

# Glass formation and glass structure of the $\text{BiO}_{1.5}\text{-PbO-CuO}$ system

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The glass-forming region of the  $\text{BiO}_{1.5}\text{-PbO-CuO}$  system has been determined by the melt-quenching technique. The glass transition temperatures,  $T_g$ , and the first crystallization peak temperatures,  $T_{x1}$ , are around 240 °C and 285 °C, respectively. The glass structure consists of  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units, and the conversion between these polyhedra mainly depends on the CuO and PbO content. The covalent characteristic in the infrared absorption spectra of the  $[\text{PbO}_n]$  pyramidal units becomes significant when the glass contains more PbO.

## 1. Introduction

Bismuthate glasses are now being extensively studied since the discovery of the Bi-Sr-Ca-Cu-O glass-ceramic superconductors [1–3]. Much effort has been extended in these studies to prepare high-performance superconducting Bi-Sr-Ca-Cu-O ceramics by the glass-ceramic route since the ceramics transformed from glass are highly dense and microstructure controllable as well as easy to fabricate in any shape [4]. Recently, the glass formation and glass structure in the  $\text{Bi}_{1.5}\text{-CuO-Ca}_{0.5}\text{Sr}_{0.5}\text{O}$  [5],  $\text{Bi}_2\text{O}_3\text{-CaO-CuO}$  and  $\text{Bi}_2\text{O}_3\text{-CaO-CuO}$  [6] glass systems have been reported. It has been found that the amount of Ca and Sr in the glass would greatly affect the transition between  $[\text{BiO}_3]$  and  $[\text{BiO}_6]$  units and thus the glass-forming ability. On the other hand, the glass-forming range can be extended by adding PbO to the Bi-Ca-Sr-Cu-O glass [7]. It has also been found that the partial substitution of lead for bismuth in the Bi-Sr-Ca-Cu-O system was very effective in increasing the volume fraction of the high- $T_c$  phase [8,9]. However, only a few studies have been conducted on the glass formation and structure of the bismuthate lead glasses [10,11], and the role of PbO in the Bi-based glasses is still ambiguous. Therefore, glass formation and structure of lead-related simple systems are of much interest. In the present work the glass formation region and the glass structure of the  $\text{Bi}_2\text{O}_3\text{-PbO-CuO}$  system were investigated.

## 2. Experimental procedure

All batches were prepared using reagent-grade bismuth trioxides (purity, 99.9%), lead oxide (purity, 99%) and copper oxide (purity, 99%) as starting materials. The masses of the batches were determined to the nearest 0.001 g, and then the batches were ground and mixed using an agate mortar. The mixture was melted in a platinum crucible in air and held at 1100 °C for 25 min. Glass sheets were obtained by

quickly pressing the cast melt between two steel plates. The cooling rate for this quench process is about  $10^2\text{-}10^3\text{ }^\circ\text{C s}^{-1}$ .

The amorphous state of the melt-quenched samples was examined by visual inspection and confirmed by X-ray diffraction analysis (Siemens diffractometer; Cu  $K\alpha$  radiation). The properties and glass structure of the as-quenched glasses were analysed in three groups according to their compositions which are listed in Table I. The glass transition temperature,  $T_g$ , and the first crystallization temperature,  $T_{x1}$ , were measured using a differential scanning Calorimeter (DuPont 2000) at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . The structure of the melt-quenched samples was analysed using the Fourier transform infrared (FTIR) transmittance spectra of the glasses by the KBr pellet technique within the range  $1200\text{-}400\text{ cm}^{-1}$ .

## 3. Results

### 3.1. The glass formation region

Fig. 1 shows the glass-forming region of the  $\text{PbO-BiO}_{1.5}\text{-CuO}$  system. The composition boundary of the glass-forming region is defined as when there is no detectable X-ray diffraction peak of a sample. The typical X-ray diffraction pattern of the glass is shown in Fig. 2. In the as-quenched glass, a large halo is observed at around  $2\theta = 30^\circ$  and a small halo is also observed at around  $2\theta = 50^\circ$ . All samples solidified by quenching were opaque and black. The glass-forming range for each component is  $20 \leq \text{BiO}_{1.5} \leq 60$ ,  $25 \leq \text{PbO} \leq 58$  and  $15 \leq \text{CuO} \leq 30$  in molar ratio.

Dimitriev and Mihailova [12] studied the glass formation in several binary systems consisting of CuO,  $\text{Bi}_2\text{O}_3$  and PbO using the roller technique (cooling rate up to  $10^3\text{-}10^4\text{ }^\circ\text{C s}^{-1}$ ). The as-reported glass-forming region for any of the  $\text{Bi}_2\text{O}_3\text{-PbO}$ ,  $\text{Bi}_2\text{O}_3\text{-CuO}$  and  $\text{PbO-CuO}$  binary systems is wider than our present results. In fact, the melting

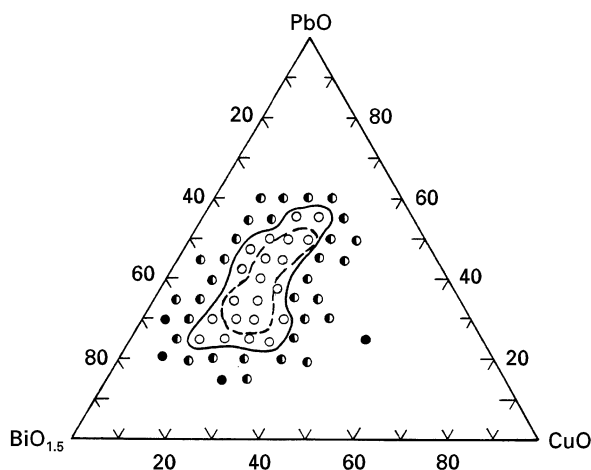


Figure 1 The glass-forming region of the  $\text{BiO}_{1.5}$ - $\text{PbO}$ - $\text{CuO}$  system. (○), glass; (◐), partially crystallized glass; (●), completely crystallized.

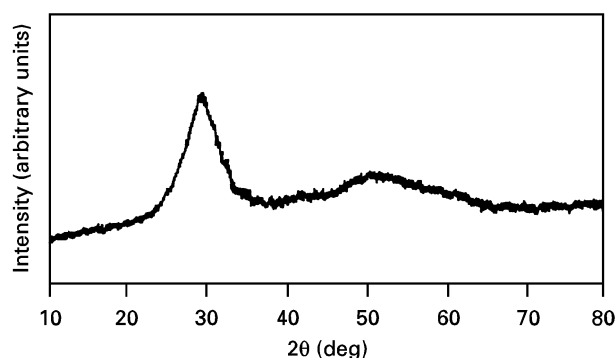


Figure 2 A typical X-ray diffraction pattern of the Bi-Pb-Cu-O glasses.

temperature and the cooling rate are the most important factors in determining the glass-forming region. Our present glass-forming region of the  $\text{BiO}_{1.5}$ - $\text{PbO}$ - $\text{CuO}$  system can be classified as a system with a melting temperature of  $1100^\circ\text{C}$  and a cooling rate of  $10^2$ - $10^3^\circ\text{C s}^{-1}$ . The area enclosed by the broken line as in Fig. 1 contains the glass compositions with  $T_{x1} - T_g > 45^\circ\text{C}$ . Since  $T_{x1} - T_g$  is one indicator of the stability of a glass, this area corresponds to compositions of the more stable glasses, which are located in an area with a narrow range of Cu contents.

### 3.2. Properties

Fig. 3 shows typical differential scanning calorimetry thermograms for the as-quenched glass. Although the exothermic temperature peaks are different for each sample, the tendencies are very similar. The glass transition temperature,  $T_g$ , and the first crystallization peak temperature,  $T_{x1}$ , of the glass are about  $238^\circ\text{C}$  and  $284^\circ\text{C}$ , respectively. The values of  $T_g$  and of  $T_{x1}$  for the glass, which are classified into three groups, are shown in Table I, Fig. 4 and Fig. 5. It can be seen that  $T_g$  decreases with increasing CuO content in group A glasses, decreases with increasing PbO

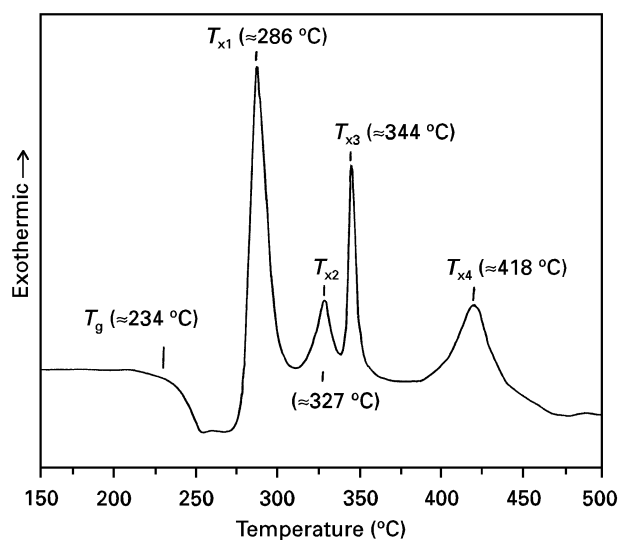


Figure 3 A typical differential scanning calorimetry curve for the Bi-Pb-Cu-O glass. The heating rate is  $10^\circ\text{C min}^{-1}$ .

TABLE I Composition and properties of the Bi-Pb-Cu-O system

Sample	$\text{BiO}_{1.5}$ (mol%)	$\text{PbO}$ (mol%)	$\text{CuO}$ (mol%)	$T_g$ ( $^\circ\text{C}$ )	$T_{x1}$ ( $^\circ\text{C}$ )	$T_{x1} - T_g$ ( $^\circ\text{C}$ )
Group A: $0.7 [x \text{ CuO} - (1-x)\text{BiO}_{1.5}] - 0.3\text{PbO}$						
A1	40	30	30	237	274	37
A2	46.67	30	23.33	241	289	48
A3	50	30	20	243	287	44
A4	55	30	15	246	283	37
Group B: $x \text{ PbO} - [(1-x)/3] (2\text{BiO}_{1.5} - \text{CuO})$						
B1	36.67	45	18.33	233	275	42
B2	40	40	20	236	293	57
B3	43.33	35	21.67	240	284	44
B4	46.67	30	23.33	242	289	47
B5	50	25	25	245	284	39
Group C: $x \text{ BiO}_{1.5} - [(1-x)/3] (\text{CuO} - 2\text{PbO})$						
C1	25	50	25	231	283	51
C2	33	44.33	22.67	234	296	58
C3	40	40	20	236	293	57
C4	49	34.67	17.33	240	294	54
C5	55	30	15	246	283	37

content in group B glasses, but increases with increasing  $\text{Bi}_2\text{O}_3$  content in group C glasses. The above results are consistent with the hypotheses that the behaviour of  $T_g$  acts as a function of glass composition [13]. The difference,  $T_{x1} - T_g$ , between the first crystallization temperature and transition temperature which can be used to estimate the workability of the glasses is shown in Fig. 6.

### 3.3. Infrared spectra

Figs 7-9 show the infrared spectra of the glasses in three groups. The absorption at  $669 \text{ cm}^{-1}$  is ascribed to the stretching vibration of the  $\text{O}=\text{C}$  group and is used as the reference of wavenumber shift. Several fundamental vibrational bands attributed to the Bi-O group, namely,  $860$ ,  $847$ ,  $617$ ,  $520$  and  $470 \text{ cm}^{-1}$ , were

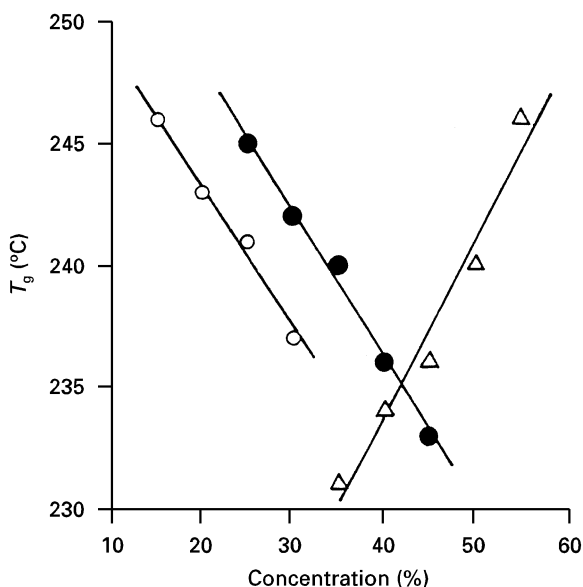


Figure 4 The effect of composition on the glass transition temperature. (○), Cu concentration for group A glasses; (●), PbO concentration for group B glasses; (△), BiO<sub>1.5</sub> concentration for group C glasses.

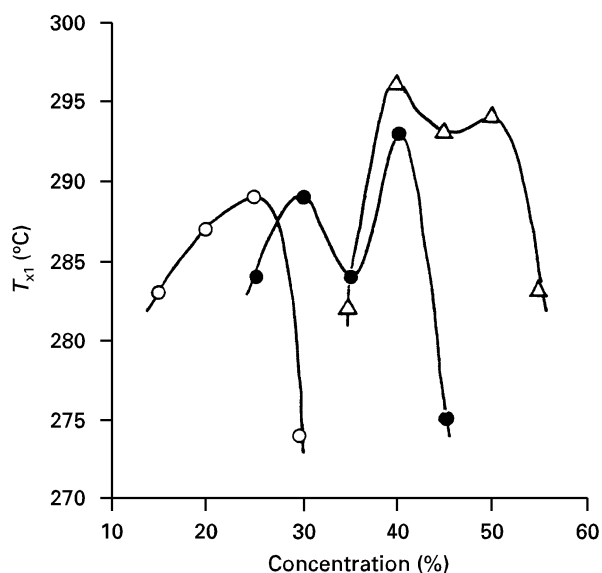


Figure 5 The effect of composition on the first crystallization peak temperature. (○), Cu concentration for group A glasses; (●), PbO concentration for group B glasses; (△), BiO<sub>1.5</sub> concentration for group C glasses.

observed in these samples. Additional absorption at 1130, 1062, 688 and 430 cm<sup>-1</sup> was also observed. These absorption bands of each glass are listed in Table II. It can be seen that there is almost no shift in the absorption peaks in the group A and B glasses, whereas slight shifts in the  $\nu_1$  and  $\nu_6^*$  absorption bands were observed in the C group glasses. The 1130 cm<sup>-1</sup> and the 1062 cm<sup>-1</sup> bands seem to be the overtones of the other lower absorption bands (i.e.,  $\nu_a = \nu_2 + \nu_3$  and  $\nu_b = 2\nu_6^*$ ). However, the 686 cm<sup>-1</sup> band is not an overtone of any other absorption bands since it exists only in samples B1, B2, C1 and C2.

The relative absorption strength ratio of [BiO<sub>6</sub>] to [BiO<sub>3</sub>] as shown in Table II was obtained from the

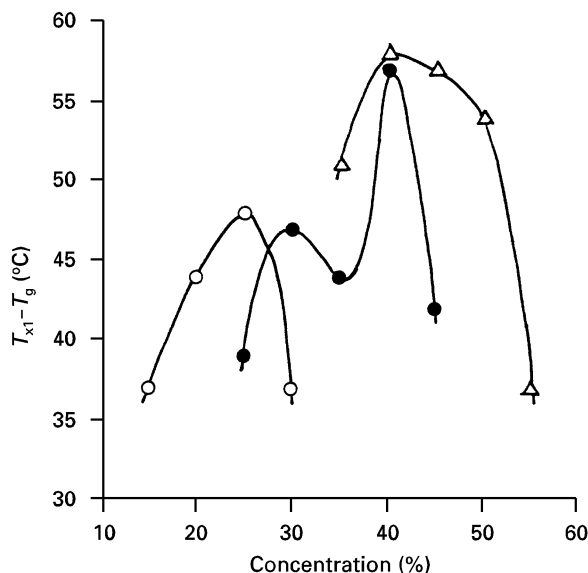


Figure 6 The dependence of  $T_{x1} - T_g$  on the glass composition. (○), Cu concentration for group A glasses; (●), PbO concentration for group B glasses; (△), BiO<sub>1.5</sub> concentration for group C glasses.

absorption intensity of the  $\nu_a^*$  band divided by that of the  $\nu_1$  band. It can be found that the ratio of [BiO<sub>6</sub>] to [BiO<sub>3</sub>] increases with increasing CuO in group A and with increasing PbO content in group B. However, the ratio of [BiO<sub>6</sub>] to [BiO<sub>3</sub>] decreases as Bi<sub>2</sub>O<sub>3</sub> content increases in group C.

#### 4. Discussion

Neither Bi<sub>2</sub>O<sub>3</sub> nor PbO is a transitional glass former. However, they behave as main glass formers in the system based on the Bi<sub>2</sub>O<sub>3</sub>-PbO matrix [11, 12]. This is because both Pb<sup>2+</sup> and Bi<sup>3+</sup> ions are highly polarizable and their asymmetry polyhedra inhibit crystallization in the molten masses. Also, bismuth and lead are heavy elements with nearly the same atomic weights.

Detailed data on the infrared spectra of the Bi-based glasses have been reported in the literature [5, 6, 10, 14, 15]. Although some arguments exist that the glass former unit is the BiO<sub>3</sub> pyramidal or BiO<sub>6</sub> distorted octahedral groups, the absorption bands of each group can be clearly distinguished. The BiO<sub>3</sub> unit belongs to the pyramidal point group C<sub>3v</sub> and has four fundamental vibrations: totally symmetric stretching vibration,  $\nu_1$ , at 840 cm<sup>-1</sup>; doubly degenerate stretching vibration,  $\nu_3$ , at 540–620 cm<sup>-1</sup>; totally symmetric bending vibration,  $\nu_2$ , at 470 cm<sup>-1</sup>; doubly degenerate bending vibration,  $\nu_4$ , at 350 cm<sup>-1</sup> [5, 10]. On the other hand, the 860, 575–600, 470–520 and 430 cm<sup>-1</sup> absorption bands in the spectra were due to the vibrations of strongly distorted BiO<sub>6</sub> octahedra [6, 14, 15]. Therefore, it is proposed that the 840 and 860 cm<sup>-1</sup> absorption bands can be used to identify the [BiO<sub>3</sub>] and [BiO<sub>6</sub>] units, respectively.

The FTIR spectra of these glasses as in Figs 7–9 show clearly the vibration bands at 861 and 847 cm<sup>-1</sup>. This indicates that these glasses consist of both [BiO<sub>3</sub>] and distorted [BiO<sub>6</sub>] units. It has been

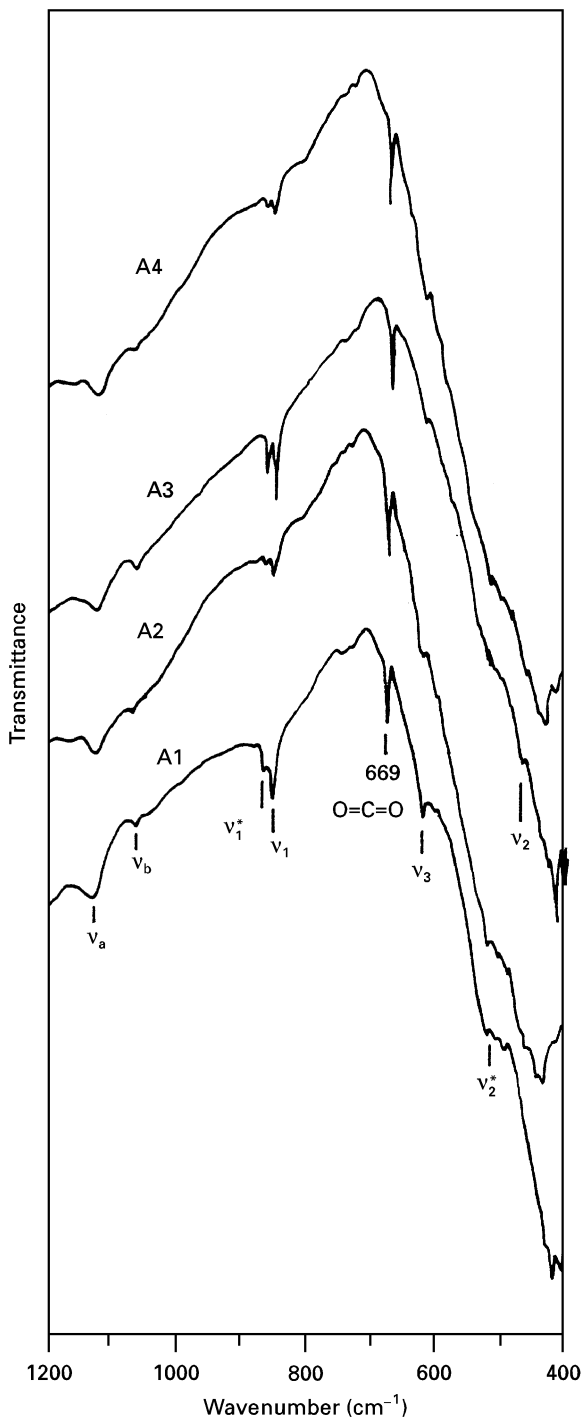


Figure 7 FTIR transmittance of group A glasses.

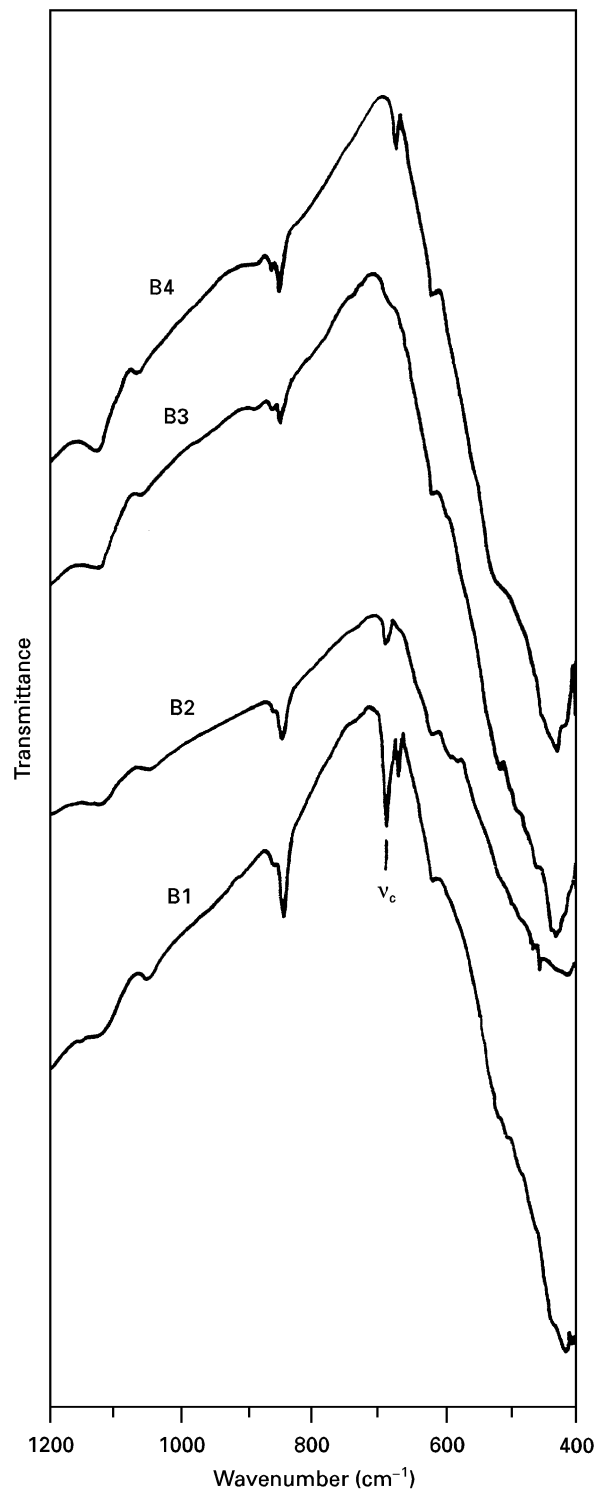


Figure 8 FTIR transmittance of group B glasses.

suggested that the distorted  $\text{BiO}_6$  octahedron involves  $\text{BiO}_3$  species when three Bi–O distances in the  $\text{BiO}_6$  octahedron are nearly equal [8]. The small or nearly no shift in the absorption peaks of these glasses as in Table II indicates that the Bi–O distance and bond strength are distinctly unchanged.

The  $[\text{BiO}_3]$  pyramidal unit acts as the glass network former unit in the Bi-based glass system and the deformed  $[\text{BiO}_6]$  octahedral units are incorporated in the glass network as modifiers as reported in the literature [5, 10]. The structure of the glass quenched from the melts may essentially be a two-dimensional network or may consist of short chains, depending on the number of glass network former  $[\text{BiO}_3]$  and

$[\text{BiO}_6]$  units. The glass network becomes more connected with more  $[\text{BiO}_3]$  units. The relative volume fraction of  $[\text{BiO}_6]$  octahedral units to  $[\text{BiO}_3]$  pyramidal units can be estimated from the relative absorption intensities at 860 and 848  $\text{cm}^{-1}$  bands in the FTIR spectra and is shown in Table II. The reason for the transition of  $[\text{BiO}_6]$  octahedral to  $[\text{BiO}_3]$  pyramidal units is probably due to the presence of strong polarizing cations.

The relative volume fraction of  $[\text{BiO}_3]$  units decreases with increasing CuO or  $\text{BiO}_{1.5}$  content in group A glasses. This is probably due to the increase

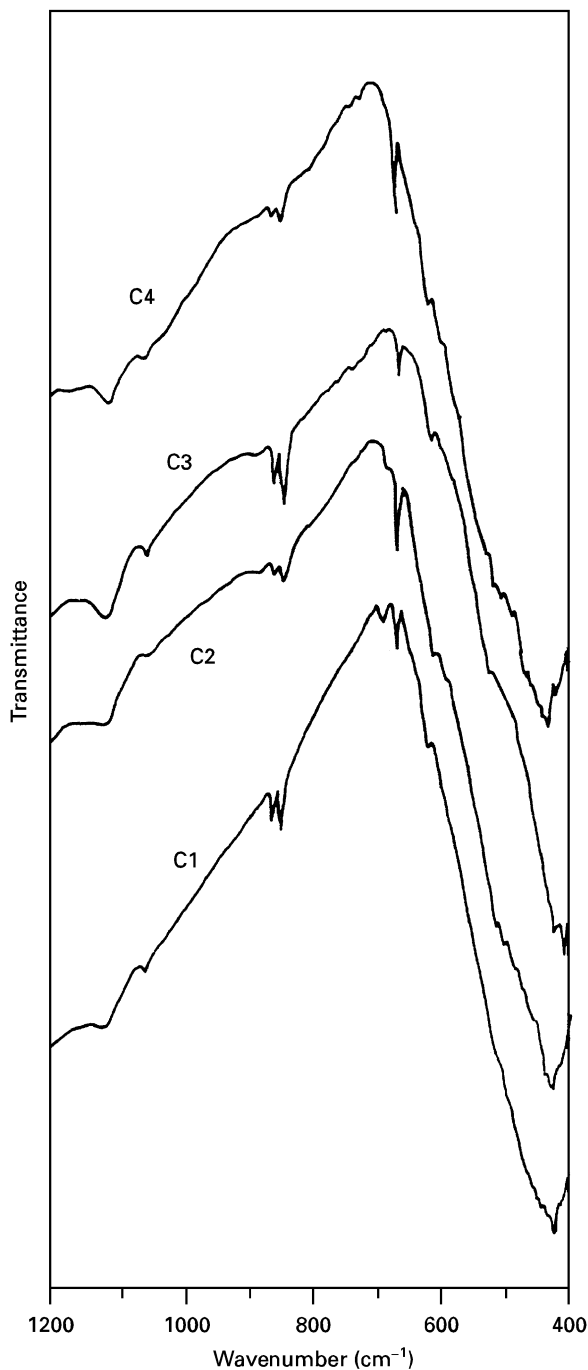


Figure 9 FTIR transmittance of group C glasses.

in the number of non-bridging oxygen atoms provided by CuO and thus converts  $\text{Bi}^{3+}$  from a glass modifier into a glass network former unit. This effect of the non-bridging oxygen atoms provided by CuO has also been observed in the  $\text{SiO}_2\text{-CuO-PbO}$  system [16]. The addition of CuO to these lead bismuthate glasses leads to the formation of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions, both of which should act as modifiers only. An increase in the number of non-bridging oxygen atoms provided by CuO in the glass would convert  $[\text{BiO}_6]$  units into  $[\text{BiO}_3]$  units, an effect similar to  $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{O}$  in the Bi-Sr-Ca-Cu-O glasses [9]. However, the increase in the number of non-bridging oxygen atoms would decrease the connectivity of the glass network, although the ratio of  $[\text{BiO}_3]$  to  $[\text{BiO}_6]$  units increases with increasing CuO content in group A glasses. This decrease in the connectivity of the glass network with increase in CuO content is reflected in the decrease in the glass transition temperature,  $T_g$ , as seen in Fig. 4 and Table I.

In group B glasses, there is a marked increase in the relative volume fraction of  $[\text{BiO}_3]$  with decreasing PbO content. PbO can be a glass modifier or a glass network former. If PbO is incorporated into the glass network as a modifier, the number of non-bridging oxygen atoms would increase with increasing PbO content and thus the number of  $[\text{BiO}_3]$  units would also increase. However, PbO seems to become a glass network former with higher PbO content since the number of  $[\text{BiO}_3]$  units decreases with increasing PbO content. It has been reported that the lead atoms can be the covalent  $[\text{PbO}_n]$  ( $n = 3, 4$ ) pyramids as glass network formers [17–20]. The average coordination number of  $\text{Pb}^{2+}$  ions is about three, and Pb–O bonds with different distances coexist [20]. It can be seen that the absorption band at  $688\text{ cm}^{-1}$ , which is assigned to the vibration absorption of the covalent Pb–O bonds in the  $[\text{PbO}_n]$  pyramids [21], becomes apparent in group B and C glasses with higher PbO contents. Such covalent oxygen polyhedra of  $[\text{PbO}_n]$  pyramids give rise to a shortage of oxygen for  $\text{Bi}^{3+}$  ions as for  $\text{Ga}^{3+}$  ions in the  $\text{PbO-Ga}_2\text{O}_3$  system [22]. The shortage of oxygen for  $\text{Bi}^{3+}$  ions will thus cause the number of octahedrally coordinated  $\text{Bi}^{3+}$  to increase. Therefore, the relative number of  $[\text{BiO}_3]$  units

TABLE II Assignment of absorption peaks and intensities of the glass samples

Sample	$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_3$ ( $\text{cm}^{-1}$ )	$\nu_2$ ( $\text{cm}^{-1}$ )	$\nu_1^*$ ( $\text{cm}^{-1}$ )	$\nu_2^*$ ( $\text{cm}^{-1}$ )	$\nu_a$ ( $\text{cm}^{-1}$ )	$\nu_b$ ( $\text{cm}^{-1}$ )	$\nu_c$ ( $\text{cm}^{-1}$ )	$[\text{BiO}_6]$ to $[\text{BiO}_3]$ ratio
A1	847	617	$\cong 475$	861	$\cong 519$	1120	1061	—	0.44
A2	847	617	$\cong 475$	861	$\cong 518$	1119	1060	—	0.47
A3	848	617	$\cong 475$	860	$\cong 517$	1120	1062	—	0.48
A4	848	617	$\cong 475$	860	$\cong 519$	1119	1062	—	0.50
B1	848	617	$\cong 475$	862	$\cong 521$	1119	1062	688	0.52
B2	847	617	$\cong 475$	861	$\cong 520$	1120	1060	687	0.50
B3	848	617	$\cong 475$	861	$\cong 519$	1121	1061	—	0.44
B4	847	618	$\cong 475$	860	$\cong 518$	1120	1060	—	0.34
C1	843	616	$\cong 475$	861	$\cong 517$	1120	1060	687	0.55
C2	846	617	$\cong 475$	861	$\cong 518$	1120	1060	687	0.53
C3	847	617	$\cong 475$	860	$\cong 519$	1121	1060	—	0.50
C4	848	618	$\cong 475$	860	$\cong 522$	1122	1061	—	0.50

decreases with increasing the PbO content as in group B glasses.

However, the connectivity of the glass network seems to be unchanged because the increase in the number of  $[\text{PbO}_n]$  pyramids will compensate for the decrease in the number of  $[\text{BiO}_3]$  pyramids. Nevertheless, the glass structure would become less rigid with a higher relative ratio of  $[\text{PbO}_n]$  to  $[\text{BiO}_3]$  because the field strength of  $\text{Pb}^{2+}$  (about 0.31) is less than that of  $\text{Bi}^{3+}$  (about 0.53) in oxide glasses [23]. The less strong glass structure would lead to a lower glass transition temperature. This effect can be observed in Fig. 4 where the glass transition temperature,  $T_g$ , decreases with increasing PbO content. Similar results have been also observed for group C glasses where the glass transition temperature,  $T_g$ , increases with increasing  $\text{Bi}_2\text{O}_3$  concentration. With increasing  $\text{Bi}_2\text{O}_3$  concentration, the glass network consists of more  $[\text{BiO}_3]$  units and the glass network becomes more rigid.

Glass formation of the bismuth-oxide-based system is possible because  $[\text{BiO}_6]$  distorted octahedra can be converted to  $[\text{BiO}_3]$  pyramidal units by strong polarizing cations. The polarizing effect in the Bi–Pb–Cu–O glass system comes from  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ions. Since the field strengths of  $\text{Pb}^{\text{II}}\text{–O}$  and  $\text{Cu}^{\text{II}}\text{–O}$  are much higher than that of  $\text{Cu}^{\text{I}}\text{–O}$ , the ratio of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  might be an important factor to affect the glass forming ability and the glass structure. However, since the  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  ratio is thermodynamically controlled as a function of melting temperature, the ratio would be a constant for a definite glass composition and a melting temperature. The nearly fixed  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  ratio in each glass sample would probably contribute to the narrow range of copper contents in the glass-forming range, as seen in Fig. 1.

## 5. Summary

The glass-forming region of the  $\text{Bi}_2\text{O}_3\text{–PbO–CuO}$  system has been determined. The glass transition temperature,  $T_g$ , decreases with increasing CuO content in group A glasses and increasing PbO content in group B glasses, and increases with increasing  $\text{Bi}_2\text{O}_3$  content in group C glasses. It is found from FTIR spectral investigation of Bi–Pb–O glasses that the glass structure consists of both  $[\text{BiO}_6]$  distorted octahedral and  $[\text{BiO}_3]$  pyramidal units. The covalent characteristic in FTIR absorption spectra of  $[\text{PbO}_n]$  glass-forming units becomes more apparent when the glass contains a high PbO content.

## Acknowledgement

This research work was supported by the National Science Council, Taiwan (Contract NSC85-2815-

0036-01-006E), and Tatung Institute of Technology (Basic Research Program B84-1712-01).

## References

1. H. MAEDA, Y. TANAKA, M. FUKUTOMI and T. ASANO, *Jpn. J. Appl. Phys.* **27** (1988) L209.
2. T. KOMATSU, K. IMAI, R. SATO, K. MATSUDA and T. YAMASHITA, *ibid.* **27** (1988) L533.
3. H. ZHENG and J. D. MACKENZIE, *Phys. Rev. B* **38** (1988) 7166.
4. D. G. HINKS, L. SODERHOLM, D. W. CAPONE, II, B. DABROSKI, A. W. MITCHELL and D. SHI, *Appl. Phys. Lett.* **53** (1988) 423.
5. A. BISHAY and C. MAGHRABI, *Phys. Chem. Glasses* **10** (1969) 1.
6. W. H. DUMBAUGH, *ibid.* **19** (1978) 121.
7. H. ZHENG, R. XU and J. D. MACKENZIE, *J. Mater. Res.* **4**, (1989) 911.
8. F. MIYAJI, T. YOKO and S. SAKKA, *J. Non-Cryst. Solids* **126** (1990) 170.
9. H. ZHENG, Y. HU and J. D. MACKENZIE, *Amer. Ceram. Soc. Proc.* **113** (1989) 735.
10. S. A. SUNSHINE, T. SIEGRIST, L. F. SCHNEEMEYER, D. W. MURPHY, R. J. CAVA, B. B. BATLOGG, R. B. VAN DOVWE, R. M. FLEMING, S. H. GLARUM, S. NAKAHARA, R. FARROW, J. J. KRAJEWSKI, S. M. ZAHURAK, J. V. WASZCZAK, J. H. MARSHALL, P. MARSH, L. W. RUPP JR and W. F. PECK, *Phys. Rev. B* **38** (1988) 893.
11. M. TAKANO, J. TAKADA, K. ODA, H. KITAGUCHI, Y. MIURA, Y. IKEDA, Y. TOMII, and H. MAZAKI, *Jpn. J. Appl. Phys.* **27** (1988) L1041.
12. Y. B. DIMITRIEV and V. T. MIHAILOVA, *J. Mater. Sci. Lett.* **9** (1990) 1251.
13. N. H. RAY, in Proceedings of the 9th International Congress on Glass, *Sci. Technol. Commun.* **1** (1971) 633.
14. V. DIMITROV, Y. DIMITRIEV and A. MONTENERO, *J. Non-Cryst. Solids* **180** (1994) 51.
15. Y. DIMITRIEV and M. MIHAILOVA, in Proceedings of the 16th International Congress on Glass, Madrid, 1992 *Bol. Soc. Esp. Ceram. Vidrio* **3** (1992) 293.
16. M. V. ROODE, T. H. HUANG, J. J. HENCHLER and K. C. COLE, *J. Amer. Ceram. Soc.* **69** (1986) 449.
17. T. YOKO, K. TADANAGA, F. MIYAJI and A. SAKKA, *J. Non-Cryst. Solids* **150** (1992) 192.
18. M. IMAOKA, H. HASEGAWA and I. YASUI, *ibid.* **85** (1986) 393.
19. H. MORIKAWA, Y. TAKAGI and I. OHNO, *ibid.* **53** (1982) 173.
20. K. YAMADA, A. MATSUMOTO, N. NIIMURA, T. FUKUNAGA, N. HAYASHI and N. WATANABE, *J. Phys. Soc. Jpn* **55** (1968) 831.
21. W. L. KONIJNENDIJK and H. VERWEIJ, Philips Research Laboratory Report (1976) p. 227.
22. F. MIYAJI, T. YOKO, J. JIN, S. SAKKA, T. FUKUNAGA and M. MISAWA, *J. Non-Cryst. Solids* **175** (1994) 211.
23. W. H. DUMBAUGH, *Phys. Chem. Glasses* **27** (1986) 119.

Received 19 April 1996  
and accepted 29 July 1997