Coherent Excitation in Superionic Conductors

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***Abstract*—Millimeter wave absorption spectra of superionic conducting glasses were measured using coherent THz light from KURRI-LINAC. Silver halides doped silver phosphate glasses have two absorption bands in millimeter wave region. These bands seem to be due to a collective motion of conduction ions.**

I. Introduction And Background

Movement of ions is not in phase and frequent scattering by other mobile ions seems to decrease the ionic conductivity. If coherent excitation of ionic movement by coherent external electric field occurs, ionic conductivity seems to increase drastically. One of authors (Awano) has investigated sub-millimeter and far-infrared spectroscopy of superionic conductors to find such a correlative movement of conduction ion with incoherent synchrotron radiation. Broad peak was observed at sub-millimeter wave region in energy loss function spectra of MA_4X_5 (M = Rb, K, NH_4; A = Ag or Cu; X = I or Cl) crystals[1-3]. This peak was able to be considered as that by "ionic plasmon".

Coherent THz wave from LINAC of Research Reactor Institute of Kyoto University (KURRI) is so strong that the excitation effect is expected to be observed. If this excitation occurs, absorption spectrum in this region should change. The coherent THz light is extremely strong so that precise absorption measurement of thick sample is possible. We have measured millimeter wave absorption spectra of silver halides - silver phosphate glasses to investigate the excitation of such a collective movement of conduction ion.

II. Results

Each content of AgI (of 99 % by Kojima Chem. Co. Ltd.), AgBr (of 98 % by Kanto Chem. Co. Ltd.), $AgNO_3$ and $NH_4H_2PO_4$ were melt at 900 K for 3 hours after chemical reaction at 500 K. Then the liquid was quenched between two copper blocks. The glass formation was checked by X-ray diffraction. Sample diameter was 20 mm and thicknesses were around 400 μm and 800 μm.

Pairs of transmittance spectra of thin and thick plates were measured to obtain absorption coefficient. They were measured by a Martin-Puplett type interferometer at KURRI-LINAC. Signal detection was done by a liquid-He-cooled Si-bolometer. The coherent millimeter wave was extremely strong so that the pre-amplifier of the bolometer was not necessary. Precisely measurable region was 4 to 10 cm^{-1}, however, because strong sample absorption made spectra uncertain above 10 cm^{-1}.

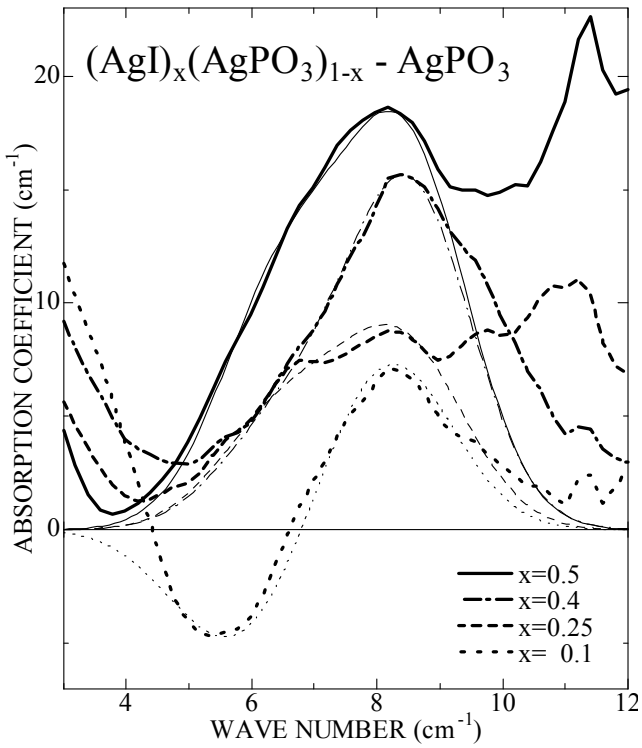

Fig. 1. Difference absorption spectra (thick lines) of AgI-doped $AgPO_3$ glasses from that of undoped $AgPO_3$ glass. Thin lines show the calculated Gaussian absorption curves.

Fig. 1 shows increment spectra of AgI-doped $AgPO_3$ glasses. Differences from the spectrum of undoped $AgPO_3$ glass are shown. Two absorption bands were separated at 8.4 cm^{-1} (A-band) and 6.3 cm^{-1} (B-band). Summations of Gaussian fitting curves of these bands are shown by thin lines respectively. Increment of intensity of the A-band is roughly proportional to the AgI content. This suggests that the A-band is related with AgI molecule or each atom in it. The intensity of B-band decreased first and then increased as the AgI content was increased.

As AgI-doped one, increase of absorption intensity by adding AgBr was observed at 8.7 cm^{-1} (A-band) and 6.1 cm^{-1} (B-band). Increment of intensity of the A-band is roughly proportional to the AgBr content. This clearly shows that the A-band is related with AgBr molecule or each atom in it. The intensity of B-band decreased first and then increased as the AgBr content was increased as that in the AgI-doped one. The averaged peak position of A-band over AgBr content, 8.65 cm^{-1}, is 3% larger than that in AgI-doped one, 8.40 cm^{-1}. This shift toward high frequency in AgBr-doped glass suggests that the A-band is related with a vibration in a silver-halogen pair. This ratio is small, however, comparing with that of inverse of

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square root of reduced mass ratio of AgBr and AgI (13%). This suggests that these absorption bands are concerned with not a single molecule but a large number of silver ions and a small number of halogen ions. Phonon band of AgI or AgBr crystal is around 80-100 cm^{-1}. Therefore these 8 cm^{-1} band should be caused by another mechanism. If this frequency difference between 80 and 8 cm^{-1} suggests that the number of concerned silver ions with this absorption is large, the number should be around one hundred. Such a large number suggests aggregation of silver ions or correlation of their movement.

The 8 cm^{-1} band was absent in the $RbAg_4I_5$ crystal, which is one of the most superionic conducting crystals at room temperature. This suggests that the movement of Ag ion in these glasses is a sort of average motion in random structure. However, this absorption band is not caused by static random structure of glass itself, because it vanished at low temperature.

Molecular dynamics simulation was also executed on the $(AgX)_{0.4}(AgPO_3)_{0.6}$ (X = Br, I) glasses. The MXDORTO program[4] by Prof. K. Kawamura of Tokyo Institute of Technology was used for the calculation. Two body potential of Born-Mayer type was adopted.

$$U_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\frac{a_i + a_j - r_{ij}}{b_i + b_j} - \frac{c_i c_j}{r_{ij}^{\,6}}$$

Parameters of the simulation calculation are summarized in Table 1.

Fig. 2 shows power spectra of each Cartesian coordinate of silver ions. The main peak around 15-20 cm^{-1} seems to be due to the "attempt mode", which is the outward movement of a silver ion within a halogen cage. The frequency difference between AgI-doped glass and AgBr-doped one seems to be due to the difference of reduced mass of AgX_4.

Another shoulder peak appeared around 7 cm^{-1} in AgI-doped glass or 8 cm^{-1} in AgBr-doped one. This band seems to correspond to the observed band in the millimeter absorption spectra.

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Table 1. Parameters of Born-Mayer potential of $(AgI)_{0.4}(AgPO_3)_{0.6}$ glass. Notations are the same as in the equation.

Element	Number of ions	Effective charge Z (e)	Ionic radius a (A)	b (A)	c (A^3)
O	900	-1.2	1.91	0.08	20.0
I	200	-0.9	2.00	0.08	50.0
P	300	3.2	0.99	0.08	0
Ag	500	0.6	063	0.10	0

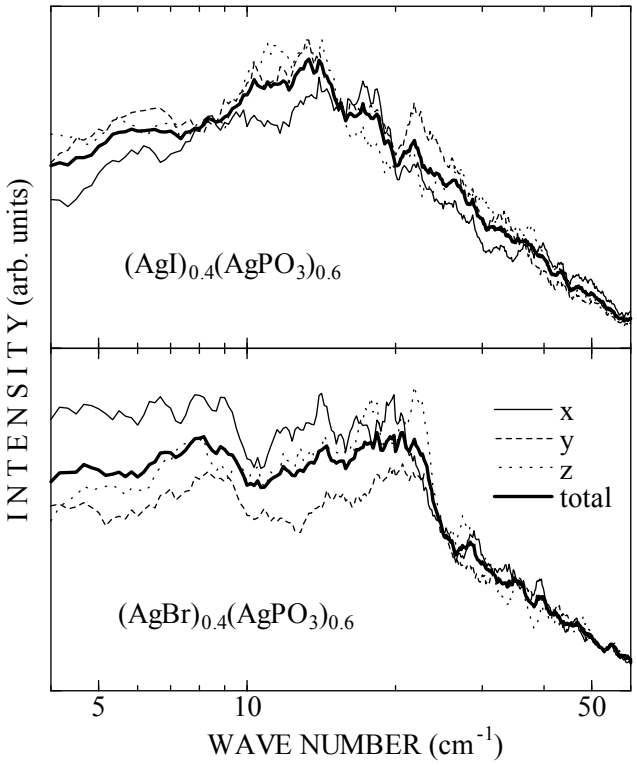

Fig. 2. Power spectra of each Cartesian coordinates of silver ions. Average spectra of three directions are shown by thick solid lines.