

13.6 Self-trapped Holes in Alkali Silver Halide Crystals

T. Awano, M. Ikezawa *and T. Matsuyama**

Department of Applied Physics, Tohoku Gakuin University, Tagajo 985, Japan

*Research Institute for Scientific Measurements, Tohoku University, Sendai 980-77, Japan

**Research Reactor Institute, Kyoto University, Osaka 590-04, Japan

Abstract γ -Ray irradiation at 77 K induces defects in M_2AgX_3 ($M=Rb, K$ and NH_4 ; $X=Br$ and I) crystals. The irradiation induces self-trapped holes of the form of I^0 in the case of alkali silver iodides, and $(halogen)_2^-$ and $(halogen)^0$ in the case of ammonium silver halides. The $(halogen)^0$ is weakly coupled with the nearest alkali metal ion or ammonium ion. It is able to be denoted as RbI^+ , KI^+ , NH_4I^+ or NH_4Br^+ . The directions of hole distribution of $(halogen)_2^-$ and $(halogen)^0$ were different in each case of the alkali silver iodides, ammonium silver halides and mixed crystal of them. The $(halogen)^0$ decayed at 160 K in annealing process. The $(halogen)_2^-$ was converted into another form of $(halogen)_2^-$ at 250 K and this decayed at 310 K. A formation of metallic layers was observed on the crystal surface parallel with the c -plane of $(NH_4)_2AgI_3$ irradiated at room temperature.

INTRODUCTION

Alkali silver halide or ammonium silver halide crystals of the formula of M_2AgX_3 ($M=Rb, K$ and NH_4 ; $X=Br$ and I) are orthorhombic and belong to the space group of D_{2h}^{16} (Brinc and Kroase, 1954). A unit cell contains four molecules as shown in Fig. 1, which shows a projection of a unit cell along the b -axis of the crystal. A silver ion is surrounded by a tetrahedron formed by halogen ions. This tetrahedron is connected along the b -axis.

The top of the valence band is mainly composed of the p -orbital of the halogen ion and the lowest conduction band is s -orbital of the silver atom. The energy levels of $Ag(4d)$ and $X(p)$ are close and they are mixed to form the uppermost valence band (Edamatsu et al., 1989).

This crystal structure and energy band structure are different from those of alkali halides, in which defect formation process has been well investigated. We have investigated the structure of defects in M_2AgX_3 by ESR measurements to study the relation between the defect formation and the energy band structure.

In the case of alkali halides and ammonium halides, there is no difference in the structure of the self trapped holes (STHs). It was found by this study that different forms of STHs are stable in alkali silver halides and ammonium silver halides. It is interesting to investigate the reason why those STHs have different stable forms in alkali silver halides from

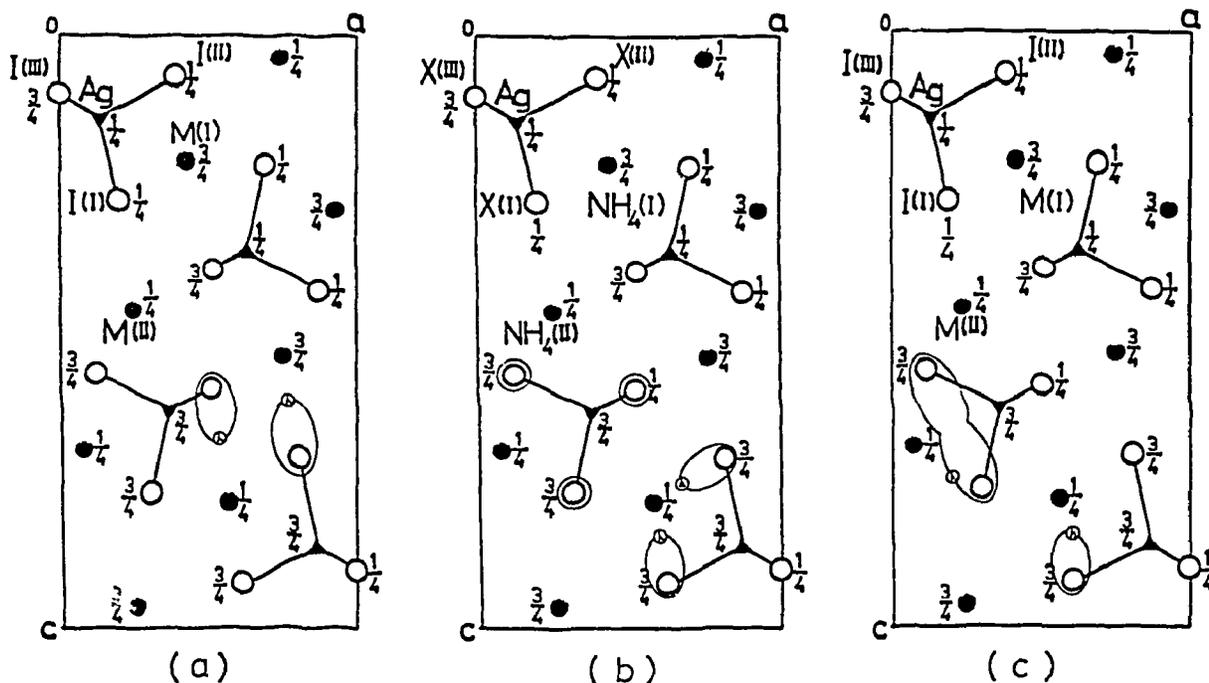


Fig. 1. Crystal structure of (a) alkali silver iodides, (b) ammonium silver halides and (c) alkali-ammonium silver halides. A unit cell is projected on ac plane. Figures show b -coordinates of each ion. "M" in (a) denotes alkali metal ion, "X" in (b) denotes halogen ion. "M" in (c) denotes rubidium or ammonium ion. Schematic distributions of self-trapped holes are shown in the figure. In (b), X_2^- is parallel to the normal of the ac plane of the crystal. It is shown as simple circle in the figure. (See text.)

those in ammonium silver halides. Thus, we also have investigated the structures of self-trapped holes in the mixed crystal of alkali silver halides and ammonium silver halides of the formula of $(M_x(NH_4)_{1-x})_2AgX_3$.

EXPERIMENTAL

Single crystals of M_2AgX_3 were prepared from saturated aqueous or hydrohalogenoid acid solution of stoichiometric compounds of MX and AgX . The dimension of obtained crystal was $7 \times 15 \times 30 \text{ mm}^3$ at maximum. γ -Ray irradiation was done by the ^{60}Co facility at the Research Reactor Institute of Kyoto University. The dose was about 50 Mrad in ammonium silver halides and 200 Mrad in alkali silver halides. Mixed crystals of alkali silver iodide and ammonium silver iodide were grown in saturated aqueous solution of a mixture of NH_4I , MI ($M=K, Rb$) and AgI . A part of alkali metal ions seems to be substituted by ammonium ions in the crystal considering from x-ray diffraction analysis. The concentration ratio of Rb and NH_4 was determined by neutron activation analysis.

RESULTS AND DISCUSSION

The characteristic feature of ESR spectra of M_2AgI_3 γ -irradiated at 77 K was as follows (Awano et al., 1989). Each of four sets of component has six hyperfine structures of

an equal intensity. Each set of hyperfine structure is due to a single iodine nucleus which has a nuclear spin of $5/2$. The g tensor and the hyperfine tensor have the uniaxial symmetry whose axes are almost coincident with directions between I(I) and the nearest alkali metal ion M(II) or I(III) and M(I) in the fig. 1(a). Super-hyperfine structure is due to a nearest alkali metal nucleus. The main contribution is due to ^{39}K of which natural abundance is 93.2 % and nuclear spin is $3/2$ in the case of K_2AgI_3 . The above results show that the defect formed in both crystals is a pair of iodine ion and an alkali ion at the sites I and III but not in the site II. It can be denoted in a simple way as KI^+ and RbI^+ molecule. The mixing of Ag $4d$ -orbital with the I $5p$ -orbital may be larger at the site II and this may be the reason of the difficulty of the localization of a hole.

In the ESR spectra of $(\text{NH}_4)_2\text{AgI}_3$ γ -irradiated at 77 K, each of two sets of component has six hyperfine structures of an equal intensity (Awano et al., 1993). The super-hyperfine structure of the three lines of an equal intensity and splitting is due to a nitrogen nucleus. The hole is located at I(I) or (II) and slightly distributed to the nearest $\text{NH}_4(\text{I})$ as shown in fig. 1(b). Hyperfine parameters of I^0 are almost the same as those in alkali silver halides. Beside the hyperfine structure of I^0 , hyperfine structure of I_2^- is observed. The I_2^- has its axis parallel with the b -axis of the crystal. Hyperfine parameters of I_2^- are almost the same as those in alkali iodides.

In the case of $(\text{NH}_4)_2\text{AgBr}_3$, each of two sets of several lines has four hyperfine structures with an equal splitting and an almost equal strength, beside the large structure centered at $g=2$ (Awano and Matsuyama, 1994). The former signal is due to Br^0 weakly coupled with a nitrogen nucleus and hydrogen nuclei. The uniaxial directions of Br^0 s are coincide with the direction between each Br^- ion located on the sites I and II and the nearest $\text{NH}_4(\text{I})$ ion as in the case of $(\text{NH}_4)_2\text{AgI}_3$.

In the case of $(\text{Rb}_{0.9}(\text{NH}_4)_{0.1})_2\text{AgI}_3$, hyperfine parameters of I^0 and I_2^- are approximately the same as those in the alkali silver iodides and the ammonium silver iodide (Awano and Matsuyama, 1994). Uniaxial directions of I^0 and I_2^- are, however, different from those in the alkali silver iodides and the ammonium silver halides. In $(\text{Rb}_{0.9}(\text{NH}_4)_{0.1})_2\text{AgI}_3$, I^0 exists only in iodine ion (II) and slightly distributes the nearest NH_4^+ (I) as shown in the fig. 1(c). I_2^- is in two iodine ions on the horizontal edge of the iodide tetrahedron.

The $(\text{halogen})^0$ decays at 150 K in the alkali silver iodides and the ammonium silver halides. The $(\text{halogen})_2^-$ decays at 180 K in the ammonium silver halides. The structural conversion of the $(\text{halogen})_2^-$ occurs in the ammonium silver halides. Fig. 2 shows an example of ESR spectra of $(\text{NH}_4)_2\text{AgI}_3$ γ -irradiated at 77K and annealed up to 190 K. Magnetic field was applied in directions in the ac plane of the crystal. Angles from the a -axis are shown in the fig. 2. This new $(\text{halogen})_2^-$ was stable up to 250K and disappeared at 280 K. This has small hyperfine parameters and large line width comparing with $(\text{halogen})_2^-$ in alkali halides. The same phenomena occurred in the case of $(\text{NH}_4)_2\text{AgBr}_3$. Fig. 3 shows an example of ESR spectra of $(\text{NH}_4)_2\text{AgBr}_3$ γ -irradiated at 77K and annealed up to 258 K.

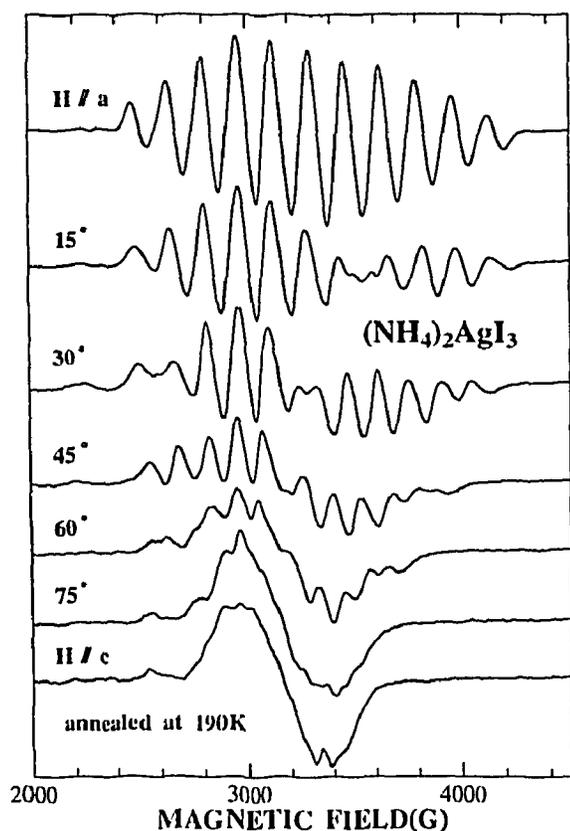


Fig. 2. ESR spectra of $(\text{NH}_4)_2\text{AgI}_3$ γ -irradiated at 77K and annealed up to 190 K. Magnetic field was applied in directions within ac plane of the crystal. Angles from the a -axis are shown in the figure. The temperature of measurement was 77 K. The microwave frequency was 9.290 GHz.

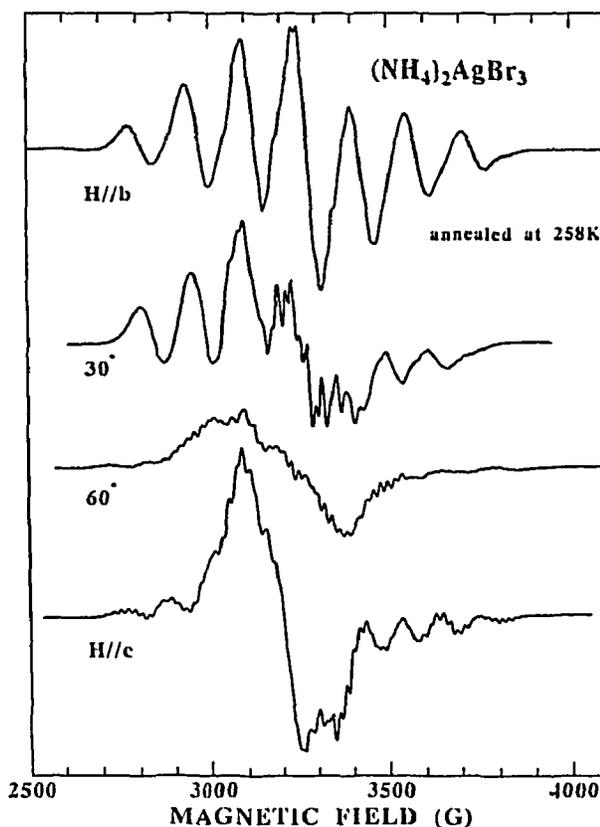


Fig. 3. ESR spectra of $(\text{NH}_4)_2\text{AgBr}_3$ γ -irradiated at 77K and annealed up to 258 K. Magnetic field was applied in directions within bc plane of the crystal. Angles from the b -axis are shown in the figure. The temperature of measurement was 77 K. The microwave frequency was 9.290 GHz.

Magnetic field was applied in directions in the bc plane of the crystal. Angles from the b -axis are shown in the fig. 3. This new V_K center disappeared at 310 K. This conversion did not occur in the $(\text{Rb}_{0.9}(\text{NH}_4)_{0.1})_2\text{AgI}_3$ crystal. Each of the I_2^- and I^0 in $(\text{Rb}_{0.9}(\text{NH}_4)_{0.1})_2\text{AgI}_3$ crystal decayed at 250 K and 240 K in an annealing process. Comparing with the alkali silver iodides and the ammonium silver iodide, I_2^- and I^0 were stable in the mixed crystal in the annealing process.

$(\text{NH}_4)_2\text{AgI}_3$ crystal turned in brown color by irradiation at room temperature. The c plane of this crystal showed silvery luster. The a plane also showed a little silvery luster. The b plane, however, showed no luster. Such a metallic coloration was reported on alkylammonium chlorides (Yoshinari et al., 1985). This phenomenon is probably due to the deposition of microcrystal layers.

CONCLUSION

A self-trapped hole of the form of I^0 was stable in Rb_2AgI_3 and K_2AgI_3 among alkali silver halides. The I^0 was weakly coupled with the nearest alkali ion and it is denoted by RbI^+ or KI^+ . On the other hand, both of X_2^- and X^0 were stable in $(NH_4)_2AgX_3$. The structures of self-trapped holes induced in the mixed crystal of the alkali silver iodide and the ammonium silver iodide are almost the same as those in each component crystal. Their orientations are, however, different from those in each component crystal. They are thermally stable comparing with those in each component crystal. These facts indicate that small differences of site energies, which is due to the energy band structures, resulted in rather large differences of the stability of the STHs.

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REFERENCES

- Brinc C. and Kroase H. A. S. (1951) Acta Cryst. **5**, 433 .
- Awano T. , Nanba T., Ikezawa M., Matsuyama T. and Yamaoka H. (1989) J. Phys. Soc. Jpn. **58**, 2570.
- Awano T., Ikezawa M., Matsuyama T. and Yamaoka H. (1993) Defect in Insulating Materials, World Scientific, Singapore.
- Awano T. and Matsuyama T. (1994) Nucl. Instrum. Methods **B91**, 227.
- Awano T. and Matsuyama T. (1994) Proc. 7th europysical conference on defects in insulating materials, Lyon (in press).
- Edamatsu K., Nanba T. and Ikazawa M. (1989) J. Phys. Soc. Jpn. **58**, 314.
- Yoshinari T., Matsuyama T., Yamaoka H. and Aoyagi K. (1985) Jpn. J. Appl. Phys. **24**, L720.