Thermal Stability and Microstructure of Bi-Sr-Ca-Cu-O Glasses

Ryuji SATO*, Takayuki KOMATSU* and Kazumasa MATSUITA*

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This paper reviews glass formation, thermal stability, some physical properties and structure of glasses based on the Bi-Sr-Ca-Cu-O (Bi-based) system. Especially, the effect of copper valence state on the thermal stability and microstructure of the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass has been clarified. The Cu$^+$/ΣCu ratio in Bi-based glasses is largely changed from 0.01 to 0.98 by adding glucose during melting or by annealing of powdered glasses in oxygen at near the glass transition temperature. The thermal stability of the glasses with high Cu$^+$ contents is extremely high compared with that of the glasses with low Cu$^+$ contents. The viscosity and density of glasses decrease steeply with increasing Cu$^+$/ΣCu ratio, implying that the structure of Bi-based glasses becomes loose with increasing Cu$^+$ content. The phase separation is observed in the glasses with high Cu$^+$ contents, but no phase separation occurs in the glasses with high Cu$^{2+}$ contents. The correlation between the phase separation and crystallization behaviors has been discussed.

KEY WORDS: Bi-Sr-Ca-Cu-O Glasses/ Thermal Stability/ Superconducting Glass-Ceramics/ Phase separation/ Cu$^+$/ΣCu

1. INTRODUCTION

Many compositions in the Bi-Sr-Ca-Cu-O system (Bi-based system) are glass-forming through the quenching of melts, and glasses are converted into high-Tc superconductors after proper annealing.\(^1-4\) This preparation technique, i.e., melt-quenching method or glass-ceramic route, is very attractive for the fabrication of superconductors with desired forms such as fibers. Many studies on superconducting properties of Bi-based glass-ceramics have been made so far. In order to fabricate superconducting glass-ceramics with more excellent properties, an in-depth understanding of the crystallization mechanism of Bi-based glasses will be necessary. It should be pointed out that a large amount (70~80\%) of copper ions in the Bi-based glasses prepared by a conventional melt-quenching method exists as monovalent Cu$^+$ ions.\(^5\) On the other hand, it is well known that the average copper valences in the Bi-based superconducting phases are over 2.0. It is, therefore, very important to clarify the effect of copper valence state in Bi-based glasses on crystallization behaviors.\(^6\)

Since Bi-based glasses are newcomers in the field of glass science and technology, the structure and properties of glasses themselves are also of particular interest. Recently, the effect of copper valence state on thermal stability and some properties such as viscosity and density in

*佐藤隆士, 小松高行, 松下和正: Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-21, Japan.
Bi-based glasses has been clarified. The data on the structure of Bi-based glasses seem to be insufficient at this moment. But, very recently, phase separation behaviors in Bi-based glasses have been reported. In this paper, we review glass formation, thermal stability, some physical properties and structure of Bi-based glasses. Especially, we focus our attention on the effects of copper valence state on the thermal stability and microstructure of the Bi2Sr2CaCu2Ox glass, which also will shed some important light on the fabrication of high-performance high-Tc superconducting glass-ceramics.

2. GLASS FORMATION REGION

The glass-forming region in the Bi-Sr-Ca-Cu-O system has been reported by several groups. The glass forming-region in the xBiO3/2+ySrO-zCaO-2CuO system (x=0.5−3, y=0.5−2 and z=0.3−2) is shown in Fig. 1. It can be seen that the BiO3/2-SrO-CaO-CuO system has a strong tendency to form a glass and that the addition of Bi2O3 is particularly effective in facilitating glass formation. The ratio of SrO and CaO is also important. Miyaji et al. examined the glass forming regions of Bi2O3-CaO-CuO and Bi2O3-SrO-CuO by using a conventional melt-quenching method. They reported that glasses are more easily formed with lower Bi2O3 compositions in the Bi2O3-SrO-CaO-CuO system than in the Bi2O3-CaO-CuO system and that the structure of SrO containing glasses is considerably different from that of CaO containing glasses. Tohge et al. also examined the glass forming region in the pseudoternary system BiO3/2-(SrO,Ca)1/2-CuO, Ca/Sr=1, by using a twin-roller rapid quenching method. They reported that the amorphous samples were obtained in a relatively wide region. Since monovalent copper ions coexist with divalent ones in the Bi-based glasses, the Cu+/2Cu ratio should be specially considered for the investigation of the glass forming region. However, there

![Fig. 1. The glass-forming region of the xBiO3/2+ySrO-zCaO-2CuO system (x=0.5−3.0, y=0.5−2.0, z=0.3−2.0). The coordinates in the figure for the glass-forming region are the mol percentages of each oxide among BiO3/2, SrO and CaO.](image-url)
has been no report on the effect of Cu⁺/ΣCu ratio on the glass forming region in the Bi-based glasses.

3. THERMAL PROPERTY IN Bi₂Sr₂CaCu₂O₅ GLASS

The glass formation of the sample with the composition of the low-Tc phase Bi₂Sr₂CaCu₂O₅ has been reported by several research groups. For example, Yoshimura et al. prepared 20 μm thick Bi₂Sr₂CaCu₂O₅ amorphous films by using twin-roller rapid quenching. Zheng and Mackenzie prepared 1 mm thick Bi₄Sr₃Ca₃Cu₄Oₓ glasses by using a conventional melt-quenching method. A differential thermal analysis (DTA) curve for the Bi₂Sr₂CaCu₂O₅ glass prepared by using a conventional melt-quenching method is shown in Fig. 2. This glass was melted using a Pt crucible. The values of glass transition, Tg, and crystallization temperatures, Tx, are 435°C and 486°C respectively.

![DTA curve for the melt-quenched sample of Bi₂Sr₂CaCu₂O₅](image)

Heating rate was 10 K/min.

Recently, Sato et al. succeeded in preparing the Bi₂Sr₂CaCu₂O₅ glasses with various Cu⁺/ΣCu ratios ranging from about 0.8 to 0.98 by adding glucose during glass melting and examined the effect of Cu⁺/ΣCu ratio on the thermal stability. In their experiment, the glasses were prepared as follows; commercial powders of high-purity Bi₂O₃, SrCO₃, CaCO₃ and CuO were mixed and calcined at 820°C for 10 h in air. Glucose was added to calcined powders and mixed in methanol. The glucose addition was 0–2.5 wt% of batch weight. The mixture was melted in an alumina crucible at 1,300°C for 10 min in an electric furnace. The melts were poured onto an iron plate and pressed quickly to a thickness of 1.5 mm. Figure 3 shows the fractions of Cu⁺ in the glass analyzed by a cerate titration method. The estimated values from thermogravimetry (TG) curves are also shown. It can be seen that the Cu⁺/ΣCu ratio increases with increasing glucose content. An equilibrium temperature of 2CuO and Cu₂O is about 1,025°C in air, meaning that the Cu⁺/ΣCu ratio in the Bi-based glasses is affected by melting and quenching conditions. That is, many Cu ions in the melt of Bi₂Sr₂CaCu₂O₅ composition at 1,300°C would exist as Cu⁺ ions. Zheng et al. prepared the Bi₄Sr₃Ca₃Cu₄Oₓ.
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The DTA curves in air for the bulk Bi$_2$Sr$_2$CaCu$_2$O$_x$ glasses with different Cu$^+$/ΣCu ratios are shown in Fig. 4(a) and (b). It is clear that the patterns are strongly dependent on the Cu$^+$/ΣCu ratio. It is noted that the onset temperature of the first crystallization peak shifts to higher temperature and the peak intensity decreases rapidly with increasing Cu$^+$/ΣCu ratio. The values of glass transition, T$_g$, crystallization onset, T$_{xon}$, and peak, T$_{xp}$, temperatures are shown in Fig. 5 as a function of Cu$^+$/ΣCu ratio. The value of T$_g$ tends to decrease slightly with increasing Cu$^+$/ΣCu ratio. On the other hand, the values of T$_{xon}$ and T$_{xp}$ for the glasses with up to Cu$^+$/ΣCu=0.85 are almost the same, but those for the glass with Cu$^+$/ΣCu=0.98 are high compared with other glasses. In the glass with Cu$^+$/ΣCu=0.98, the difference between T$_{xon}$ and T$_g$, $\Delta T = T_{xon} - T_g$, was 70°C. It indicates that the thermal stability of Bi$_2$Sr$_2$CaCu$_2$O$_x$ glasses with different Cu$^+$/ΣCu ratios (0.66–0.85) by changing melting temperature. It is clear from Fig. 3 that the addition of glucose being a reducing agent accelerates the transformation of Cu$^{2+}$ ions into Cu$^+$ ions in the melt of Bi-Sr-Ca-Cu-O system and is effective in controlling the copper valence in Bi-based glasses.
glass is improved by increasing Cu$^+$/ΣCu ratio. Indeed, in the sample with Cu$^+$/ΣCu = 0.98, a perfect glass is obtained without any press (rapid quenching) but just pumping up (slow quenching) into silica glass tubes with 3 mm diameter.

Figure 6 shows the DTA curves for the powdered glasses with different Cu$^+$/ΣCu ratios. The value of Tg for the powdered glass is higher than that for the bulk glass with the same Cu$^+$/ΣCu ratio, and the value of Txon is lower. The first exothermic peak due to the crystallization for powdered glasses is very broad. Figure 7 shows the TG curves for the bulk and powdered samples of the glass with Cu$^+$/ΣCu = 0.98, together with the DTA curves. In the powdered sample, an increase in the weight occurs rapidly at above 300°C and a gradual decrease is observed above 650°C. In the bulk sample, an increase in the weight is very small below 650°C and a rapid increase occurs at 700°C. The maximum increase is observed at around 850°C. The increase in the weight for the powdered sample occurs rapidly at temperature below Tx, indicating that in the powdered sample with large surface area the oxidation of Cu$^+$ to Cu$^{2+}$ is accelerated. This oxidation would be a cause of the decrease in crystallization temperature for the powdered glasses. These results clearly indicate that the thermal stability of the Bi-based glasses in which Cu ions exist almost completely as Cu$^+$ ions is much higher than that of glasses in which a large amount of Cu$^{2+}$ ions are included. Since the initial crystalline phase appearing during heating of the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass is the Bi$_2$Sr$_2$CuO$_x$ phase in which Cu ions exist almost completely as Cu$^{2+}$ ions, the presence of Cu$^+$ ions would decrease the rate of the crystallization of glasses.

Although the role of Cu$^+$ ion in the glass structure is not clear, it is expected that Cu$^+$ ions play an important role in the glass structure and that the structure of Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass varies with copper valence state in glass. Nakagawa et al. investigated a local structure around Cu atoms in the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass by the EXAFS analysis and proposed that some fraction of Cu
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It is worth to remind the effect of copper valence state on the structure and properties of copper aluminosilicate glasses. It is well recognized that Cu$^{+}$ ions play an important role in the unique properties of copper aluminosilicate glasses, i.e., low thermal expansions and low viscosities. Makishima et al. proposed that copper aluminosilicate glasses have low values of packing densities of atoms, and the low thermal expansion may correlate with an open structure. Kamiya et al. investigated a local structure around Cu atoms in copper aluminosilicate glasses by the EXAFS analysis and reported that the Cu$^{+}$ ion in copper aluminosilicate glasses is coordinated to two oxygens through covalent Cu$^{+}$-O bonds. They suggested that the Cu$^{+}$-O bond in copper aluminosilicate glasses is covalent as in Cu$_2$O and CuAlO$_2$ crystals, since Cu$^{+}$-O distance in the copper aluminosilicate glasses is 0.190 nm, which is relatively small compared to the sum of the Pauling's ionic radii of Cu$^{+}$, 0.096 nm, and O$^{2-}$, 0.140 nm. Nakagawa et al. reported that the average Cu-O distance in the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass is 0.189 nm. These studies support the suggestion that the structure of Bi-based glass varies significantly with the Cu$^{+}$/ΣCu ratio and the Cu$^{+}$-O bond in the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass is also covalent. The increase in the covalency of Cu$^{+}$-O bonds would be a significant reason for the improvement of thermal stability.

Fig. 7. TG and DTA curves for the bulk and powders of the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glasses with Cu$^{+}$/ΣCu=0.98.
for the Bi-based glasses with high Cu⁺/ΣCu ratios.

4. PHYSICAL PROPERTY OF Bi₂Sr₂CaCu₂O₉ GLASS

The effect of Cu⁺/ΣCu ratio on the density of the Bi₂Sr₂CaCu₂O₉ glass is shown in Fig. 8 as a function of Cu⁺/ΣCu ratio. The density decreases almost linearly with increasing Cu⁺ content. The large decreases imply that the structure of glasses changes with the Cu⁺ content. If one assumes that the structures of the glasses such as Bi₂Sr₂CaCu⁺₁.₅Cu²⁺₀.₄O₇.₂ and Bi₂Sr₂CaCu⁺₁.₉Cu²⁺₀.₁O₇.₀₅ are the same and the difference in the density arises only from oxygen content, the density change with the Cu⁺/ΣCu ratio is expected as shown by a dotted line in Fig. 8. It is known that the oxygen coordination numbers of Cu ions in Cu₂O and CuO crystals are two and four, respectively and the densities of Cu₂O and CuO crystals are 6.04 and 6.31 g/cm³, respectively. If the oxygen coordination numbers of Cu ions in Bi-based glasses are similar to those in the crystals, i.e. two for Cu⁺ ions and four or five for Cu²⁺ ions, a large decrease in the density would be expected, as is the case shown in Fig. 8.

![Fig. 8. Values of the density for the Bi₂Sr₂CaCu₂O₉ glasses with different Cu⁺/ΣCu ratios.](image)

![Fig. 9. Temperature dependence of viscosity for the Bi₂Sr₂CaCu₂O₉ glasses with different Cu⁺/ΣCu ratios: ○, Cu⁺/ΣCu=0.82; ●, Cu⁺/ΣCu=0.88; □, Cu⁺/ΣCu=0.98.](image)
The viscous flow behaviors were also reported. The Arrhenius plots of the viscosity of the glasses with different Cu+/ΣCu ratios are shown in Fig. 9. It is seen that the viscosity in the temperature range of 431 and 467°C obeys the Arrhenius law. The isoviscous temperatures of these glasses decrease with increasing Cu⁺ content. The activation energies, $E_a$, for viscous flow estimated from the data in Figs. 9 are shown in Fig. 10 as a function of Cu⁺/ΣCu ratio. The value of $E_a$ decreases rapidly with increasing Cu⁺ content from 987 to 637 kJ/mol. These values for the Bi₂Sr₂CaCu₂Oₓ glasses are similar to the values of 800–980 kJ/mol for BiₓSrCaCu₂Oₓ glasses (x=1.5 and 2.7) reported by Tatsumisago et al.. The results shown in Figs. 9 and 10 indicate that the viscosity of Bi-based glasses is very sensitive to the copper valence state. In other words, the decrease of $E_a$ for the viscous flow indicates that the size of flow unit decreases with increasing Cu⁺ content or the amount of free volume increases. It is clear that the dependence of the copper valence state on the viscosity shown in Figs. 9 and 10 is very similar to that on the density shown in Fig. 8, suggesting again that the structure of Bi-based glasses becomes loose with increasing Cu⁺ content.

The thermal expansion coefficients for the Bi₂Sr₂CaCu₂Oₓ glasses are shown in Fig. 11 as a function of Cu⁺/ΣCu ratio. The values obtained are about $120 \times 10^{-7}$ K⁻¹ and insensitive to the Cu⁺ content. It is well known that the thermal expansion coefficient of ordinary oxide glasses containing copper ions such as Cu₂O-Al₂O₃-4SiO₂ depends strongly on the Cu⁺/ΣCu ratio. For Bi-based glasses with low Cu⁺ contents such as Cu⁺/ΣCu≤0.5, if possible, some change in the thermal expansion coefficient might be observed.

5. OXIDATION OF Cu⁺ IONS IN Bi₂Sr₂CaCu₂Oₓ GLASS

The preparation and investigation of the Bi-based glasses with high Cu⁺²⁺ contents are very important. However, the Bi-based glasses with high Cu⁺²⁺ contents can not be prepared by using a conventional melt-quenching method. Very recently, Sato et al. succeeded in
preparing the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass powders with low Cu$^+$ contents, i.e. Cu$^+$/ΣCu = 0.01–0.8, by oxidizing of Cu$^+$ to Cu$^{2+}$ through the annealing in oxygen at near the glass transition temperature without causing any crystallization. In their experiment, the bulk glass was first ground, and then the glass powders with diameters less than 37 μm were oxidized.

Figure 12 shows X-ray powder diffraction patterns at room temperature for the samples annealed at 390, 430, and 450°C for 72 h in oxygen. In the as-quenched glass, a large halo is observed at around 2θ = 30° and a small one is also observed at around 2θ = 20°. The value of the half width of the large halo is about 5.5°. In the powdered samples annealed at 390°C and 430°C, a large halo is also observed and any sharp diffraction peak cannot be seen. The values of the half width of these large halos are almost the same as that of as-quenched glass. An annealing at 450°C leads to the appearance of the peaks due to the precipitation of a crystalline phase. This phase is assigned to the Bi$_2$Sr$_2$CuO$_y$ phase. These results indicate that the glassy state is kept in the powdered glasses annealed at 430°C for 72 h in oxygen but a crystallization occurs at annealing of about 450°C.

The values of the Cu$^+$/ΣCu ratio analyzed by a cerate titration for the powdered glasses annealed at 430°C are shown in Fig. 13 as a function of annealing time. A decrease in the Cu$^+$/ΣCu ratio occurs rapidly within a short annealing time below 4 h. This result indicates that the Cu$^+$ ions in the powdered glasses are easily oxidized through the annealing at 430°C. 

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without causing any crystallization, i.e. with keeping the amorphous state.

The DTA curves in oxygen for the powdered glasses annealed at 430°C for various periods in oxygen are shown Fig. 14. The exothermic peaks due to the crystallization are observed in all glasses. In the as-quenched glass, two exothermic peaks are observed at around 460 and 500°C. In the annealed samples, the intensity of the exothermic peak at around 460°C decreases with increasing annealing time and such a peak is not observed in the glass annealed for 180 min. On the other hand, the intensity of the exothermic peak at around 500°C increases with increasing annealing time. Figure 15 shows the expanded DTA curves at near the glass transition for the
powdered glasses annealed at 430°C. The endothermic peak due to the glass transition is clearly observed in all glasses. This result also indicates that the glassy state is kept in the powdered glasses annealed at 430°C in oxygen. The values of $T_g$ and $T_x$ for the powdered glasses obtained by annealing in oxygen are given in Fig. 16 as a function of $\text{Cu}^+/\Sigma\text{Cu}$ ratio. It is seen

Fig. 15. Expanded DTA curves at near glass transition for the samples obtained by annealing at 430°C.$^9$

Fig. 16. Values of glass transition, $T_g$, crystallization onset, $T_x$, temperatures as a function of $\text{Cu}^+/\Sigma\text{Cu}$ ratio for the Bi$_2$Sr$_2$CaCu$_2$O$_x$ samples obtained by annealing at near the glass transition.$^{10}$

Fig. 17. Intensities of the exothermic peaks measured by DSC as a function of $\text{Cu}^+/\Sigma\text{Cu}$ ratio for the Bi$_2$Sr$_2$CaCu$_2$O$_x$ samples obtained by annealing at near the glass transition.$^{10}$
that the values of $T_g$ or $T_x$ for the glasses with $Cu^+/\Sigma Cu < 0.3$ are much higher than those for the glasses with $Cu^+/\Sigma Cu > 0.3$. The highest values of glass transition and crystallization temperatures are 474°C and 513°C, respectively. In Bi-based glasses, these are the highest values of all data reported so far.

The intensities of the exothermic peaks due to the crystallization for the Bi$_2$Sr$_2$CaCu$_2$O$_x$ powdered glasses, which were measured by a differential scanning calorimetry (DSC), are shown in Fig. 17 as a function of $Cu^+/\Sigma Cu$ ratio. The intensity of the first exothermic peak, $DH$, decreases gradually and that of the second crystallization peak increases with decreasing $Cu^+/\Sigma Cu$ ratio. Particularly, in the glasses with $Cu^+/\Sigma Cu < 0.2$, a rapid increase is observed. These results shown in Figs. 16 and 17 also indicate that the structure of the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass is largely affected by the $Cu^+/\Sigma Cu$ ratio and particularly changes drastically at around $Cu^+/\Sigma Cu = 0.2$.

6. MICROSTRUCTURE OF BI-BASED GLASSES

The microstructure of Bi-based glasses using transmission electron microscopy (TEM) has been reported by several researchers. Kim et al. and Aruchamy reported that the phase separation occurs in the Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass and the Bi$_{1.68}$Pb$_{0.32}$Sr$_{1.75}$Ca$_2$Cu$_3$O$_{x}$ glass. However, the chemical compositions of those phases and the origin of the phase separation have not been clarified yet. Kasuga et al. reported that the addition of Al$_2$O$_3$ to a BiSrCaCu$_2$Ox melt enhances a droplet-like phase separation.

The TEM micrograph of the as-quenched Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass ($Cu^+/\Sigma Cu = 0.81$) is shown in Fig. 18. The electron diffraction pattern, which is inserted in the figure, is a typical amorphous ring. The microstructure shown in Fig. 18 has a characteristic of liquid-liquid phase separation, demonstrating that the as-quenched glass is phase separated. The feature size found

![Fig. 18. TEM bright-field image from the as-quenched Bi$_2$Sr$_2$CaCu$_2$O$_x$ glass. Insert is an electron diffraction pattern.](image-url)
in this sample is in the range of 4–10 nm. Similar microstructures were observed for some other Bi-based glasses.\textsuperscript{8,9} Figure 19 shows the TEM micrograph of the Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{x} glass (Cu\textsuperscript{+}/\Sigma\textsubscript{Cu}=0.01) annealed at 430°C for 72 h in oxygen. Any fine structure composed of clear different contrasts is not seen. This result suggests that the phase separation in the as-quenched glass disappears due to the annealing in oxygen. In other words, the phase separation behaviors of Bi-based glasses depend largely on the copper valence state. It is considered that the presence of Cu\textsuperscript{+} ion in the Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{x} glass is a key factor for the phase separation. That is, it is considered that one of the phases observed in the as-quenched glass contains most of Cu\textsuperscript{+} ions.

In the DTA curve of the as-quenched Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{x} glass powders shown in Fig. 14, two exothermic peaks were observed and the intensity of lower exothermic peak decreased with decreasing Cu\textsuperscript{+}/\Sigma\textsubscript{Cu} ratio. On the other hand, the intensity of the second peak increased with decreasing Cu\textsuperscript{+}/\Sigma\textsubscript{Cu} ratio. These crystallization behaviors might be closely related to the phase separation behaviors. That is, the glasses with a phase separation have two crystallization peaks and the glasses with no phase separation have only one crystallization peak.

As shown in Fig. 16, a rapid increase in T\textsubscript{g} was observed at around Cu\textsuperscript{+}/\Sigma\textsubscript{Cu}=0.3. It is known that some glasses in which a phase separation occurs have two glass transition temperatures.\textsuperscript{30} However, two glass transition temperatures are not observed in the Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{x} glass, as shown in Fig. 15. In the glasses with Cu\textsuperscript{+}/\Sigma\textsubscript{Cu}≥0.3, the glass transition and lower crystallization temperatures are observed at about 420°C and 460°C, respectively. On the other hand, the glasses with Cu\textsuperscript{+}/\Sigma\textsubscript{Cu}=0.01, in which a phase separation is not observed, exhibited a glass transition at about 470°C. From these results, it would be expected that although the as-quenched glass separates into two glass phases having T\textsubscript{g} of about 420°C and 470°C, an endothermic peak due to the higher glass transition is overlapped by the lower crystallization peak and would not be observed in a DTA curve.
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