

## Glass Transition and Crystallization Behavior of Binary Divalent Metal Vanadate Glasses

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*Received November 12, 1993*

The glass transition and crystallization behavior of various binary divalent metal vanadate glasses have been investigated by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The values and compositional dependences of the glass transition temperature,  $T_g$ , and the crystallization temperature,  $T_x$ , of alkaline earth vanadate glasses were similar to each other.

The  $T_g$ 's of lead vanadate glasses were low compared with those of alkaline earth vanadate glasses. The results obtained were interpreted in terms of the difference in the vanadate groups contained in these glasses. It was noted that as for  $50MO \cdot 50V_2O_5$  glasses ( $M = Sr, Pb$ ), the process of crystallization depends on the kinds of the vanadate groups present in the glasses.

**KEY WORDS:** Structure of binary divalent metal vanadate glasses/ Glass transition/ Crystallization

### 1. INTRODUCTION

It is of practical and scientific importance to know the glass transition and crystallization temperatures, and the softening point of glass. These properties are directly related to the thermal stability of glasses. They also sometimes give significant information concerning the network structure of glasses.

It has been shown from  $^{51}V$  NMR study<sup>1,2)</sup> that the network structure of divalent metal vanadate glasses mainly consists of  $VO_4$ -tetrahedra, and is very similar to each other except for the local environment of divalent metals. It is also found that the local environment around vanadium atoms is influenced by the presence of the second neighboring divalent metal, as evidenced by the  $^{51}V$  NMR isotropic chemical shift. Therefore, it is interesting to know the effects of the kind of divalent metal ( $M$ ) and the  $MO$  content on the thermal properties of glasses, such as glass transition and crystallization temperatures, and the crystallization process.

In the present work, the glass-forming region of various binary divalent metal vanadate glasses has been first established, and the glass transition and the crystallization behavior have been investigated by means of differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The results obtained have been discussed in relation to the glass structure revealed by previous  $^{51}V$  NMR study.<sup>1,2)</sup>

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## 2. EXPERIMENTAL

Compositions of the glasses used in the present work are shown in Table 1. Binary divalent metal vanadate glasses of the compositions  $x\text{MO} \cdot (100-x)\text{V}_2\text{O}_5$  ( $M=\text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, x=30, 40, 45, 50, 55$ ) were prepared using reagent-grade  $\text{V}_2\text{O}_5$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{PbO}$  chemicals supplied by Nacalai Tesque. Starting materials were well mixed and then melted in a Pt-5% Au crucible in an electric furnace at temperatures of 950 to 1,100°C. The melts were poured onto a brass plate and immediately pressed by another one. For  $50\text{CaO} \cdot 50\text{V}_2\text{O}_5$ ,  $55\text{SrO} \cdot 45\text{V}_2\text{O}_5$  and  $55\text{PbO} \cdot 45\text{V}_2\text{O}_5$  the crucible containing a small quantity of melt ( $\sim 1$  g) was directly soaked into ice water to cool down more quickly. DSC curves were recorded in air for bulk samples of about 20 mg. The scans were made at 10°C/min using a Rigaku Thermoflex TG8110 calorimeter. The glass transition temperature,  $T_g$ , and crystallization temperature,  $T_x$ , were estimated from the DSC curves. The glass samples 1–2 mm thick was heat-treated in an electric furnace in air to identify the precipitated crystalline phases by XRD, using a Rigaku Geigerflex RAD-IIA diffractometer.

## 3. RESULTS

## 3.1 Glass-forming region

Table 1 shows the glass-forming region of the glasses, in which all the marks except crosses mean glasses to be formed. The triangles denote that glasses cannot be prepared by the usual vitrification method with 10 g batch but can be prepared by rapid cooling of a small quantity of melt ( $\sim 1$  g). The closed circles denote that the glasses are apt to be hydrated by moisture in ambient atmosphere. It is seen that the glass-forming regions are almost the same irrespective

Table 1. Glass forming range of binary vanadate glasses melted at 950–1,100°C.

MO /mol%	Ca	Sr	Ba	Pb
55	×	△	×	△
50	△	○	○	○
45	△	○	○	○
40	○	○	○	○
30	●	○	●	○
20	●	●	●	●

×: crystal, △: glass and crystal, ○, ●: glass, ●: These glasses are subject to the moisture attack.

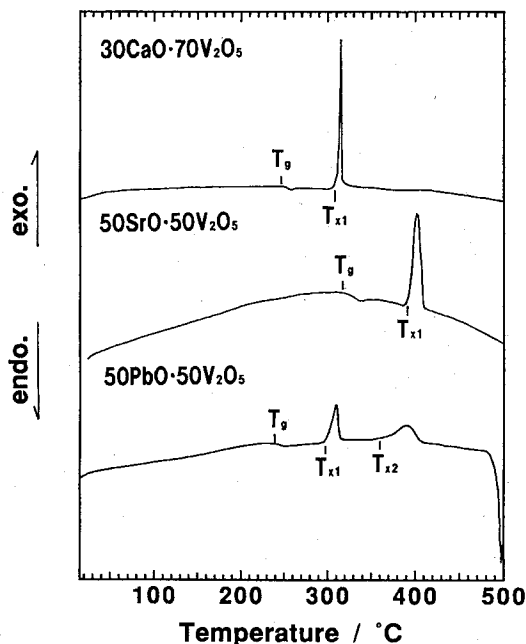


Fig. 1. DSC curves of  $30\text{CaO} \cdot 70\text{V}_2\text{O}_5$ ,  $50\text{SrO} \cdot 50\text{V}_2\text{O}_5$  and  $50\text{PbO} \cdot 50\text{V}_2\text{O}_5$  glasses.

of the kind of the divalent metal, although the sensitivity to moisture attack is slightly different from each other.

### 3.2 Glass transition and crystallization temperatures

In Fig. 1 typical DSC curves taken for 50SrO·50V<sub>2</sub>O<sub>5</sub> and 50PbO·50V<sub>2</sub>O<sub>5</sub> glasses are shown. All lead vanadate glasses and several alkaline earth vanadate glasses have more than two exothermic peaks. The glass transition temperature,  $T_g$ , and the crystallization temperature,  $T_x$ , are shown in Table 2.

Table 2. The glass transition temperature ( $T_g$ ) and the crystallization temperature ( $T_x$ ) of binary vanadate glasses.

Glass sample	$T_g$ (°C)	$T_x$ (°C)
50CaO·50V <sub>2</sub> O <sub>5</sub>	314	378
40CaO·60V <sub>2</sub> O <sub>5</sub>	276	314
30CaO·70V <sub>2</sub> O <sub>5</sub>	247	312
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55SrO·45V <sub>2</sub> O <sub>5</sub>	348	399
50SrO·50V <sub>2</sub> O <sub>5</sub>	319	396
40SrO·60V <sub>2</sub> O <sub>5</sub>	275	367
30SrO·70V <sub>2</sub> O <sub>5</sub>	251	294,391 (w)
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50BaO·50V <sub>2</sub> O <sub>5</sub>	318	382,422 (w)
40BaO·60V <sub>2</sub> O <sub>5</sub>	271	355
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55PbO·45V <sub>2</sub> O <sub>5</sub>	242	297,359 (w)
50PbO·50V <sub>2</sub> O <sub>5</sub>	240	298,360
40PbO·60V <sub>2</sub> O <sub>5</sub>	222	256,303 (w)
30PbO·70V <sub>2</sub> O <sub>5</sub>	214	237,405 (w)

w : The intensity of the exothermic peak is very weak.

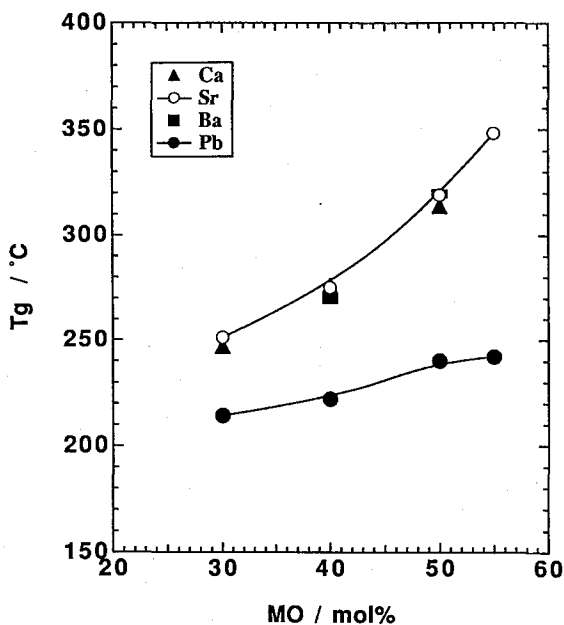


Fig. 2. Plots of the  $T_g$  vs. the MO content for divalent metal vanadate glasses.

In Fig. 2 the  $T_g$  is plotted against the MO content. It is seen that in every glass system the  $T_g$  values of glasses increase with increasing MO content.

### 3.3 Crystallization behavior

The XRD profiles of two glass systems,  $x$ SrO·(100- $x$ )V<sub>2</sub>O<sub>5</sub> ( $x=30, 40, 50$ ) and  $x$ PbO·(100- $x$ )V<sub>2</sub>O<sub>5</sub> ( $x=30, 40, 50$ ) after heat-treatment at various temperatures are shown in Fig. 3 and 4, respectively. Table 3 summarizes the crystalline phases precipitated from the glass samples heated at different temperatures in air. For 50SrO·50V<sub>2</sub>O<sub>5</sub> glass, many distinct peaks due to Sr(VO<sub>3</sub>)<sub>2</sub> crystal were observed when heat-treated at 450°C for 1 hour. When the heat-treatment time was extended up to 120 hours, the diffraction peaks due to new Sr(VO<sub>3</sub>)<sub>2</sub> crystalline phase appeared. For 40SrO·60V<sub>2</sub>O<sub>5</sub> glass, Sr(VO<sub>3</sub>)<sub>2</sub> crystals first precipitated at 350°C, followed by the precipitation of VO<sub>2</sub> crystals and unknown phases at 500°C. For 30SrO·70V<sub>2</sub>O<sub>5</sub> glass, V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O crystals first precipitated at 300°C and grew up to 350°C. At 500°C clear peaks due to VO<sub>2</sub> crystals were observed together with those due to unknown phases, but V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O crystals were no longer present.

For 50PbO·50V<sub>2</sub>O<sub>5</sub> glass, many distinct peaks due to Pb(VO<sub>3</sub>)<sub>2</sub>(III)<sup>3)</sup> and Pb<sub>2</sub>V<sub>2</sub>O<sub>7</sub>

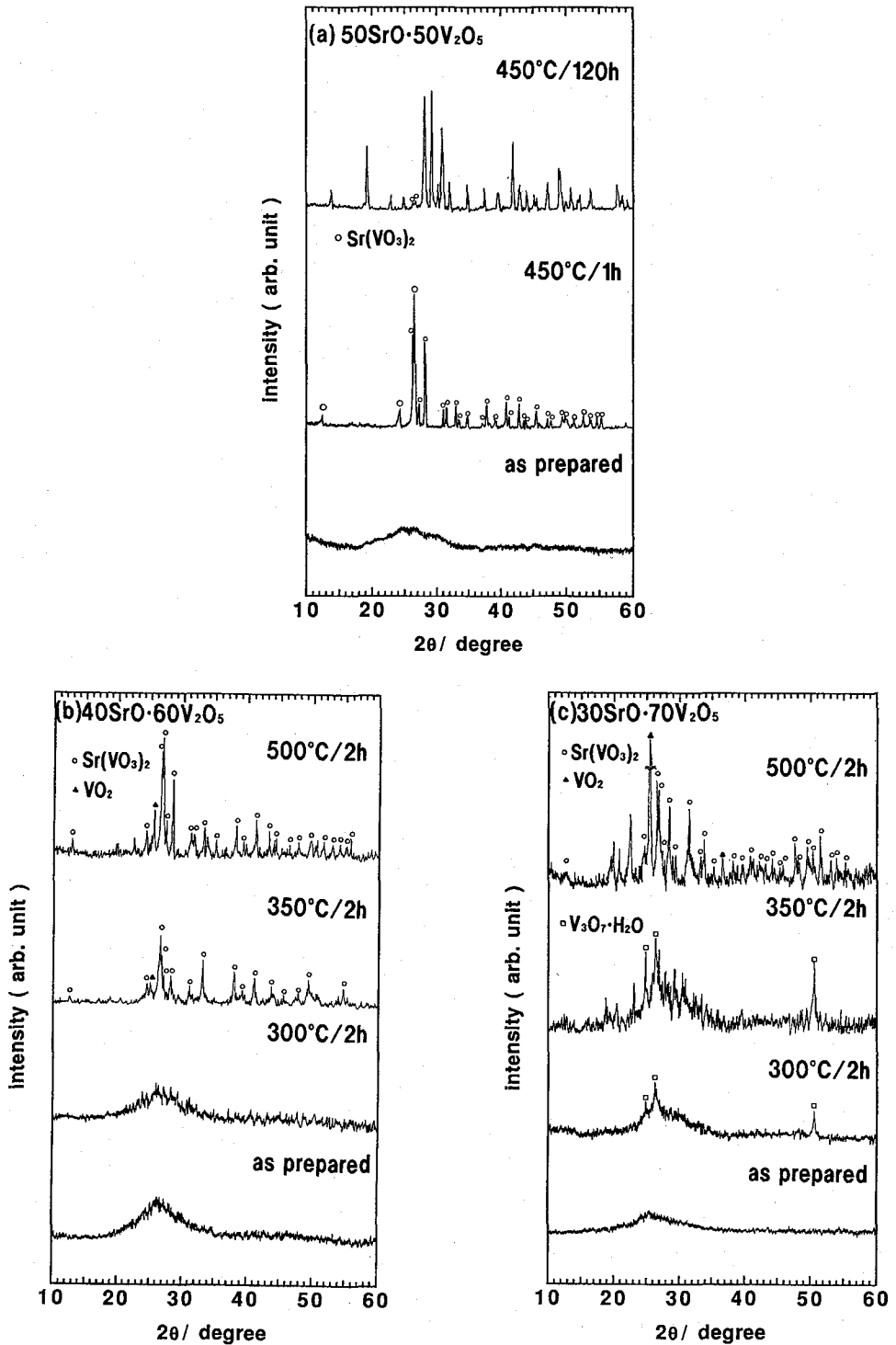


Fig. 3. X-ray diffraction patterns of (a) 50SrO·50V<sub>2</sub>O<sub>5</sub>, (b) 40SrO·60V<sub>2</sub>O<sub>5</sub> and (c) 30SrO·70V<sub>2</sub>O<sub>5</sub> glasses before and after heat-treatment.

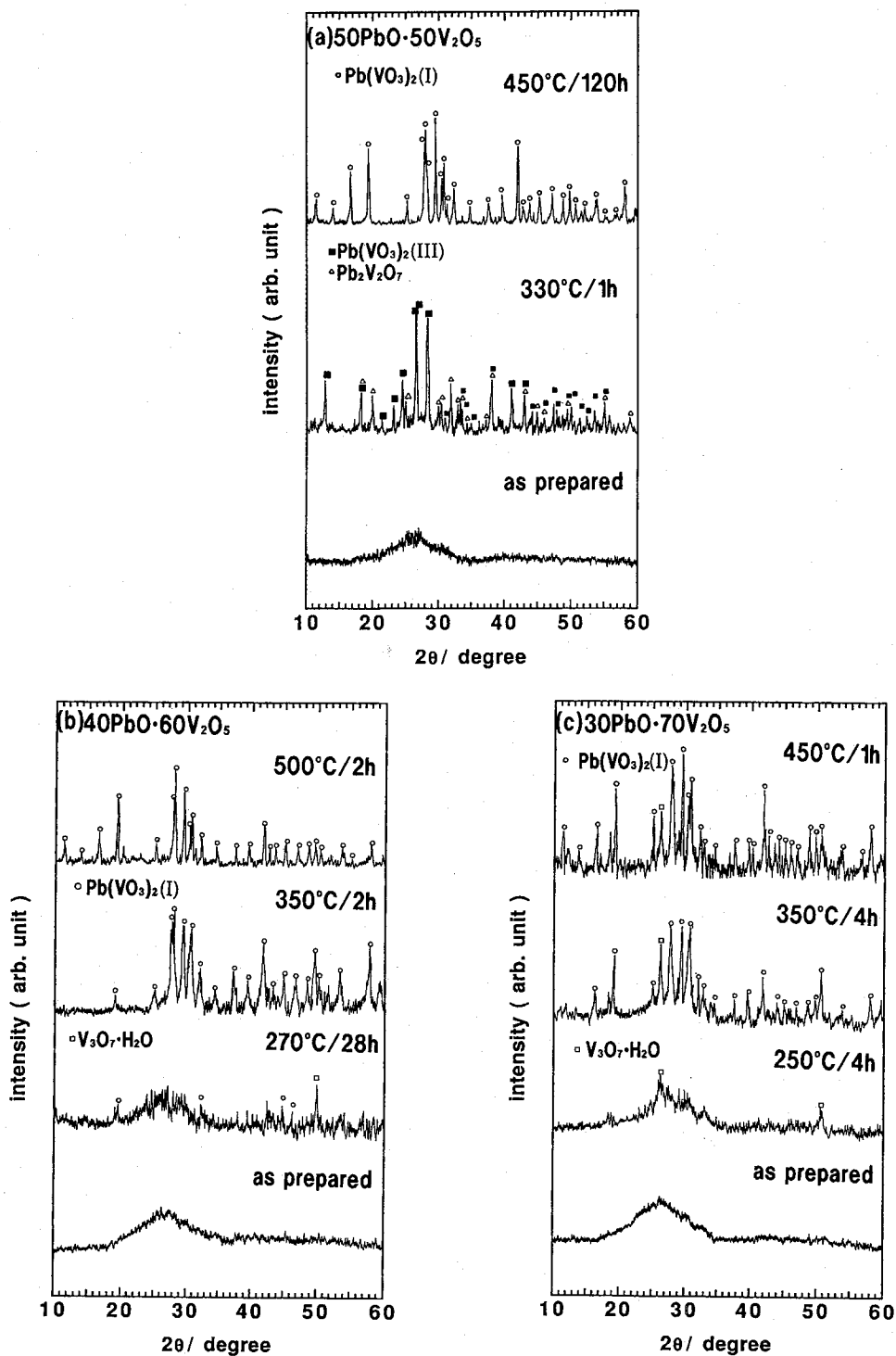


Fig. 4. X-ray diffraction patterns of (a) 50PbO·50V<sub>2</sub>O<sub>5</sub>, (b) 40PbO·60V<sub>2</sub>O<sub>5</sub> and (c) 30PbO·70V<sub>2</sub>O<sub>5</sub> glasses before and after heat-treatment.

Table 3. Characterization of annealed SrO-V<sub>2</sub>O<sub>5</sub> and PbO-V<sub>2</sub>O<sub>5</sub> glass samples.

Annealing temperature/°C	Phase		
	50SrO·50V <sub>2</sub> O <sub>5</sub>	40SrO·60V <sub>2</sub> O <sub>5</sub>	30SrO·70V <sub>2</sub> O <sub>5</sub>
as-prepared	Am <sup>a)</sup>	Am	Am
300	—	Am	Am, V <sub>3</sub> O <sub>7</sub> ·H <sub>2</sub> O
350	—	Sr(VO <sub>3</sub> ) <sub>2</sub>	Sr(VO <sub>3</sub> ) <sub>2</sub> , VO <sub>2</sub> , V <sub>3</sub> O <sub>7</sub> ·H <sub>2</sub> O
450	Sr(VO <sub>3</sub> ) <sub>2</sub>	—	—
500	—	Sr(VO <sub>3</sub> ) <sub>2</sub> , VO <sub>2</sub> , Un <sup>b)</sup>	Sr(VO <sub>3</sub> ) <sub>2</sub> , VO <sub>2</sub> , Un
	50PbO·50V <sub>2</sub> O <sub>5</sub>	40PbO·60V <sub>2</sub> O <sub>5</sub>	30PbO·70V <sub>2</sub> O <sub>5</sub>
as-prepared	Am	Am	Am
250	—	—	Am, Pb(VO <sub>3</sub> ) <sub>2</sub> (I), V <sub>3</sub> O <sub>7</sub> ·H <sub>2</sub> O
270	—	Am, Pb(VO <sub>3</sub> ) <sub>2</sub> (I), V <sub>3</sub> O <sub>7</sub> ·H <sub>2</sub> O	—
330	Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub> , Pb(VO <sub>3</sub> ) <sub>2</sub> (III)	—	—
350	—	Pb(VO <sub>3</sub> ) <sub>2</sub> (I), V <sub>3</sub> O <sub>7</sub> ·H <sub>2</sub> O	Pb(VO <sub>3</sub> ) <sub>2</sub> (I), V <sub>3</sub> O <sub>7</sub> ·H <sub>2</sub> O, Un
450	Pb(VO <sub>3</sub> ) <sub>2</sub> (I)	—	Pb(VO <sub>3</sub> ) <sub>2</sub> (I), V <sub>3</sub> O <sub>7</sub> ·H <sub>2</sub> O, Un
500	—	Pb(VO <sub>3</sub> ) <sub>2</sub> (I), Un	—

a) Am: amorphous phase, b) Un: unknown crystalline phase.

crystals were observed when heat-treated at 330°C between T<sub>x1</sub> and T<sub>x2</sub>. At 450°C the diffraction peaks from Pb<sub>2</sub>V<sub>2</sub>O<sub>7</sub> crystals were no longer observed and instead those from Pb(VO<sub>3</sub>)<sub>2</sub>(I)<sup>4)</sup> crystals were observed. For 40PbO·60V<sub>2</sub>O<sub>5</sub> glass, the diffraction peaks due to V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O and Pb(VO<sub>3</sub>)<sub>2</sub>(I) crystals were observed at 270°C. The Pb(VO<sub>3</sub>)<sub>2</sub> crystals grew on heating to 500°C, while the V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O crystals disappeared. For 30PbO·70V<sub>2</sub>O<sub>5</sub> glass, the diffraction peaks due to V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O crystal were observed together with the small peaks due to Pb(VO<sub>3</sub>)<sub>2</sub>(I) crystal at 250°C. When the heat-treatment temperature was raised above 350°C, Pb(VO<sub>3</sub>)<sub>2</sub>(I) crystals became a major crystalline phase.

#### 4. DISCUSSION

##### 4.1 Glass transition temperature

The T<sub>g</sub> values of alkaline earth vanadate glasses are found to be almost the same irrespective of the kind of the alkaline earth cation. This well corresponds to our previous finding that the structure of alkaline earth vanadate glasses are very similar to each other irrespective of the kind of the alkaline earth cation.<sup>1,2)</sup>

Another interesting finding is that the T<sub>g</sub> increases with increasing content of modifier, MO. Recently, we have determined the compositional changes of different vanadate groups present in alkaline earth metal and lead vanadate glasses based on the <sup>51</sup>V NMR measurements.<sup>2)</sup> Figure 5 shows the results for (a) SrO-V<sub>2</sub>O<sub>5</sub> and (b) PbO-V<sub>2</sub>O<sub>5</sub> glasses. The fractions of V<sub>2</sub>O<sub>7</sub><sup>4-</sup> groups and (VO<sub>3</sub>)<sub>n</sub>-single chains increase with increasing MO while those of branched-VO<sub>4</sub> tetrahedra and (V<sub>2</sub>O<sub>8</sub>)<sub>n</sub>-zigzag chains decrease. It therefore follows that the coexistence of V<sub>2</sub>O<sub>7</sub><sup>4-</sup> groups and (VO<sub>3</sub>)<sub>n</sub>-single chains increase the stability of vanadate glasses probably due to the increased randomness. Contrarily, the presence of (V<sub>2</sub>O<sub>8</sub>)<sub>n</sub>-zigzag chains or three dimensional corner-sharing branched VO<sub>4</sub>-tetrahedral groups lowers T<sub>g</sub>. This result may be

explained as follows. Tsuzuki et al.<sup>5)</sup> have shown that amorphous  $V_2O_5$  film crystallizes at very low temperature of  $210^\circ\text{C}$  without a glass transition. This indicates that the branched- $\text{VO}_4$  groups transform into  $(V_2O_8)_n$ -zigzag chains at relatively low temperatures, because the thermodynamic stability of the former is low at low temperatures.

It is noted that the  $T_g$ 's of lead vanadate glasses are very low compared with those of alkaline earth vanadate glasses. This is possibly because the fraction of thermodynamically unstable  $(V_2O_8)_n$ -zigzag chains is much smaller in  $\text{SrO-V}_2\text{O}_5$  glasses than in  $\text{PbO-V}_2\text{O}_5$  glasses.

#### 4.2 Crystallization behavior of $\text{SrO-V}_2\text{O}_5$ and $\text{PbO-V}_2\text{O}_5$ glasses

In  $V_2O_5$ -rich glass ( $x=30$ ) the crystalline phases precipitated from the glasses were mainly  $M(\text{VO}_3)_2$  and  $\text{VO}_2$ , although several unknown phases were precipitated. The diffraction peaks due to  $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$  crystal were observed at lower temperature of  $270\text{--}300^\circ\text{C}$ , indicating that the  $V_2O_5$ -rich phases are present in the glass sample. The formation of hydrated phase, such as  $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$  are explained as follows. The first precipitating phase,  $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$ , is formed by the reaction of the  $V_2O_5$ -rich phase with a small amount of  $\text{H}_2\text{O}$  present in the glass as well as

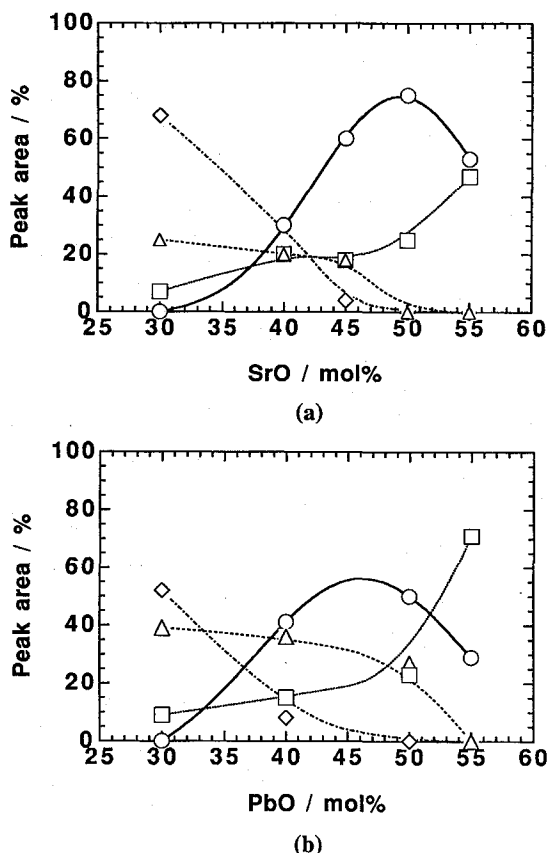


Fig. 5. Plots of the percentage of the vanadate groups in several vanadate glasses vs. the MO content ( $M=\text{Sr, Pb}$ ). (a)  $\text{SrO-V}_2\text{O}_5$ , (b)  $\text{PbO-V}_2\text{O}_5$ .  $\square$ :  $\text{V}_2\text{O}_7^{4-}$ ,  $\circ$ :  $(\text{VO}_3)_n$ -single chain,  $\diamond$ : branched- $\text{VO}_4$  group,  $\triangle$ :  $(\text{V}_2\text{O}_8)_n$ -zigzag chain.

moisture in ambient atmosphere. As described in previous study,<sup>1)</sup> the  $V_3O_7 \cdot H_2O$  phase is readily formed by the reaction between  $V_2O_5$ -rich glass and  $H_2O$  from ambient moisture even at room temperature.

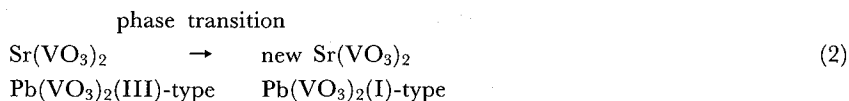
In 40MO-60 $V_2O_5$  glasses the crystalline phases precipitated from the glasses were mainly  $M(VO_3)_2$  and  $VO_2$ . It is noted that in 40SrO-60 $V_2O_5$  glass the diffraction peaks due to  $VO_2$  crystal are very intense. In 40PbO-60 $V_2O_5$  glass the diffraction peaks due to  $V_3O_7 \cdot H_2O$  crystal were observed at 270°C, indicating that the  $V_2O_5$ -rich phases are present in the glass sample. On the other hand, the diffraction peaks due to  $V_3O_7 \cdot H_2O$  crystal were not observed in 40SrO-60 $V_2O_5$  glass, indicating that the fraction of the  $V_2O_5$ -rich phases of 40SrO-60 $V_2O_5$  glass is small compared with that of 40PbO-60 $V_2O_5$ . This is in good agreement with the result of NMR study in Fig.5.

In 50SrO-50 $V_2O_5$  glass,  $Sr(VO_3)_2$  crystals were first precipitated on heating at 450°C for 1 hour and then transformed into new  $Sr(VO_3)_2$  crystal on further heating at 450°C for 120 hours. This indicates that crystallization proceeds as follows:

at 450°C for 1 hour



and for 120 hours



Therefore, it is found that  $Sr(VO_3)_2$  crystal first precipitated out of metavanadate glasses is a metastable and high temperature phase, while new  $Sr(VO_3)_2$  crystal is a stable and low temperature phase. The metastable  $Sr(VO_3)_2$  crystal consists of  $(VO_3)_n$ -single chains and its structure is very similar to that of  $Ba(VO_3)_2$  and  $Pb(VO_3)_2(\text{III})$  crystals. However, at temperatures just below the crystallization temperature metastable  $Sr(VO_3)_2$  crystal is transformed into stable new  $Sr(VO_3)_2$  crystal. The structure of new  $Sr(VO_3)_2$  crystal is assumed to be identical to that of  $Pb(VO_3)_2(\text{I})$  crystal consisting of  $(V_2O_8)_n$ -zigzag chains, because their X-ray diffraction patterns are very similar to each other, and the profiles and peak positions of their infrared spectra, which are not shown here, are also very similar to each other. The structural analysis of this crystal will be made elsewhere.

In 50PbO-50 $V_2O_5$  glass, first  $Pb(VO_3)_2(\text{III})$  and  $Pb_2V_2O_7$  crystals are precipitated by heating at 330°C and then transformed into single phase,  $Pb(VO_3)_2(\text{I})$  crystal on heating to 450°C. Taking into account the glass composition, this indicates that the crystallization proceeds as follows:

at 310°C

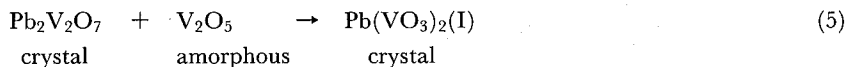


and at 390°C

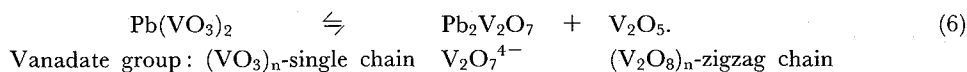




## Glass Transition and Crystallization of Vanadate Glasses



As seen from Fig. 5(b), 50PbO-50V<sub>2</sub>O<sub>5</sub> glass consists of many kinds of vanadate groups, such as V<sub>2</sub>O<sub>7</sub><sup>4-</sup>, (VO<sub>3</sub>)<sub>n</sub>-single chains and (V<sub>2</sub>O<sub>8</sub>)<sub>n</sub>-zigzag chains. This can be expressed by the following equilibrium reactions:



In 50PbO-50V<sub>2</sub>O<sub>5</sub> glass, the equilibrium is shifted to the left to a considerable extent as known from Fig. 5(b). This may be related to the fact that Pb(VO<sub>3</sub>)<sub>2</sub>(I) crystal melts incongruently at 482°C[6], that is, Pb(VO<sub>3</sub>)<sub>2</sub> is not thermodynamically stable at high temperatures. It can be therefore concluded that the Pb<sub>2</sub>V<sub>2</sub>O<sub>7</sub> crystal and metastable Pb(VO<sub>3</sub>)<sub>2</sub>(III) crystal are precipitated directly from the corresponding vanadate groups present in the glass. The low temperature stable phase, Pb(VO<sub>3</sub>)<sub>2</sub>(I), is mainly formed as a result of the phase transition of Pb(VO<sub>3</sub>)<sub>2</sub>(III) crystal. Since in 50SrO-50V<sub>2</sub>O<sub>5</sub> glass the glass network consists of only (VO<sub>3</sub>)<sub>n</sub>-single chains, a single phase of metastable Sr(VO<sub>3</sub>)<sub>2</sub> crystal is precipitated from the beginning.

### 5. CONCLUSION

The glass-forming region and glass transition and crystallization temperatures for binary divalent metal vanadate glasses have been discussed. The following conclusions were drawn.

(1) The T<sub>g</sub> and the T<sub>x</sub> of alkaline earth metavanadate glasses are almost the same irrespective of the kind of the alkaline earth metal.

(2) The T<sub>g</sub> values of lead vanadate glasses are small compared with those of alkaline earth vanadate glasses.

(3) The V<sub>2</sub>O<sub>5</sub>-rich phase readily crystallizes as the hydrate, V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O, from vanadate glasses by the reaction with a small amount of H<sub>2</sub>O in the glass and in ambient atmosphere.

(4) As for 50MO-50V<sub>2</sub>O<sub>5</sub> glasses (M=Sr, Pb), the process of crystallization depends on the vanadate groups present in these glasses.

### 6. ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 02403016).

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