<table>
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<th>Title</th>
<th>Some Physical Properties of BiO₁.₅-BaO-CuO Glasses (Commemoration Issue Dedicated to Professor Sumio Sakka On the Occasion of His Retirement)</th>
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<td>Author(s)</td>
<td>Miyaji, Fumiaki; Fujimine, Satoshi; Yoko, Toshinobu; Sakka, Sumio</td>
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Kyoto University
Some Physical Properties of BiO$_{1.5}$-BaO-CuO Glasses

Fumiaki MIYAJI*, Satoshi FUJIMINE**, Toshinobu YOKO*** and Sumio SAKKA***

Received May 27, 1994

The density, refractive index, glass-transition temperature and crystallization temperature were investigated for BiO$_{1.5}$-BaO-CuO ternary glasses in relation to copper valence and glass structure. It was found that the Cu$^+$-Cu$^{2+}$ equilibrium moves toward reduction side (Cu$^+$) with increasing melting temperature and the BaO content. Judging from the additivity of the measured properties, the glass structure hardly changes with glass composition when Cu$^+$/Cu$^++$Cu$^{2+}$ ratio is constant. On the other hand, the glass structure might be more open structure at the Cu$^+$/Cu$^++$Cu$^{2+}$ ratio higher than 60%. The molar volume and refractive index of fictive Bi$_2$O$_3$ glass estimated by extrapolation are almost the same as those of α-Bi$_2$O$_3$ crystal. The local structure around Bi$^{3+}$ ions were therefore assumed to resemble that in α-Bi$_2$O$_3$ crystal. The Cu$_4$O$_3$ crystal-like structural units might also be present in the Bi-Ba-Cu-O glasses, contributing to wide glass-forming region in the present system.

KEY WORDS : BiO$_{1.5}$-BaO-CuO glasses/ Density/ Molar volume/ Refractive index/ Cu$^+$-Cu$^{2+}$ equilibrium/ Glass structure

1. INTRODUCTION

Since Komatsu et al. found that Bi-Sr-Ca-Cu-O composition corresponding to high $T_c$ superconductor form a glass by ordinary melt quenching technique, those and related glasses containing Bi$_2$O$_3$, CuO and alkaline earth oxides (CaO, SrO and/or BaO) have attracted an attention not only as a precursor of superconductors but also as a new family of so-called “non-conventional” oxide glasses. There have been many studies on preparation of Bi-Sr-Ca-Cu-O superconductor ceramics by crystallizing the melt-quenched glasses. On the other hand, several researchers investigated the structure and properties of the glasses. Zheng et al. measured the density, glass-transition temperature and crystallization onset temperature of Bi-Sr-Ca-Cu-O glasses and presumed their structure by infrared spectroscopy. Moreover, specific heat, viscosity, and electrical conduction have been investigated for the glasses so far.

It is, however, difficult to clarify the compositional dependence of structure and properties of Bi-Sr-Ca-Cu-O glasses, since they consists of four kinds of oxides. For simplified analysis, the present authors determined the glass-forming regions in the BiO$_{1.5}$-CaO-CuO, BiO$_{1.5}$-SrO-CuO and BiO$_{1.5}$-BaO-CuO ternary systems and investigated the structure and properties of these glasses. It was suggested that glass structure of these three systems may be considerably...
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different one another.$^{10,11}$ On the other hand, Sato et al. examined the crystallization behavior of Bi$_2$Sr$_2$CuO$_y$ glasses.$^{12}$

Taking into consideration that the glass-forming region in the Bi-Ba-Cu-O system is widest among all the Bi-R-Cu-O ternary systems, the Bi-Ba-Cu-O system will be most appropriate in order to clarify the compositional dependence of properties of the Bi$_{0.5}$- and CuO-based glass systems. The authors have already studied the crystallization behavior$^{11,13,14}$ and electrical conduction$^{15}$ of Bi-Ba-Cu-O glasses. In the present work, some physical properties viz. the density, refractive index, glass-transition and crystallization temperatures were studied in relation to the valence state of copper ions and the glass structure.

2. EXPERIMENTAL

2.1 Sample preparation

Bi-Ba-Cu-O glasses with various compositions and Bi$_2$Sr$_2$CaCu$_2$O$_y$ glass were prepared. 10 g well-mixed glass batches containing reagent-grade Bi$_2$O$_3$, RCO$_3$ (R=Ca, Sr, Ba) and CuO were melted in a high-grade alumina crucible with a lid in an electric furnace at 1,250°C for the Bi$_2$Sr$_2$CaCu$_2$O$_y$ composition and at 1,350°C for the Bi-Ba-Cu-O systems for 10 min. The melt was poured onto a brass plate and quickly pressed by another plate. Black-colored glasses were obtained. Glasses of some compositions were also prepared in a similar manner but at various melting temperatures (950-1,350°C), in order to realize wide variations of Cu$^+$/ (Cu$^+ + $Cu$^{2+}$) ratio in the glasses.

2.2 Determination of copper valence

The valence state of copper ions in the glasses was determined by the following technique. First, Cu$^+$ was determined by potential-difference titration. About 0.1 g glass sample was dissolved in an aqueous solution containing Fe$_2$(SO$_4$)$_3$•H$_2$O and HCl. In this process, Cu$^+$ is oxidized to Cu$^{2+}$.

\[ \text{Cu}^+ + \text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} \tag{1} \]

Another aqueous solution containing MnSO$_4$•5H$_2$O, H$_2$SO$_4$ and H$_3$PO$_4$ was added to the solution to avoid yellow-coloration of Fe$^{3+}$ and the interference of titration by the presence of Cl$^-$. Fe$^{2+}$ produced by eq. (1) were determined by back-titration using 0.01 M KMnO$_4$ solution.

\[ 5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O} \tag{2} \]

The end point was determined as the inflection point of potential curve.

Next Cu$^{2+}$ was determined by iodimetric titration. Excess KI was added to 1 M HCl solution and about 0.1 g glass sample was dissolved in this solution.

\[ 3\text{I}^- + \text{Cu}^{2+} \rightarrow \text{I}_2 + \text{CuI} \tag{3} \]

I$_2$ produced by eq. (3) was determined by back titration using 0.01 M Na$_2$S$_2$O$_3$ solution.

\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-} \tag{4} \]

Just before the end point, the starch solution as indicator was added to the solution. The end point was determined as the point that the color of the solution was changed from purple to
colorless. N₂ gas was bubbled in the solution during the above operation to avoid the air-
oxidation of Cu⁺ and I⁻.

2.3 Density and refractive index
The densities of the glasses were measured by Archimedean method using kerosene as an
immersion liquid. The refractive indices were measured on the series of (100−3x)
BiO₁·₅·BaO·₂xCuO (x=5, 10, 20) glasses. The glass sample was polished to 0.1–0.2 mm thick.
A Mizojiri-Kogaku model DVA-36VW ellipsometer was employed in order to measure the
refractive index in the range 500–1,050 nm.

2.4 Thermal analyses
The glass transition temperature, Tg, and the crystallization onset temperature, Tx, of the
glasses with various Cu⁺/(Cu⁺+Cu²⁺) ratio were measured by a Rigaku-Denki model
Thermoflex TG 8110 DSC/DTA apparatus. The measurements were performed on bulk
samples of about 40 mg under an air atmosphere.

3. RESULTS

3.1 Copper valence
Figure 1 shows the results of valence determination of copper ions in the (100−2x)
BiO₁·₅·BaO·CuO glasses melted at 1,350°C. It is found that Cu⁺/(Cu⁺+Cu²⁺) ratio (a) is
almost constant around 75%. Figure 2 shows the variation of the Cu⁺/(Cu⁺+Cu²⁺) ratio in
50BiO₁·₅·25BaO·25CuO, 60BiO₁·₅·10BaO·30CuO and 80BiO₁·₅·5BaO·15CuO glasses as a
function of melting temperature. As to all the compositions, the Cu⁺/(Cu⁺+Cu²⁺) ratio
increases with increasing melting temperature and most of copper ions are present as Cu⁺ for the

![Graphs showing Cu⁺/(Cu⁺+Cu²⁺) ratio and mean valence of copper as a function of CuO content](image)

Fig. 1. (a) Cu⁺/(Cu⁺+Cu²⁺) ratio and (b) mean valence of copper as a function of CuO
content for (100−2x)BiO₁·₅·xBaO·xCuO glasses. The melting temperature was
fixed at 1,350°C for all the glasses.
some physical properties of BiO{sub 1.5-BaO-CuO} glasses

Fig. 2. Variation of Cu{sup +}/(Cu{sup +}Cu{sup 2+}) ratio in 50BiO{sub 1.5}25BaO25CuO, 60BiO{sub 1.5}10BaO30CuO and 80BiO{sub 1.5}5BaO15CuO glasses as a function of melting temperature.

melting temperatures higher than 1,250°C. It is also found that the higher the BaO content, the higher the Cu{sup +}/(Cu{sup +}Cu{sup 2+}) ratio at lower temperatures than 1,100°C.

3.2 Density and refractive index

The density and molar volume of BiO{sub 1.5}-BaO-CuO glasses are listed in Table 1, in which V_m and V_o denote the molar volume per one total-cation mol and per one oxygen mol, respectively.
In calculation, the $\text{Cu}^+/(\text{Cu}^++\text{Cu}^{2+})$ ratio is fixed at 0.75 based on the results in figure 1(a). Figure 3 shows the contours of (a) density, (b) $V_m$ and (c) $V_o$ in $\text{BiO}_{1.5}\cdot\text{BaO}\cdot\text{CuO}$ glasses. It is found that the density increases and decreases with increasing $\text{BiO}_{1.5}$ and $\text{BaO}$ contents, respectively and that $V_m$ decreases with increasing CuO content and $V_o$ decreases with increasing $\text{BiO}_{1.5}$ content.

Figure 4 shows the (a) density, (b) $V_m$ and (c) $V_o$ in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, 60$\text{BiO}_{1.5}\cdot10\text{BaO}\cdot30\text{CuO}$ and 80$\text{BiO}_{1.5}\cdot5\text{BaO}\cdot15\text{CuO}$ glasses as a function of $\text{Cu}^+/(\text{Cu}^++\text{Cu}^{2+})$ ratio. The density and
Some Physical Properties of BiO$_{1.5}$-BaO-CuO Glasses

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1) $V_m$; molar volume per one total-cation mol, 2) $V_o$; molar volume per one oxygen mol, 3) Melting temperature was fixed at 1,350°C for all the compositions, 4) $\text{Cu}^+/\text{(Cu}^++\text{Cu}^{2+})$ ratio is fixed at 0.75 in calculation.

the molar volume decreases and increases with increasing the $\text{Cu}^+/\text{(Cu}^++\text{Cu}^{2+})$ ratio, respectively.

Figure 5 shows the wavelength dependence of refractive index in (100-3x) BiO$_{1.5}$ BaO-2xCuO (x=5, 10, 20) glasses. It is found that the refractive index becomes higher as the BiO$_{1.5}$ content increases.

3.3 Thermal analysis

Figure 6 shows the DSC curves of 80BiO$_{1.5}$5BaO-15CuO glass prepared at various melting temperatures. It is found that $T_\beta$, $T_x$ and $T_\phi$ decreases with increasing melting temperature. Figure 7 shows the (a) $T_x$ and (b) $(T_x-T_\beta)$ in Bi$_2$Sr$_2$CaCu$_2$O$_{8_\delta}$, 50BiO$_{1.5}$25BaO-25CuO, 60BiO$_{1.5}$:10BaO:30CuO and 80BiO$_{1.5}$:5BaO:15CuO glasses as a function of $\text{Cu}^+/\text{(Cu}^++\text{Cu}^{2+})$ ratio. It is found that $(T_x-T_\beta)$ shows the maximum at 55–65% of $\text{Cu}^+/\text{(Cu}^++\text{Cu}^{2+})$ ratio.
4. DISCUSSION

4.1 Cu\(^+\)-Cu\(^{2+}\) equilibrium

It is found that the Cu\(^+\)/(Cu\(^+\)+Cu\(^{2+}\)) ratio increases with increasing melting temperature, agreeing with other copper-containing oxide glasses such as 30Na\(_2\)O-70B\(_2\)O\(_3\),\(^{10}\) 30R\(_2\)O-70SiO\(_2\) (R=alkali metal),\(^{17}\) 15Na\(_2\)O-10Al\(_2\)O\(_3\)-75B\(_2\)O\(_3\),\(^{18}\) 19.2Na\(_2\)O-4CaO-76.8SiO\(_2\)^{19} and Bi\(_4\)Sr\(_3\)Ca\(_3\) Cu\(_4\)O\(_{20}\) glasses.
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![Graph showing refractive index vs. wavelength](image)

**Fig. 5.** Wavelength dependence of refractive index in (100−3x)BiO$_{1.5}$xBaO$_x$CuO (x=5, 10, 20) glasses. The melting temperature was fixed at 1,350°C for all the glasses.

![DSC curves](image)

**Fig. 6.** DSC curves of 80BiO$_{1.5}$-5BaO-15CuO glass prepared at various melting temperatures. The heating rate is 10°C/min.

![Graphs showing T$_g$ and T$_x$](image)

**Fig. 7.** (a) T$_g$ and (b) (T$_x$-T$_g$) in Bi$_2$Sr$_2$CaCu$_2$O$_y$, 50BiO$_{1.5}$-25BaO-25CuO, 60BiO$_{1.5}$-10BaO-30CuO and 80BiO$_{1.5}$-5BaO-15CuO glasses as a function of Cu$^+/(Cu^++Cu^{2+})$ ratio.
It is also seen that the Cu$^+$-Cu$^{2+}$ equilibrium moves toward reduction side (Cu$^+$) with increasing BaO content, which is consistent with the case for copper ions in 30R$_2$O-70SiO$_2$ glass with various R$_2$O content.\textsuperscript{17) Singh et al. expressed the equilibrium of copper ions in the melt as follows.\textsuperscript{18)}

\[ \text{Cu}^+ + \frac{1}{4} \leftrightarrow \text{Cu}^{2+} + \frac{1}{2} \text{O}^{2-} \tag{5} \]

The equilibrium constant of the above equation is therefore expressed by

\[ K = \frac{[\text{Cu}^{2+}](a_{\text{O}^{2-}})^{1/2}}{[\text{Cu}^+]^{1/2}(p\text{O}_2)^{1/4}} \tag{6} \]

The activity of O$^{2-}$ ions, $a_{\text{O}^{2-}}$, is assumed to increase with increasing BaO content, since the Ba-O bond is more ionic compared with the Bi-O and Cu-O bonds. That is, the Cu$^+$-Cu$^{2+}$ equilibrium moves toward reduction side with increasing basicity\textsuperscript{21} of glass.

4.2 Density

Figure 8 shows the relation between the $V_m$ and Bi$_{0.5}$ content in Bi$_{0.5}$-BaO-CuO glasses. The linear relation holds for all the Ba/Cu series, indicating the additivity of $V_m$ in the pseudobinary Bi$_{0.5}$-(Ba$_x$Cu$_y$O$_z$) system. This also suggests that the local structure around Bi$^{3+}$ ions does not significantly change with glass composition. The average $V_m$ of single Bi$_{0.5}$ glass estimated by extrapolation for each line is 26.7 cm$^{-3}$mol$^{-1}$, which is slightly larger than $V_m$ of $\alpha$-Bi$_2$O$_3$ crystal, viz. 25.32 cm$^{-3}$mol$^{-1}$.\textsuperscript{22) This indicates that the packing around Bi$^{3+}$ ions is not denser in the present glasses than in $\alpha$-Bi$_2$O$_3$ crystal. However, the small difference in the $V_m$ values between them may indicate that Bi$^{3+}$ ions are present as BiO$_3$ or BiO$_5$ form as in $\alpha$-Bi$_2$O$_3$ crystal, similarly to Bi$_{0.5}$-Ga$_{0.5}$ glass.\textsuperscript{23)}

Figure 9 shows the calculated $V_m$ for fictive BaO-CuO binary glasses as a function of...
CuO/(CuO+BaO) ratio. It is found that $V_m$ does not depend on BiO$_{1.5}$ content and the $V_m$ linearly decreases with increasing CuO/(CuO+BaO) ratio, where the $V_m$ of BiO$_{1.5}$ is fixed at 26.7 cm$^{-3}$mol$^{-1}$. This suggests that the coordination environments around Cu$^{2+}$ and Ba$^{2+}$ ions are hardly affected by glass composition.

As shown in figure 4(b), $V_m$ is nearly constant up to 60% of Cu$^+/(Cu^++Cu^{2+})$ ratio and starts to increase from this point. It may be explained by assuming that oxygen atoms are eliminated without the change in configuration of cations up to 60% of Cu$^+/(Cu^++Cu^{2+})$ ratio, whereas at Cu$^+/(Cu^++Cu^{2+})$ ratio higher than 60% of copper ions rearrange resulting in the increase in $V_m$. As a result, more open glass structure may be realized in high Cu$^+/(Cu^++Cu^{2+})$ region. The coordination of copper ions will be discussed later.

4.3 Refractive index

The high refractive index (>2.2) of the present glasses is ascribed to high concentration of Bi$^{3+}$ ions with high polarizability. According to Wemple, the following equation holds at high photon energies,

$$
\frac{1}{n^2-1} = \frac{E_0}{E_d} - \frac{E^2}{E_0E_d}
$$

where $E$, $E_0$ and $E_d$ represent the photon energy, the average excitation energy and the electronic oscillation strength, respectively. Figure 10 shows the relation between $1/(n^2-1)$ and $E^2$. As expected from eq. (7), the linear relationship between $1/(n^2-1)$ and $E^2$ is seen for all the compositions. The refractive index at any wavelength can be therefore estimated from interpolation or extrapolation of these straight lines. Table 2 lists the refractive index at various wavelengths, Abbe number, $\nu_d$, and molar refraction, $R_m$. The $n_d$, $n_F$, $n_C$ and $n_\infty$ represent refractive indices at the wavelengths of 587.6, 486.1, 656.3 nm and infinity, respectively. The $R_m$ is calculated by

![Fig. 10. Plot of $1/(n^2-1)$ vs. $E^2$ for (100-3x)BiO$_{1.5}$xBaO-2xCuO glasses.](image)

The melting temperature was fixed at 1,350°C for all the glasses.
Table 2. Refractive index (n), Abbe number (v) and molar refraction ($R_m$) of (100-3x)BiO$_{1.5}$-BaO-2xCuO glasses.

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* Values estimated from extrapolation.

The $n_d$ values of the present glasses are in the range 13–30, classified into high dispersion glasses.

Figure 11 shows the compositional dependence of (a) $n_d$ and $n_\infty$ and (b) $R_m$ of (100–3x)BiO$_{1.5}$-BaO-2xCuO glasses. It is found that the additivity completely holds for both n and $R_m$ similarly to molar volume. It has been reported that the refractive index of thin α-Bi$_2$O$_3$ film at 550 nm is 2.45. The refractive index of fictive Bi$_2$O$_3$ glass at 550 nm is estimated at 2.46 by extrapolation, agreeing with this value. This also supports that coordination environment around Bi$^{3+}$ ions resembles that in α-Bi$_2$O$_3$ crystal which is constructed by BiO$_5$ and BiO$_6$ polyhedra, which is also the case for BiO$_{1.5}$-GaO$_{1.5}$ glasses.

4.4 Thermal properties and glass structure in relation to copper valence

The $(T_c-T_g)$ in the present glasses shows the maximum at 55–60% of the Cu$^+$/$(Cu^++Cu^{2+})$ ratio. This may be explained by the presence of Cu$_4$O$_3$ crystal-like clusters in the present Bi-Ba-Cu-O glasses. The in situ high-temperature XRD measurement indicated that Cu$_4$O$_3$ crystal is precipitated in 50BiO$_{1.5}$-25BaO-25CuO glass on heating, although the
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crystal is finally transformed to Cu$_2$O or CuO crystal. In Cu$_4$O$_3$ crystal the Cu$^+/(\text{Cu}^++\text{Cu}^{2+})$ ratio is just 50% and Cu$^+$ and Cu$^{2+}$ ions form Cu-O-Cu colinear bond and CuO$_4$ square plan, respectively. Therefore, the amount of Cu$_4$O$_3$ crystal-like units may become maximum at about 50% of the Cu$^+/(\text{Cu}^++\text{Cu}^{2+})$ ratio. The wide glass-forming region in the present system instead of high concentration of CuO may be attributed to the presence of complex Cu$_4$O$_3$ crystal-like structural units, increasing randomness of the system. Consequently, it seems reasonable that the Bi-Ba-Cu-O glasses may be most stable at about 50% of the Cu$^+/(\text{Cu}^++\text{Cu}^{2+})$ ratio.

5. CONCLUSION

Some physical properties of BiO$_{1.5}$-BaO-CuO ternary glasses were investigated and they were correlated with glass structure. It was found that the glass structure depends on Cu$^+/(\text{Cu}^++\text{Cu}^{2+})$ ratio rather than glass composition. It was assumed that the local structure around Bi$^{3+}$ ions resembles that in α-Bi$_2$O$_3$ crystal. On the other hand, the Cu$_4$O$_3$ crystal-like units might be present in the present glasses.

REFERENCES