THz Spectroscopy of Superionic Conducting Glasses

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***Abstract*—Far-infrared and millimeter wave reflectivity spectra of iodides-doped silver phosphate glasses were measured. Increase of absorption intensity around 100cm^{-1} shows a structural change of these glasses by the doping. This structural change seems to make these glasses superionic conducting.**

I. Introduction And Background

Enhancement of ionic conductivity by doping of PbI_2 in $AgPO_3$ glass was reported previously[1]. Swenson et al. investigated mechanism of the enhancement on the PbI_2-$AgPO_3$ glass by diffraction measurements and reverse Monte Carlo simulation[2]. They explain the increase of ionic conductivity by that the doped Pb^{2+} substitutes Ag^+ which was connected with non-bonding oxygen and the released Ag^+ contributes to ionic conduction.

The enhancement of ionic conductivity by metal iodide doping has also been reported on BiI_3, CdI_2 and other metal iodides[3]. The increase of ionic conductivity is proportional to dopant concentration and valence number of the metal ion. This paper reports results of far-infrared spectra of dense metal iodides-doped silver phosphate glasses to investigate correlation effect of released silver ions on the enhancement of ionic conductivity, besides the above mentioned structural model.

II. RESULTS

MI_n (M = Bi, Cd and Ag) doped $AgPO_3$ glasses were obtained by quenching melt product by chemical reaction of $NH_4H_2PO_4$, $AgNO_3$ and MI_n at 500 K for 4 hours and subsequent heating at 900 K for 2 hours. Far-infrared and millimeter wave reflectivity spectra were measured by JASCO FARIS spectrometer at UVSOR-II, the Institute for Molecular Science, Okazaki, Japan.

Fig. 1 shows absorption spectra obtained by Kramers-Kronig analysis from the reflectivity spectra of $(BiI_3)_{0.05}(AgPO_3)_{0.95}$, $(CdI_2)_{0.1}(AgPO_3)_{0.9}$ and $(AgI)_{0.5}(AgPO_3)_{0.5}$ glasses. The Ag-O vibration absorption band in $AgPO_3$ glass was reported at 135cm^{-1} [4]. In iodides doped glasses of this study, it was observed at different positions with different band strengths. In $(CdI_2)_{0.1}(AgPO_3)_{0.9}$, the peak was at 128 cm^{-1} and shift slightly toward low wave number. In $(BiI_3)_{0.05}(AgPO_3)_{0.95}$, the strength is more than that in $(CdI_2)_{0.1}(AgPO_3)_{0.9}$ as shown in fig. 1. In $(AgI)_{0.5}(AgPO_3)_{0.5}$, the peak was at 115 cm^{-1} which is rather lower than that in $AgPO_3$. These shift seems to be due to Ag-I production in the doped glasses.

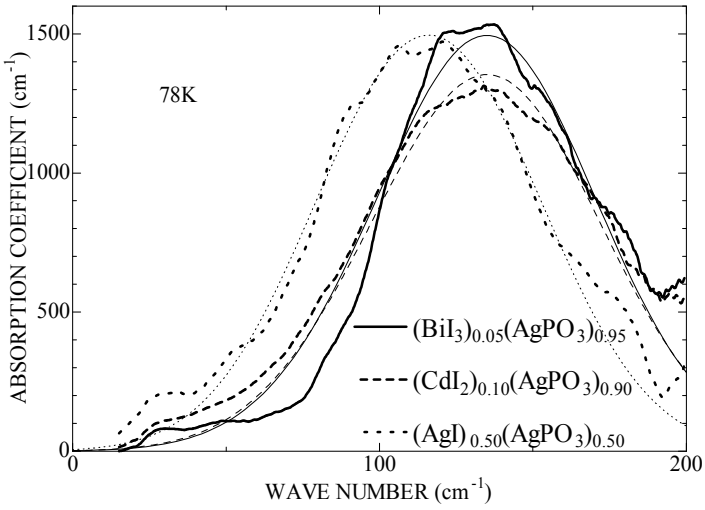

Fig. 1. Absorption spectra of iodides doped silver phosphate glasses. Absorption coefficients were obtained from reflectivity spectra by K-K transformation. Simulation curves (thin lines) by Gaussian components of Ag-I, Ag-O and Bi- or Cd-O vibration were drawn as described in the text.

In the above mentioned model of structural change of the glass, the number of the released silver ions is proportional to the dopant concentration and also the valence number of the doped metal ion. Therefore intensities of newly induced absorption bands by Ag-I are expected to be proportional to the product of the dopant concentration and the valence number. On the other hand, intensity of newly induced absorption band by Cd- or Bi-O is expected to proportional only to the dopant concentration. The intensity of Ag-O vibration should decrease by the product of the dopant concentration and the valence number. The simulation curves in fig. 1 shows the sum of each Gaussian component of Ag-O, Ag-I and Cd- or Bi-O vibration, which are centered at 135, 100 and 165 cm^{-1}. The intensity of each band is added or subtracted as above mentioned. Net absorption spectra calculated by these component bands are shown by thin lines in fig. 1. These simulation spectra well agree with the observed one.

The far-infrared spectral change showed the mechanism of the enhancement of ionic conductivity in iodides doped silver phosphate glasses. A doped metal ion substitutes a silver ion which is connected with a non-bonding oxygen. The released silver ion is coordinated weakly with an iodine ion and conducts easily. This mechanism is the same as that in PbI_2-$AgPO_3$ glass. The correlation effect seems to exist in lower wave number region.

Classical molecular dynamics simulation was done using MXDORTO program[5]. Two-body potential of Born-Mayer

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type was adopted in the simulation program. Number of atoms was 291 for silver ion and those of others were as in the formula of $(BiI_3)_{0.05}(AgPO_3)_{0.95}$. Simulation calculation was also executed on $AgPO_3$ for comparison. Effective charge of each ion was reduced by 60 percent. The start temperature was 1000 K and reduced to 300 K in 10000 steps (20 ps). Then simulation was continued for 50000 steps at 300 K and some physical properties were acquired. Ionic conductivity of silver ion estimated from the inclination of the mean square distribution was 1.2×10^{-3} Scm^{-1}, which almost agreed with the observed one.

Fig. 2 shows pair correlation functions of each ion pair. In Bi-O pair, distribution peak was at 1.75 Å. The distance between Ag and O was also 1.75 Å as seen in the figure. This suggests that all the doped Bi^{3+} ions replaced silver ions and combined with nonbonding oxygen ions. There was no additional peak between silver and other ions in doped glasses comparing with undoped $AgPO_3$. This suggests that the replaced silver ions move in the glasses. The released Ag^+ ions were coordinated with I^- ions with distance of 2.1 Å. This seems to help the conducting silver ions for reducing activation energy and keeping conduction pathways. Other pair correlation functions were the same as those in $AgPO_3$.

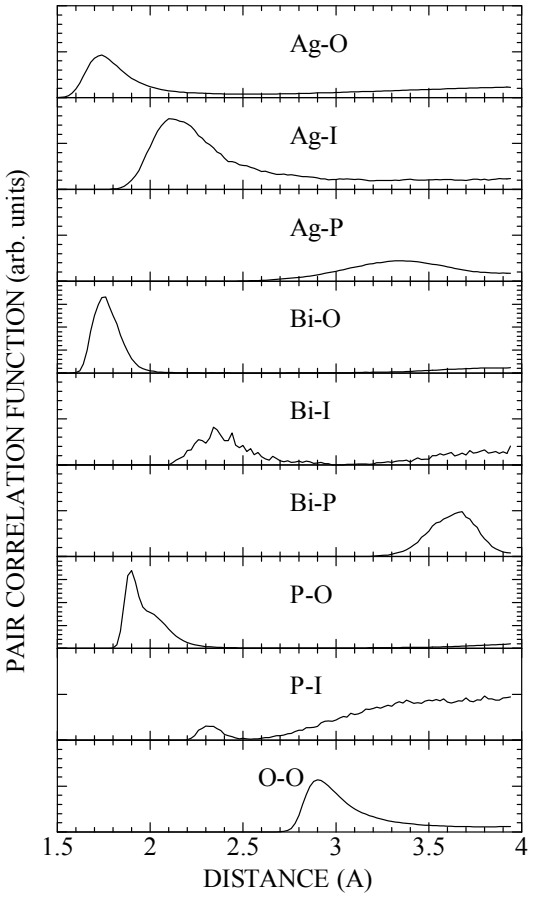

Fig. 2. Pair correlation function of $(BiI_3)_{0.05}(AgPO_3)_{0.95}$.

Fig. 3 shows velocity autocorrelation function (VAC) of each ion. The VAC corresponds to absorption spectrum by movement of each ion. The intense band at low wave number of

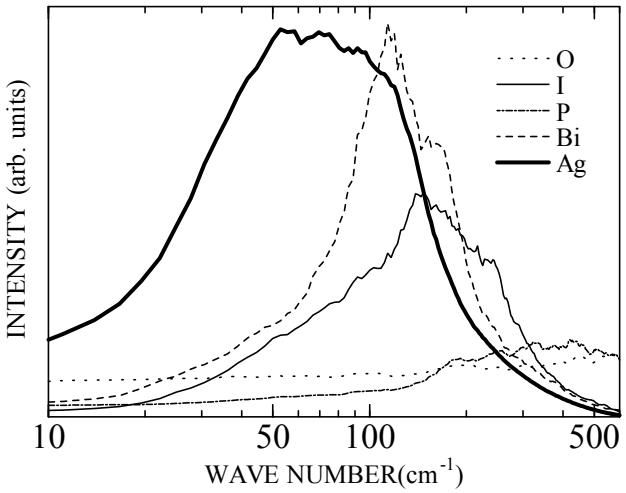

Fig. 3. Velocity autocorrelation function of each ion in $(BiI_3)_{0.05}(AgPO_3)_{0.95}$.

silver ion is due to large movement of conduction ion. The THz peak shift between Ag-I and Bi-O in fig.1 corresponds to the peak position difference between Ag and Bi in fig. 3.

All these facts mean that all the doped metal ions substitute silver ions which were connected with nonbonding oxygen ions. The released silver ions are coordinated weakly with iodine ions and conduct easily.

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