger than the voids in the alkali free borosilicate network. The voids in the assumed network $\text{KBO}_{4/2}+\text{SiO}_{4/2}$ are as large as accommodating a

potassium ion.

The voids as large as 6.6 and $14.6\text{cm}^3/\text{mol}$ associated with the $\text{BO}_{4/2}$ units in sodium and potassium borate glasses are larger than those both in the hypothetical h-c structure constructed by $\text{BO}_{4/2}$ units ($2.7\text{cm}^3/\text{mol}$) and in the alkali borosilicate network. This represents the difference in structure between the alkali borate and borosilicate glasses, showing that the borate glass networks cannot be approximated by the h-c network.

7.3.2 Glasses in the system $\text{GeO}_2\text{-SiO}_2$

The voids in glasses in the system $\text{GeO}_2\text{-SiO}_2$ are considerably larger than sodium and potassium ions. Ordinarily, the glasses in this system can be considered as solid solutions of the terminal glasses. Thus, the volumes of the voids in glasses $\text{GeO}_2 \cdot r\text{SiO}_2$ might change smoothly with the mixing ratio $r = \text{GeO}_2/\text{SiO}_2$. However, they do not change monotonously with r as is shown in Table 7.2. The reasons for such variation of the void volumes are not clear, though it can be pointed out that coexistence of GeO_2 and SiO_2 might affect the arrangements and the partial molar volumes of the $\text{GeO}_{4/2}$ and $\text{SiO}_{4/2}$ units.

7.3.3 Disilicate network

Table 7.2 also shows that the void associated with the disilicate units is significantly larger than that of the

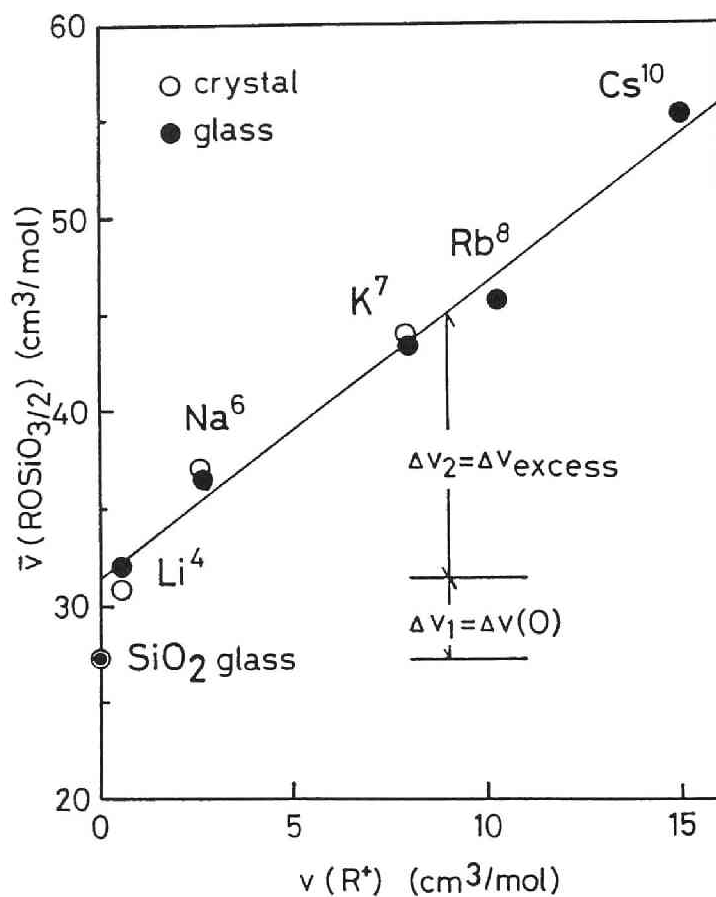


Fig. 7.2. Partial molar volumes of disilicate units, ROSiO_3 , plotted as a function of the volume of alkali ions, $v(\text{R}^+)$. The arabic numeral on the shoulder of R represents the assumed coordination number.

other units and the alkali ions. This fact can be attributed to the difference in the glass constitution, that is, the network of borate, borosilicate and GeO_2 containing glasses is constructed only by the bridging bond, even if the alkali oxide is added to the NWF oxides, while non-bridging bonds take part in the disilicate network. The volumes of the disilicate units $v(\text{ROSiO}_{3/2})$ in the alkali disilicate glasses and crystals ($\text{R}=\text{Li}, \text{Na}$ and K) [11-13] have been plotted in Fig. 7.2 as a function of the volume of the alkali ions $v(\text{R})$. The CN of each R is indicated on the shoulder of R. The CN of Li, Na and K in the crystals are the same as assumed in the glasses. It is clearly seen in the figure that the volumes of the disilicate units in the glasses and crystals increase linearly with $v(\text{R})$. The volume extrapolated to 0 in $v(\text{R})$ represents that of an assumed disilicate unit in which the alkali ion is substituted by a unipositive point charge; $v(\text{OSiO}_{3/2})=31.3 \text{ cm}^3/\text{mol}$. The difference $\Delta v_1=4.0 \text{ cm}^3/\text{mol}$ between $v(\text{OSiO}_{3/2})$ and $v(\text{SiO}_{4/2})$ is equivalent to $v(\text{NBO})-1/2v(\text{BO})$, where $v(\text{NBO})$ and $v(\text{BO})$ represent respectively the apparent volumes of non-bridging and bridging oxygens. Since $v(\text{BO})=V_o=8.9 \text{ cm}^3/\text{mol}$, $v(\text{NBO})$ is estimated to be $8.4 \text{ cm}^3/\text{mol}$. It has been indicated that the apparent volume of an NBO is almost as large as that of a BO in the alkali disilicate glasses and crystals. The difference $\Delta v_2 (= \Delta v_{\text{excess}})$ between $v(\text{ROSiO}_{3/2})$ and $v(\text{OSiO}_{3/2})$ represents the increased volume due to introduction of the alkali ions replacing the point charge. The effects of the non-bridging oxygen are not involved in Δv_2 and the increment of the volume can be attributed to the size

of the alkali ions. Since V_o , that is, $v(BO)$ is nearly equal to $v(NBO)$, the network structure built by $OSiO_{3/2}$ units has a spherical void $V_v = 31.3 - 8.9 \times 2.5 = 9.1$ (cm^3/mol), which can accommodate as large spheres as potassium ion. Therefore, a large increase in the volume Δv_2 of the disilicate units with introducing large alkali ions can be accounted as follows: the repulsive forces between the NBOs conquer the smaller network tightening effect of larger alkali ions and, as the results, the Si-Si distance at the non-bridging bonds is elongated and, finally, it becomes long enough to permit a linear arrangement of the two non-bridging bonds as Si-O O-Si in the rubidium and cesium glasses[1].

7.4 Characteristic aspects of GeO_4 containing networks

It has already been proposed in sect. 2.3 and in Chap. 5 as to a structure model of the alkali germanate and germanosilicate glasses in which SiO_4 , GeO_4 and GeO_6 component units are arranged in a high-cristobalite like network structure. Consider the structure of $LiNaGe_4O_9$ [14] as the example of such network. It can be seen that the structure has no 1:1 correspondence in number between the NWF cations and the voids though the 1:1 correspondence is present in the h-c structure as indicated above. The tetramolecular unit cell of the tetragermanate crystal contains 16 Ge atoms, which compose 12 GeO_4 and 4 GeO_6 units ($N_6=1/4$). Those units enclose 12 voids, 8 of which are occupied by the alkali ions. Thus, 3

voids are associated with 4 Ge atoms.

The crystal with $N_6=1/4$ other than $\text{LiNaGe}_4\text{O}_9$ is $\text{K}_2\text{Ge}_4\text{O}_9$ [15]. In the hexamolecular unit cell, 12 voids are constructed by 6 Ge_3O_9 rings and 6 GeO_6 units, showing that one void is associated with 2 Ge atoms as in h-t structure.

No 1:1 correspondences are found between the number of void and NWF cation in the germanate crystals as indicated in the tetragermanate ones. Thus, if one can assume the germanate crystal structure as the model structure of the GeO_2 containing glasses, the absence of the correspondence of the voids and NWF cations is a characteristic aspect of the glasses.

7.5 Summary

The sizes of voids in the alkali silicate, borate, borosilicate and alkali free germanosilicate glass networks have been evaluated from the volume of the largest spheres occupied in the voids. They are compared with those of the alkali ions. It has been shown that the sodium borosilicate glasses have voids large enough to accommodate Li^+ and Na^+ ions, while the voids in the potassium borosilicate are as large as K^+ ions. The voids in alkali disilicate glasses are considerably larger than the corresponding alkali ions. This is caused by the repulsion of the non-bridging oxygens and structure tightening effect of the alkali ions. When the network of the alkali germanate crystal can be taken as the

model of the alkali germanate glasses, the structure of the glasses is dissimilar to that of h-c in that the network of the former glasses has lesser number of void than that of the NWF cation.

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Chapter 8

ADDITIVITY RULE AND THERMOCHEMISTRY OF GLASSES

Among network forming (NWF) oxides, P_2O_5 is similar to SiO_2 in respect to the fact that neither of P nor Si change their coordination number (=4) under normal condition. However, P_2O_5 is dissimilar to SiO_2 in that P_2O_5 has P=O double bonds, a variation of non-bridging bonds, where 3d-2p π -interaction play an important role. On addition of network modifying (NWM) oxides, the phosphate units PO_4 are ordinarily changed from three-branched state in P_2O_5 to two-branched one according to interruption of the P-O-P bridging bonds. It is to be noted, however, that the P=O double bonds are fissured producing four-branched silica type $PO_{4/2}$ units by addition of B_2O_3 .

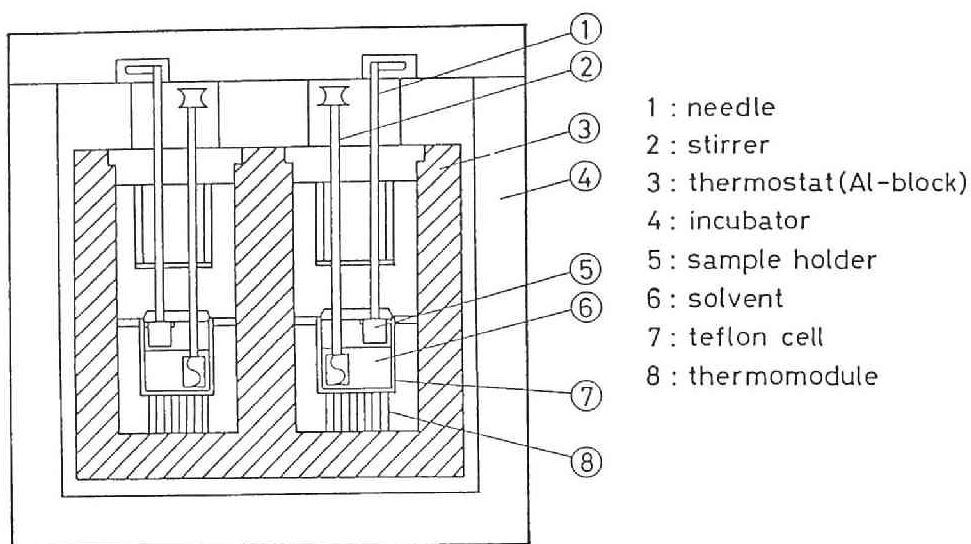
In this chapter thermochemical behavior of alkali and alkaline earth phosphate glasses is discussed on the basis of additivity rule. The heats of solution have been measured for the glasses in the systems $R_2O-P_2O_5$ and $MO-P_2O_5$ where R=Li, Na and K, and M=Mg, Ca and Sr. Their composition dependences are discussed in order to obtain knowledges on the constitution of the glasses. In order to examine the difference of the role of the alkaline earth oxide from that of alkali oxide, the thermochemical behavior of the alkaline earth silicate glasses is also discussed and compared with that of the alkali silicate glasses reported previously [1]. The heats of solution of $MO \cdot 2SiO_2$ glasses where M=Mg, Ca, Sr and Ba have

been derived. This is done by extrapolation of the heats of solution data of glasses in the pseudo-binary systems $R_2Si_2O_5$ - MSi_2O_5 . Using these data, the heats of formation have been calculated for RPO_3 , $M(PO_3)_2$ and MSi_2O_5 glasses. Thermochemical quantities employed here are represented in kcal/mol in chapters 8 and 9: 1 kcal/mol = 4.184 kJ/mol.

8.1 Determination of heats of solution and thermochemical quantities

Heats of solution ΔH_s of several series of binary glasses have been measured at 25°C by a twin type conduction calorimeter. Fig. 8.1 shows schematically mechanism of the calorimeter. 50g solvent (6) and sample holders (5) having 0.2g pulverized specimen were set at both side cells (7). After the temperature of the whole unit was kept at 25°C for a half day (steady state of former period), the needle (1) was pressed to drop the sample together with the holder into the solvent. The heat of reaction was taken out as an increase or decrease in solvent temperature, which was monitored and measured by a thermocouple (8). Let A the observed output of the thermocouple, being integrated during the dissolution reaction, when the completion of the reaction was assured by the steady state of latter period. Before measuring the heats of solution of glasses, known heat of reaction of TRIS (SIGMA Co.) ((trishydroxymethyl) aminomethane) with 0.1M HCl (=7.11 kcal/mol) [2] was measured by the same way. Let B the output

Fig. 8.1. A schematic representation of the twin-type conduction calorimeter.



for this reaction per 1 mol TRIS, the heat of solution of the glass was given by 7.11 (A/B) (kcal/0.2g-glass). Measurements were conducted for several times for each glass, the averaged value of which was taken as the heat of solution of the glass. The error was within 2%. The solvents employed here were 3N-HNO₃ and 2.5wt% HF solution respectively for phosphate and silicate materials.

The difference in heat of solution of the crystal and corresponding glass represents the difference in enthalpy of the two, that is, the heat of crystallization, ΔH_{cryst} . Therefore, the heat of formation ΔH_f of the glass is spontaneously obtained when ΔH_f of the crystal is known. If

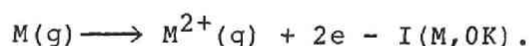
Table 8.1. Thermochemical data (kcal/mol).
1 kcal/mol=4.184 kJ/mol.

	ΔH_f	ref.		ΔH_f	ref.
a-quartz	-217.7	5	Si(g)	107.7	5
SiO ₂ glass	-215.7	5	Ge(g)	89.5	8
GeO ₂ (c,hex)	-132.6	6	B(g)	132.8	5
GeO ₂ (c,tet)	-138.6	7	P(g)	75.6	5
B ₂ O ₃ (c)	-304.0	5	O(g)	59.6	5
B ₂ O ₃ glass	-299.6	9	O ⁻ (g)	24.3	5
P ₂ O ₅ (c)	-359.7	5	O ²⁻ (g)	208.6	9
Li ₂ O(c)	-143.1	5	Li ₂ CO ₃ (c)	-290.6	5
Na ₂ O(c)	-99.9	5	Na ₂ CO ₃ (c)	-270.3	5
K ₂ O(c)	-86.8	5	K ₂ CO ₃ (c)	-274.9	5
CO ₂ (g)	-94.1	5	H ₂ O(l)	-68.32	4
Li(g)	38.4	5	Li ⁺ (g)	164.2	5
Na(g)	25.8	5	Na ⁺ (g)	145.8	5
K(g)	21.3	5	K ⁺ (g)	122.9	5
Li ⁺ (aq)	-66.5	5	Na ⁺ (aq)	-57.4	5
K ⁺ (aq)	-60.3	5			
MgO(c)	-143.8	5	Mg(g)	35.3	5
CaO(c)	-151.6	5	Ca(g)	42.8	5
SrO(c)	-141.5	5	Sr(g)	39.2	5
BaO(c)	-131.0	5	Ba(g)	42.8	5
Mg ²⁺ (g)	561.1	3	Sr ²⁺ (g)	427.7	3
Ca ²⁺ (g)	460.4	3	Ba ²⁺ (g)	396.6	3

the crystal is not present or its ΔH_f is not known, one can calculate ΔH_f of the glass by means of measuring the heats of solution of the component oxides into the same solvent. Table 8.1 shows ΔH_f data of a number of chemical species [3-9]. Those of $R^+(g)$ and $M^{2+}(g)$ are necessary in the following calculations. Since $\Delta H_f(M^{2+}(g))$ data have not been given in literatures, they are calculated by the present author [18] as follows.

$$\Delta H_f(M^{2+}(g), 298K) = \Delta H_f(M(g), 0K) + I(M, 0K) + 4.4 + \\ H(M(c), 298K) - H(M(c), 0K)$$

Here $I(M, 0K)$ represents the ionization potential of M at 0K, defined as



The other data in Table 8.1 have been cited from JANAF Thermochemical Tables [5] and other literatures [6-9]. It must be inferred here that in this study "kcal/mol" is adopted as the energy unit in order to compare directly the bond energies from the present study with single bond strengths of Sun and Huggins [10] and bond dissociation energies of Pauling [11].

8.2 Thermochemistry of alkali and alkaline earth phosphate glasses and additivity rule

In this section the dependence of the heats of solution on the composition of the glasses in the systems R_2O - and $MO-P_2O_5$ is first described. Then, the branching states of the PO_4 units are correlated with the thermochemical stabilities. The

increment of bond energy of the P-O-P bridging bonds in the alkali and alkaline earth phosphate glasses from those of P_2O_5 crystal is evaluated. Moreover, with an aid of the other thermochemical data of relevant chemical species, the heats of formation of the metaphosphate glasses will be calculated.

8.2.1 Experimental procedures and results

Dried reagent grade R_2CO_3 ($R=Li, Na$ and K), MgO , MCO_3 ($M=Ca$ and Sr) and P_2O_5 or $NH_4H_2PO_4$ were mixed to give about 50g glass. The batches were melted in a Pt crucible placed in an electric furnace for 2hr at temperatures ranging from 1000 to 1300°C, depending on the composition. In the course of melting, dry O_2 gas was bubbled in the melts led by a Pt pipe for the sake of stirring and eliminating water. The melts were poured onto a sheet of stainless steel plate to obtain quenched glasses. All the annealed specimens were analysed chemically [12]. Employed methods were ZnO substitution method for H_2O , a phosphorous molybdate method for P_2O_5 . The rest was assigned to the portion of the alkali and alkaline oxides. It was shown that about 2 or 3 mol% H_2O and about 1 mol% H_2O were left respectively in the alkali and alkaline earth phosphate glasses. Behavior of H_2O in glass, that is, the site and role of protons in glass structure has been investigated by means of spectroscopy [13] and internal friction measurements [14-16]. It is assumed in the present study that water plays a role of an NWM oxide. H_2O interrupts the P-O-P bridging bonds

and the protons are present in the vicinity of thus created non-bridging oxygens as charge compensating modifier cation. Therefore, molar ratio $(R_2O+H_2O)/P_2O_5$, later denoted as x , has been taken for the parameter to represent the composition of the alkali phosphate glasses, and the molar ratio $(MO+H_2O)/P_2O_5$ for that of the alkaline earth glasses. Parameter x represents the amount of the non-bridging oxygens in the glass containing 1 mol P_2O_5 . The following crystalline materials were also prepared [3], namely, $NaPO_3$ (Maddrell salt), $Na_4P_2O_7$, Na_3PO_4 , $Mg(PO_3)_2$, $Mg_3(PO_4)_2$, $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$.

Their heats of solution were measured by twin type conduction calorimeter at 25°C as mentioned in the preceding section 8.1. 3N- HNO_3 solution was employed as the solvent for all the specimens so that the heats of solution data should be compared in both systems. The results were shown in Tables 8.2 and 8.3 respectively for the alkali and alkaline earth phosphates. The heat of solution of $P_2O_5(c)$, $\Delta H_S(P_2O_5(c))$, has been calculated by

$$H_S(P_2O_5(c)) = H_f(H_3PO_4(aq)) - H_f(P_2O_5(c)) - H_f(H_2O(l)). \quad (8.1)$$

Here, the heats of solution and formation, ΔH_S and ΔH_f are represented by $-H_S$ and $-H_f$, respectively. The letters in parentheses such as c , aq and l denote respectively crystalline, hydrolysed and liquid states of substances. Eq. 8.1 results in $H_S(P_2O_5(c)) = 53.9$ kcal/mol from $H_f(H_3PO_4(aq)) = 309.8$ kcal/mol [3] and other heats of formation data available in Table 8.1.

Table 8.2. Heats of solution of alkali phosphate glasses and crystals in 3N-HNO₃ at 25°C (kcal/mol P₂O₅). The analysed compositions of the glasses are also indicated.

Analysed composition ^a (R ₂ O+H ₂ O)/P ₂ O ₅ -ΔH _S				
P ₂ O ₅	R ₂ O	H ₂ O		
R=Li				
60.9	36.4	2.7	0.64	27.8
53.3	36.4	2.3	0.87	12.8
49.5	48.5	2.0	1.02	18.5
45.9	52.1	2.0	1.18	22.4
45.5	52.7	1.8	1.20	22.3
43.8	54.1	2.1	1.28	22.9
42.1	55.9	1.9	1.37	26.8
R=Na				
58.1	36.5	5.4	0.721	23.9
59.1	37.6	3.3	0.692	21.0
56.3	40.6	3.1	0.78	18.3
52.8	44.3	2.9	0.89	15.2
51.7	45.5	2.8	0.93	13.3
48.0	48.8	3.2	1.08	15.3
47.0	50.0	3.0	1.13	16.1
46.7	50.3	3.0	1.14	16.0
45.6	51.6	2.8	1.19	17.8
41.1	57.0	1.9	1.43	20.3
R=K				
50.3	46.1	1.9	0.988	13.6
Crystal	P ₂ O ₅	NaPO ₃	Na ₄ P ₂ O ₇	Na ₃ PO ₄
-ΔH _S	54.9 ^b	8.1	16.1	37.1

a: mole fraction.

b: ΔH_S in H₂O.

Table 8.3. Heats of solution of alkaline earth phosphate glasses and crystals in 3N-HNO₃ at 25°C (kcal/mol-P₂O₅). The analysed compositions of the glasses are also indicated.

Analysed composition ^a (MO+H ₂ O)				
P ₂ O ₅	MO	H ₂ O	P ₂ O ₅	-ΔH _s
M=Mg				
55.6	43.2	1.2	0.80	38.5
50.0	49.0	1.0	1.0	35.6
43.7	55.2	1.1	1.29	39.0
41.7	57.3	1.0	1.40	38.7
M=Ca				
52.9	45.9	1.2	0.89	28.5
51.5	47.4	1.1	0.94	27.0
50.9	48.1	1.1	0.97	26.2
48.1	50.9	1.0	1.08	25.1
47.3	51.7	1.0	1.12	25.8
44.1	54.9	1.0	1.27	25.6
43.1	55.9	1.0	1.32	24.4
42.4	56.6	1.0	1.36	24.5
M=Sr				
50.0	48.8	1.2	1.00	22.4
Crystal	-ΔH _s *	Crystal	-ΔH _s	
2CaO·P ₂ O ₅	13.1	2MgO·P ₂ O ₅	25.3	
3CaO·P ₂ O ₅	34.3	2.5MgO·P ₂ O ₅	38.3	
1.5MgO·P ₂ O ₅	23.9	3MgO·P ₂ O ₅	51.4	
MgO	39.3	CaO	50.9	
SrO	61.8			
a: Mole fraction.		* kcal/mol		

8.2.2 Composition dependence of the heats of formation

a) Results and composition ranges

In Figs. 8.2 and 8.3 the heats of solution of the glasses and crystals in the systems of $R_2O-P_2O_5$ and $MO-P_2O_5$ have been plotted as a function of x . The heats of solution of the glasses and crystals in each system can be represented by segments of lines, showing bendings at 1 and 2 in x , and they are minimum at 1 in x . The glasses and crystals in the barium phosphate system have also been prepared, whereas they are dissolved into the solvent very sluggishly and give only scattered data. Thus the data of the barium phosphates have been considered unreliable and are not plotted in the figure. However, it seems that their H_s data should vary as those of the other systems. The two bendings divide the whole composition range into three ranges, I ($0 < x < 1$), II ($1 < x < 2$) and III ($2 < x < 3$).

b) Heat of solution vs. composition relations

Let the system $R_2O-P_2O_5$ taken as the example for describing the H_s vs. x relation. Addition of 1 mol R_2O interrupts one P-O-P bond, creating two P-OR non-bridging bonds. Since P_2O_5 has 6 P-O bridging bonds, an alkali phosphate glass or crystal of the composition $xR_2O \cdot P_2O_5$ has $(6-2x)$ P-O bridging and $2x$ P-OR non-bridging bonds. The heat of solution H_s is a sum of the following three energies:

- * an energy necessary to interrupt P-O-P bond ($2E(P-O)$, endothermic quantity),

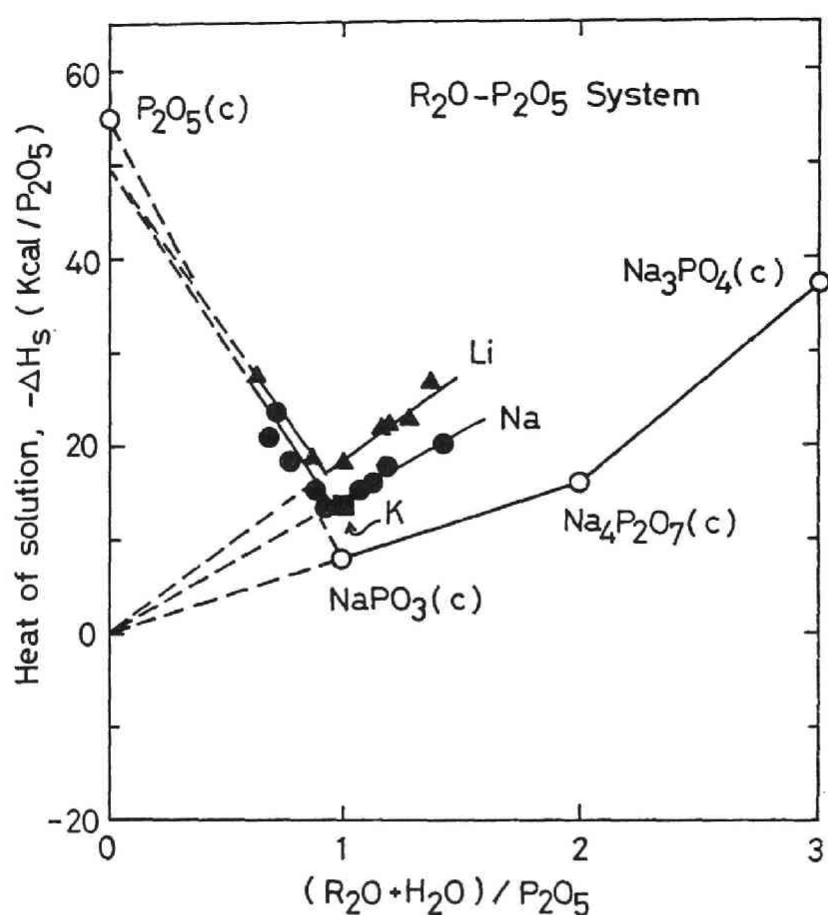
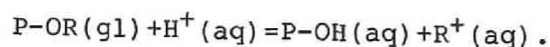


Fig. 8.2. Variation of heats of solution of the alkali phosphate glasses in 3N-HNO₃ at 25°C.

* a heat of reaction between the interrupted bonds and H₂O, and solvation energy of thus resulted 2 P-OH bonds (2H_h, exothermic)

* a heat of exchange (H_{ex}, exothermic) accompanied by the process,



Thus, H_s is expressed as

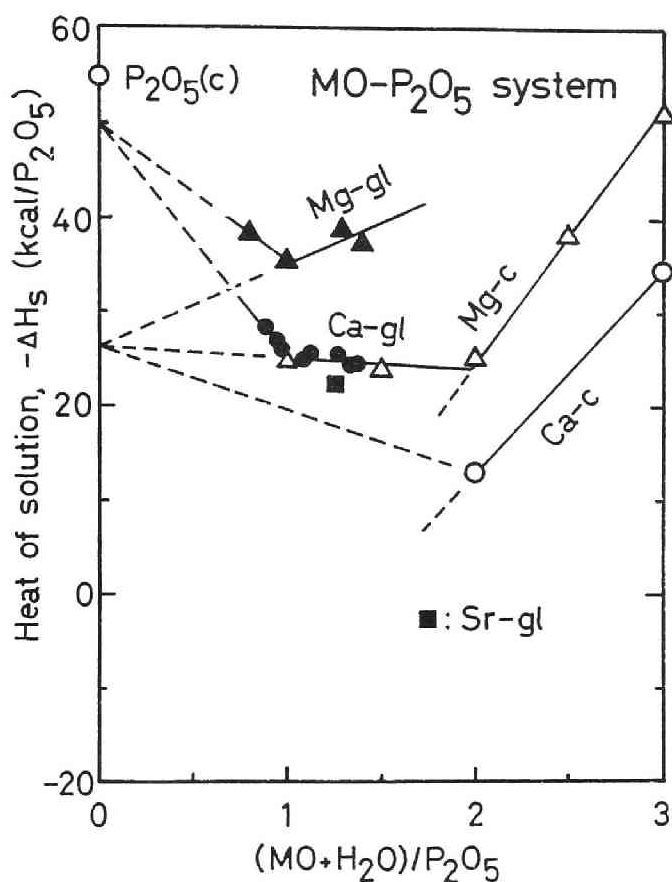


Fig. 8.3. Variation of heats of solution of the alkaline earth phosphate glasses in 3N-HNO₃ at 25°C.

$$H_s(xR_2O \cdot P_2O_5) = 6(-E(P-O) + H_h) + 2x(H_{ex} + H_h - E(P-O)). \quad (8.2)$$

A similar equation can be derived for the alkaline earth phosphate glasses.

c) Energy of the P-O bridging bond, $E(P-O)$

Equation 8.2 can represent the linear H_s vs. x relation in ranges I, II and III found in Fig. 8.2 [12]. This indicates

that the bond energies and enthalpies in eq. 8.2 are constant in each range. Especially, the value of H_s extrapolated from each composition range to 0 in x , namely $H_s(x=0) = 6(-E(P-O) + H_h)$, is related only to the P-O bridging bond, being H_s of the imaginary $P_2O_5(c)$ or $P_2O_5(gl)$ which has the bridging bond energy $E(P-O)$ of the glasses and crystals in the extrapolated range. The extrapolated H_s data for the glasses in range I are $H_s(P_2O_5(gl)) = 50$ kcal/mol irrespective of the alkali and alkaline earth ions. This $H_s(P_2O_5(gl))$ is less exothermic by 4.9 kcal/mol than that of $P_2O_5(c)$, 54.9 kcal/mol. The difference of the two from the present study agrees well with that in the cited data of H_f of the two: $H_f(P_2O_5(c)) = 359.7$ and $H_f(P_2O_5(am)) = 363.5$ kcal/mol [4], indicating

$$E(P-O)(c) < E(P-O)(gl).$$

On the other hand, the H_s data extrapolated from range II are 0 kcal/mol for the alkali phosphate glasses and crystals, and 26.5 kcal/mol for the alkaline earth phosphate ones. The extrapolated data represent similarly H_s of imaginary $P_2O_5(c)$ consisting of the P-O bonds as strong as that in RPO_3 and $M(PO_3)_2$ glasses and crystals. Therefore, the values of $E(P-O)$ for these metaphosphates are larger by 54.9 and 28.4 kcal/mol P_2O_5 in the alkali and alkaline earth phosphates, respectively, than that of actual $P_2O_5(c)$. It can also be seen that the extrapolation from range III gives $H_s = -30$ kcal/mol for the alkaline earth crystals, showing that the dissolving reaction is endothermic. Thus it has been shown that the values of H_s extrapolated from each range to 0 in x

are more endothermic in the order $I < II < III$, and that the glasses or crystals with the more NWM oxide content have the greater bridging bond energy. This conclusion can be interpreted by a resonance in a PO_4 unit. In range I ($x < 1$) three-branched PO_4 units with 3 bridging bonds are present while in ranges II and III those with one or two bridging bonds are present. van Wazer discussed the stabilities of the three- and two-branched PO_4 units in terms of resonance [17] and concluded that the two-branched units were stabler than the three-branched ones. Kadota et al. [18] proposed, however, that the minima in the heat of solution vs. x relations in Figs. 8.2 and 8.3 caused by strengthening of the structure due to a formation of interlinked three-dimensional network. However, the intermolecular link cannot present in ranges II and III because the three-branched PO_4 units are changed to two-branched ones by the end of range I. The thermochemical unstability of the three-branched units due to lesser number of resonance hybrids can interpret the change in the structure. The unstable three-branched units are decomposed by addition of R_2O into the stable two-branched units. This causes modification of the structure of the glasses or crystals to chain type one. It is considered that the structural change in the glasses and crystals has resulted in the composition dependence of the heat of solution indicated in Fig. 8.2. That is, the number of resonance hybrids and that of electrons taking part in the resonance increase as the three-branched PO_4 units are modified gradually to metaphosphate (PO_3^-), pyrophosphate ($P_2O_7^{2-}$) and

orthophosphate anions (PO_4^{3-}). The rapid increase in H_s with increase in x in ranges II and III then can be attributed to increasing portions of H_{ex} in H_s with increasing number of the non-bridging oxygens.

d) Effect of alkali and alkaline earth ions

It can be seen in Fig. 8.2 that H_s of the lithium glasses are more exothermic than that of any other alkali glasses. Generally, a stronger bond will be formed by the cation with smaller ionic radius than the cation with larger radius. Thus one might naturally expect that the lithium glasses should give the smaller H_s values than any other alkali glasses, being dissolved most endothermically. The experiments have shown contradictory results. It has already been described that the energies evolved in the following three processes result in the heat of solution of a phosphate: (1) the interruption energy $E(\text{P-O})$ (endothermic), (2) solvation energy of thus produced P-OH bonds H_h (exo), and (3) solvation energy of P-OR bonds at the reaction $\text{P-OR}(\text{gl}) + \text{H}^+(\text{aq}) \longrightarrow \text{P-OH}(\text{aq}) + \text{R}^+(\text{aq})$ (exo). Since in the glasses with the same alkali content the energies related to the bridging bonds are all the same, the O-R bond energy E_R and solvation energy of P-O^- and R^+ should cause the difference in the values of H_s . Therefore, the result, $H_s(\text{an Li-glass}) > H_s(\text{an Na-glass})$, seems attributable to that the solvation energy of lithium ions is much larger than that of sodium ions, and it compensates in excess the difference in O-Li and O-Na bond energies. Let these energies evaluated. Consider as a first order

approximation that the alkali ion R^+ is bonded to the non-bridging oxygen by the coulombic interaction at a distance of the sum of the ionic radii given by Pauling in glass. The bond energy between O and R with a formal charge of unity is 166.6 kcal/mol for $R=Li$ and 141.3 kcal/mol for $R=Na$. $-H_f(R^+(g)) + H_f(R^+(aq))$ can be a measure of the solvation energy of the alkali ion. They are 230.8 and 203.2 kcal/mol for Li^+ and Na^+ ions. Thus the contribution of the O-R bond to the H_s in the lithium and sodium glasses is estimated as 64.2 and 61.9 kcal/mol-R, respectively. It is indicated that the dissolution reaction of the lithium glass is more exothermic by about 2 kcal/mol-R than that of the sodium one. The values estimated as the measure of the H_s values, about 60 kcal/mol-R, might be incorrect since they are based on a very simple model without considering the heat of formation of $H^+(aq)$ and omitting the repulsive terms in the O-R bonds. However, the difference among the estimated values is reliable, and the fact that the lithium glass will give slightly larger H_s than the sodium glass agrees well with the experimental result that $H_s(LiPO_3(gl))$ is 2 kcal/mol larger than $H_s(NaPO_3(gl))$.

Similarly, in the alkaline earth phosphate glasses and crystals, H_s is in the order $Sr < Ca < Mg$. This relation can also be explained in terms of coulombic energy of the O-M bonds and approximated solvation energy of M^{2+} ions.

It has been reported [19] that the glasses in the system $MgO-P_2O_5$ behave anomalously in several property vs. composition relations when compared with those in the other

alkaline earth phosphate systems. As for the H_S vs. x relation, however, the magnesium phosphates exhibit similar behavior as the other systems.

When the P-O bridging bond energy $E(P-O)$ is compared between the alkali and alkaline earth phosphates in ranges I, II and III, $E(P-O)$ of the alkali glasses or crystals is always larger than that of the alkaline earth ones. This can be attributed to the polarizing ability of M^{2+} ions stronger than that of R^+ ions. The divalent cations attract the electrons on the bridging bonds more than the monovalent cations, resulting in a reduced electron density of the bonds.

8.2.3 Heats of formation of RPO_3 and $M(PO_3)_2$ glasses

a) Heats of formation of RPO_3 glasses

It is conventional to calculate H_f of a glass employing H_S of the glass, and H_S and H_f of the corresponding crystal. This method cannot be applied to $LiPO_3$ and KPO_3 glasses because the reliable H_f data of the crystals have not been reported. Since $H_f(NaPO_3(c))$ [20] and $H_f(R^+(aq))$ ($R=Li, Na$ and K) [9] have been known, the value of H_f of $LiPO_3(gl)$ and $KPO_3(gl)$ can be calculated as in the following way.

$H_f(NaPO_3(gl))$ can be represented as

$$H_f(Na-gl) = H_f(Na-c) + H_S(Na-c) - H_S(Na-gl),$$

yielding

$$H_f(Na-gl) = 294.7 \text{ kcal/mol},$$

since $H_S(Na-gl) = 7.2 \text{ kcal/mol}$ in Table 8.2. Here $Na-gl$ and $Na-c$ denote respectively $NaPO_3(gl)$ and $NaPO_3(c)$, and the similar

representations are employed to other alkali and alkaline earth metaphosphates. Based on the dissolution reaction of an $RPO_3(gl)$ and the formation reaction of $R^+(aq)$, $H_f(R-gl)$ is represented as

$$H_f(R-gl) = -H_s(R-gl) + H_s(Na-gl) + H_f(R^+(aq)) - H_f(Na^+(aq)).$$

Data in Table 8.2 yield the values of $H_f(R-gl)$.

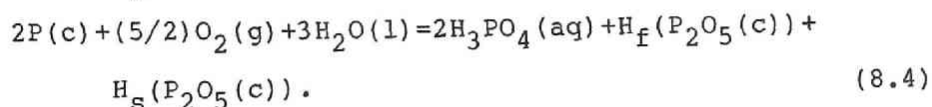
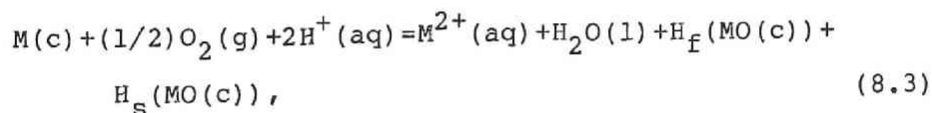
$$H_f(LiPO_3(gl)) = 301.7 \text{ kcal/mol},$$

$$H_f(KPO_3(gl)) = 298.4 \text{ kcal/mol},$$

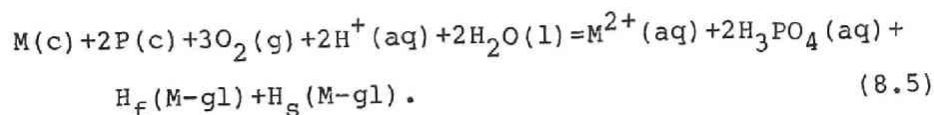
where the values of H_s of a lithium glass with $x=1.02$ and a potassium glass with $x=0.988$ have been employed.

b) Heats of formation of $M(PO_3)_2$ glasses

Since reliable $H_f(M^{2+}(aq))$ data are not available, the $H_f(M-gl)$ data have been obtained by means of the following thermochemical cycle. Formation reactions of $MO(c)$ and $P_2O_5(c)$ and their dissolution reactions in $3N-HNO_3$ derive eqs. 8.3 and 8.4.



From the formation and dissolution reactions of $M-gl$, eq. 8.5 is derived.



A heat of mixing of the solutions produced by reactions (8.3) and (8.4) can be neglected on comparison with other heats of reaction. Thus (8.5) is equal to (8.3)+(8.4), resulting in

eq. 8.6.

$$H_f(M-g1) = H_s(M-g1) - H_f(MO(c)) - H_f(P_2O_5(c)) - H_s(MO(c)) - H_s(P_2O_5(c)). \quad (8.6)$$

The values of H_f and H_s appearing in the right hand side of eq. 8.6 have been known in Tables 8.1 and 8.3. Thus, eq. 8.6 gives $H_f(M-g1)$ and H_f of the alkaline earth phosphate crystals in a similar way. The results have been shown in Table 8.4.

Table 8.4. Heats of formation of $RPO_3(g1)$, $M(PO_3)_2(g1)$ and $M(PO_3)_2(g1)$ (kcal/mol).

Glass	$-\Delta H_f$	Crystal	$-\Delta H_f$
$LiPO_3$	301.7	$2CaO \cdot P_2O_5$	806.9
$NaPO_3$	294.7	$3CaO \cdot P_2O_5$	988.4
KPO_3	298.1	$Mg(PO_3)_2$	572.6
$Mg(PO_3)_2$	562.1	$2MgO \cdot P_2O_5$	755.5
$Ca(PO_3)_2$	591.5	$3MgO \cdot P_2O_5$	912.5
$Sr(PO_3)_2$	592.5		

8.3 Thermochemistry of MSi_2O_5 glasses and additivity rule

In the systems $MO-SiO_2$ in the composition range $MO < 50$ mol%, liquidus temperatures are high and a liquid-liquid immiscibility is present, nor any $MO \cdot 2SiO_2$ crystals are found other than $BaO \cdot 2SiO_2$ crystal. Thus binary alkaline earth silicate glasses are difficult to be obtained and the mixed

cation glasses are usually prepared [21]. Those mixed cation glasses are improper for obtaining M-O bond energies and the single bond strengths, and comparing with those given by Sun [22]. Since the Si-O skeleton of $R_2Si_2O_5$ crystal [23] is similar to that of $BaSi_2O_5$ crystal [24]. On this basis, the glasses have been prepared in the pseudo-binary systems, $Na_2Si_2O_5$ - MSi_2O_5 (M=Mg, Ca and Ba) and $Li_2Si_2O_5$ - $SrSi_2O_5$, and the heats of solution of the glasses have been measured. The H_s data are extrapolated to obtain those of MSi_2O_5 glasses, and H_f of them is calculated with use of other thermochemical quantities. Let (R,M) represent the pseudo-binary system. The employed systems are (Na,Mg), (Na,Ca), (Li,Sr) and (Na,Ba). In order to study whether a specific mixing of R and M causes anomalous structural change or not, Li has been chosen as one of the mixing counterparts.

8.3.1 Experimental procedures and results

The compositions of the glasses in the pseudo-binary systems were $xR_2Si_2O_5 \cdot (1-x)MSi_2O_5$ ($0.2 < x < 1.0$). Reagent grade R_2CO_3 (R=Li and Na), MCO_3 (M=Ca, Sr and Ba), MgO and SiO_2 were mixed to give about 50g glass and placed in a Pt crucible in an electric furnace. The batches were melted for 3 hr at temperatures ranging from 1200 to 1400°C, depending on the composition. After being refined, they were poured onto a sheet of stainless steel plate and pressed by an iron block to give quenched plate samples. They were annealed for 30 min,

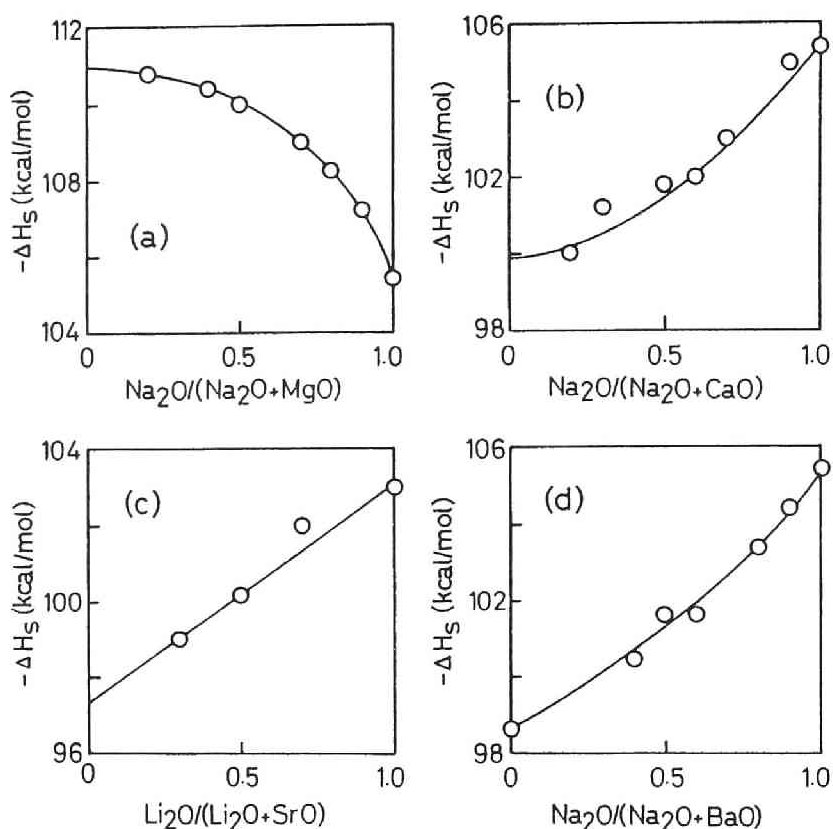


Fig. 8.4. Variation of heats of solution of the glasses in the pseudo-binary systems $R_2Si_2O_5$ - MSi_2O_5 in 2.5 wt% HF solution at 25°C.

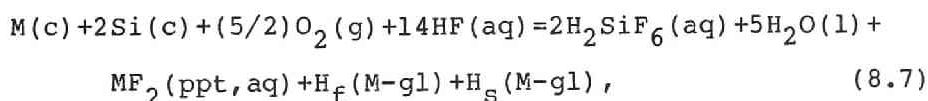
pulverized in dry benzen, and served for the heats of solution measurements. The solvent was 2.5wt% HF aqueous solution.

The measured H_S data of the glasses have been plotted in Fig. 8.4 as a function of the molar ratio $MO/(MO+R_2O)$ which is denoted as x later. The H_S vs. x relation for the system (Na,Mg) is represented by a convex curve, while those for (Na,Ca) and (Na,Ba) by concave curves. H_S of glasses in the

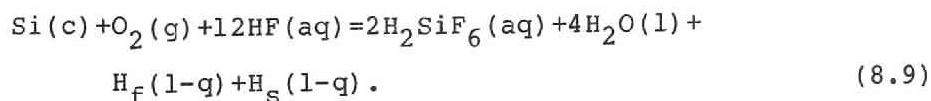
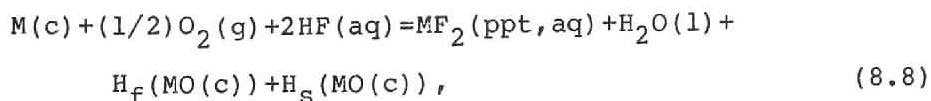
system (Li,Sr) varies linearly with x. Such dependence of H_s on x represents the implicit stabilities of the ternary glasses at mixing the $R_2Si_2O_5$ and MSi_2O_5 glasses. On mixing, the glasses in the system (Na,Mg) have smaller enthalpies than expected from additivity and become unstable, while those in the systems (Na,Ca) and (Na,Ba) have larger enthalpies and become more stable. The glasses in the system (Li,Sr) behave as expected from additivity. In any systems, the H_s data vary smoothly with x, indicating that the mixing causes no anomalous structural changes. Therefore, it is concluded that the H_s data extrapolated to 0 in x can be taken for those of the MSi_2O_5 glasses. They have been shown in Table 8.5.

8.3.2 Heats of formation of the MSi_2O_5 glasses

As in $M(PO_3)_2$ glasses, formation and dissolution reactions of an MSi_2O_5 glass (denoted as M-gl) derive eq. 8.7.



where ppt represents the state of precipitation. Further, the reactions of $MO(c)$ and low-quartz (denoted as l-q) derive eqs. 8.8 and 8.9.



Since heats of mixing of the solutions produced by reactions (8.8) and (8.9) can be neglected as in the phosphate glasses,

the mixture of the two solutions is equivalent to that produced by reaction (8.7). Therefore, eq. 8.10 can be derived.

$$H_f(M-gl) = H_s(M-gl) - H_f(MO(c)) - H_f(l-q) - H_s(MO(c)) - H_s(l-q). \quad (8.10)$$

Since all of the enthalpies in eq. 8.10 are known, $H_f(M-gl)$ can be calculated and shown in Table 8.5.

Incidentally, it might be necessary to examine the equations involving precipitation process as to the behavior of M. Let $[M]_1$ the amount of M^{2+} ions present in the solutions as the state $M^{2+}(aq)$, and $[M]_2$ that of M^{2+} ion present in a specimen employed in the heat of solution measurement. $[M]_1$ can be calculated by the solubility product of $MF_2(c)$ [4] and by the concentration of F^- ion in the solutions. The ratios $[M]_1/[M]_2$ are lesser than 10^{-4} for any specimen. Therefore, it can be concluded that the all of M^{2+} ions in the specimens have been precipitated as $MF_2(ppt, aq)$ in the solution and that eqs. 8.7 and 8.8 are valid.

Table 8.5. Heats of solution and formation of MSi_2O_5 glasses and pertinent crystals.

	Mg	Ca	Sr	Ba
Heat of solution (kcal/mol)				
MSi_2O_5 glass	-111.0	-99.8	-97.4	-99.0
MO(c)	-31.8	-58.8	-66.3	-65.8
α -quartz		-27.1		
Heat of formation (kcal/mol)				
MSi_2O_5 glass	-553.9	-600.2	-599.8	-587.8

8.4 Summary

Heats of solution, ΔH_s , in 3N-HNO₃ have been measured for the glasses and crystals in the systems R₂O-P₂O₅ (R=Li, Na and K) and MO-P₂O₅ (M=Mg, Ca, Sr and Ba) in order to discuss the dependence on composition. Variation of the constitution of the glasses and the P-O bridging bond energy E(P-O) in ranges I (0<x<1), II (1<x<2) and III (2<x<3) have been discussed. It has been found that E(P-O) is larger in the order, range I < range II < range III. The order in E(P-O) is interpreted in terms of a concept of resonance in PO₄ units. It is also indicated that H_s of the glasses with smaller network modifying cations is larger than that with the larger cations. This is explained in terms of the polarizing power of the cations. The heats of formation of the metaphosphate glasses and crystals, RPO₃ and M(PO₃)₂, have been calculated.

The heats of solution of the glasses of composition xR₂Si₂O₅·(1-x)MSi₂O₅ have also been measured, where the combined pairs of R and M are (Na,Mg), (Na,Ca), (Li,Sr) and (Na,Ba). The thermochemical stability of the pseudo-binary systems depends on the pair. The glasses in the system (Na,Mg) become unstable on mixing the sodium and magnesium disilicate glass, those in the systems (Na,Ca) and (Na,Ba) become stable, and those in the system (Li,Sr) behave as expected from additivity. The heats of solution and formation of MSi₂O₅ glasses have been obtained.

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Chapter 9

ADDITIVITY RULE AND CHEMICAL BONDS IN GLASSES

The energy of bonds such as Si-O, P-O and O-R in glass differs from one glass to another. It depends on the kind of second neighbor cations and on glass composition. Accordingly, if one can proportionate the total bond energy of a glass to each component bond, one would be able to elucidate characteristics of the bond, such as degree of π -interaction and that of polarization of oxygen atoms.

In this chapter it is attempted to characterize each bond on the basis of calculated bond energies. A total bond energy of a glass D, defined as an energy necessary to dissociate the glass into the elements in a monoatomic gaseous state, is calculated using the heats of formation (ΔH_f , denoted as $-H_f$) of the glass and related chemical species. The H_f data of RPO_3 , $M(PO_3)_2$ and MSi_2O_5 glasses have been described in Chapter 8. Those of $R_2Si_2O_5$ and R_2SiO_3 glasses have already been reported [1]. However, recalculation will be made here, considering that the H_f data of some chemical species employed in ref. 1 are inconsistent with those in JANAF Thermochemical Tables [2] which are the most reliable accumulations of the thermochemical data at present.

The total bond energy is then proportionated with a few assumptions to the component bonds of the glass. It is discussed how O-M and O-R bond energies are dependent on the polarizing ability of R^+ and M^{2+} ions and electrostatic shield

of the cations by surrounding oxygens. The variation of NWF cation-oxygen bond energy is also discussed when one alkali or alkaline earth cation is replaced by another.

9.1 Physical meaning of bond energy and assumptions for calculations

9.1.1 Physical meaning of bond energy

There are two definitions in the bond energy as indicated below.

- (a) Bond dissociation energy, after Pauling [3], represents the energy necessary to interrupt a bond at each step on the way of dissociating a substance to the elements in monoatomic gaseous state. For example, the C-H bond energy of methane, on this basis, varies from one dissociation product to another, such as CH_4 , CH_3 , CH_2 , etc.
- (b) Single bond strength, after Sun [4], of an M-O bond of an oxide M_mO_n is calculated by dividing its atomization energy with the coordination number CN of the metal ion M in the oxide. Here, the atomization energy, later denoted as the total bond energy D, represents an energy necessary for dissociating the substance to a mixture of the elements in monoatomic gaseous state.

Thus the single bond strength is dependent upon heats of formation of the oxide M_mO_n , $\text{O}(\text{g})$ and $\text{M}(\text{g})$, and the coordination number CN which must be assumed in glass.

The chemical bonds in glass are partly ionic and partly covalent in character. Ionic character should be predominant in the bonding between a non-bridging oxygen and a network modifying (NWM) cation. However, the bonding between a bridging oxygen and a network forming (NWF) cation has a greater degree of covalency, about 50% according to an ionicity vs. electronegativity correlation postulated by Pauling [4]. Hence, it should be improper to employ the concept of ionic bond for all of the bonds composing the glasses.

Considering these, the bond energies of metal-oxygen bonds in glass such as Si-O and Na-O are obtained by proportionating the total bond energy D to each component bond. Then the single bond energy can be calculated by dividing D by assumed CN of the metals. Therefore, the bond energy here is not directly based on the heats of formation of the component oxides as is Sun's single bond strength. Sun approximated the energy of metal-oxygen bond in glass by that in corresponding oxide. However, the bond energy of Sun and the present study is concerned with the atomization processes of the crystalline oxides and glasses.

9.1.2 Bond energy relations and assumptions on calculations

Taking an alkali disilicate glass $R_2O \cdot 2SiO_2$ as the example, bond energy relations will be described. The dissociation processes of the glass are indicated in Fig. 9.1. (Al) Additivity in the bond energy is assumed for

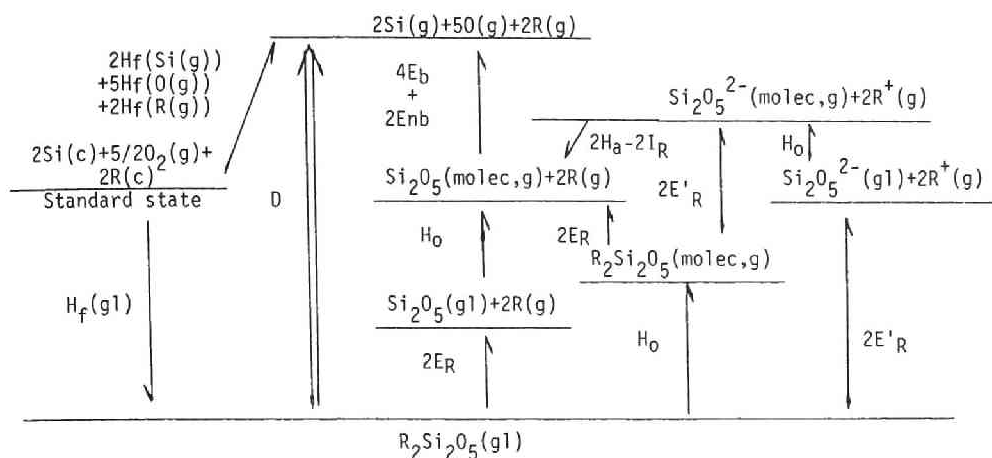


Fig. 9.1. Dissociation process of an $R_2Si_2O_5$ glass.

proportionating D to each bond energy.

The disilicate glass consists of 6 Si-O bridging, 4 Si-O⁻ non-bridging and 4 O-R bonds. The bond energies are represented by E_b , E_{nb} and E_R , respectively. Then, D is described from definition as follows.

$$D = 6E_b + 2E_{nb} + 2E_R, \quad (9.1a)$$

$$D = H_f(R_2O \cdot 2SiO_2(g1)) - 2H_f(Si(g)) - 2H_f(R(g)) - 5H_f(O(g)), \quad (9.1b)$$

where the heat of formation $-\Delta H_f$ of a chemical species is denoted by H_f . It is also assumed that

(A2) contrary to the concept of bond dissociation energy, the energy of each bond is independent of the dissociated state of the glass.

Namely, the bond energies in the assumed chemical species appearing in each step of the dissociation process shown in

Fig. 9.1 are taken equal to those in the original glass. In $\text{Si}_2\text{O}_5(\text{molec},\text{g})$, assumed to be in the configuration $(\text{O})_2\text{Si}-\text{O}-\text{Si}(\text{O})_2$, the bridging oxygen in the midst of Si-Si tie line is unique, while the other four oxygen atoms cannot be distinguished from each other. Nevertheless, according to the above assumptions (A1) and (A2), an energy $4E_b+2E_{nb}$ is needed to atomize the molecule into $2\text{Si}(\text{g})+5\text{O}(\text{g})$ since two of the four oxygens are originally the non-bridging ones.

On this basis, one can obtain a bond energy relation for the disilicate glass referring to Fig. 9.1 which represents every step in the dissociation process and the involved bond energy. When an energy H_0 is applied to the glass $\text{R}_2\text{Si}_2\text{O}_5(\text{gl})$, an $\text{R}_2\text{Si}_2\text{O}_5(\text{molec},\text{g})$ is produced, which is subsequently dissociated to $\text{Si}_2\text{O}_5(\text{molec},\text{g})$ and $2\text{R}(\text{g})$ by application of $2E_R$. These two species are also produced by applying first $2E_R$ to $\text{R}_2\text{Si}_2\text{O}_5(\text{gl})$, and subsequently H_0 to thus produced $\text{Si}_2\text{O}_5(\text{gl}) + 2\text{R}(\text{g})$. Thus, E_R corresponds to the energy necessary to take an $\text{R}(\text{g})$ from the glass. Further, since $4E_b+2E_{nb}$ is needed for dissociating $\text{Si}_2\text{O}_5(\text{gl})$ into $2\text{Si}(\text{g})+5\text{O}(\text{g})$, the total energy needed to atomize the glass is represented as $H_0+4E_b+2E_{nb}+2E_R$. This must be equivalent to D in eq. 9.1, and $H_0=2E_b$ is derived. This is the physical aspect of the bridging bond energy. Let $E(\text{Si}-\text{O})$, $E(\text{P}=\text{O})$ and $E(\text{P}-\text{O}^-)$ represent the energy of the corresponding bond. $E(\text{Si}-\text{O})$ and $E(\text{P}-\text{O})$ can be obtained from the composition dependence of heats of solution H_s of glasses and the H_s data of the NWF oxides. It has been indicated [1] that $E(\text{Si}-\text{O})$ in $\text{R}_2\text{Si}_2\text{O}_5(\text{gl})$ and $\text{R}_2\text{SiO}_3(\text{gl})$ is equal to $E(\text{Si}-\text{O})$ of low-quartz, and the $E(\text{P}-\text{O})$ in $\text{RPO}_3(\text{gl})$ and

$M(\text{PO}_3)_2(\text{gl})$ has specific relation with that in $\text{P}_2\text{O}_5(\text{c})$ [5,6] (sect. 8.2). Then, since D has been known according to eq. 9.1b, all of the bond energies can be calculated if either of E_{nb} or E_{R} can be evaluated in eq. 9.1a.

Table 9.1. Thermochemical data (kcal/mol).

	Li	Na	K
Heats of crystallization, $\Delta H_{\text{c}}^{\text{a}}$			
$\text{R}_2\text{O} \cdot 2\text{SiO}_2(\text{gl})$	-12.6	-7.4	-3.4
$\text{R}_2\text{O} \cdot \text{SiO}_2(\text{gl})$		-8.6	-2.1
Heats of formation, $\Delta H_{\text{f}}^{\text{b}}$			
$\text{R}_2\text{O} \cdot 2\text{SiO}_2(\text{c})$	-612.1	-590.4	-593.5 ^c
$\text{R}_2\text{O} \cdot \text{SiO}_2(\text{c})$	-394.2	-373.2	-370.0
$\text{R}_2\text{O} \cdot 2\text{SiO}_2(\text{gl})$	-599.5	-583.0	-590.3
$\text{R}_2\text{O} \cdot \text{SiO}_2(\text{gl})$		-364.6	-367.9
Heats of formation, ΔH_{f}			
	ref.		ref.
l-quartz	-217.7	2	SiO_2 glass -215.7 2
$\text{GeO}_2(\text{c, hex})$	-132.6	8	$\text{GeO}_2(\text{c, tetr})$ -138.6 9
GeO_2 glass	-128.8	8	$\text{B}_2\text{O}_3(\text{c})$ -304.0 11
B_2O_3 glass	-299.6	10	$\text{P}_2\text{O}_5(\text{c})$ -359.7 2
P_2O_5 glass	-365.6	5	

a: ref. 1, b: ref. 2, c: ref. 7.

9.2 Proportionation of D to each bond

The calculation for proportionating D to each bond energy is described in this section. The thermochemical data have been shown in Table 9.1, such as the heats of formation of several alkali silicate crystals [2,7], the heats of crystallization of the corresponding glasses, and heats of formation of NWF oxides [5,8-11]. The heat of crystallization represents the difference in enthalpy of the glass and corresponding crystal. The previous values of heats of formation of the alkali silicate glasses [1] are based on the H_f data of the crystals different from those in JANAF Thermochemical Tables [2]. Considering this, the heats of formation of the alkali silicate glasses have been recalculated by the present author, using the heats of crystallization data [1] and heats of formation data cited from JANAF Thermochemical Tables.

9.2.1 Bond energies of NWF cation-O skeleton bonds

Here, the energy of bonds constituting the glass skeleton will be evaluated. For example, low-temperature modification of quartz (denoted as l-q) gives the total bond energy D as

$$D(1-q) = H_f(1-q) - H_f(\text{Si}(g)) - 2H_f(\text{O}(g)),$$

and the bond energy $E(\text{Si-O})$ of an Si-O bond in the SiO_4 tetrahedra of l-q is obtained as D divided by the oxygen coordination number, $\text{CN}=4$, of the Si atom.

$$E(\text{Si-O}) = D(1-q)/4.$$

E_b such as $E(\text{Ge-O})$ and $E(\text{B-O})$ for GeO_2 and B_2O_3 has been obtained in a similar way.

On the other hand, $E(\text{P-O})$ in P_2O_5 cannot be equalized to $D(\text{P}_2\text{O}_5)/4$ because of the presence of P=O double bond. $E(\text{P-O})$ has a different character from that of the other E_b in SiO_2 and B_2O_3 . Sun [4] employed the both cases, $E(\text{P=O})=2E(\text{P-O})$ and $E(\text{P=O})=E(\text{P-O})$ and did not evaluate the ratio $E(\text{P=O})/E(\text{P-O})$. In the present study, a range of the ratio is tentatively evaluated as follows.

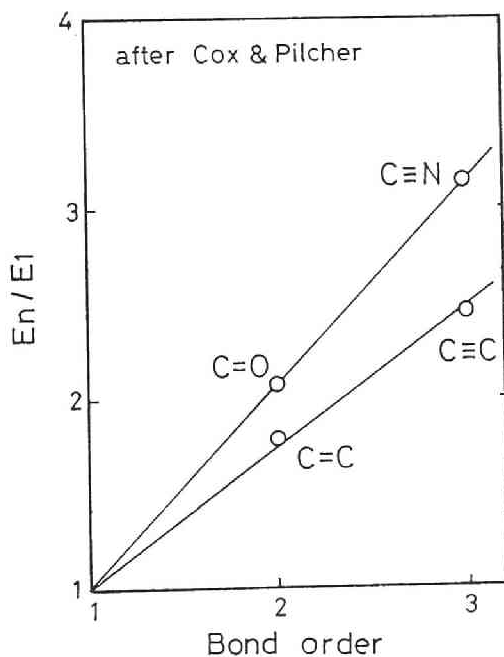


Fig. 9.2. The ratio of bond energy of a multiple bond E_n to that of corresponding single bond energy E_1 is plotted as a function of the multiplicity n . (ref. 12).

(a) Bond energy vs. bond order relation

In Fig. 9.2 the ratio of multiple bond energy to single bond energy, E_n/E_1 , is plotted as a function of apparent multiplicity of the bond, n , for homoatomic and heteroatomic bonds. The bond energy data have been cited from Cox and Pilcher [12]. One might evaluate the ratio of bond energies $E(P=O)/E(P-O)$ on the basis of E_n/E_1 vs. n relations. The 2p-2p π -interaction is effective in C-C, C-O and C-N bonds, while 3d-2p π -interaction is significant in the P-O bonds. The data of Cox and Pilcher [12] should be applied only to organic compounds. It seems, however, that whether the system is organic or inorganic, the ratio of the multiple bond energy to the single bond one should be correlated to the fractions of σ - and π -interactions of the multiple bonds. Linear approximation of E_n/E_1 vs. n relations result in 1.75 and 2.0 in the ratio E_2/E_1 for the homoatomic and heteroatomic bonds, respectively [6].

(b) $E(P=O)$ and $E(P-O)$

- * The overlap of electron clouds in 3d-2p π -interaction of P=O bonds is less than that in 2p-2p one. Thus, the relation $E_2/E_1 < 1.75$ is implied.
- * However, P-O and P=O bonds are heteroatomic ones. The difference in the electronegativities 1.4 between O and P is much larger than that 1.0 between O and C. This causes the contribution of ionic character to the bond energy to be much effective. On this basis, it is implied that E_2/E_1 for P-O bonds is greater than that estimated above.

Consequently, it can be evaluated that $E(P=O)/E(P-O)$ ranges from 1.75 to 2.0 [5]. Later the calculations will be performed employing both values of the ratio, and the results corresponding to $E(P=O)/E(P-O)=2.0$ are represented in parentheses.

Table 9.2 represents thus obtained energy of the bridging bond in the NWF oxides. These bond energies should replace Sun's single bond strengths for the NWF cation-oxygen bonds.

Table 9.2. Single bond energy of network forming cation-O bonds (kcal/mol).

Bridging bond	CN	Single bond energy (kcal/mol)	Notes
Si-O	4	111.1	in α -quartz, $R_2O \cdot 2SiO_2$ (gl),
	4	110.6	$R_2O \cdot SiO_2$ (gl) in SiO_2 glass
Ge-O	4	85.3	in hex. GeO_2
	4	84.3	in GeO_2 glass
	6	57.9	in tet. GeO_2
B-O	3	124.7	in B_2O_3 (c)
	3	124.0	in B_2O_3 (gl)
P-O*	4	85.1(80.9)	in P_2O_5 (c)
	4	86(82)	in P_2O_5 (gl)
	4	90(86)	in RP_2O_3 (gl)

* Calculated for $E(P=O)/E(P-O)=1.75$ and 2; the results in the latter case were shown in parentheses.

9.2.2 O-R and O-M bond energies, E_R and E_M

The O-R bond energy has already been defined as the energy necessary to take $R(g)$ out of glass. E_M can be similarly defined. Sun [4] obtained those by dividing the total bond energies D of $R_2O(c)$ and $MO(c)$ with coordination numbers CN of R^+ and M^{2+} ions assumed in glass. In the present study the bond energies will be calculated based on D of glass, assuming that

(A3) O-R and O-M interactions in glass are ionic as in $R_2O(c)$ and $MO(c)$.

Let E_R' and E_M' the energies necessary to take $R^+(g)$ and $M^{2+}(g)$ out of glass in order to distinguish from E_R and E_M . The calculation of E and E' is described by taking an $R_2Si_2O_5$ glass as the example. E_R and E_R' are concerned with the following reactions.

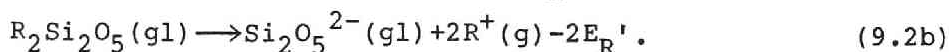
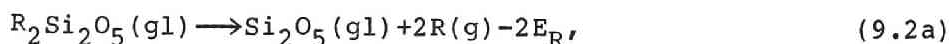
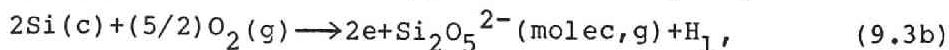
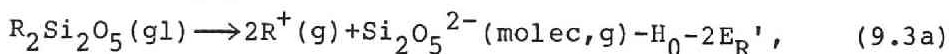
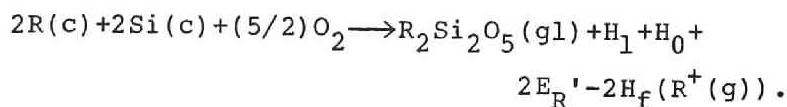


Fig. 9.1 indicates that application of $H_0 + 2E_R'$ on $R_2Si_2O_5(gl)$ produces $Si_2O_5^{2-}(molec, g) + 2R^+(g)$. Letting $-H_1$ the heat of formation of $Si_2O_5^{2-}$, eq. 9.3 is derived.



Thus, the formation reaction of the glass is derived by summing eqs. 9.3a, 9.3b and 9.3c.



The heat of reaction in above equation is equal to $H_f(R_2Si_2O_5(gl))$. Therefore, E_R' is described as

$$2E_R' = H_f(R_2Si_2O_5(gl)) - 2H_f(R^+(g)) - (H_1 + H_0). \quad (9.4a)$$

In glass the formal charge of the non-bridging oxygen may be reduced to $-(1-a)$ due to polarizing effect of alkali ions. In eq. 9.2, therefore, an electron transfer occurs and changes the formal charge on the non-bridging oxygen and alkali ion from $\equiv Si-O^- R^+$ to $\equiv Si-O^{-(1-a)} R^{+(1-a)}$. The energy accompanied with the electron transfer is included in E_R' . Thus, H_0 and H_1 is independent of the alkali species, showing that E_b and E_{nb} are independent of the alkali species. This is also valid in any other glasses. The equations similar to eq. 9.4a representing E_R' and E_M' of the glasses, namely RPO_3 , R_2SiO_3 , MSi_2O_5 and $M(PO_3)_2$ ones, can be derived in the same way. For example, E_M' of an $M(PO_3)_2$ glass is described as

$$E_M' = H_f(M(PO_3)_2(gl)) - H_f(M^{2+}(g)) - H, \quad (9.4b)$$

where H represents the heat of formation of 2 mol metaphosphate anions ($2PO_3^-$). Simultaneous equations of eq. 9.4a for $R=Li, Na$ and K cannot be solved uniquely, since they have three unknown bond energies such as E_{Li}' , E_{Na}' and E_K' and one unknown constant ($H_0 + H_1$). Therefore, one more assumption should be introduced in order to solve the equations and obtain the O-R and O-M bond energies.

9.2.3 Ionic bond and parameters

The ionic bond energy E' such as E_R' and E_M' in glass is assumed to be described as

$$(A4) \quad E' = (A/d) (1 - p/d), \quad (9.5)$$

where d and p represent O-R or O-M distance and repulsion parameter, respectively, and A is related to the Madelung constant. It is also assumed [13] that

$$(A5) \quad E_{Na}'/E_K' = k_R, \quad E_{Ca}'/E_{Sr}' = k_M. \quad (9.6)$$

Then, let evaluate those parameters followingly.

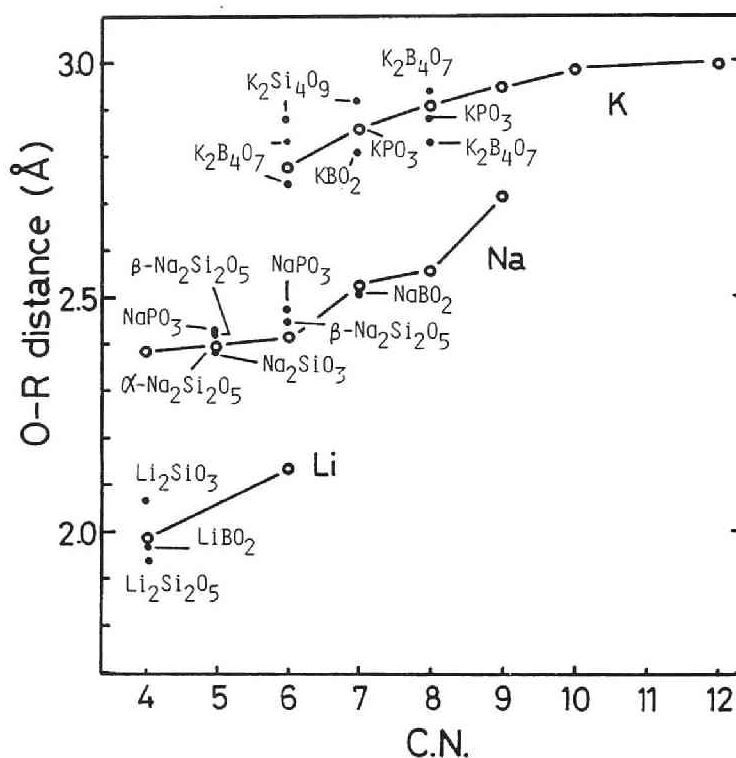


Fig. 9.3. O-R distance (10^{-1} nm) found in several silicate, borate and phosphate crystals, and that due to Shannon-Prewitt's effective ionic radii, plotted as a function of CN of the alkali ions.

(a) O-R and O-M distances

Shannon and Prewitt (denoted as S&P) [14] have reported the effective ionic radii of cations and anions as a function of their coordination number CN. The distance between the non-bridging oxygen and alkali ion, $d(O-R)$, and CN in glass might be different from those in the ordinary inorganic salts such as halides and sulfides. The $d(O-R)$ data are plotted in Fig. 9.3 as a function of CN for several alkali borate, silicate and phosphate crystals [13]. The values of $d(O-R)$ are calculated from the effective ionic radii of the alkali ions given by S&P and the radius of O^{2-} ion, 0.14nm. These $d(O-R)$ are indicated by the open circles in Fig. 9.3. It seems that the O-R distances in the crystals are scattered near the solid curves representing the calculated $d(O-R)$ vs. CN relations. Moreover, one might consider that $d(O-R)$ in the glasses should not differ so much from that in the crystals, if one could permit them distributed in a wider range. Therefore, considering the ranges of scattering about $\pm 0.01\text{nm}$ of $d(O-R)$ in the crystals, one can assume each $d(O-R)$ as follows. $d(O-Li)=0.199\text{nm}$, $d(O-Na)=0.242\text{nm}$ and $d(O-K)=0.287\text{nm}$. On this basis, CN of the alkali ions in glass can be assumed as 4, 6 and 7 for Li^+ , Na^+ and K^+ ions, respectively.

Thus it has been shown that the effective radii of S&P well approximate the O-R distances if CN of each alkali is properly evaluated. Hence, the radii of S&P are also applied to evaluating the O-M distances. Almost all Mg^{2+} ions are six-coordinated in oxides, among the possible CN, 4, 6 and 8. Thus $CN(Mg)=6$ might also be plausible in glass. For Ca^{2+} ions,

CN of 6, 7 and 8 are seen. Waseda [15] has reported $d(\text{Ca-O})=0.249\text{nm}$ (CN=6.9) and 0.241nm (CN=7.2) in $45\text{CaO}\cdot 55\text{SiO}_2$ glass by means of X-ray and neutron diffraction studies. Then, $\text{CN}(\text{Ca})=7$ is assumed in glass. CN of 9 for Ba^{2+} ions is seen in BaSi_2O_5 crystal [16], which is only one alkaline earth disilicate crystal to be vitrified. Thus $\text{CN}(\text{Ba})=9$ is assumed in glass. CN might be considered in the order $\text{Mg}<\text{Ca}<\text{Sr}<\text{Ba}$. Then, $\text{CN}(\text{Sr})=8$ might be adopted for Sr^{2+} ions. Then, a sum of each effective ionic radius of an M^{2+} ion of S&P corresponding to the assumed CN and radius of six-coordinated O^{2-} ion 0.14nm is taken for $d(\text{M-O})$ in glass.

(b) Repulsion parameter

It was shown previously [1] that coulombic O-R interactions could describe the O-R bond energies. However the repulsive energy term must be taken into consideration so that the O-R and O-M interactions should be stable chemical bonds. Lattice energies of $\text{R}_2\text{O}(\text{c})$ and $\text{MO}(\text{c})$ can be represented by a simplified Born-Mayer equation,

$$U = -N A z_+ z_- e^2 (1/d) (1-p/d), \quad (9.7)$$

where N and A are the Avogadro's number and the Madelung constant of each lattice, z_+ and z_- the cation and anion charges, and d and p the O-R or O-M distance and the repulsion parameter, respectively. The Madelung constants of antifluorite and rock salt lattices are 2.519 and 1.746. The lattice energy of each alkali and alkaline earth oxide is obtained by

$$U(\text{R}_2\text{O}(\text{c})) = H_f(\text{R}_2\text{O}(\text{c})) - 2H_f(\text{R}^+(\text{g})) - H_f(\text{O}^{2-}(\text{g})),$$

$$U(\text{MO}(\text{c})) = H_f(\text{MO}(\text{c})) - H_f(\text{M}^{2+}(\text{g})) - H_f(\text{O}^{2-}(\text{g})).$$

Table 9.3. O-R and O-M bond energy and related parameters.

	Li	Na	K	
d(R-O) (10^{-1} nm)	1.99	2.44	2.87	
CN	4	6	7	
p _R (10^{-1} nm)		0.332	0.247	
O-R bond energy, E' _R (kcal/mol)				
R ₂ O·2SiO ₂	197	170	151	
R ₂ O·SiO ₂		188	166	
R ₂ O·P ₂ O ₅	198	172	153	
Coulombic energy, E _c (OR)				
	166.8	134.4	115.7	
	Mg	Ca	Sr	Ba
d(M-O) (10^{-1} nm)	2.12	2.47	2.65	2.87
CN	6	7	8	9
p _M (10^{-1} nm)		0.360	0.350	
O-M bond energy, E' _M (kcal/mol)				
MO·2SiO ₂	679	625	591	548
MO·P ₂ O ₅	611	540	511	
Coulombic energy, E _c (OM)				
	626.6	537.8	501.2	462.8

All of the H_f data are available in the previous tables. Thus applying U to eq. 9.7, the repulsion parameter p for Na, K and Ca, Sr has been obtained. Table 9.3 represents the parameters used in the calculations, the calculated bond energy and the coulombic energy E_c working between O and R or M at distance $d(R-O)$ or $d(M-O)$.

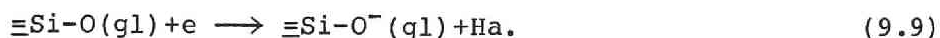
It must be noted that as far as one uses the fifth assumption A5 (eq. 9.6), the differences between any pairs of E_R' or E_M' , e.g., $E_{Na}' - E_K'$ are independent of R-O or M-O distance and the repulsion parameter [13]. Therefore, one can compare the bond energies within the O-R or O-M bonds regardless to those parameters. It might also be plausible to adopt Pauling's crystal radii and neglect the repulsive term. However, the O-R and O-M bond energies evaluated here are the most probable ones at the present stage because the effects of the bond lengths and coordination numbers and the repulsive term have been taken into consideration. When more reliable values of those parameters are available, the bond energies will be recalculated.

9.2.4 Bond energy relations in the glasses

According to eq. 9.2, E_R is related to E_R' by

$$2E_R = 2E_R' - 2(R^+(g) - R(g)) - (Si_2O_5^{2-}(gl) - Si_2O_5(gl)). \quad (9.8)$$

The term $R^+(g) - R(g)$ thermochemically represents the ionization potential of R (denoted as $I_R(>0)$). The last term in the right hand side of eq. 9.8 involves the following electron transfer.



where $H_a(>0)$ is the heat of reaction and can be called the electron affinity of the non-bridging oxygen. Then, application of eq. 9.9 modifies eq. 9.8 to eq. 9.10a.

$$E_R = E_R' - I_R + H_a, \quad (9.10a)$$

Similarly, the relation between E_M and E_M' is represented by

$$E_M = E_M' - I_M + 2H_a. \quad (9.10b)$$

It can be assumed [5] that H_a is equal to the electron affinity of $O(g)$,



This is a rough estimation but there may be no other plausible ways to evaluate H_a . Then, knowing E_R due to eq. 9.10, all of the bond energies can be estimated by eq. 9.1 for the alalkali disilicate glasses. In similar ways, the bond energy relations can be obtained for the glasses other than the disilicate ones. Table 9.4 represents the bond energies for the alkali silicate and phosphate glasses, and Table 9.5 represents that for the alkaline earth glasses. In the tables, the bond energies corresponding to $H_a=0$ are indicated in brackets. Moreover, the bond energies of the phosphate glasses are calculated with applying 1.75 and 2.0 in the ratio $E(P=O)/E(P-O)$ and those corresponding to the latter case in parentheses, as noted previously.

9.3 Properties of bonds viewed from additivity rule

In this section the properties of each bond such as polarization of oxygen and electrostatic shield of the NWM

Table 9.4. Bond energy relation in the alkali silicate and phosphate glasses.

Glass	Bond energies (kcal/mol)					
	D	E_b	$E_{nb}+E'_R$	E'_R	E_R	E_{nb}
$Li_2O \cdot 2SiO_2$	1190		261	197	106[71]	
$Na_2O \cdot 2SiO_2$	1148	111	241	170	85[50]	155 [191]
$K_2O \cdot 2SiO_2$	1146		240	151	84[49]	
$LiPO_3$	595		256 (251)	198	107[72]	
$NaPO_3$	575	90 (88)	236 (231)	172	88[52]	143 (138)
KPO_3	574		235 (230)	153	86[51]	178 (173)
$Na_2O \cdot SiO_2$	703		240	188	103[68]	
$K_2O \cdot SiO_2$	697	111	237	166	100[65]	137 [173]

Table 9.5. Bond energy relation in the alkaline earth silicate and phosphate glasses.

Glass	Bond energies (kcal/mol)					
	D	E_b	$E_{nb}+E_M/2$	E'_M	E_M	E_{nb}
$MgO \cdot P_2O_5$	1106		223(218)	611	155[85]	
$CaO \cdot P_2O_5$	1143	88 (84)	241(237)	540	192[122]	145(141) [180(176)]
$SrO \cdot P_2O_5$	1144		241(237)	511	192[122]	
$MgO \cdot 2SiO_2$	1102		218	679	223[153]	
$CaO \cdot 2SiO_2$	1156	111	245	625	277[207]	106[141]
$SrO \cdot 2SiO_2$	1152		243	591	273[203]	
$BaO \cdot 2SiO_2$	1143		238	548	264[194]	

cations will be discussed on the basis of the bond energies.

9.3.1 E_R , E_M and the single bond energy

(a) Single bond energy

Compare in Table 9.3 E_R' and E_M' with coulombic energies $E_C(OR)$ and $E_C(OM)$. The ratios $E_R'/E_C(OR)$ and $E_M'/E_C(OM)$ can be called apparent Madelung constants for the cations in the glasses. They are in the range from 1.18 for $R=Li$ to 1.30 for K , and from 1.08 for $M=Mg$ to 1.21 for Ba . The Madelung constants of R_2O and MO are 2.519 and 1.74, respectively. Thus it is shown that the R^+ and M^{2+} ions are significantly shielded electrostatically by coordinating oxygens in the glasses. Mg^{2+} ions with the ratio about 1 suffer greatly from the effect, polarize the oxygens and attract their electron cloud.

It can be seen from comparison of O-R bond energies that E_R and E_R' of RPO_3 glasses are similar to those of $R_2Si_2O_5$ glasses rather than those of R_2SiO_3 glasses. The metasilicate glasses have a chain-like structure as the metaphosphate ones. However, the ratio NWM cation/NWF cation in the metaphosphate, R/P is equal to the ratio in the disilicate, R/Si . It seems, therefore, that the O-R bond energies depend on the ratio NWM cation/NWF cation rather than the glass structure. However, O-M bond energy of an $MO \cdot 2SiO_2$ glass is not similar to that of an $MO \cdot P_2O_5$ glass with the same cation M . The results indicate a difference in properties of the alkali and alkaline earth cations.

Table 9.6. Single bond energy of O-R and O-M bonds
in $R_2Si_2O_5$ and MSi_2O_5 glasses (kcal/mol).

O-R	Li	Na	K	
Sun [9]	36	20	10	
CN	4	6	9	
D(R ₂ O(c))/CN	35	18	16	
E _R /CN*	26	14	12	
E _R '/CN*	49	28	22	
CN	4	6	7	
O-M	Mg	Ca	Sr	Ba
Sun [9]	37	32	32	33
CN	6	8	8	8
D(MO(c))/CN	40	36	30	26
E _M /CN#	37	40	34	29
E _M '/CN#	113	89	74	61
CN	6	7	8	9
* R ₂ O·2SiO ₂ (gl) # MO·2SiO ₂ (gl)				

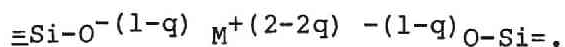
Table 9.6 shows single bond energy of O-R and O-M bonds in $R_2O \cdot 2SiO_2$ and $MO \cdot 2SiO_2$ glasses. Sun's single bond strength data should be replaced by $D(R_2O(c))/CN$ and $D(MO(c))/CN$ because the updated data have been employed for D/CN . E_R/CN and E_M/CN data are different from corresponding D/CN by 4 to 10 kcal/mol for O-R bonds and by 3 or 4 kcal/mol for O-M ones, respectively. Thus, if one notices those deviations, D/CN can be used as their single bond energy. It must be noted, however, that one should not compare E_R/CN or E_M/CN with

activation energy of cation transfer phenomena, because the activation energy is concerned with the ionic states of the metals and related to E_R' or E_M' rather than E_R or E_M .

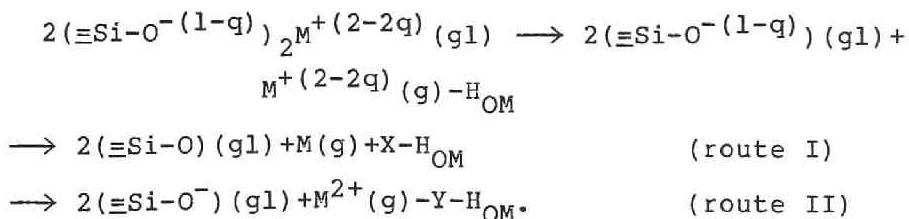
(b) Dependence of the bond energy on NWM and NWF cations

E_M , H_f and D of the alkaline earth glasses are generally in the order $Mg < Ba < Sr < Ca$. The quantities related with ionic state of M such as E_M' and $E_c(OM)$ are in the order $Ba < Sr < Ca < Mg$, and their effective radii of S&P in the reverse order $Mg < Ca < Sr < Ba$. Moreover, E_M' and E_M in the disilicate glasses are larger than those in the metaphosphate glasses irrespective of M . Such orders found in the alkaline earth glasses can be interpreted qualitatively.

In glass the formal charges of the non-bridging oxygens and alkaline earth cations are reduced to $-(1-q)$ and $+(2-2q)$ ($q < 1$) owing to polarizing power of M^{2+} ions, hence the non-bridging bond can schematically be represented as



The species $2(\equiv Si-O^{-(1-q)})(gl)$ and $M^{+(2-2q)}(g)$ are created by application of $H_{OM}(>0)$ to the non-bridging bond. The subsequent electron transfer produces either pair of the species, $2(\equiv Si-O^-)(gl) + M^{2+}(g)$ or $2(\equiv Si-O)(gl) + M(g)$. The procedures are represented as



The heats of reaction X and Y ($X, Y > 0$) are evolved at the

electron transfer, which might be expressed by $(1-q)(I_M - 2H_a)$ and $q(I_M - 2H_a)$, respectively. Because I_M is greater than $2H_a$, X and $-Y$ are exo- and endothermic quantities. Therefore, along the electron transfer, a part of the ionization potential of M and electron affinity of the non-bridging oxygens is added to or reduced from $O-M$ bond dissociation energy, H_{OM} . The results are observed as E_M or E_M' . That is, in route I involving E_M , exothermic quantity X reduces the endothermic quantity H_{OM} . Either of larger q or smaller I_M , which are characteristic of smaller and larger ions, respectively, give a larger value of $H_{OM} - X$, that is, E_{OM} . Contrarily, endothermic quantity $-Y$ is added to H_{OM} in route II, where both larger q and larger I_M values give a larger value of $H_{OM} + Y$, that is, E_{OM}' . I_M of each M at 0 K is 558, 457, 425 and 394 kcal/mol for $M = Mg, Ca, Sr$ and Ba , respectively. In spite of the fact that I_{Ca} and I_{Sr} are greater by about 60 and 30 kcal/mol than I_{Ba} , the E_M values for $M = Ca, Sr$ and Ba are almost the same and different only by about 10 kcal/mol. This can be interpreted as follows. The effect of the polarization q reducing X and giving a larger E_{OM} is greater in the order $Ba < Sr < Ca < Mg$. The effect of I_M increasing X and giving a smaller E_{OM} is in the order $Ba < Sr < Ca$. As the results of the two contrary effects of q and I_M on E_{OM} , E_M becomes larger in the order $Ba < Sr < Ca$. In short, the effect of the polarization is cancelled excessively by that of the ionization potential. Similarly, the fact that E_{Mg}' is the greatest and E_{Mg} is the smallest among the E_M' and E_M values can be attributed to very large value of I_{Mg} , greater by 100 kcal/mol than I_{Ca} . As a result, it has been

shown that O-Ba bond is the most ionic and O-Mg bond is the most covalent.

The fact that O-M bond energies are larger in the silicate glasses than in the phosphate glasses can be explained in terms of the polarization as follows. The electrons on the non-bridging oxygens of the phosphate glasses are strongly bound in PO_4 units due to 3d-2p π -interactions with the P atom, and they are polarized little by the adjacent M^{2+} ions, giving a small q . Contrarily, the non-bridging oxygens in the silicate glasses can be polarized more than those in the phosphate ones, and this causes a larger q because of trace 3d-2p π -interaction in the silicates. Thus, X is reduced in the silicate glasses, resulting in a larger value of $H_{\text{OM}}-X$, that is, E_{M} . The polarization of the non-bridging oxygens causes a larger Y and a larger $H_{\text{OM}}+Y$, that is, E_{M}' .

O-R bond energies are in the order $\text{Li} > \text{Na} > \text{K}$, while the effective ionic radii of S&P are in the reverse order. Moreover, O-R bond energies of the silicate glasses are smaller than those of the phosphate glasses, contrarily to the O-M bond energies. On application of the interpretation of the order of O-M bond energies, it is considered that such behavior of O-R bonds may be caused by the following items.

- (1) The ionization potential of the alkali atoms ranges from 126 for Li to 102 kcal/mol for K, being in much narrower range and much smaller than that of the alkaline earth atoms.
- (2) The polarizing power of R^+ ions are considerably smaller than that of M^{2+} ions.

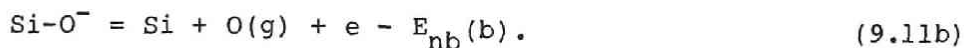
Items (1) and (2) reduce the influence of the electron transfer and the polarization of the non-bridging oxygens to the O-R bond energies. As a result, the ionic bond energy term becomes predominant in the O-R energies and is dependent on the bond lengths, namely the sizes of the R^+ ions. This might be the reason why the bond energies are in the order $Li > Na > K$ that might be usually supposed.

9.3.2 NWF cation-O bonds

On obtaining E_{nb} in the previous section, the value of H_a is assumed to be 0 and 35 kcal/mol. The former case, $H_a=0$ kcal/mol gives E_{nb} corresponding to the heat of the following reaction,



In the latter case, $H_a=35$ kcal/mol, E_{nb} is related to the reaction,



The state of Si atoms are not significant in both cases. The important thing is that $E_{nb}(a)$ indicated in brackets in Tables 9.4 and 9.5 would essentially represent the energy of the bond between NWF cation and non-bridging oxygen. However, the definition of the bond energy here involves the process of atomization. Hence $E_{nb}(b)$ as the heat of reaction of (9.11b) should be assigned to the bond energy E_{nb} .

Incidentally, compare the ratio E_{nb}/E_b between the silicate and phosphate systems. The elements on and after the third period in the periodic tables have d-p π -interaction

with oxygens employing their d orbitals. The elements with such interaction may have larger E_{nb} compared to E_b . In the alkali disilicate and metaphosphate glasses of the same alkali and NWM cation/NWF cation ratio, it is shown that the ratio E_{nb}/E_b is in the order

$$E_{nb}/E_b(\text{silicate}) < E_{nb}/E_b(\text{phosphate}).$$

The $P-O^-$ non-bridging bond is in resonance with the $P=O$ bond through d-p π -interaction. Thus it is natural to give a large ratio 1.6. A similar effect of d-p π -interaction can be seen in the silicate glasses with the ratio $E_{nb}/E_b=1.4$. This is confirmed by the fact that $Si-O^-$ bond length 0.156nm is shorter than the bridging bond length 0.163nm in $Na_2O \cdot 2SiO_2$ crystal [17].

9.4 Summary

The total bond energies, calculated with the heats of formation of RPO_3 , $M(PO_3)_2$ and MSi_2O_5 glasses described in Chap. 8, have been proportionated to each bond. The physical meaning of the bond energies have also been discussed. The O-R bond energies E_R in RPO_3 glasses are similar to those in $R_2Si_2O_5$ glasses, having the same NWM cation/NWF cation ratio. The energies E_R in the RPO_3 glasses are not similar to those in R_2SiO_3 glasses which resemble the metaphosphate glasses in structure. O-M bond energy E_M is larger in the order $Mg < Ba < Sr < Ca$ in $M(PO_3)_2$ and MSi_2O_5 glasses. Moreover, E_R is in the order $K < Na < Li$. Such behavior of E_R and E_M has been

interpreted in terms of the ionization potentials of $R(g)$ and $M(g)$, the polarizing power of R^+ and M^{2+} ions, and the electron density on the non-bridging oxygens. It has also been shown that each E_M is larger in the silicate glass than in the phosphate glass, whereas E_R is larger in the phosphate one. This is the effect of d-p π -interaction which is greater in the phosphates than in the silicates.

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SUMMARY

In order to understand the network structure of binary and ternary glasses, obtain the structure models and clarify changes in glass structure due to a mixing of two network forming (NWF) oxides, detailed experimental studies were conducted on dependences of molar volumes, elastic constants, thermochemical and optical properties on the composition of glass. The results were discussed in relation to the arrangements of the fundamental units constituting the glasses such as SiO_4 , BO_4 , GeO_6 and PO_4 , properties of the NWF cation-oxygen and network modifying (NWM) cation-oxygen bonds, oxygen coordination numbers of NWF cations, and thermochemical stabilities. The following two principles were employed as the essential and fundamental basis: additivity rule and void as a major constituent of glass structure.

In Chapter 1, fundamental concepts of network structure of glasses composed by oxygen tetrahedra were discussed on the basis of the molar volume vs. composition relation in alkali silicate glasses, $x\text{R}_2\text{O} \cdot \text{SiO}_2$ ($\text{R}=\text{Li}, \text{Na}, \text{K}, \text{Rb}$ and Cs , $0 \leq x \leq 0.5$). A high-cristobalite (h-c) type cage structure model was proposed, assuming additivity in the two units, $\text{SiO}_{4/2}$ and $\text{ROSiO}_{3/2}$. The correlation of the alkali ions and voids associated to the units was discussed as to their size and distribution in the glass. Bulk modulus vs. mean atom-pair volume relation (K-V relation) was also explained in terms of

the cage structure model and effects of alkali ions occupying the voids.

In Chapter 2, structure of the glasses $x\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ ($0 < x \leq 0.5$) was described in relation to boron oxide anomaly. The presence of first and second anomalies was inferred. Particular arrangements of the borate units, BO_3 and RBO_4 , were found in the crystals of the composition corresponding to the first anomaly. The presence of such arrangements was also suggested in the glasses. Another specific arrangements were proposed at 0.3 in x from K-V relation for the glasses. The second anomaly at 0.5 in x was caused by the decrease of BO_4 units in number and formation of the non-bridging oxygens, and was suggested to be related to unstability of BO_3 - BO_4 bond relative to BO_3 - BO_3 one. The elastic constants became maximum at the composition corresponding to maximum fraction N_4 of the RBO_4 units.

In Chapter 3, the network structure of alkali germanate glasses of the compositions $x\text{R}_2\text{O}\cdot\text{GeO}_2$ ($\text{R}=\text{Na}$ and K , $0 < x < 1.5$) was investigated. Variations of the molar volume and elastic constants with x indicated the presence of two composition ranges, I and II. On referring to the molar volume and fraction N_6 of GeO_6 units vs. x relations in the alkali germanate crystals, the structure of the alkali germanate glasses was derived. In range I the added Na_2O changed GeO_4 units to Na_2GeO_6 ones, and Na^+ ions filled the voids associated with the GeO_6 units without expanding the glass skeletons. This caused that the molar volume of the sodium glasses was independent of x in range I. K^+ ions played the

same role as Na^+ ions. However, the molar volume of the potassium germanate glasses increased because of larger size of K^+ ions than that of the void in the sodium glasses. N_6 followed the relation $N_6=x$ in the sodium and potassium glasses in range I. In range II, decomposition of GeO_6 units to ROGeO_3 ones occurred and interruption of the bridging bonds took place simultaneously creating the ROGeO_3 units. The structural changes agreed well with that indicated by the K-V relation for the sodium and potassium germanate glasses. A cage type network model was proposed for the glasses.

In Chapter 4, the structure of alkali borosilicate glasses of the compositions $x\text{R}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot r\text{SiO}_2$ ($\text{R}=\text{Na}$ and K , $r=1$ and 2 , $0 < x \leq 2.0$) was discussed from the composition dependence of the molar volume, Dq of Ni^{2+} ions and elastic constants. The behavior of B_2O_3 and R_2O was different in the three composition ranges. In range I, added R_2O changed BO_3 units to RBO_4 ones. In range II, the alkali oxide created ROSiO_3 units and in range III it caused decomposition of the RBO_4 units and interruption of the bridging bonds creating ROSiO_3 and ROBO_2 units. From the K-V relation and void volume associated with the BO_4 units, it was indicated that in range I Na^+ ions filled the voids neighboring to the BO_4 units without expanding the borosilicate network, while K^+ ions expanded the network due to its larger size. The correlation of the size of the voids and that of the alkali ions explained the composition dependence of the molar volumes of the borosilicate glasses and the difference in structure between the borosilicate and borate glasses. The glasses with molar

ratio $r = \text{SiO}_2/\text{B}_2\text{O}_3$ ranging from 1 to 4 had characteristic network of borosilicate. This network was different from that of the borosilicate glasses with $r < 1$, resembling the borate network, and from that with $r \geq 5$, resembling silica glass network. Furthermore, the second boron oxide anomaly was explained thermochemically. It was indicated that the $\text{BO}_4\text{-BO}_4$ bond was not so stable as $\text{BO}_3\text{-BO}_4$ one.

In Chapter 5, the network structure of the alkali germanosilicate glasses of the compositions $x\text{R}_2\text{O} \cdot \text{GeO}_2 \cdot r\text{SiO}_2$ ($\text{R} = \text{Na}$ and K , $r = 1/3$ and 1 , $0 < x \leq 1.0$) was described. The role of R_2O was presented in two ranges I and II. In range I GeO_4 units were changed to R_2GeO_6 ones. N_6 was proposed to follow the relation $N_6 = x$. The maximum values of N_6 , $N_{6\text{max}}$, were larger in the sodium glasses than in the potassium ones. This was a contrary trend of $N_{4\text{max}}$ in the borosilicate glasses, where $N_{4\text{max}}$ of the potassium glasses was larger than that of the sodium ones. Moreover, the K-V relation was correlated to the effects of the alkali ions filling the voids on the glass network. It was indicated that the germanosilicate glass network was derived when the SiO_4 units substituted the GeO_4 ones in the alkali germanate glasses with keeping the configurations of the GeO_4 tetrahedra. In range II where non-bridging oxygens were created, the partition coefficients of Na_2O and K_2O to GeO_2 and SiO_2 were calculated assuming additivity. The amount of alkali oxide partitioned to GeO_2 was considerably larger than that partitioned to SiO_2 . All of K_2O were associated with GeO_2 in the glasses with $r \leq 1/3$.

In Chapter 6, the constitution of potassium borophosphate

glasses of the compositions $K_2O \cdot 2(1-x)B_2O_3 \cdot 2xP_2O_5$ ($0 \leq x \leq 1$) was presented. Two factors were considered for constructing the glass network: one was the change in coordination number of B atoms and the other was the presence of P=O double bond which could play both roles of the non-bridging and bridging bond. The molar volume increased by substitution of P_2O_5 for B_2O_3 showing a plateau near 0.5 in x. The elastic constants showed complicated dependence on x. They became minimum at 0.25 in x and maximum at 0.5 in x. A structure model was proposed for the glasses; K_2O first associated with B_2O_3 yielding KBO_4 and free BO_3 units, the rest of K_2O was reacted with P_2O_5 resulting in KPO_3 units, and the free B_2O_3 and P_2O_5 were reacted to create BPO_4 units. The model explained well the composition dependence of the molar volume and elastic constants. The variation of N_4 predicted by the model agreed with the cited one.

In Chapter 7, the size of the voids in so far investigated glasses was summarized and compared with that of the alkali ions. The volume of the void in the borate, silicate and borosilicate glasses was compared. The difference of the borate network from the other ones was recognized by the larger void than that in the other glasses. The effects of presence of the non-bridging oxygens in the networks on the void volume were also discussed. Significantly larger voids in the alkali disilicate networks occupied by the alkali ions were attributed to the repulsion between the non-bridging oxygens and structure tightening effect of the alkali ions.

In Chapter 8, composition dependence of heats of solution

of the phosphate glasses of compositions $xR_2O \cdot P_2O_5$ ($R=Li, Na$ and K) and $xMO \cdot P_2O_5$ ($M=Mg, Ca, Sr$) was discussed. The heats of solution varied linearly with molar ratio $x=R_2O/P_2O_5$ or MO/P_2O_5 in each composition range, I ($0 < x < 1$), II ($1 < x < 2$) and III ($2 < x < 3$). The minima in the heat of solution vs. x relations found for the crystalline and vitreous metaphosphates were explained in terms of a resonance in the PO_4 units. The bond energy of the P-O bridging bond was independent of R in the alkali phosphate glasses and independent of M in the alkaline earth ones in each range. In range I, the P-O bond energy was the same for all of the glasses. In ranges II and III, the alkali glasses had stronger P-O bonds than the alkaline earth ones. The P-O bond energy increased with increase in the NWM oxide content. Moreover, the heats of solution of $MO \cdot 2SiO_2$ glasses ($M=Mg, Ca, Sr$ and Ba) were obtained from those of pseudo-binary systems $R_2Si_2O_5$ - MSi_2O_5 . The heats of formation of RPO_3 , $M(PO_3)_2$ and MSi_2O_5 glasses were given.

In Chapter 9, the total bond energy D of the glasses RPO_3 , $M(PO_3)_2$, $R_2Si_2O_5$ and MSi_2O_5 was described. D was proportioned to each bond composing the glasses. The NWF cation-O and NWM cation-O bond energies were compared within them. M-O and R-O bond energies were in the order $Mg < Ba < Sr < Ca$, and $K < Na < Li$, respectively. The orders were explained in terms of the ionization potential of M and R , the polarizing power of M^{2+} and R^+ ions and the electron density on the non-bridging oxygens dependent upon the adjacent NWF cations. Ba-O bond was the most ionic and Mg-O the most covalent and ionic energy

term was predominant in R-O bonds.

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