

# Structural study of semiconducting and superionic conducting silver vanadate glasses

TETSUAKI NISHIDA, HIROSHI IDE, YOSHIMASA TAKASHIMA  
*Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan*

TOSHIROU YAGI, SATORU TOMARIGUCHI, TOHRU ISHIZUKA,  
 AKIRA SAKAI  
*Department of Physics, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan*

A structural study of semiconducting and superionic conducting silver vanadate glasses, containing 40 mol% AgI and 1 mol%  $^{57}\text{Fe}_2\text{O}_3$ , is performed by means of Mössbauer spectroscopy. Distinct composition dependency of Mössbauer parameters ( $\Delta$  and  $\Gamma$ ) of  $\text{Fe}^{3+}$  ions, having a minimum when  $\text{Ag}_2\text{O}$  content is 30 mol%, suggests that increasing  $\text{Ag}_2\text{O}$  content results in a gradual change of the glass matrix from a two-dimensional layer structure composed of  $\text{VO}_5$  tetragonal pyramids to a chain structure composed of  $\text{VO}_4$  tetrahedra. An increase in the Mössbauer parameters observed when the  $\text{Ag}_2\text{O}$  content is higher than 30 mol%, corresponding to a metavanadate structure ( $\text{Ag}_2\text{O}/\text{V}_2\text{O}_5 = 1$ ), indicates a reverse change of the glass matrix into a complicated two- or three-dimensional network structure composed of  $\text{VO}_4$  tetrahedra. These conclusions are in good agreement with those obtained from a distinct composition dependency of glass transition temperatures ( $T_g$ ). Composition dependency of electrical conductivity at room temperature suggests that the structural change of glass matrix primarily affects the semiconductivity caused by a step-by-step electron hopping from  $\text{V}^{4+}$  to  $\text{V}^{5+}$  ions.

## 1. Introduction

Electrical conductivity of so-called superionic conducting glasses is known to reach the order of  $10^{-2} \text{ S cm}^{-1}$  [1-7], which is comparable to that of aqueous solution of  $\text{AgNO}_3$  and  $\text{NaCl}$ . High electrical conductivity in the superionic conducting glasses is due to migrating cations such as  $\text{Ag}^+$  and  $\text{Li}^+$  ions present at interstitial sites in the network structure. Two types of  $\text{Ag}^+$  ions in the superionic conducting glasses are reported [1-3]; those originating from  $\text{AgX}$  molecules ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) and those from  $\text{Ag}_2\text{O}$  molecules. The former type of  $\text{Ag}^+$  ions are considered to be ionically bonded with halide ions at interstitial sites in the network structure, and to be mobile under the electric field. On the other hand,  $\text{Ag}^+$  ions originating from  $\text{Ag}_2\text{O}$  molecules are assumed to be covalently and therefore statically bonded with oxygen atoms. Raman and EXAFS studies of superionic conducting glasses revealed that each mobile  $\text{Ag}^+$  ion is surrounded by four halide ions at interstitial sites in the network structure, forming a microdomain or a distorted sublattice of  $\alpha\text{-AgI}$  type which is known to have a high electrical conductivity [4-6]. Chiodelli and co-workers [7] ruled out the presence of electrical conducting  $\alpha\text{-AgI}$  phase dispersed in the network structure. Electrical conductivity of binary  $\text{Ag}_2\text{O}-\text{B}_2\text{O}_3$  glasses also proved to be much higher than that of ordinary alkali borate glasses. Matusita and Sakka [8] and Tsuchiya

and colleagues [9] report that the conductivity of  $30\text{Ag}_2\text{O} \cdot 70\text{B}_2\text{O}_3$  glass is about  $10^{-6} \text{ S cm}^{-1}$  at  $100^\circ\text{C}$  and is higher than  $10^{-8} \text{ S cm}^{-1}$  at room temperature.

Electrical conductivity of semiconducting vanadate glasses [10-12] is almost comparable to that of superionic conducting oxide glasses described above [1-7]. High electrical conductivity of semiconducting vanadate glasses is reported to be due to a step-by-step electron hopping from  $\text{V}^{4+}$  ions, produced during the sample preparation as a result of thermal decomposition [13], to  $\text{V}^{5+}$  ions originally present in a  $\text{V}_2\text{O}_5$  matrix [14-16]. The electric conduction mechanism in these glasses has been described by using a "small polaron hopping theory" proposed by Mott [17-19]. The crystal structure of  $\text{V}_2\text{O}_5$  was proposed by Byström and colleagues [20] and subsequently by Jansen and Sperlich [21]. The latter authors suggested that each  $\text{V}^{5+}$  ion is surrounded by five oxygen atoms in a distorted  $\text{VO}_5$  tetragonal pyramid, and that  $\text{VO}_5$  tetragonal pyramids form a layer structure by sharing edges and corners with each other. An IR study of semiconducting vanadate glasses performed by Dimitriev and co-workers [22] revealed that an introduction of alkali or alkaline earth oxides into the  $\text{V}_2\text{O}_5$  matrix results in a structural change from  $\text{VO}_5$  tetragonal pyramids to  $\text{VO}_4$  tetrahedra. Furthermore, network structure of the alkali or alkaline earth metavanadate glasses was reported to consist of only

VO<sub>4</sub> tetrahedra [22]. Similar conclusions were obtained in an NMR study of potassium metavanadate (KVO<sub>3</sub>) glass [23]. In contrast to the IR [22] and NMR [23] studies, a neutron diffraction study showed that networks of P<sub>2</sub>O<sub>5</sub>-V<sub>2</sub>O<sub>5</sub>, BaO-V<sub>2</sub>O<sub>5</sub> and PbO-V<sub>2</sub>O<sub>5</sub> glasses consist of VO<sub>5</sub> tetragonal pyramids [24]. A similar conclusion was obtained in the cases of EXAFS and XANES [25] and NMR and ESR [26] studies of P<sub>2</sub>O<sub>5</sub>-V<sub>2</sub>O<sub>5</sub> glasses. <sup>57</sup>Fe-Mössbauer spectroscopy was also applied to the structural study of vanadate glasses by several groups [27-30]. The conclusions obtained from the Mössbauer spectroscopy were inconsistent with each other; the coordination number of Fe<sup>3+</sup> ions was reported to be 6 in the case of BaO-V<sub>2</sub>O<sub>5</sub> glasses [27] and both 6 and 4 in the cases of CaO-B<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> [28], BaO-B<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> [29] and Na<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> [30] glasses.

Mössbauer spectroscopy has so far been applied to a structural study of several kinds of inorganic glasses [31-35]. A relationship between the coordination number of iron in glasses and Mössbauer parameters has been reviewed by Kurkjian [31], Coey [32] and Müller-Warmuth and Eckert [33]. Fe<sup>3+</sup> ions have been reported to occupy tetrahedral sites in borate and silicate glasses [32]. Nishida and co-workers also showed that the coordination number of Fe<sup>3+</sup> ions is 4 in alkali borate [36-42] and alkali borosilicate [42-44] glasses. In the Mössbauer studies of glasses [36-44], isomer shift values of Fe<sup>3+</sup> ions fall in a range of 0.22-0.38 mm sec<sup>-1</sup> with respect to metallic iron. Judging from the experimental results shown in the reviews [31-33] and papers [36-44], we can conclude that the isomer shift of Fe<sup>3+</sup> ions is less than ~0.40 (±0.01) mm sec<sup>-1</sup> when they are tetrahedrally coordinated with oxygen atoms. On the other hand, octahedrally coordinated Fe<sup>3+</sup> ions have been observed in several phosphate glasses [45-48], where the isomer shift values are greater than 0.42 (±0.01) mm sec<sup>-1</sup>. These symmetries do not correspond to "regular" tetrahedra or octahedra, but to "distorted" ones because the iron-oxygen polyhedra in glasses have widely distributed bond angles and bond lengths.

Differential thermal analysis (DTA) measurements are effective when we deduce a structural change of glasses from the glass transition temperatures (*T<sub>g</sub>*). Several experimental results proved that *T<sub>g</sub>* is sensitive to a change of the coordination number of network-forming atoms (network former) and to a formation of non-bridging oxygen, chlorine and fluorine atoms in the network [49-56]. DTA measurements are also useful when we confirm that the structural information obtained from Mössbauer spectroscopy is representative of the whole glass matrix. Based on this idea, Mössbauer spectroscopy and DTA have been applied to the structural studies of superionic conducting silver borate glasses [57-59] and semiconducting alkali vanadate [60-63], alkaline earth vanadate [62, 63], and phosphorus vanadate [64] glasses. The present study was carried out in order to elucidate the structure of silver vanadate glasses and a relationship between the structure and physical properties (*T<sub>g</sub>* and electrical conductivity). In the silver vanadate glasses containing AgI, an ionic conductivity due to Ag<sup>+</sup> ions co-exists

with semiconductivity caused by the electron hopping from V<sup>4+</sup> to V<sup>5+</sup> ions.

## 2. Experimental procedure

Semiconducting and superionic conducting silver vanadate glasses denoted by 40AgI · *x*Ag<sub>2</sub>O · (59 - *x*)V<sub>2</sub>O<sub>5</sub> · 1<sup>57</sup>Fe<sub>2</sub>O<sub>3</sub> were prepared by fusing each mixture of weighed quantities of AgI, Ag<sub>2</sub>O, V<sub>2</sub>O<sub>5</sub> and <sup>57</sup>Fe<sub>2</sub>O<sub>3</sub> of guaranteed reagent grade. Each mixture (0.5 g) in a platinum crucible was fused at 900°C for 1 h, and quenched with ice-cold water. Semiconducting silver vanadate glasses without AgI, denoted by *x*Ag<sub>2</sub>O · (90 - *x*)V<sub>2</sub>O<sub>5</sub> · 10Fe<sub>2</sub>O<sub>3</sub>, were also prepared similarly. Black glasses could be prepared in the compositional ranges of 20 ≤ *x* ≤ 35 and 5 ≤ *x* ≤ 45 for 40AgI · *x*Ag<sub>2</sub>O · (59 - *x*)V<sub>2</sub>O<sub>5</sub> · 1<sup>57</sup>Fe<sub>2</sub>O<sub>3</sub> and *x*Ag<sub>2</sub>O · (90 - *x*)V<sub>2</sub>O<sub>5</sub> · 10Fe<sub>2</sub>O<sub>3</sub> glasses, respectively. All the silver vanadate glasses were preserved in a desiccator placed in the dark. Mössbauer measurements were performed on pulverized sample by a conventional acceleration method, by using a source of <sup>57</sup>Co (10 mCi) diffused into a palladium foil. As a reference of isomer shift, a piece of iron foil enriched with <sup>57</sup>Fe was used. DTA measurements were performed on pulverized sample at the heating rate of 5°C min<sup>-1</sup>, by using α-Al<sub>2</sub>O<sub>3</sub> as a standard. Mössbauer and DTA measurements were carried out under a dry nitrogen atmosphere to prevent the glass sample from absorbing atmospheric moisture. Electrical conductivities were obtained by measuring d.c. resistivities at room temperature.

## 3. Results and discussion

### 3.1. *x*Ag<sub>2</sub>O · (90 - *x*)V<sub>2</sub>O<sub>5</sub> · 10Fe<sub>2</sub>O<sub>3</sub> glasses

A Mössbauer spectrum of semiconducting silver vanadate glasses without AgI consists of a symmetric quadrupole doublet peak due to paramagnetic Fe<sup>3+</sup> ions homogeneously distributed in the glass matrix. This is the case for semiconducting alkali vanadate [60-63], alkaline earth vanadate [62, 63], and phosphorus vanadate [64] glasses studied by Nishida and co-workers. In the case of superionic conducting AgCl-Ag<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> [57], AgI-Ag<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> [58] and AgBr-Ag<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> [59] glasses containing 1 mol % <sup>57</sup>Fe<sub>2</sub>O<sub>3</sub> as a Mössbauer probe, each spectrum consists of an asymmetric quadrupole doublet peak due to Fe<sup>3+</sup> ions substituted for distorted and asymmetric BO<sub>4</sub> units. Isomer shift values of Fe<sup>3+</sup> ions in *x*Ag<sub>2</sub>O · (90 - *x*)V<sub>2</sub>O<sub>5</sub> · 10Fe<sub>2</sub>O<sub>3</sub> glasses are located in a range of 0.38-0.41 mm sec<sup>-1</sup>, having an average of 0.395 mm sec<sup>-1</sup> (Fig. 1). This indicates that all the Fe<sup>3+</sup> ions are present in tetrahedral environments, as observed in several alkali borate [36-42], alkali borosilicate [42-44], and several vanadate [60-64] glasses. In Fig. 1, a composition dependency of the isomer shift for Fe<sup>3+</sup> ions in *x*K<sub>2</sub>O · (90 - *x*)V<sub>2</sub>O<sub>5</sub> · 10Fe<sub>2</sub>O<sub>3</sub> glasses [60] is also shown with a dotted line. Relatively large isomer shift values obtained in the present *x*Ag<sub>2</sub>O · (90 - *x*)V<sub>2</sub>O<sub>5</sub> · 10Fe<sub>2</sub>O<sub>3</sub> glasses will be due to a decreased 4s-electron density at the iron nucleus, caused by the covalency between Ag<sup>+</sup> ion and oxygen atom present at the neighbouring site of Fe<sup>3+</sup> ion. (The Ag<sup>+</sup> ion is generally known to be covalently

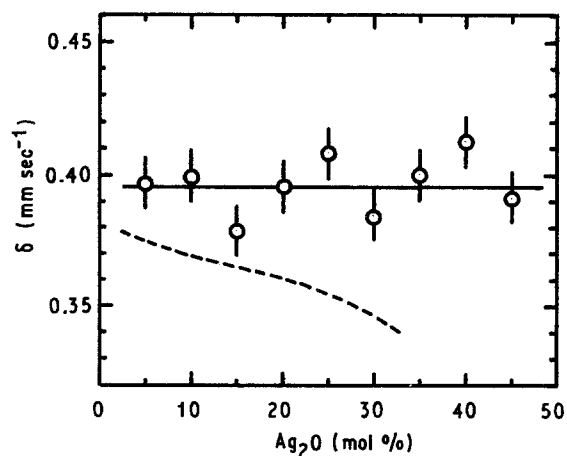


Figure 1 Composition dependency of the isomer shift ( $\delta$ ) of  $\text{Fe}^{3+}$  ions in  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses.

bonded with oxygen atom.) Almost invariable isomer shift values observed in  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses (Fig. 1) will also be correlated with the covalent bond between  $\text{Ag}^+$  ion and oxygen atom.

The formation of non-bridging oxygen atoms in  $\text{VO}_4$  (and  $\text{FeO}_4$ ) tetrahedra was confirmed by the composition-dependent decrease in quadrupole splitting, as is shown with a dotted line in Fig. 2 in the case of  $x\text{K}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses [60]. The composition dependency of quadrupole splitting observed in  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses (Fig. 2) is also ascribed to the formation of non-bridging oxygen atoms in  $\text{FeO}_4$  and  $\text{VO}_4$  tetrahedra. The composition dependency of quadrupole splitting obtained in the present study, which is less pronounced than that of potassium vanadate glasses [60], will be due to the covalent bond between  $\text{Ag}^+$  ion and oxygen atom. The steric configuration of oxygen atoms will be less affected by the covalently bonded  $\text{Ag}^+$  ions than ionically bonded  $\text{K}^+$  ions. It is noted that an ionic radius of  $\text{Ag}^+$  ion is almost comparable to that of  $\text{K}^+$  ion. A gradual decrease in the linewidth of Mössbauer absorption peak (Fig. 3a) may be correlated with the formation of nonbridging oxygen atoms in  $\text{FeO}_4$  and  $\text{VO}_4$  tetrahedra. In Fig. 3, the linewidth of  $\text{Fe}^{3+}$  ions in the semiconducting and superionic conducting  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses is also shown for comparison.

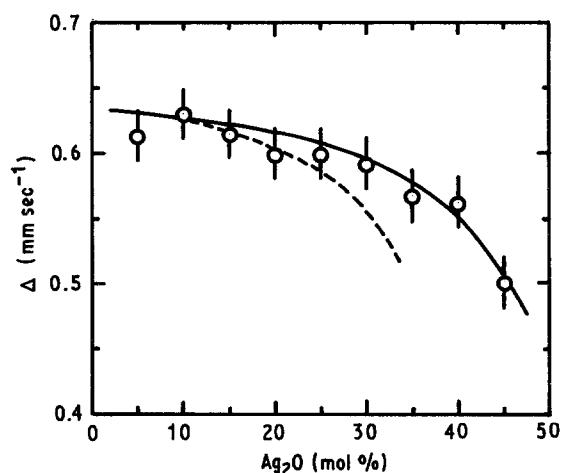


Figure 2 Composition dependency of the quadrupole splitting ( $\Delta$ ) of  $\text{Fe}^{3+}$  ions in  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses.

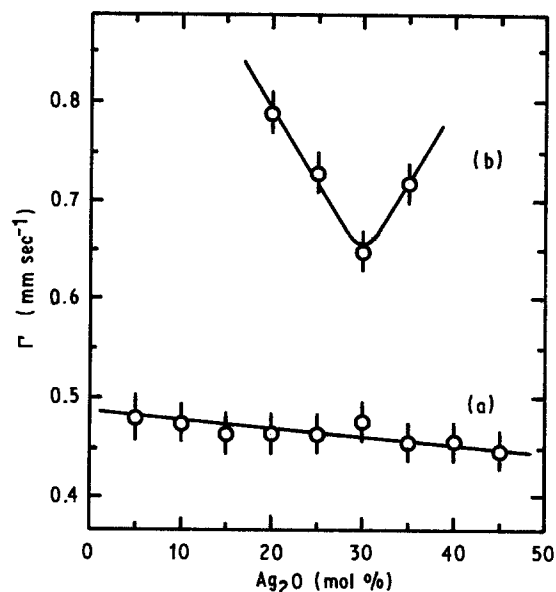


Figure 3 Composition dependencies of the linewidth ( $\Gamma$ ) of absorption peak due to  $\text{Fe}^{3+}$  ions in (a)  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  and (b)  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses.

Composition dependency of  $T_g$  obtained from DTA measurements of  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses is shown in Fig. 4a, which is similar to that of the quadrupole splitting values shown in Fig. 2. In Fig. 4, a dotted line refers to the composition-dependent  $T_g$  values of  $x\text{K}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses [60]. Distinct decrease in  $T_g$  observed with an increasing  $\text{Ag}_2\text{O}$  content is correlated with the formation of non-bridging oxygen atoms in  $\text{VO}_4$  and  $\text{FeO}_4$  tetrahedra and a decrease in the coordination number of  $\text{V}^{5+}$  (or  $\text{V}^{4+}$ ) ions from 5 to 4, as was observed in alkali vanadate glasses [60–63]. The concordant composition dependencies of quadrupole splitting (Fig. 2) and  $T_g$  (Fig. 4a) indicated that the structural information obtained from Mössbauer measurements is representative of the whole matrix of silver vanadate glasses. This is also the case for semiconducting and superionic conducting  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses described later. From the Mössbauer and DTA results obtained for

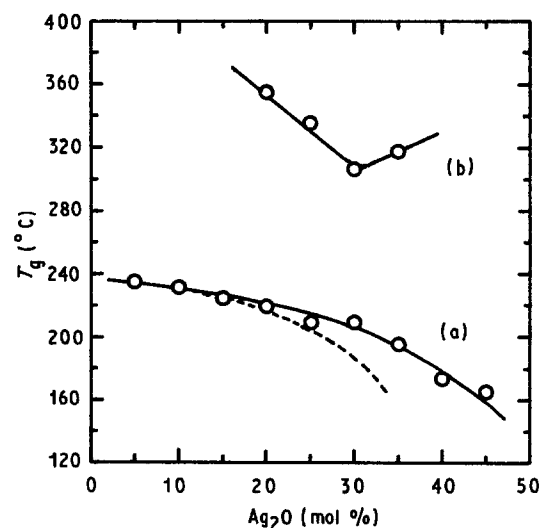


Figure 4 Composition dependencies of the glass transition temperature ( $T_g$ ) of (a)  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  and (b)  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses.

$x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses, we conclude that the structure of silver vanadate glasses is similar to that of alkali vanadate glasses [60–63], except that the chemical bond between  $\text{Ag}^+$  ion and oxygen atom is essentially covalent. The glass matrix (skeleton) gradually changes from a layer structure composed of  $\text{VO}_5$  tetragonal pyramids to a chain structure composed of  $\text{VO}_4$  tetrahedra, where the fraction of non-bridging oxygen atoms increases with an increasing  $\text{Ag}_2\text{O}$  content.

### 3.2. $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$ glasses

A Mössbauer spectrum of semiconducting and superionic conducting  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses consists of a quadrupole doublet peak due to  $\text{Fe}^{3+}$  ions. Isomer shift of the  $\text{Fe}^{3+}$  ions is almost constant irrespective of the composition (Fig. 5a), similarly to that of  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses described above. The isomer shift values indicate the presence of  $\text{Fe}^{3+}$  ions with tetrahedral symmetry. Composition dependency of the quadrupole splitting of  $\text{Fe}^{3+}$  ions in the semiconducting and superionic conducting silver vanadate glasses is shown in Fig. 5b, which shows a minimum when the  $\text{Ag}_2\text{O}$  content is 30 mol %. The quadrupole splitting shows a decrease with increasing  $\text{Ag}_2\text{O}$  content, similarly to the case of quadrupole splitting observed in  $x\text{Ag}_2\text{O} \cdot (90 - x)\text{V}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3$  glasses (Fig. 2). The skeleton of  $40\text{AgI} \cdot 30\text{Ag}_2\text{O} \cdot 29\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glass is equivalent to that of alkali metavanadate glasses ( $\text{R}_2\text{O}/\text{V}_2\text{O}_5 = 1$ ) having a chain structure composed of  $\text{VO}_4$  tetrahedra [22, 23, 60–63]. Therefore, the decrease in quadrupole splitting is ascribed to a change of the glass matrix from a layer structure composed of  $\text{VO}_5$  tetragonal pyramids to a chain structure composed of  $\text{VO}_4$  tetrahedra. At the same time, non-bridging oxygen atoms will be produced in  $\text{VO}_4$  tetrahedra. These conclusions suggest that the structure of semiconducting and superionic conducting silver vanadate glasses containing AgI is essentially the same as that of ordinary silver vanadate glasses without AgI, when the  $\text{Ag}_2\text{O}/\text{V}_2\text{O}_5$  ratio is equal to or less than unity. On the contrary, an increase in the quadrupole splitting, observed when the  $\text{Ag}_2\text{O}$  content is higher than 30 mol %, indicates a decreased symmetry of  $\text{FeO}_4$  and  $\text{VO}_4$  tetrahedra. A

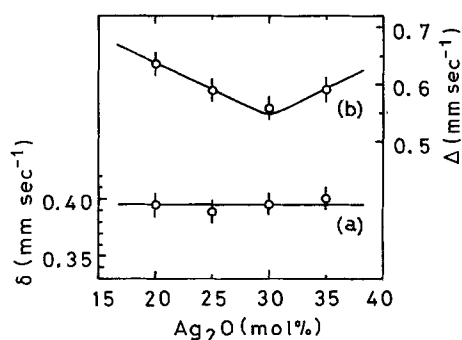


Figure 5 Composition dependencies of (a) isomer shift ( $\delta$ ) and (b) quadrupole splitting ( $\Delta$ ) of  $\text{Fe}^{3+}$  ions in  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses.

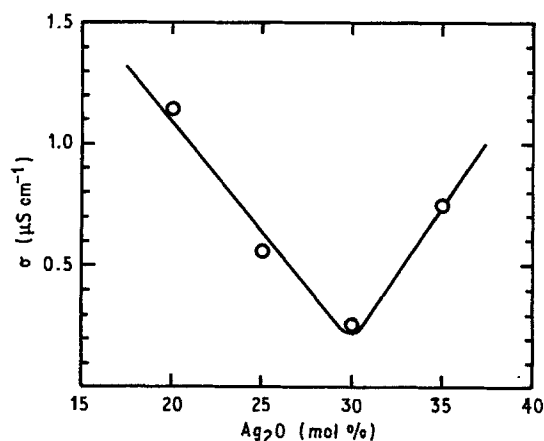


Figure 6 Composition dependency of the electrical conductivity ( $\sigma$ ) of  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses.

similar composition dependency is observed in the linewidth of absorption peak (Fig. 3b). Comparing Fig. 3a with b, we can speculate that bond length and bond angle between  $\text{Fe}^{3+}$  (and  $\text{V}^{5+}$  or  $\text{V}^{4+}$ ) ion and oxygen atom are widely distributed when AgI molecules are incorporated into interstitial sites of the glass matrix. The present Mössbauer results (Figs 3b and 5b) suggest that a reverse change occurs in the glass matrix from the one-dimensional chain structure composed of  $\text{VO}_4$  tetrahedra to a two- or three-dimensional network structure composed of  $\text{VO}_4$  tetrahedra when the  $\text{Ag}_2\text{O}/\text{V}_2\text{O}_5$  ratio is greater than unity.

Such a structural change will be reflected in the physical properties such as  $T_g$  and electrical conductivity. Figure 4b shows the  $T_g$  values of  $40\text{AgI} \cdot x\text{Ag}_2\text{O} \cdot (59 - x)\text{V}_2\text{O}_5 \cdot 1^{57}\text{Fe}_2\text{O}_3$  glasses. A minimum  $T_g$  is observed when the  $\text{Ag}_2\text{O}$  content is 30 mol %. Increased  $T_g$  values indicate a complicated structure of the glass matrix, in which a fraction of bridging oxygen atoms will increase. The structural change of glass matrix is also reflected in the electrical conductivity (Fig. 6), indicating that semiconductivity caused by the electron hopping from  $\text{V}^{4+}$  to  $\text{V}^{5+}$  ions is primarily affected by the structural change of glass matrix. The minimum electrical conductivity (Fig. 6) suggests that an electron hopping from  $\text{V}^{4+}$  to  $\text{V}^{5+}$  ions decreases with a decreasing degree of bridging (cross-linking) of the glass matrix. Ionic conductivity due to  $\text{Ag}^+$  ions migrating at interstitial sites will be enhanced when the size of “space” or “tunnel” is large, where  $\text{Ag}^+$  ions actually pass through under the electric field. This is already observed in silver borate glasses having AgI [58]. If this is the case for silver vanadate glasses, the composition dependency of electrical conductivity will show a maximum when the  $\text{Ag}_2\text{O}/\text{V}_2\text{O}_5$  ratio is unity. However, the experimental result shown in Fig. 6 is quite opposite to this expectation. This suggests that the ionic conduction due to  $\text{Ag}^+$  ions, migrating at interstitial sites of the glass matrix, is less affected by the structural change of glass matrix (skeleton). Apart from  $\text{Cl}^-$  and  $\text{Br}^-$  ions originating from  $\text{AgCl}$  [57] and  $\text{AgBr}$  [59] molecules, respectively,  $\text{I}^-$  ions in silver borate glasses proved to be present at interstitial sites of the glass matrix together with  $\text{Ag}^+$  ions, irrespective

of the composition [58]. This will be true in the case of silver vanadate glasses containing AgI.

#### 4. Conclusion

Structure of semiconducting and superionic conducting silver vanadate glasses containing AgI is to be essentially the same as that of ordinary semiconducting silver vanadate glasses without AgI. When the  $\text{Ag}_2\text{O}/\text{V}_2\text{O}_5$  ratio is smaller than unity, the glass matrix gradually changes from a layer structure composed of  $\text{VO}_5$  tetragonal pyramids to a chain structure composed of  $\text{VO}_4$  tetrahedra with an increasing  $\text{Ag}_2\text{O}$  content. In the case of silver vanadate glasses having the  $\text{Ag}_2\text{O}/\text{V}_2\text{O}_5$  ratio greater than unity, the glass matrix is reversely changed from the chain structure composed of  $\text{VO}_4$  tetrahedra to a two- or three-dimensional network structure composed of  $\text{VO}_4$  tetrahedra. A step-by-step electron hopping from  $\text{V}^{4+}$  to  $\text{V}^{5+}$  is primarily affected by the structural change of glass matrix. An ionic conduction at room temperature, due to  $\text{Ag}^+$  ions migrating at interstitial sites of the glass matrix, seems to be less affected by the structural change.

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