7.4 Radiation Damages on Superionic Conductors

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Abstract Irradiation coloration on superionic conductors of MA_4X_5 (M=K, Rb, NH_4; A=Ag, Cu; X=Cl, I) was observed. Five absorption bands were observed at 1.4, 1.8, 2.1, 2.3 and 2.9 eV in $RbAg_4I_5$. In these crystals, stable coloration was observed at lower temperature than in alkali halides. The absorption bands due to electronic centers and hole one were classified from the results of optical breaching and electron or hole doping. Growth rate and induced spectra by irradiation changed drastically at the temperatures just above the superionic phase transition. The growth rate increased drastically also at 40 K. ESR signal of γ-irradiated $RbCu_4Cl_3I_2$ showed that one of the induced defects is a hole trapped by a monovalent copper ion (Cu^{2+}).

INTRODUCTION

Superionic conductors contain a lot of ion vacancies. If the vacancies trap electrons or holes, color centers may be created as in alkali halides and coloration may occur easily. The induced defects may show characters which reflect the high ionic mobility. There have been, however, few studies on the radiation damages on superionic conductors.

MA_4X_5 (M=K, Rb, NH_4; A=Ag, Cu; X=Cl, I) have the highest ionic conductivity at room temperature and hold it even at the low temperature region, for example, above 122 K in $RbAg_4I_5$ (Owens and Argue, 1967). It has been reported that coloration occurs on $RbAg_4I_5$ in iodine vapor at room temperature (Andreev et al., 1984). This means that the critical temperature of additive coloration is very low comparing with that in alkali halides. We have investigated irradiation coloration at low temperature.

EXPERIMENTAL

Single crystals of MAg_4I_5 were grown from the hydroiodic acid solution saturated with the stoichiometric compounds. Crystals of $RbCu_4Cl_3I_2$ were grown from melt of stoichiometric compound. The crystals were composed of several small domain of single crystals. γ-Ray irradiation and ESR measurement were done at ^{60}Co facility of Research Reactor Institute, Kyoto University. X-ray irradiation was done under the condition of W-target, 40 kV and 20 mA.

RESULTS AND DISCUSSION

Irradiation induced absorption bands were at 1.35, 1.80, 2.05, 2.32 and 2.85 eV in $RbAg_4I_5$ and 1.71, 2.00, 2.35 and 2.95 eV in KAg_4I_5 and 1.75, 2.05 and 2.98 eV in $NH_4Ag_4I_5$ (Awano et al., 1990, 1992). Only the band around 2.9 eV appears by additive coloration by iodine vapor. This means that the 2.9 eV band is due to trapped holes and others are due to trapped electrons. This is supported by the results of coloration on electron or hole doped crystal. Electron doping enhanced the bands except the 2.9 eV band and hole doping enhanced the 2.9 eV band. The results of optical bleaching also support that. The intensities of all bands except the 2.9 eV band were decreased by illumination of the light of corresponding photon energies of each band.

A drastic increase of the coloration rate at temperatures just above the superionic phase transition was observed on MAg_4I_5. This seems to be due to the competition of the increase of the number of the vacancy of the conduction ion and the increase of the mobility of it.

Coloration rate by x-ray irradiation on $RbAg_4I_5$ increased drastically also at 45 K. Fig. 1 shows the growth rate of induced absorption bands by x-ray irradiation. No

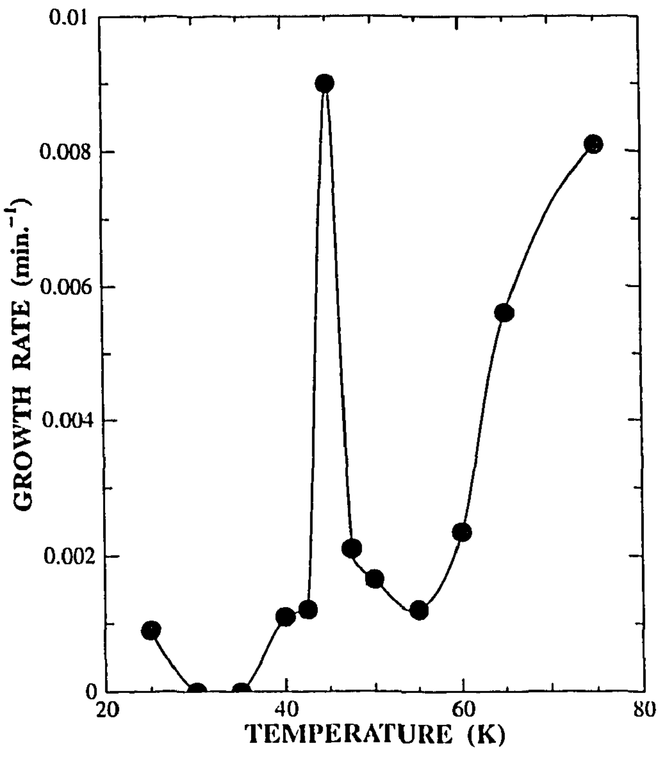

Fig. 1. Irradiation temperature dependence of the growth rate of each absorption bands induced by x-ray irradiation. No coloration was induced by irradiation at the temperature between 30 and 37 K. Below 30 K, the induced absorption bands were very broad as shown in fig. 2.

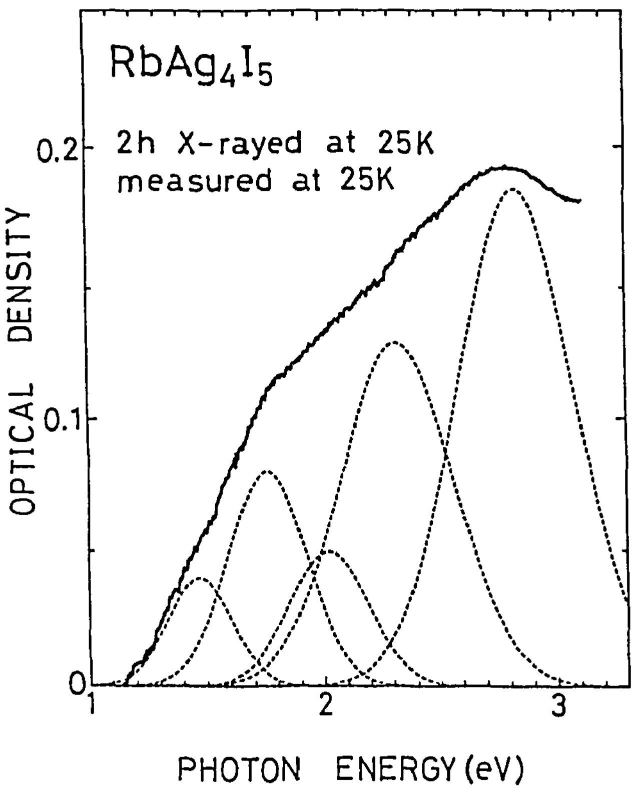

Fig. 2. Induced absorption spectrum by x-ray irradiation on $RbAg_4I_5$ at 25 K. The dashed lines show Gaussian components assuming the same peak energies as those above 45 K.

absorption bands were induced by irradiation at around 35 K. The induced absorption spectra by irradiation below 30 K were different from those above 40K. An example of the induced absorption spectra is shown in fig. 2. The dashed lines show Gaussian components assumed to have the same peak energies as those by higher temperature irradiation. The absorption bands by irradiation at temperature lower than 30K were very broad. This temperature is around the phase transitions in non-superionic phase at 44K and 30K, which were recently reported by Volkov et al. from the measurement of submillimeter transmission (Volkov et al., 1986).

In the case of $RbCu_4Cl_3I_2$, irradiation induced absorption spectrum were different from those of MAg_4I_5. Fig. 3 shows the induced net absorption spectrum of $RbCu_4Cl_3I_2$ x-ray irradiated at 77 K. Absorption bands were induced at 1.9, 2.4 and 2.8 eV. These bands were disappeared at 110 K in annealing process. Examples of ESR spectra from an irradiated crystal are shown in fig. 4. Angular dependence on the direction of external magnetic field was observed as shown by curve a and b. Curve b in fig. 4 has peaks at g = 2.43, 2.34, 2.26, 2.18 and 2.11. These g-values indicate that the defect is a hole. The spectrum b in the fig. 4 is similar to that of the hyperfine structure of Cu^{2+}, for example in AgCl crystal, which has four lines of the hyperfine structure by the nuclear spin of 3/2 (Fukui et al., 1973). Therefore, observed ESR spectra are able to be interpleted as that of a hole trapped by a Cu^+ ion. The large width of lines seems to be due to the polycrystalline sample. This signal vanished at 160 K in annealing process and

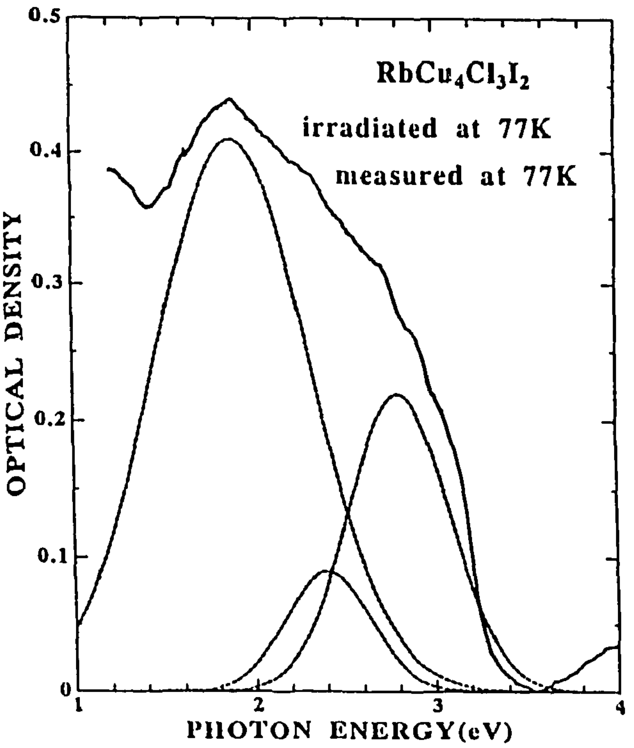

Fig. 3 Induced absorption spectrum by x-ray irradiation on $RbCu_4Cl_3I_2$ at 77 K. The dashed lines show Gaussian components.

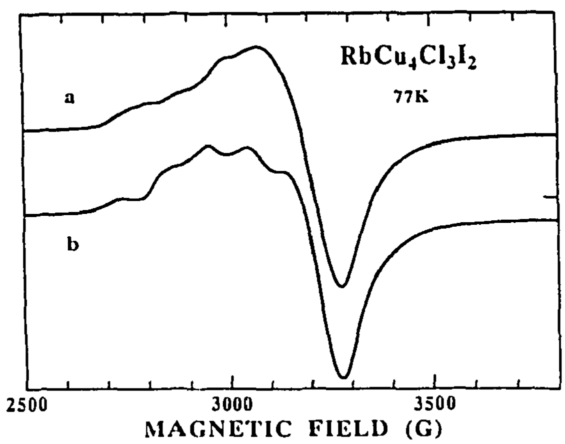

Fig. 4. ESR spectra of γ-irradiated $RbCu_4Cl_3I_2$ at 77 K. The direction of the magnetic field is 90 degrees apart from each other for lines a and b. The microwave frequency is 9.288 GHz.

another weak signal grew at g = 2.13. This new signal disappeared at 210K.

CONCLUSIONS

Irradiation induced signals of ESR and optical absorption were different between silver ion conductors and the copper ion conductor. This suggests that different electronic structure cause different radiation damages even in the crystals with the same crystal structure.

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REFERENCES

Andreev V. N. and Goffman V. G. (1984) Sov. Phys. Solid State **25**, 2004.

Awano T., Ikezawa M., Matsuyama T. and Yamaoka H. (1990) Solid State Ionics **40/41**, 324.

Awano T., Nanba T. and Ikezawa M. (1992) Solid State Ionics **53-56**, 1269.

Owens B. B. and Argue G. R. (1967) Science, **157**, 308.

Volkov A. A., Goncharov Y. G., Goffman V. G., Kozlov G. V., Mirzoyanz G. I. and Torgashev V. I.(1986) Zh. eksper. teor. Fiz. Pisma **43**, 280.

Fukui M., Hayashi Y. and Yoshioka H. (1973) J. Phys. Soc. Jpn., **34**, 1226.