

## Preparation and Electrical Conductivity of CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> Glass for Solid State Batteries

Dong Jin Jeong, Hee Chan Park, Heun Soo Lee\*, Myung Mo Shon\*,  
Seong Soo Park\*\* and Chan Young Park\*\*

Department of Inorganic Materials Engineering, Pusan National University,  
Pusan 609-735, Korea

\*Department of Ceramics, Daegu Technical College, Daegu 704-120, Korea

\*\*Department of Polymer Engineering, Pukyong National University,  
Pusan 608-739, Korea

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The crystallization behavior and electrical conductivity of the CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> glasses with various CuO content were investigated. The glass formation region was 0~20 mol% Bi<sub>2</sub>O<sub>3</sub>, 5~55 mol% CuO, and 30~90 mol% V<sub>2</sub>O<sub>5</sub> with  $T_f=275^\circ\text{C}\sim 290^\circ\text{C}$ . Among glasses with various compositions, the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glass heat-treated at 358°C for 8 h showed the highest conductivity of  $\sim 1.51 \times 10^2 \Omega^{-1} \text{cm}^{-1}$  at room temperature. The heat-treated glasses increased in electrical conductivity by the order of  $10^4$  compared to non heat-treated glass. The linear relationship between  $\ln(\sigma T)$  and  $T^{-1}$  indicated that electrical conduction in the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glass occurred by a small polaron hopping.

**Key words :** CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub>, Crystallization, DTA, Electrical conductivity, Small polaron hopping

### I. Introduction

Oxide glasses containing transition metal ions showing semiconductivity have recently reported by several authors.<sup>1-4)</sup> Among the oxide glasses, vanadate glasses are of growing interest, because they are characterized by several properties that make them promising materials for technological applications such as electrodes, solid state batteries, or sensors. The electrical conductivity of the vanadate glasses has generally been understood in terms of Mott's theory with a small-polaron hopping: electrical conduction proceeds by the electron hopping between high- and low- valence transition-metal ions.<sup>6-8)</sup>

In vanadate glass system, glass modifier-oxide with high ionic character will break the bridging bond V-O-V and is believed to be sensitive to the electron hopping. On the other hand, glass forming oxide with high covalent character is reported to have a slight effect on the electron hopping.<sup>7)</sup> Vanadate glasses with the electron hopping from V<sup>4+</sup> to V<sup>5+</sup> ion within glass matrix have been reported to show semiconductivity with electrical conductivity of the order of about  $10^5$  to  $10^7 \Omega^{-1} \text{cm}^{-1}$  at 300°K.<sup>8-12)</sup> The CuO addition to the vanadate glasses will increase electrical conductivity due to the possibility of promoting the reduction of V<sup>5+</sup> ion in the molten state.<sup>13)</sup>

The heat treatment of oxide glasses brings about the crystallization and structural relaxation of glass matrix. In general, crystallization of the oxide glasses results in the decrease of electrical conductivity. However, if conducting crystalline phase precipitates in vanadate glasses,

the electrical conductivity of the glasses crystallized after heat treatment will become higher than that of non heat-treated glasses.<sup>14,15)</sup> Distortion of structure units of the vanadate glasses after heat treatment will be reduced as a result of the cooperative movement of the clusters composed of VO<sub>4</sub> and VO<sub>5</sub> units.<sup>7)</sup> It has been assumed that the increase of electrical conductivity in vanadate glasses can be ascribed to increasing probability of an electron hopping, which is brought about as a result of decreasing distortion of VO<sub>4</sub> and VO<sub>5</sub> units. Vanadate glasses such as V<sub>2</sub>O<sub>5</sub>-Bi<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>-CuO, V<sub>2</sub>O<sub>5</sub>-ZnO, V<sub>2</sub>O<sub>5</sub>-Sb<sub>2</sub>O<sub>3</sub>-Te<sub>2</sub>O<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub>-SrO-V<sub>2</sub>O<sub>5</sub> systems have been extensively studied.<sup>8,10,11,14,16,17)</sup> However, electrical conductivity of CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> ternary system has not been studied.

In this study, the crystallization behavior and electrical properties of the CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> glasses with various compositions were investigated to seek the glass composition and optimum heat-treatment condition for high electrical conductivity. DTA, XRD, SEM analyses and DC conductivity measurement were carried out. The DC conductivity data were analyzed by applying small polaron hopping theory.

### II. Experimental Procedure

#### 1. Sample Preparation

Batches to produce glasses with various compositions of CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> system were prepared from well-mixed powders containing appropriate amounts of reagent-grade 99.99% Bi<sub>2</sub>O<sub>3</sub>, 99.9% CuO and 99.9% V<sub>2</sub>O<sub>5</sub> as starting ma-

terials. The batches were placed in a platinum crucible, thereafter melted at 950°C for 1 h in an electric furnace. The melts were quenched by pouring them into ice-cooled water. The resulting frits were dried at 100°C, pulverized in an alumina mortar, then sieved to yield the powder of particle size below 45  $\mu\text{m}$ . The powders were cold-pressed into pellets using a pressure of approximately 10 MPa. The pellets were heat-treated at various temperatures for each time in an air atmosphere.

## 2. Methods of Characterization

The glass transition temperature and crystallization temperature of powder samples were determined using differential thermal analysis (DTA) (SPS-7700, Seiko, Japan) at a heating rate of 5°C min<sup>-1</sup>. The bulk density of the samples was measured by using the Archimedes method. The phases of the samples were identified by X-ray diffractometry (XRD) (D Max-III, Rigaku, Japan) using Ni-filtered CuK $\alpha$  radiation. High-purity quartz was used as a standard material. The morphology of the samples was examined using scanning electron microscopy (SEM) (JSM-5400, Jeol, Japan). Samples for SEM observation were polished with 1  $\mu\text{m}$  diamond paste, then chemically etched with 1% HF+HCl solution for 1 min. The DC conductivity of the samples was measured using high voltage generator measurement (Keithley-237, Keithley, U. S.A.). The DC conductivity measurement was performed in the range of 25°C to 200°C at a heating rate of 5°C min<sup>-1</sup> using two-probe method.

## III. Results and Discussion

### 1. Glass Formation Regions

From DTA and XRD analyses, the glass formation region in the CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> system was obtained as shown in Fig. 1. The chemical composition and physical properties of samples in the present system are shown in Table 1. The composition ranges for glass formation were found to be 5 to 55 mol% CuO, 0 to 20 mol% Bi<sub>2</sub>O<sub>3</sub> and 30 to 90 mol% V<sub>2</sub>O<sub>5</sub>. The glass formation region for the present system was larger than that for the Bi<sub>2</sub>O<sub>3</sub>-SrO-V<sub>2</sub>O<sub>5</sub> system.<sup>16</sup> This suggests that enlarged glass formation region is related to the substitution CuO for SrO. Studies on the reasons for glass formation enlargement are now in progress.

### 2. DTA analysis

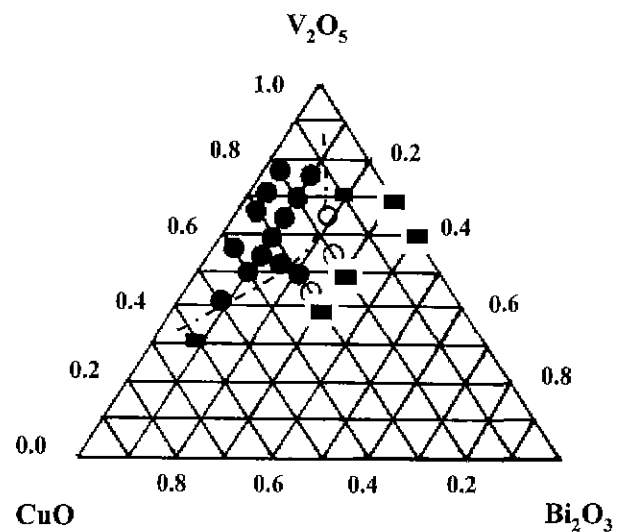


Fig. 1. Compositions studied in the CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> system; ● for glass, ○ for glass and crystal and ■ for crystal.

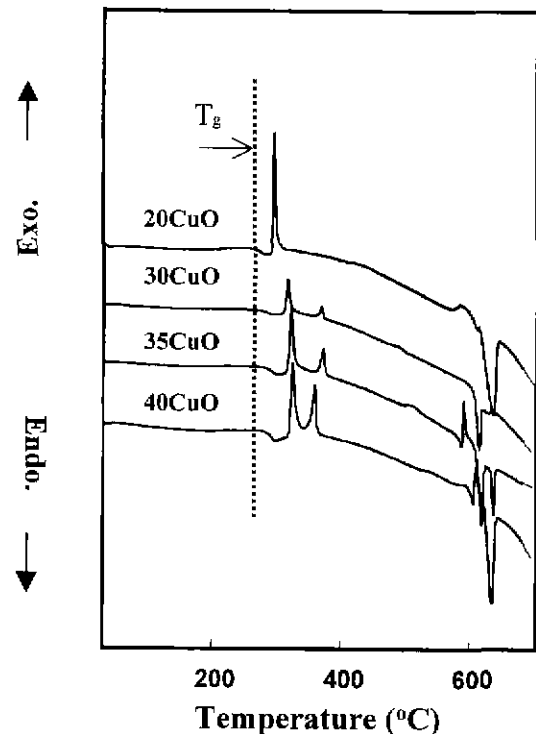


Fig. 2. DTA curves of the xCuO-10Bi<sub>2</sub>O<sub>3</sub>-(90-x)V<sub>2</sub>O<sub>5</sub> glasses with various CuO content at a heating rate of 5°C/min.

Table 1. Chemical Compositions and Properties of the CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> Glass System

Chemical composition (mol%)			Glass Transition Temperature* (T <sub>g</sub> )	Crystallization temperature* (°C)			Conductivity after heat treatment**	Density
Bi <sub>2</sub> O <sub>3</sub>	CuO	V <sub>2</sub> O <sub>5</sub>		1st	2nd	3rd		
10	15	75	273	302	390	417	4.26	3.61
10	20	70	275	320	370	-	7.90	3.81
10	25	65	280	315	370	-	9.40	3.93
10	30	60	282	328	370	-	15.10	3.34
10	40	55	290	320	353	-	9.87	4.48

\*determined by DTA analysis. \*\*heat-treated for 8 h at 2nd crystallization temperature of each sample

Fig. 2 shows the DTA curves of the  $\text{CuO-Bi}_2\text{O}_3\text{-V}_2\text{O}_5$  glasses with various CuO content as a network modifier. Glass transition temperatures of the glasses are at 275 °C-290°C. The first exothermic peaks for crystallization are observed at 302°C-327°C and the second peaks are observed at 353°C-390°C due to complicated crystallization of  $\text{BiVO}_4$ ,  $\text{CuVO}_3$ , and unknown crystalline phases. With increasing CuO content, the glass transition temperature ( $T_g$ ) and first crystallization temperature increased. The increase of  $T_g$  would make glass closer packing in the glass network structure, resulting in an increase in the thermal stability of the glass.<sup>13,17,18</sup> It has been reported that closer packing of glass network structure in the vanadate glasses results in the decrease of V-O-V site spacing.<sup>19,16</sup> Meanwhile, in the  $\text{V}_2\text{O}_5\text{-CuO}$  glass system, the  $\text{Cu}^{2+}$  ion added to  $\text{V}_2\text{O}_5$  is placed between vanadate layers as a glass modifier and changes oxygen coordination around vanadium ion in the glass network from  $\text{VO}_5$  polyhedron with one short V-O bond to  $\text{VO}_5$  polyhedron without that.<sup>13</sup> In this study, it is assumed that the decrease in  $T_g$  is ascribed to the increase in the formation of  $\text{VO}_4$  tetrahedra at the expense of  $\text{VO}_5$  pyramids and to the formation of non-bridge oxygen in  $\text{VO}_4$  tetrahedra as reported by Nishida et al.<sup>14</sup>

With increasing CuO content, the electrical conductivity of glasses was increased as given in Table 1. Electron transport in the present vanadate glass system is considered to occur by an electron hopping between  $\text{V}^{4+}$  and

$\text{V}^{5+}$  ions, mainly due to the increase in  $\text{V}^{4+}$  ion.<sup>13</sup> Further studies on the electron hopping behavior between  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions by CuO addition are currently being investigated using FT-IR spectroscopy and analytical chemical analysis. With increasing CuO content, the density of glasses increased from 3.8 to 4.6  $\text{g cm}^{-3}$  as given in Table 1. This might be related to the  $T_g$  shifting and electrical conductivity variation, reflecting structural differences.

### 3. Crystallization Behavior

Among the glasses with different composition, the 31CuO-14 $\text{Bi}_2\text{O}_3$ -55 $\text{V}_2\text{O}_5$  (mol%) glass showed the highest electrical conductivity. Thus, the 31CuO-14 $\text{Bi}_2\text{O}_3$ -55 $\text{V}_2\text{O}_5$  glass was heat-treated at various temperatures and holding times to investigate crystallization behavior. Fig. 3 shows the XRD patterns of the 31CuO-14 $\text{Bi}_2\text{O}_3$ -55 $\text{V}_2\text{O}_5$  (mol%) glasses heat-treated at 332°C, 358°C, 382°C, 400°C and 450°C for 8h, respectively. No diffraction peak was observed in the XRD pattern of non heat-treated glass, but several sharp diffraction peaks were observed in the XRD patterns of the heat-treated glasses due to the formation of  $\text{BiVO}_4$ ,  $\text{CuVO}_3$  and unknown crystalline phases during the heat treatment. With increasing heat-treatment temperature, the XRD peaks of the heat-treated glasses become more intense. However, the XRD peak of  $\text{CuVO}_3$  crystalline phase was disappeared in the glass heat-treated at 450°C for 8h.

Fig. 4 shows the XRD patterns of the 31CuO-14 $\text{Bi}_2\text{O}_3$ -

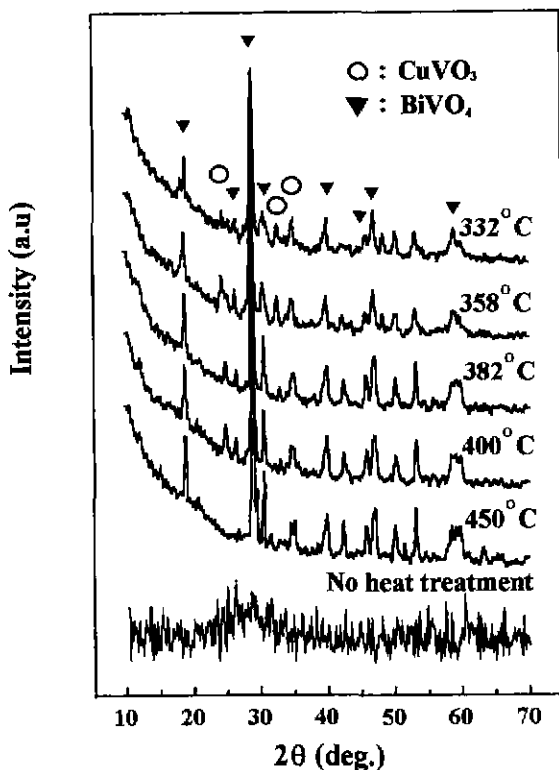


Fig. 3. XRD patterns of the 31CuO-14 $\text{Bi}_2\text{O}_3$ -55 $\text{V}_2\text{O}_5$  (mol%) glasses heat-treated at various temperatures for 8 h.

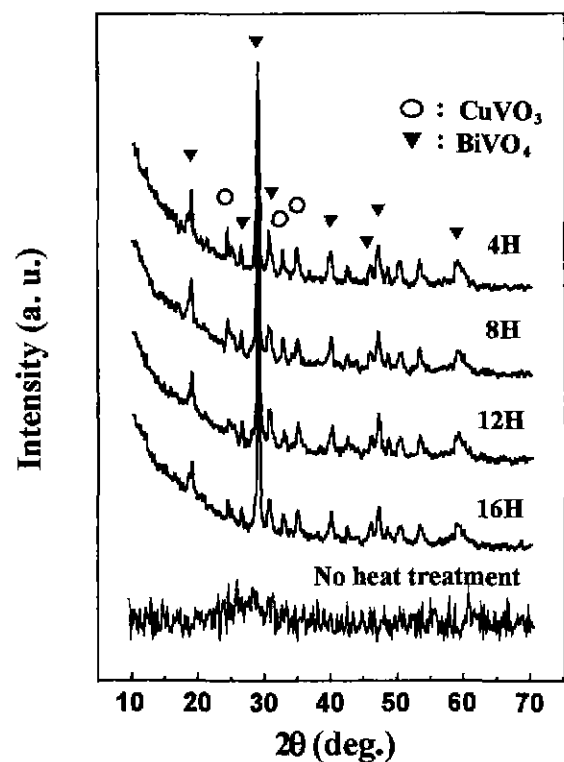
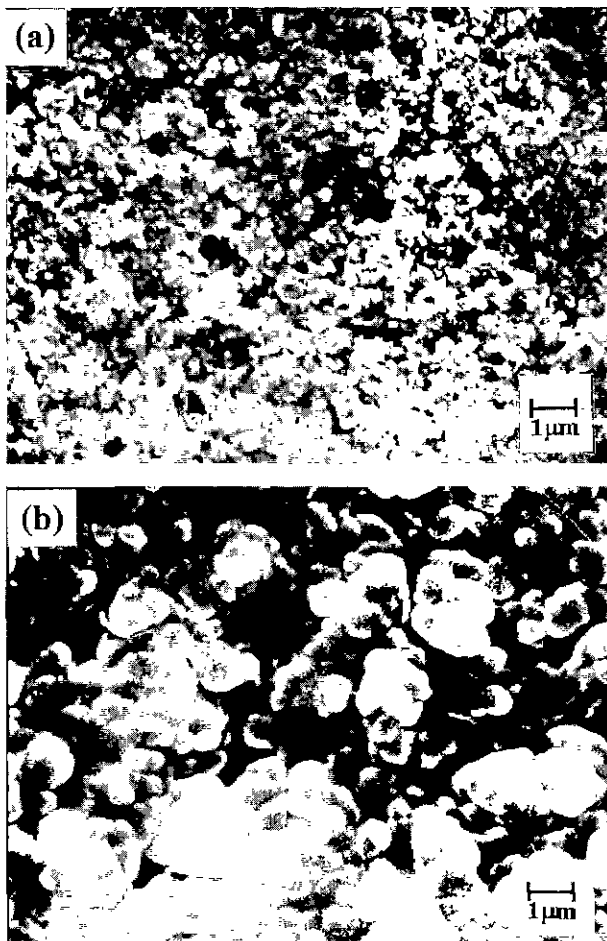


Fig. 4. XRD patterns of the 31CuO-14 $\text{Bi}_2\text{O}_3$ -55 $\text{V}_2\text{O}_5$  (mol%) glasses heat-treated at 358°C for various times.



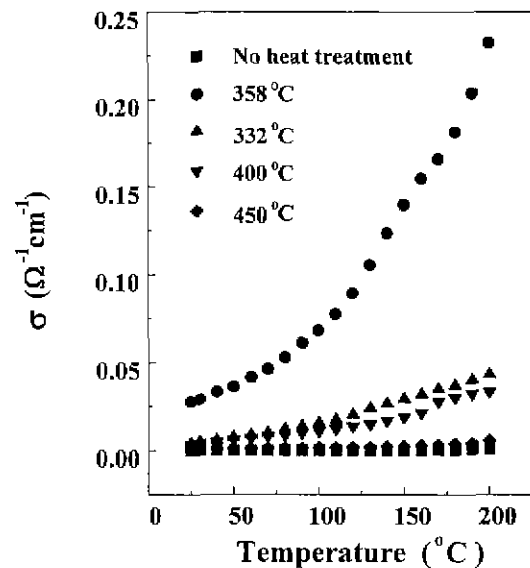
**Fig. 5.** SEM micrographs of the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol %) glasses heat-treated at (a) 358°C and (b) 450°C for 8 h.

55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at 358°C for 4 h, 8 h, 12 h, and 16 h, respectively. With increasing holding time, the XRD peaks of the heat-treated glasses were not much changed. It indicated that crystallization behavior of the heat-treated glasses depended upon heat-treatment temperature more than holding time.

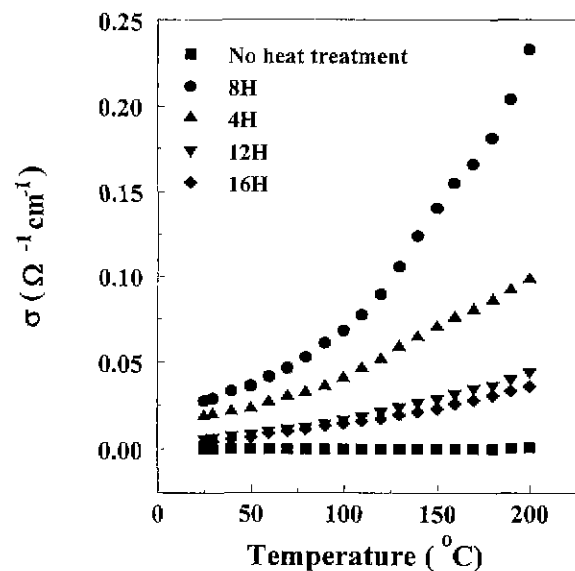
Fig. 5 shows the SEM micrographs of the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at 358°C and 450°C for 8 h. Both the glasses showed that the crystalline phases, such as BiVO<sub>4</sub> and CuVO<sub>3</sub> were grown within glass matrix. The size of crystallites in the glass heat-treated at 358°C was much higher than that in the glass heat-treated at 450°C. This SEM result was consistent with the result of XRD analysis, although crystalline phases were not distinguished each other.

#### 4. Electrical Conductivity

Fig. 6 shows the electrical conductivity of the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) samples heat-treated at various temperatures for 8 h. It is interesting to note that the glass heat-treated at 358°C shows much higher electrical conductivity compared to the glasses heat-treated at various temperatures over 358°C. Fig. 7 shows the electrical



**Fig. 6.** The variation of electrical conductivity as a function of temperature in the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at various temperatures for 8 h.



**Fig. 7.** The variation of electrical conductivity as a function of temperature in the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at 358°C for various holding times.

conductivity of the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at 358°C for various holding times. The electrical conductivity ( $\sim 2.67 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$ ) of the glass heat-treated at 358°C for 8 h was higher than that ( $\sim 2.88 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ ) of non heat-treated glass by the order of  $10^4$ .

Fig. 8 and 9 show the linear relationships between  $\ln(\sigma T)$  and  $T^{-1}$  of the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at various temperatures for 8 h and at 358°C for various holding times. These linear relationships between  $\ln(\sigma T)$  and  $T^{-1}$  suggest that the electrical conduction will be due to a small polaron hopping resulting from electron exchange between V<sup>4+</sup> and V<sup>3+</sup> ions within

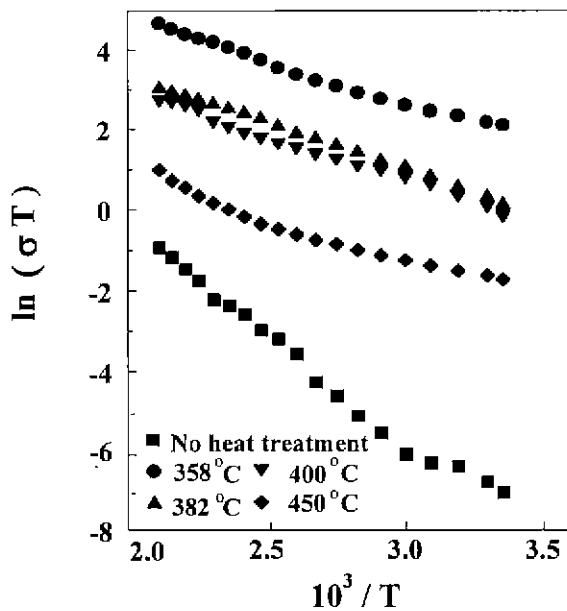


Fig. 8.  $\ln(\sigma T)$  versus  $10^3/T$  in the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at various temperatures for 8 h.

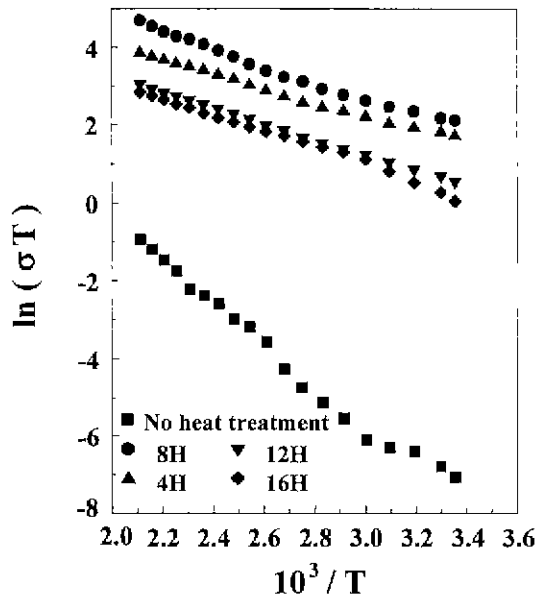


Fig. 9.  $\ln(\sigma T)$  versus  $10^3/T$  in the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glasses heat-treated at 358°C for various holding times.

the glass matrix.<sup>5)</sup> These straight lines in Fig. 8 and 9 can be described in terms of the equation as follows:

$$\sigma = \sigma_0 \exp(-W/kT)$$

where  $W$  is the activation energy for electrical conduction,  $\sigma_0$  is the pre-exponential factor,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The values of activation energy ( $W$ ) as estimated from the data in Fig. 8 were found to be 0.2 to 0.101 eV for the heat-treated glasses and 0.42 eV for non heat-treated glass. It means

that heat treatment for the glasses causes activation energy to decrease and electrical conductivity to increase.

The enhanced electrical conductivity of heat-treated glasses could be ascribed to the increased probability of an electron hopping from  $V^{4+}$  to  $V^{5+}$  which was brought about as a result of the decreasing distortion of VO<sub>4</sub> and VO<sub>5</sub> units and the formation of conducting crystalline phases.<sup>10)</sup> With increasing heat-treatment temperature above 358°C and holding time above 8 h, the electrical conductivity of the heat-treated glasses decreased. That could be ascribed to the decreased probability of an electron hopping from  $V^{4+}$  to  $V^{5+}$  indicating the increase in distortion of VO<sub>4</sub> and VO<sub>5</sub> units due to crystal growth and dissociation of conducting crystalline phases.

#### IV. Conclusions

In the CuO-Bi<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> glass system, glasses were obtained in the composition range of 5 to 55 mol% CuO, 0 to 20 mol% Bi<sub>2</sub>O<sub>3</sub> and 30 to 90 mol% V<sub>2</sub>O<sub>5</sub>. With increasing CuO content,  $T_g$ , first crystallization temperature and density increased due to closer packing of glass network structure. The 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glass with higher density showed the highest electrical conductivity ( $\sim 1.51 \times 10^2 \Omega^{-1} \text{cm}^{-1}$ ) among the glasses with various CuO content.

Compared to non heat-treated glass, the 31CuO-14Bi<sub>2</sub>O<sub>3</sub>-55V<sub>2</sub>O<sub>5</sub> (mol%) glass heat-treated at 358°C for 8h increased in the electrical conductivity by the order of  $10^4$ . The linear relationship between  $\ln(\sigma T)$  and  $T^{-1}$  suggests that the electrical conduction in the present glass system will be due to a small polaron hopping. The values of activation energy were found to be 0.2 to 0.101 eV for heat-treated glasses and 0.42 eV for non heat-treated glass.

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