

Review

## Formation of Metastable Pyrochlore-Type Crystals in Glasses

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Structures of metastable crystals in  $K_2O-Ta_2O_5-Nb_2O_5-Al_2O_3-SiO_2$  and  $PbO-TiO_2-Al_2O_3-SiO_2$  glasses as well as conditions of formation of the crystals were investigated to speculate the structures of the mother glasses.

### I INTRODUCTION

In the course of investigations on glass-ceramics essentially composed of ferroelectric perovskite-type crystals, the present authors have found that metastable pyrochlore-type crystals tend to form in glasses on heating prior to precipitation of the stable perovskite-type crystals and that the crystals of this type can form only through crystallization of glasses, but not through sintering of their raw materials.

These facts suggest that the structures of the metastable pyrochlore-type crystals are very similar to those of the mother glasses from which the crystals precipitated. If so, detailed studies of the structures of the metastable crystals as well as conditions of their formation might furnish the important key to investigations of the structures of the mother glasses.

The present paper is a summary of the authors' investigations<sup>1-4)</sup> on the formation of metastable pyrochlore-type crystals in  $K_2O-Ta_2O_5-Nb_2O_5-Al_2O_3-SiO_2$  and  $PbO-TiO_2-Al_2O_3-SiO_2$  glasses which are finally transformed, by heating, into glass-ceramics essentially composed of perovskite-type  $K(Ta, Nb)O_3$  and  $PbTiO_3$  crystals, respectively.

### II EXPERIMENTAL AND DISCUSSION

#### 1. $K_2O-Ta_2O_5-Nb_2O_5-Al_2O_3-SiO_2$ Glasses

##### 1.1. Preparation of Glasses and their Crystallization

Batch mixtures of the compositions given in oxide mol % in Table I were prepared from reagent grade chemicals of  $K_2CO_3$ ,  $Ta_2O_5$ ,  $Nb_2O_5$ ,  $Al(OH)_3$  and  $SiO_2$ . About 10 g of each of the batch mixtures except for compositions Nos. 10 and 11 was melted in a Pt-10%Rh crucible at 1300°–1500°C for 1 hr in an electric furnace. The melts were poured on a steel plate and pressed into plates approximately 1 mm thick. Since compositions Nos. 10 and 11 were unable to be formed into glasses by this method about 0.1 g of their batch mixtures were melted directly on a platinum strip heater and

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Table I. Batch Compositions

Glass No.	Composition (mol %)				
	KO <sub>0.5</sub>	TaO <sub>2.5</sub>	NbO <sub>2.5</sub>	AlO <sub>1.5</sub>	SiO <sub>2</sub>
1	40.0	26.0	14.0	20.0	—
2	40.0	26.0	14.0	13.3	6.7
3	47.8	22.6	12.2	—	17.4
4	48.9	22.1	11.9	11.3	5.7
5	47.8	22.6	12.2	11.6	5.8
6	33.3	28.9	15.6	14.8	7.4
7	25.0	32.5	17.5	16.6	8.4
8	42.8	7.6	30.5	12.7	6.4
9	42.8	26.7	11.4	12.7	6.4
10*	50.0	32.5	17.5	—	—
11*	48.0	30.5	16.7	—	4.8

\* Splat quenching

blown off by a compressed oxygen gas against a microscopic slide held at room temperature by using a splat quenching apparatus similar to that described by Sarjeant *et al.*<sup>5)</sup>

All the glasses thus obtained were analyzed by X-ray fluorescent method to determine their final compositions. They are listed in Table II which indicates that fairly large amount of K<sub>2</sub>O evaporated from each of the glass melts.

The glass specimens were heated to various temperatures at a rate of 5°C/min in an electric furnace, and allowed to cool in the ambient atmosphere. The crystalline phases present in the heat-treated specimens were identified by powder X-ray diffraction analyses with Ni-filtered CuK $\alpha$  radiation. The results are shown in Table III.

It can be seen from the table that the unidentified crystal denoted by X is formed prior to precipitation of perovskite-type K(Ta, Nb)O<sub>3</sub> crystal (abbreviated to KTN crystal hereafter) in the glasses with a wide range of compositions; the X crystal is formed even in glass No. 10 consisting only of K<sub>2</sub>O, Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>.

Table II. Analyzed Compositions of Glasses

Glass No.	Composition (mol %)				
	KO <sub>0.5</sub>	TaO <sub>2.5</sub>	NbO <sub>2.5</sub>	AlO <sub>1.5</sub>	SiO <sub>2</sub>
1	30.4	30.2	16.3	23.1	—
2	32.2	29.3	15.7	15.1	7.6
3	36.3	27.6	15.0	—	21.2
4	40.3	25.8	13.9	13.3	6.6
5	38.2	26.8	14.4	13.8	6.9
6	23.9	32.9	17.8	16.9	8.5
7	15.7	36.6	19.7	18.7	9.3
8	34.0	8.8	35.3	14.6	7.4
9	31.7	31.8	13.5	15.2	7.8
10	40.5	38.7	20.8	—	—
11	36.0	37.7	20.3	—	5.9

## Metastable Pyrochlore-Type Crystals in Glasses

Table III. Crystals Precipitated in the Heat-treated Glasses

Glass No.	Temperature (°C)					
	550	650	750	850	950	1050
1	—	—	—	X, A, P	P, A	P, A
2	—	—	X	X	P, B	P, B
3	—	—	X	P	P	P
4	—	—	—	C	P	P
5	—	—	X	P	P	P
6	—	—	—	X	P, D	P, D
7	—	—	—	X	E	E
8	—	—	—	P, F	P, F	P, F
9	—	—	X	X	P, X	P
10	—	X, G	P	P	P	P
11	—	X	X	P	P	P

—; Glass, X and A-G; Unidentified crystals,  
P; Perovskite-type  $K(\text{Ta}, \text{Nb})\text{O}_3$  crystal

1. 2. *Stability of the X Crystal and Conditions for its Formation*

Several pieces of glass No. 2 were put into an electric furnace previously heated to 850°C and after held for various lengths of time at this temperature, allowed to cool in the ambient atmosphere. The intensities of the most intensive X-ray diffraction peaks of the X crystal and the perovskite-type KTN crystal precipitated in each of the specimens thus heat-treated were measured and plotted in Fig. 1 against the heat-treatment time. The figure shows that when the glass is heat-treated at a constant temperature the X crystal first precipitates in the glass and then the perovskite-type KTN crystal commences to precipitate with consumption of the X crystal. This result indicates that the X crystal is a metastable phase formed prior to formation of the perovskite-type KTN crystal which is stable at this temperature.

In order to investigate conditions for formation of the X crystal, the batch mixture of composition No. 10, which consists only of  $\text{K}_2\text{O}$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ , was melted in 10 g amounts in a Pt-10%Rh crucible, poured on a steel plate and pressed into a plate

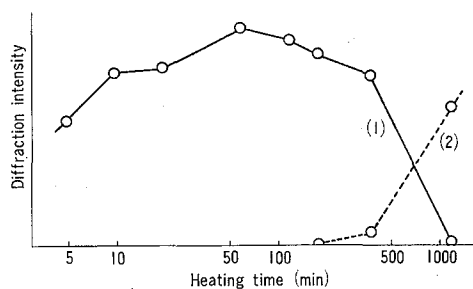


Fig. 1. Intensity of X-ray diffraction lines of the X crystal and the perovskite-type KTN crystal precipitated in glass No. 2 vs. the heat-treatment time.

- (1) Diffraction line of the X crystal at  $d=2.66$   
(2) (110) reflection of the perovskite-type KTN crystal.

approximately 1 mm thick. The as-cooled plate appeared to be fully devitrified. X-ray diffraction analyses of the devitrified product revealed that the X crystals precipitated only at its surface whereas the perovskite-type KTN crystals precipitated in its interior.

In a separate experiment, the two batch mixtures with the same compositions those analyzed for glasses Nos. 2 and 10 (Table II) were pressed into discs, sintered by heating to various temperatures ranged from 600° to 850°C at a rate of 5°C/min, and cooled to room temperature. X-ray diffraction analyses of these sintered specimens revealed that only the perovskite-type KTN crystal formed from the initial stage of the sintering by solid state reaction; no X crystal was formed at any stages.

These results indicate that the X crystal is formed only through crystallization of glasses (supercooled melts) but not through ordinary solid state reaction of their raw materials.

### 1.3. Similarity of Structure between the X Crystal and the Mother Glass

The main factors determining the nucleation rate of crystal in a glass at a fixed temperature are free energy change associated with the bulk transformation of the glass into crystal,  $\Delta G$ , activation energy associated with this atomic rearrangement process,  $\Delta G^*$ , and free energy of the crystal-glass interface,  $\sigma^6$ . Of these factors,  $\Delta G$  is lower in the case of formation of the X crystal than in that of the perovskite-type KTN crystal, because the latter is more stable in the present system. Therefore, the initial precipitation of the X crystal from the glass must be attributed to a lower  $\Delta G^*$  and/or to a lower  $\sigma$  for formation of the X crystal. This could be achieved if the structure of the X crystal is more similar to that of its mother glasses than the structure

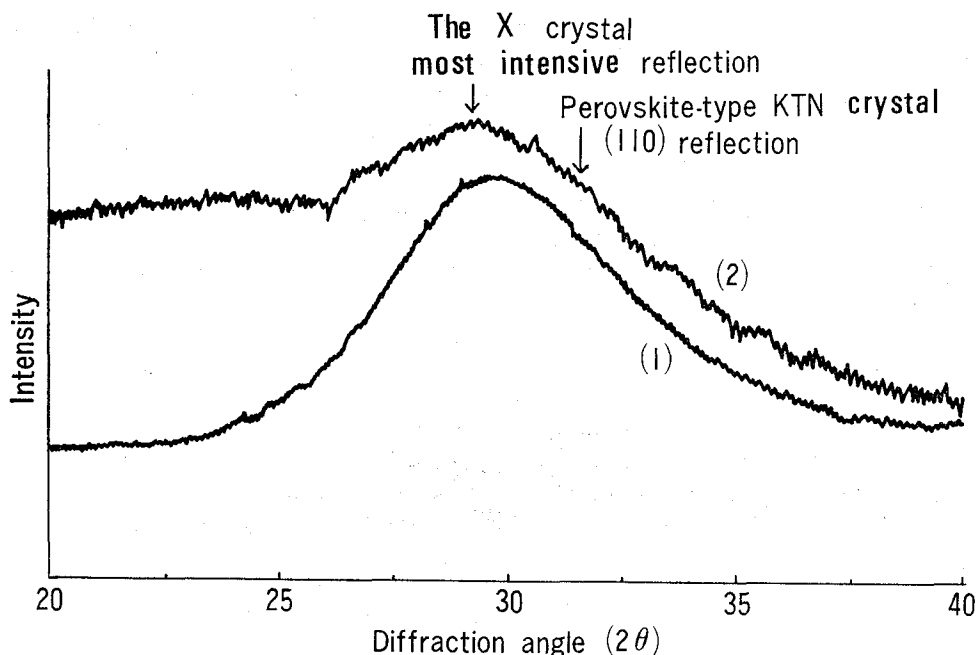


Fig. 2. X-ray diffraction patterns of (1) glass No. 2 and (2) glass No. 10.

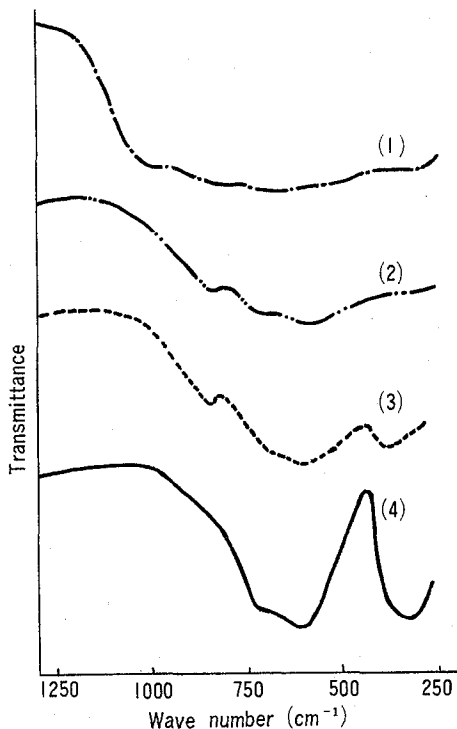


Fig. 3. Infrared spectra of crystals and glasses.  
 (1) Glass No. 2    (2) Glass No. 10  
 (3) X crystal    (4) Perovskite-type KTN crystal

of the perovskite-type KTN crystal. Following experimental results indicate that the structure of the X crystal is very similar to that of the mother glasses.

Figure 2 shows the powder X-ray diffraction patterns of glasses Nos. 2 and 10, of which the latter is enlarged along the longitudinal axis. In the figure the positions of the most intensive diffraction peaks of the X crystal and the perovskite-type KTN crystal are also shown. The most intensive diffraction peaks of the two glasses are both much nearer in position to that of the X crystal than that of the perovskite-type KTN crystal.

Figure 3 shows the infrared spectra of glasses Nos. 2 and 10, as well as those of the X crystal separated from the surface of the fully devitrified product No. 10 (section 1.2) by scratching, and the perovskite-type KTN crystal prepared by a solid state reaction (section 1.2). The spectra were obtained by using the KBr disc method. Although detailed assignment of the absorption bands is impossible because available data on their bands are few at present, it is apparent from the figure that the absorption patterns of the two glasses are more similar to that of the X crystal than that of the perovskite-type KTN crystal. Particularly, the absorption band at the wave number  $850\text{ cm}^{-1}$  is characteristic to the infrared spectra of glass No. 10 and the X crystal. Indistinct absorption at the same wave number in the spectrum of glass No. 2 is probably due to the effect of the strong absorption near  $1000\text{ cm}^{-1}$  caused by Si-O stretching vibration.

1. 4. *Composition and Structure of the X Crystal*

In order to extract the X crystal precipitated in the glass, glass No. 2 which had been heat-treated for 1 hr at 850°C was immersed in 2 N hydrochloric acid for 8 hr at 80°C. The residue was confirmed by X-ray diffraction analysis to be composed almost only of the X crystal. The relative intensities of the X-ray diffraction lines of the residue were, however, somewhat different from those of the X crystal as-precipitated in the mother glass. Then, the residue was immersed in 2 N potassium hydroxide solution for 8 hr at room temperature. By this treatment the X-ray diffraction lines of the residue came close to those of the original X crystal as-precipitated in the mother glass. The chemical composition of the X crystal thus extracted from glass No. 2 was determined by X-ray fluorescent analysis and shown in Table IV. In the table the composition of the X crystal separated from the surface of the fully devitrified plate No. 10 (section 1.2) by scratching is also shown for comparison.

For both of the X crystals, their major components are  $K_2O$ ,  $Ta_2O_5$  and  $Nb_2O_5$ , and the mol content of  $KO_{0.5}$  is less than the sum of the mol contents of  $TaO_{2.5}$  and  $NbO_{2.5}$ .

Figure 4 shows the X-ray diffraction pattern of the X crystals as-precipitated in glass No. 2. This pattern is almost the same as those<sup>7-9)</sup> generally observed for the cubic pyrochlore-type compounds. The cell length calculated from the pattern is 10.62 Å. Pyrochlore-type compounds are crystals with the general formula  $A_2B_2O_7$  and the unit cell length of 10.00 to 10.70 Å, where A and B are cations with valence of 2 or 3 and 5 or 4, and the ionic radius of 0.9 to 1.2 Å and 0.6 to 0.7 Å, respectively.<sup>8)</sup> Since potassium, tantalum and niobium ions comprised in the X crystal usually have the valences of 1+, 5+ and 5+, and the radius of 1.33, 0.68 and 0.69<sup>10)</sup> respectively,

Table IV. Composition of X Crystal

	Composition (mol %)				
	$KO_{0.5}$	$TaO_{2.5}$	$NbO_{2.5}$	$AlO_{1.5}$	$SiO_2$
X crystal extracted from glass No. 2	26.3	45.2	22.6	2.5	3.4
X crystal separated from the surface of devitrified product No. 10	39.3	39.3	21.4		

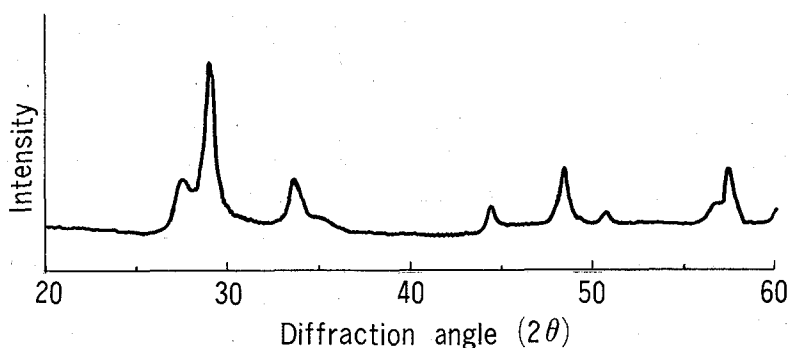


Fig. 4. X-ray diffraction pattern of the X crystal as-precipitated in glass No. 2.

the Ta<sup>5+</sup> and Nb<sup>5+</sup> ions would occupy the B ion sites in the pyrochlore-type structure. Although the K<sup>+</sup> ions seem to have the too large radius and too low valence to enter into the A ion sites, there are reports saying that the K<sup>+</sup> ions can replace some ions at A ion sites<sup>9)</sup> and also that oxygen-deficient pyrochlore-type compounds really exist.<sup>11)</sup> Therefore, it is expected that all the K<sup>+</sup> ions comprized in the X crystal occupy the A ion sites of the pyrochlore-type structure, being accompanied by some vacancies at oxygen ion sites. Furthermore, since the amount of K<sup>+</sup> ions in the X crystal is less than the sum of the Ta<sup>5+</sup> and Nb<sup>5+</sup> ions as shown in Table IV, a part of the A ion sites must be left vacant and as the result there must be more oxygen deficiencies at oxygen ion sites. Therefore, the formula of the X crystal would be K<sub>2-2δ</sub>(Ta, Nb)<sub>2</sub>O<sub>6-δ</sub>, where 2δ is the number of vacancies at the A ion sites.

On the basis of these considerations, the relative intensities of the X-ray diffraction peaks were calculated for the pyrochlore-type compounds having the formula K<sub>2-2δ</sub>(Ta, Nb)<sub>2</sub>O<sub>6-δ</sub> by reference to the atomic positions given in No. 227 in Volume 1 of *International tables for X-ray crystallography*. In the calculations, the Ta<sup>5+</sup> and Nb<sup>5+</sup> ions were assumed to occupy the B ion sites at random but by the mol ratio equal to that in the mother glass, *i.e.*, 0.65 to 0.35. The parameter,  $x$ , representing the position of the oxygen ions was assumed to be 5/16 in view of relative radius of the constituent ions. The calculated relative intensities of the X-ray diffraction peaks are shown in Table V, in comparison with those observed for the X crystal as-precipitated in glass No. 2. The relative intensities of the X-ray diffraction peaks of the X crystal well fit those of the pyrochlore-type crystal having the formula K<sub>2-2δ</sub>(Ta<sub>0.65</sub>Nb<sub>0.35</sub>)<sub>2</sub>O<sub>6-δ</sub>, where δ=0.25. Consequently, it can be concluded that the X crystal is the pyrochlore-type crystal with a composition of approximately K<sub>1.5</sub>(Ta<sub>0.65</sub>Nb<sub>0.35</sub>)<sub>2</sub>O<sub>5.75</sub>.

### 1.5. Speculated Structure of the Glass

One of most popular pyrochlore-type compound, Cd<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> has the structure shown in Fig. 57). It can be seen from the figure that the structure is built up of a three dimensional network of NbO<sub>6</sub> octahedra and Cd<sup>2+</sup> ions sitting in the holes of the network. In the X crystal, it is considered that some of the NbO<sub>6</sub> octahedra are replaced with TaO<sub>6</sub> octahedra at random and all of the Cd<sup>2+</sup> ions are replaced with

Table V. X-ray Powder Diffraction Data for X Crystal and Pyrochlore-type K<sub>2-2δ</sub>(Ta<sub>0.65</sub>Nb<sub>0.35</sub>)<sub>2</sub>O<sub>6-δ</sub> Crystal

hkl	I/I <sub>0</sub> for X crystal (observed)	I/I <sub>0</sub> for K <sub>2-2δ</sub> (Ta <sub>0.65</sub> Nb <sub>0.35</sub> ) <sub>2</sub> O <sub>6-δ</sub> crystal (calculated)		
		δ=0	δ=0.25	δ=0.50
311	0.36	0.29	0.38	0.51
222	1.00	1.00	1.00	1.00
400	0.35	0.34	0.34	0.34
331	0.076	0.062	0.085	0.13
333) 511)	0.13	0.091	0.12	0.16
440	0.37	0.41	0.41	0.41
531	0.15	0.12	0.16	0.20
533	0.06	0.052	0.066	0.083
622	0.33	0.42	0.42	0.42

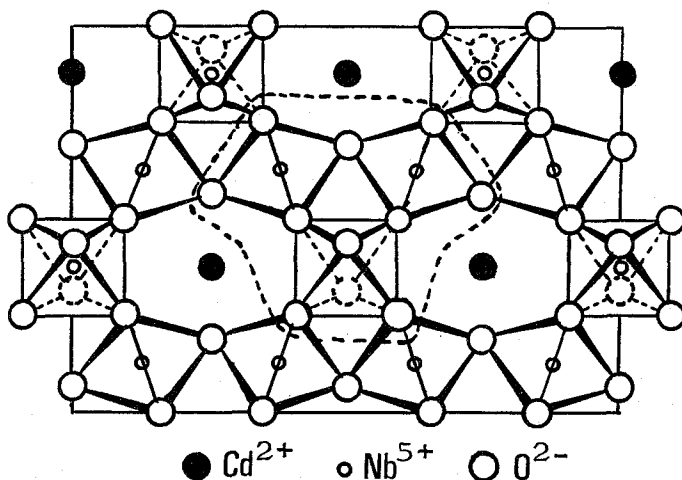


Fig. 5. Structure of pyrochlore-type crystal,  $\text{Cd}_2\text{Nb}_2\text{O}_7$  projected on (110) plane.<sup>7)</sup>

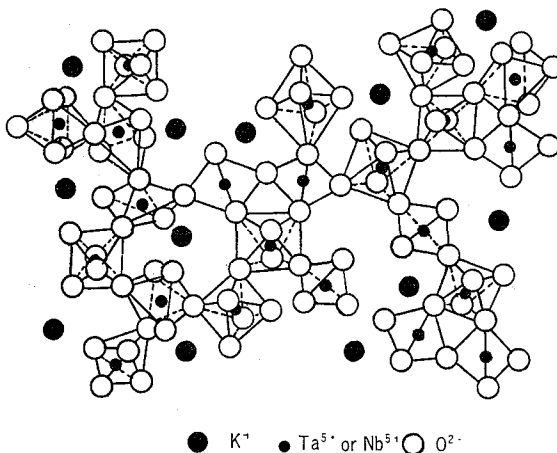


Fig. 6. A structural model of  $\text{K}_2\text{O}-\text{Ta}_2\text{O}_5-\text{Nb}_2\text{O}_5$  glasses.

$\text{K}^+$  ions and some vacant sites. Furthermore, among eight oxygen ions expected to surround one  $\text{K}^+$  ion, the two oxygens which do not participate with the network are missing and also some of the oxygen ions joining  $\text{TaO}_6$  or  $\text{NbO}_6$  octahedra are missing, and as the results many breaks are induced at some points of the network.

If the structure of the  $\text{K}_2\text{O}-\text{Ta}_2\text{O}_5-\text{Nb}_2\text{O}_5-\text{Al}_2\text{O}_3-\text{SiO}_2$  glasses is similar to that of this pyrochlore-type crystal, it is considered to be composed essentially of a random network of  $\text{TaO}_6$  and  $\text{NbO}_6$  octahedra and  $\text{K}^+$  ions being situated in some holes of the network, as shown in Fig. 6.

As to the structure of  $\text{K}_2\text{O}-\text{Nb}_2\text{O}_5-\text{SiO}_2$  glasses, Rao<sup>12)</sup> early speculated on the basis of the physical and chemical properties of the glasses that most of the  $\text{Nb}^{5+}$  ions in the glasses are octahedrally coordinated with oxygen ions and act as nearly network-forming ions. This speculation is consistent with the present conclusion.



## Metastable Pyrochlore-Type Crystals in Glasses

Tabel VI. Batch Compositions

Group No.	Glass No.	Composition (mol %)					
		PbO	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> +SiO <sub>2</sub>
I	1	38.0	17.0	—	45.0	0	
	2	38.0	17.0	6.4	38.6	1/6	45.0
	3	38.0	17.0	12.9	32.1	2/5	
	4	38.0	17.0	19.3	25.0	3/4	
II	5	33.8	21.2	—	45.0	0	
	6	33.8	21.2	6.4	38.6	1/6	45.0
	7	33.8	21.2	12.9	32.1	2/5	
III	8	45.0	20.0	—	35.0	0	
	9	45.0	20.0	5.0	30.0	1/6	
	10	45.0	20.0	10.0	25.0	2/5	35.0
	11	45.0	20.0	15.0	20.0	3/4	
IV	12	40.0	25.0	—	35.0	0	
	13	40.0	25.0	5.0	30.0	1/6	
	14	40.0	25.0	10.0	25.0	2/5	35.0
	15	40.0	25.0	15.0	20.0	3/4	
V*	16	48.0	48.0	—	4.0	0	
	17	53.0	33.0	14.0	—	∞	
	18	50.0	50.0	—	—	—	

\* Splat quenching

2. PbO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Glasses

## 2.1. Preparation of Glasses

Batch mixtures of the compositions given in oxide mol % in Table VI were prepared from reagent grade chemicals of Pb<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, Al(OH)<sub>3</sub> and SiO<sub>2</sub>. About 150 g of each of the batch mixtures except for Group V were melted in a Pt-10%Rh crucible at 1400°C for 1 hr in an electric furnace. The melts were poured on a steel plate and pressed into plates approximately 3 mm thick. The batch mixtures of group V were melted and formed into glasses by the splat quenching method<sup>5)</sup> described in the previous chapter.

## 2.2. Crystallization of Glasses

The glass specimens were heated to various temperatures at a rate of 10°C/min and allowed to cool in the ambient atmosphere from the various temperatures. The crystal phases present in the heat-treated specimens were identified by powder X-ray diffraction analyses. The results are shown in Table VII. Some unidentified crystals present in small amount in some specimens were ignored in the table. It can be seen from the table that the crystal denoted by X is formed in many glasses of this system prior to precipitation of the perovskite-type PbTiO<sub>3</sub> crystal. Martin<sup>9)</sup> already found that this X crystal is formed metastably in a system similar to the present one and is pyrochlore-type compound composed of PbO, TiO<sub>2</sub> and SiO<sub>2</sub>. He also reported that it can be formed only through crystallization of glasses but not through ordinary

Table VII. Crystals Precipitated in the Heat-treated Glasses

Group No.	Glass No.	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	Temperature (°C)							
			550	600	650	700	750	800	850	900
I	1	0	—	—	—	—	P, X	P, X	P	P
	2	1/6	—	—	—	P	P	P	P	P
	3	2/5	—	—	—	P	P	P	P	P
	4	3/4	—	—	—	P	P	P	P	P
II	5	0	—	—	—	—	P	P	P	P
	6	1/6	—	—	—	X, P	P, X	P	P	P
	7	2/5	—	—	—	—	P	P	P	P
III	8	0	—	—	X	X, P	P	P	P	P
	9	1/6	—	—	X	X, P	P	P	P	P
	10	2/5	—	—	X, P	X, P	P	P	P	P
	11	3/4	—	—	—	P	P	P	P	P
IV	12	0	—	—	—	X	P	P	P	P
	13	1/6	—	—	—	P	P	P	P	P
	14	2/5	—	—	P	P	P	P	P	P
	15	3/4	—	—	—	P	P	P	P	P
V	16	0	X	X	X, P	P	P	P	P	P
	17	∞	—	P	P	P	P	P	P	P
	18		—	P	P	P	P	P	P	P

—; Glass, X; Pyrochlore-type lead titanate,  
P; Perovskite-type PbTiO<sub>3</sub> crystal

solid state reaction of the raw materials. In his study, however, the compositions of the glasses investigated were limited to a narrow range, and there was no data on the effects of the glass compositions, especially on the effect of the Al<sub>2</sub>O<sub>3</sub> addition, on the formation of this X crystal. The present authors have found that the formation of the pyrochlore-type crystal becomes difficult as a ratio of the Al<sub>2</sub>O<sub>3</sub> to the SiO<sub>2</sub> in furthermore, in contrast to the K<sub>2</sub>O-Ta<sub>2</sub>O<sub>5</sub>-Nb<sub>2</sub>O<sub>5</sub> glass, the pyrochlore-type crystal is not formed in glass No. 18 consisting only of PbO and TiO<sub>2</sub>.

### 2. 3. Structures of Glasses

In order to find the reasons why the metastable pyrochlore-type crystals become difficult to precipitate while the stable perovskite-type PbTiO<sub>3</sub> crystals become easy to precipitate as the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio in content increases, the structures of glasses Nos. 12 and 14 were investigated by means of electronmicroscopic observation and infrared spectroscopic analyses *etc.* The amounts of PbO, TiO<sub>2</sub> and the sum of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in these glasses were same, respectively, but the ratios of Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> were different, *i.e.*, 0/35 for glass No. 12, 10/25 for glass No. 14.

#### 2. 3. 1. Glass No. 12

The fracture surfaces of glass No. 12 as-annealed and heated to 700°C to form the pyrochlore-type crystals were etched with 10 % HCl and replicated with carbon film preliminarily shadowed by platinum-palladium. Their electronmicrographs are shown in Fig. 7. It can be seen from the micrographs that glass No. 12 as-annealed

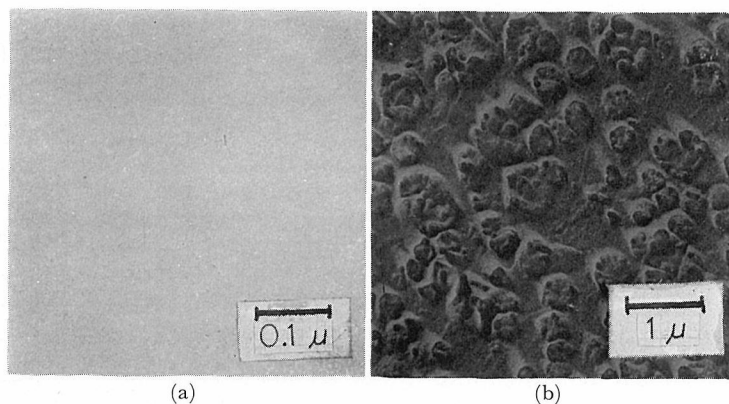


Fig. 7. Electronmicrographs of glass No. 12.  
 (a) As-annealed (b) Heat-treated to 700°C.

has a homogeneous structure and crystals identified as the pyrochlore-type one by an X-ray analysis precipitate directly from the homogeneous glass by heating. The homogeneous microstructure of the as-annealed glass No. 12 is also indicated by its infrared spectrum. Figure 8 shows its infrared spectra, obtained KBr disc method, together with those of glass No. 14 as-annealed and heated to 630°C as well as that of PbO 50, SiO<sub>2</sub> 50 mol % glass as-annealed. All the absorption bands near the wave

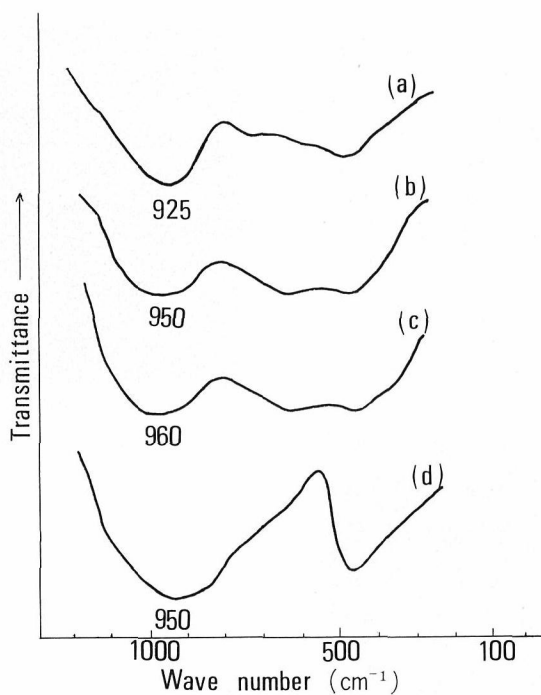


Fig. 8. Infrared spectra of glasses.  
 (a) Glass No. 12 as-annealed (b) Glass No. 14 as-annealed  
 (c) Glass No. 14 heat-treated to 630°C  
 (d) PbO 50, SiO<sub>2</sub> 50 mol % glass

number of  $950\text{ cm}^{-1}$  observed for the four specimens are assigned to Si-O stretching vibration. Among them, however, that of glass No. 12 is found at a little lower wave number in comparison with those of the other glasses. This indicates that the  $\text{SiO}_4$  tetrahedra in glass No. 12 exist in rather isolated form,<sup>13,14</sup> *i.e.*, they are uniformly distributed.

### 2.3.2. Glass No. 14

The electronmicrographs of the fracture surfaces of glass No. 14 as-annealed, heated to  $630^\circ\text{C}$  but not crystallized, and heated to  $650^\circ\text{C}$  to form the perovskite-type  $\text{PbTiO}_3$  crystals were obtained by the same method as that described above. Their photographs are shown in Fig. 9. It can be seen from the photographs that glass No. 14 as-annealed is already separated into two glassy phases, *i.e.*, glassy droplets and continuous glassy matrix, and that on heat treatment the glassy droplets first grow in size and then the perovskite-type  $\text{PbTiO}_3$  crystals precipitate in the droplets.

In view of this crystallization process, it is probable that the glassy droplets are enriched with  $\text{PbO}$  and  $\text{TiO}_2$  whereas the glassy matrix is enriched with  $\text{SiO}_2$ . The enrichment with the  $\text{SiO}_2$  is also indicated by the infrared spectra of glass No. 14; the absorption bands due to Si-O stretching vibration of glass No. 14 as-annealed and heated to  $630^\circ\text{C}$  are found at higher wave number than that for glass No. 12, as shown in Fig. 8, indicating that the  $\text{SiO}_4$  tetrahedra exist in rather condensed form<sup>13,14</sup> in the glass. On the other hand, X-ray fluorescent spectroscopic analyses of glass No. 14 as-annealed and heated to  $630^\circ\text{C}$  show that the positions of  $\text{AlK}\alpha$  peaks of both the

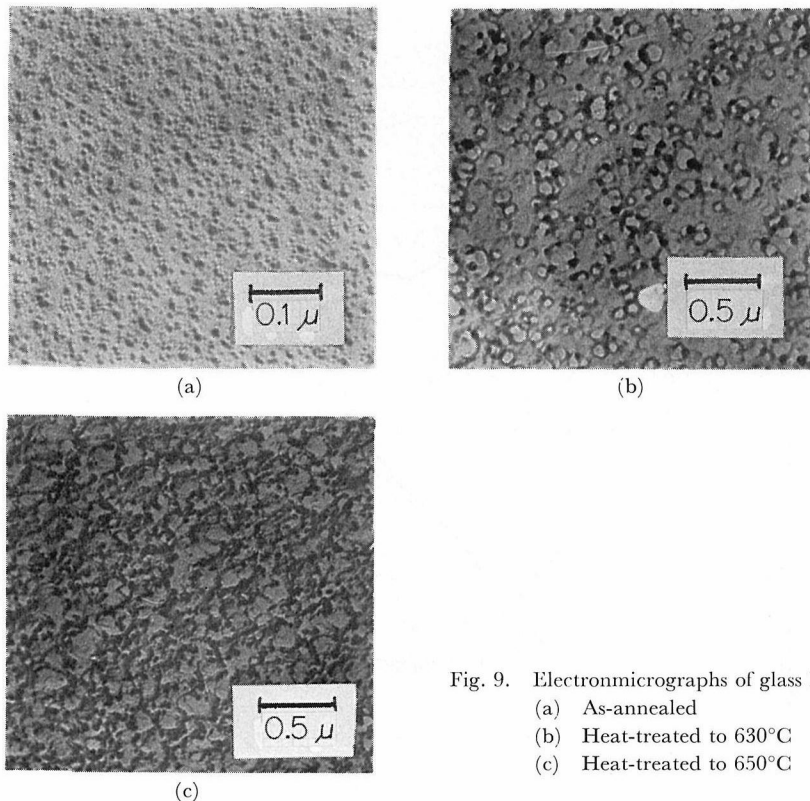


Fig. 9. Electronmicrographs of glass No. 14.

- (a) As-annealed
- (b) Heat-treated to  $630^\circ\text{C}$
- (c) Heat-treated to  $650^\circ\text{C}$

### Metastable Pyrochlore-Type Crystals in Glasses

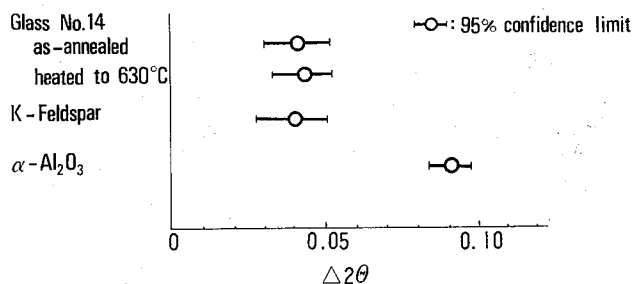


Fig. 10. Graphical representation of  $\Delta 2\theta$ , difference in diffraction angle of AlK radiation between Al metal and Al ions in various crystals and glass No. 14.

specimens are almost the same as that of K-feldspar containing  $\text{AlO}_4$  tetrahedra but not as that of  $\alpha$ - $\text{Al}_2\text{O}_3$  containing  $\text{AlO}_6$  octahedra, as shown in Fig. 10. This indicates<sup>15)</sup> that  $\text{Al}^{3+}$  ions form  $\text{AlO}_4$  tetrahedra in glass No. 14. Since typical non-bridging oxygen ions are probably not present in this type of glass, each of the  $\text{Al}^{3+}$  ions is expected to form the  $\text{AlO}_4$  tetrahedron by utilizing an extra oxygen ion already bridging the other two network-formers<sup>16)</sup> besides the three oxygen ions originally accompanied by itself. As this extra oxygen ion, the highly polarizable oxygen ion bridging  $\text{Pb}^{2+}$  or  $\text{Ti}^{4+}$  ions will be utilized, but not less polarizable oxygen ion bridging  $\text{Si}^{4+}$  ions, because the  $\text{Al}^{3+}$  ion having fairly high ionic field strength has a strong demand to be screened by the polarizable oxygen ion. Accordingly,  $\text{Al}_2\text{O}_3$  will enter into the glassy droplets enriched with  $\text{PbO}$  and  $\text{TiO}_2$ . The experimental results on crystallization process of glass No. 17 (cf. Table VII) show that the perovskite-type  $\text{PbTiO}_3$  crystals are able to precipitate from the glass with such composition.

#### 2. 4. Relation between Crystalline Species and Glass Structure

As described above, a big difference in structure between the two as-annealed glasses, Nos. 12 and 14, is that the former is homogeneous whereas the latter already consists of the two glassy phases. The fact that the metastable pyrochlore-type crystals precipitate easily from glass No. 12 but not from glass No. 14 suggests that the microstructure of the pyrochlore-type crystals is much alike to that of No. 12 than that of No. 14. In glass No. 14 even in the as-annealed state,  $\text{SiO}_2$  is already separated from the  $\text{PbO}$  and  $\text{TiO}_2$  by the glassy two-phase separation. Hence, it is natural that the pyrochlore-type crystals composed of the  $\text{SiO}_2$ ,  $\text{PbO}$  and  $\text{TiO}_2$ <sup>9)</sup> is unable to precipitate from any of the two glassy phases, but instead, the perovskite-type crystals composed only of the  $\text{PbO}$  and  $\text{TiO}_2$  do precipitate from the  $\text{PbO}$ - and  $\text{TiO}_2$ -enriched phase.

The role of the  $\text{Al}_2\text{O}_3$  in glass No. 14 is, in a brief summary, to separate the  $\text{SiO}_2$  from the  $\text{PbO}$  and  $\text{TiO}_2$  in the glass by the mechanism of glassy two-phase separation, thus enhancing the precipitation of the stable perovskite-type crystals.

### III SUMMARY

1. A metastable pyrochlore-type crystals with a composition of  $\text{K}_{1.5}(\text{Ta}_{0.65}\text{Nb}_{0.35})\text{O}_{5.75}$  precipitates in the  $\text{K}_2\text{O}-\text{Ta}_2\text{O}_5-\text{Nb}_2\text{O}_5$  glasses with addition of small amounts of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  on heating prior to precipitation of a stable perovskite-type  $\text{K}(\text{Ta}$ ,

Nb) $O_3$  crystals. The pyrochlore-type crystal is formed only through crystallization of the glasses, but not through ordinary solid state reaction of their raw materials. The X-ray diffraction pattern and infrared spectrum of the mother glasses are both more alike to those of the pyrochlore-type crystal than those of the perovskite-type crystal. The structures of the glasses are speculated to be composed of a random network of TaO<sub>6</sub> and NbO<sub>6</sub> octahedra and K<sup>+</sup> ions being situated in some holes of the network.

2. A metastable pyrochlore-type crystal composed of PbO, TiO<sub>2</sub> and SiO<sub>2</sub> precipitates also in many glasses in the system PbO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> on heating prior to precipitation of a stable perovskite-type PbTiO<sub>3</sub> crystal. The formation of the pyrochlore-type crystal becomes difficult as the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> mol ratio of the mother glass increases, and instead, the perovskite-type crystal becomes easy to precipitate in the glass. Its cause is ascribed to a change in glass structure brought about by glassy two-phase separation; the Al<sub>2</sub>O<sub>3</sub> in the glasses separate the SiO<sub>2</sub> from the PbO and TiO<sub>2</sub> by the mechanism of glassy two-phase separation, enhancing the precipitation of the stable perovskite-type crystals.

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