

## Electrical Ionic Conductivity and Optical Absorption Studies on Superionic Compound $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$ Films

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Electrical ionic conductivity studies on thin films of the superionic compound  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  ( $x = 0$  to  $0.4$ ) have been carried out from  $438$  to  $150$  K. From the conductivity plots, the activation energy for  $\text{Ag}^+$  ion conduction has been calculated. Optical absorption studies on the above films indicate (i) the existence of silver colloids in the film, (ii) a forbidden internal transition in the free  $\text{Ag}^+$  ion becoming activated because of the structure of  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$ , and (iii) a well-defined exciton state in the above material.

### Introduction

The study of superionic compounds in thin-film form has gained much importance because a thin-film solid-state battery finds itself useful in a variety of low-power applications and has low internal resistance. Though a lot of work has been done on  $\text{MAg}_4\text{I}_5$  ( $M = \text{Rb}, \text{K}, \text{NH}_4$ , and to a limited extent,  $\text{Cs}$ ) family of materials in the bulk form, not much work has been done on the above material in thin film form. It is known that  $\text{AgI}$  and  $\text{CuI}$  have similar physico-chemical properties.  $\text{CuI}$  is a hole-type semiconductor (1), and synthesized  $\text{RbAg}_4\text{I}_5$  has electron-type conductivity (2). It is reported (3) that addition of copper makes it possible to decrease electron conductivity of the solid electrolyte by a factor of  $10^2$ . Hence, addition of  $\text{CuI}$  to  $\text{RbAg}_4\text{I}_5$  may partially compensate the electron conductivity and increase the shelf life of the battery. Again, thin films coated on transparent substrates can be conveniently used

for optical absorption studies provided the crystal structure and perfection of these films compare with those of good single crystals. In view of the above facts, the present study of thin-film ionic conductivity and optical absorption has been carried out on  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  with  $x = 0$  to  $0.4$ .

### Experimental

Specpure-grade rubidium iodide (99.99%) and analar-grade silver iodide and cuprous iodide (99.95%) were used in the preparation of  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  compound. The reactants were vacuum sealed in a quartz tube, melted together and then quenched. The product was ground and again annealed in vacuum at  $438$  K for  $24$  hr. In a similar way, the  $\text{RbAg}_4\text{I}_5$  compound was prepared by taking the appropriate quantities of iodides of rubidium and silver ( $\text{AgI} : \text{RbI} = 80 : 20$ ). The compounds so formed were used for evaporation. In the present study, the thickness of the films

was kept constant by taking the same amount of material for all the compositions and also by monitoring the thickness using a quartz crystal thickness monitor. Microscope glass slides (of dimensions  $7.5 \times 2.5 \times 0.1$  cm) were used as substrates. For optical absorption studies, films coated on NaCl and fused quartz also were used. The glass plates were first cleaned with dilute chromic acid, washed with deionized water, and later degreased with isopropyl alcohol. Thick silver films were coated on either end of the glass substrate with a gap of 4 cm in the middle. The experimental film covers the 4-cm gap in the middle and also overlaps about 0.5 cm on the silver films. Pressure contacts were applied on these silver films by using copper plates. For the above arrangement, it was observed that the contact and lead resistances were negligibly small. The vacuum during evaporation was  $3 \times 10^{-5}$  Torr and the deposition rate was about  $50 \text{ \AA}/\text{sec}$ . The coated films were annealed at 438 K for about 2 hr *in situ* after the film formation and then the conductivity studies were carried out. Resistance measurements were

made using a GR 1644 A (General Radio) megohm bridge and also by measuring the voltage drop across the film by passing a known current through the film from a stabilized power supply. The polarization effects are negligible in the present conductivity measurements, since the current varied linearly with voltage and also on reversing the voltage polarity, no change in the current was observed. In order to establish that the film formed is indeed  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$ , X-ray diffractograms were taken of the films using a Philips X-generator Model 1140. Optical absorption measurements were done using a Cary 14 spectrophotometer. For studies at low temperatures, a cryostat of conventional design was used.

### Results and Discussion

Table I shows  $d$  values and the corresponding planes of reflection. Table II compares the unit cell dimensions for  $\text{RbAg}_4\text{I}_5$  obtained in the present study with earlier results (4, 5). From the above two tables it is seen that the X-ray diffraction pattern

TABLE I  
X-RAY DATA FOR  $\text{RbAg}_4\text{I}_5$  FILM

Manning <i>et al.</i> (4) observed							
$(h k l)$	Fused salt cooled and ground (diffractometer)		Small single crystals, ground (film)		Bradley and Greene (5) observed (film)		Present work, thin film (vacuum evaporated)
	$d$ (Å)	$I/I_1$	$d$ (Å)	$I$	$d$ (Å)	$I$	$d$ (Å)
311	3.39	100	3.35	S	3.36	S	3.37
(221)(300)	3.75	47	3.70	MS	3.72	MS	3.72
(110)	7.96	39	7.72	M	7.85	W	7.84
(510)	2.20	39	2.19	S	2.19	S	2.19
(222)	3.24	16	3.21	MW	3.21	W	3.22
(520)(432)	2.09	21	2.08	MS	2.07	M	2.07
(411)(330)	2.65	13	2.63	MW	2.63	W	2.64

TABLE II  
UNIT CELL DIMENSIONS FOR  $\text{RbAg}_4\text{I}_5$

Author	Method	Unit cell (Å)
Bradley and Greene	Film (powder) Single crystal	11.15 11.22
Manning <i>et al.</i>	Film (powder) Diffractometer (powder)	11.16 11.23
Present work	Thin film (vacuum evaporated)	11.15

and the lattice parameter ( $a = 11.15 \text{ \AA}$ ) of and  $\text{RbAg}_4\text{I}_5$  films in the present study agree well with those reported in the literature (4).

#### A. Electrical Ionic Conductivity

The conductivity values at room temperature (300 K) for  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  films where  $x = 0, 0.04, 0.1, 0.2,$  and  $0.3$  are, respectively,  $0.31, 0.26, 0.21, 0.18,$  and  $0.13(\text{ohm cm})^{-1}$ . Typical plots of  $\log \sigma T$  versus  $10^3/T$  for three compositions are shown in Figs. 1a, b, and c. The conductivity of  $\text{RbAg}_4\text{I}_5$  at 300 K ( $0.31(\text{ohm cm})^{-1}$ ) is higher than the best reported bulk value  $0.27(\text{ohm cm})^{-1}$ . This may be due to the assumption that the density of the film is the same as that of the bulk ( $5.38 \text{ g/cm}^3$ ) (6) in the calculation of the film thickness by the quartz oscillator method. On the other hand, one can expect the density of the film to be lower than that of bulk due to the presence of pores in the film.

The slope of the  $\log \sigma T$  versus  $10^3/T$  plot is found to be the same for films of different compositions and it represents the activation energy for  $\text{Ag}^+$  ion conduction (7). In the present investigation the activation energy turns out to be  $0.10 \pm 0.01 \text{ eV}$  which is in good agreement with the reported value  $0.1 \text{ eV}$  for  $\text{RbAg}_4\text{I}_5$  compound (7). Referring to Fig. 1a, it is seen that at 210 K, there is a discontinuity in  $d\sigma/dT$  while  $\sigma$  is continuous. The point at which the slope of the graph changes (i.e., at 210 K) lies at the

second phase transition of the compound which has two phase transitions at 121.8 and 209 K (8). The activation energies before and after this phase transition were found to be 0.1 and 0.2 eV.

As already stated, the conductivity of  $\text{RbAg}_4\text{I}_5$  at 300 K is found to decrease as the concentration of copper increases. It is reported (9) that electrical conductivity in materials which have a channel structure like  $\text{RbAg}_4\text{I}_5$  has a maximum value for a particular relationship between the radius of the ion and width of the channel. In the above work, calculations made for ions of different sizes in the  $\text{AgI}$  lattice showed that there is a set of minimum energy paths which do not follow the center line of the tunnel but deviate periodically with both direction and magnitude depending upon the cation size. From the above calculations, one can expect that mixtures of cations of different sizes like  $\text{Ag}^+$  and  $\text{Cu}^+$  will become ordered among different sets of sites, due to the influence of ionic size upon preferred location. Such related variations in site preference for different monovalent cations have also been reported in the  $\beta$ -alumina structure (9). In the present case, it can be expected that the  $\text{Cu}^+$  ion would tend to become oriented in a direction different from that of  $\text{Ag}^+$ . Introduction of  $\text{Cu}^+$  ion might alter the channel dimensions and hence there is a decrease in conductivity as the concentration of copper increases.

#### B. Optical Absorption

Figure 2 (curve 1) shows the optical absorption spectrum at 300 K of  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  ( $x = 0.3$ ) of thickness  $3740 \text{ \AA}$  coated on a glass substrate. There are three well-defined bands at  $\sim 5100, 4300, 3800 \text{ \AA}$ . In explaining the optical absorption results of  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  thin films, it is worthwhile to compare the optical properties of  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  with those of  $\beta\text{-AgI}$  and  $\text{CuI}$ , since the above systems share a host of

equivalent properties. The electronic states of  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  can be described in terms of a homogeneous solid solution  $\text{RbI}(\text{AgI})_{4-x}(\text{CuI})_x$ . The fact that for all thicknesses the bands appear at the same posi-

tion, irrespective of the substrate on which the film is coated, excludes an interference origin of the above bands.

The broad band at  $5100 \text{ \AA}$  has the characteristics of colloidal centers in alkali and silver halides (10-12). The position of the band and its half-width were hardly affected when the temperature of the film was lowered from 300 to 80 K (see Fig. 2, Curves 1 and 2). Since colloid particles should not be coupled with the lattice vibrations, the half-width and peak positions should not be affected by temperature as observed in the present study. When the thickness of the film increases, there is a slight shift ( $\sim 100 \text{ \AA}$ ) toward longer wavelength in the position of the band. The band intensity decreases and the band becomes broad due to aging of the film and subsequent annealing (see Fig. 3). The broadening of the absorption band has been said to be due to the growth of the particles. With larger particles, the scattering should increase, the absorption should be largely determined by this phenomenon, and the transmitted light should be complementary in color to the scattered light. The peak of the band should move toward longer wavelength as the particle size increases. In the present study the position of the band is found to vary between  $5100$  to  $5200 \text{ \AA}$ . in the films of different thicknesses. This variation may be due to the difference in colloid particle size in different films. Thus the broad band around  $5100 \text{ \AA}$  can be attributed to the presence of silver colloids in the films.

Let us next consider the band at  $4300 \text{ \AA}$ . A band at  $4230 \text{ \AA}$  has been reported in the optical studies (13) on  $\text{AgI}$  thin film. It is known (10) that silver and cuprous halides have a system of levels associated with the  $4d^{9s}$  and  $3d^{9s}$  states of  $\text{Ag}^+$  and  $\text{Cu}^+$  ions, respectively, which have the same parity as the ground state ( $d^{10}$ ) and hence the transition  $d^{10}-d^{9s}$  is dipole forbidden. In the wurtzite lattice of  $\text{AgI}$  as well as in the  $\text{RbAg}_4\text{I}_5$  lattice,  $\text{Ag}^+$  ion has tetrahedral

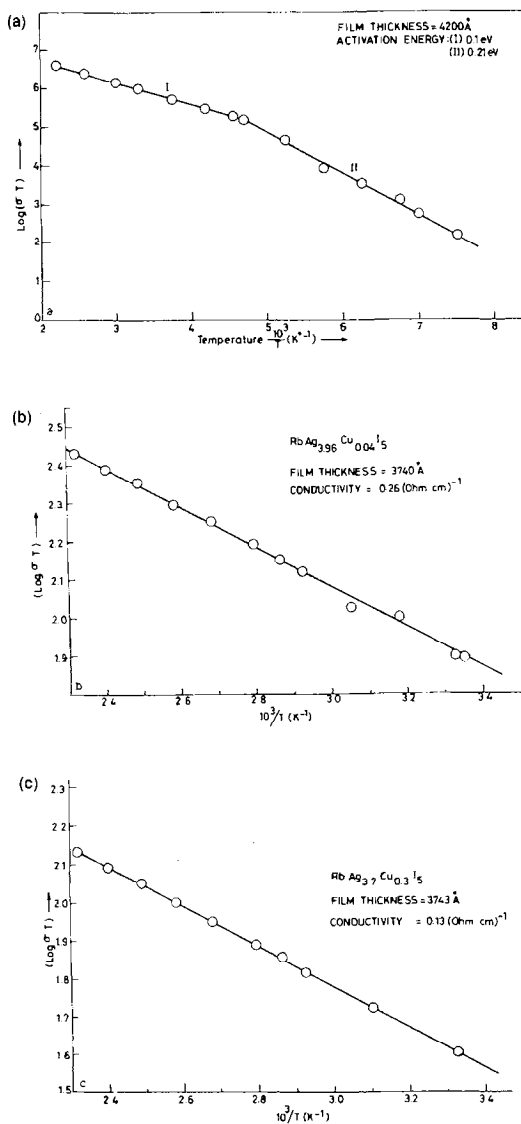


FIG. 1. (a) Conductivity plotted against temperature for  $\text{RbAg}_4\text{I}_5$  film. Also shown is the conductivity variation below room temperature showing the phase transition around 210 K. (b) Conductivity plotted against temperature for  $\text{RbAg}_{3.96}\text{Cu}_{0.04}\text{I}_5$  films. (c) Conductivity plotted against temperature for  $\text{RbAg}_{3.7}\text{Cu}_{0.3}\text{I}_5$  film.

coordination of  $\text{I}^-$  ions and hence there can be mixing of the states of opposite parity, namely, the states of  $\text{Ag}$  ( $4d^+$ ) and  $\text{I}$  ( $5p^-$ ). Hence the weak band at  $4300 \text{ \AA}$  can be attributed to the forbidden internal transition in the free  $\text{Ag}^+$  ion which becomes permitted because of tetrahedral coordination of  $\text{Ag}^+$  ion in the  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  lattice.

The well-defined band at  $3800 \text{ \AA}$  shifts to  $3750 \text{ \AA}$  when the spectrum is recorded at  $80 \text{ K}$  (see Fig. 2, curves 1 and 2). This band is attributed to the exciton state in the material with an energy of  $3.26 \text{ eV}$  at room temperature ( $300 \text{ K}$ ). Bauer and Huberman (14) have reported a well-defined exciton state in the  $\text{RbAg}_4\text{I}_5$  single crystal at  $3.338 \text{ eV}$  (at  $4.2 \text{ K}$ ) and that the temperature coefficient for  $\text{RbAg}_4\text{I}_5$  is  $-5.2 \times 10^{-4} \text{ eV/K}$  below  $122 \text{ K}$ . Accordingly the exciton state at  $80 \text{ K}$  will go to  $3.30 \text{ eV}$ . In the present study on  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$ , the exciton state is identified at  $3.31 \text{ eV}$  at  $80 \text{ K}$ .

It is worthy to point out here that the bands which were observed at  $4250$  and  $3750 \text{ \AA}$  in the case of  $\text{RbAg}_4\text{I}_5$  (15) have been shifted to the longer wavelengths  $4300$  and  $3800 \text{ \AA}$  in the case of  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$

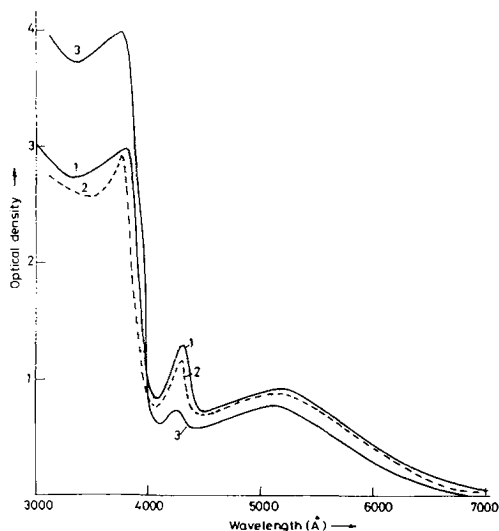


FIG. 2. Optical absorption spectrum curves of (1)  $\text{RbAg}_{3.7}\text{Cu}_{0.3}\text{I}_5$  at  $300 \text{ K}$ . (2)  $\text{RbAg}_{3.7}\text{Cu}_{0.3}\text{I}_5$  at  $80 \text{ K}$ . (3)  $\text{RbAg}_4\text{I}_5$  at  $300 \text{ K}$ .

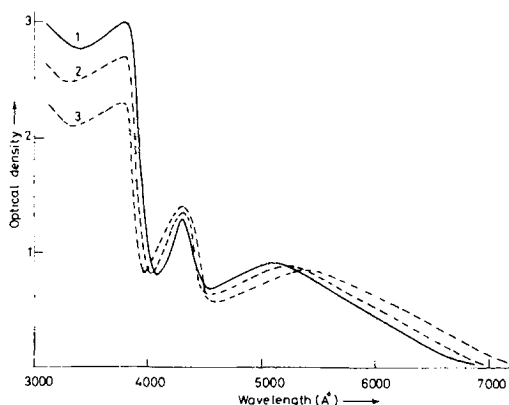


FIG. 3. Effect of aging on the optical absorption bands. Curve 1—immediately after preparation. Curve 2—after 24 hr. Curve 3—after 72 hr.

with  $x = 0.3$  (see Figure 2, curves 1 and 3). A probable explanation for the above observed shifts can be given as follows. Cardona (16) has reported the energy of exciton peaks versus concentration in the  $\text{AgI-CuI}$  system. It is known that  $\text{AgI}$  and  $\text{CuI}$  have similar optical properties. Both of them exhibit three excitonic peaks. Only the position of the peaks are different. For different concentrations in  $\text{AgI-CuI}$  system, the peak positions are different. From the plot (16), it is seen that for a small addition of  $\text{CuI}$  to  $\text{AgI}$ , the energy of the exciton peaks is lower than the corresponding peak energy for pure  $\text{AgI}$ . Having the above reported facts in mind and also considering  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  as a solid solution of  $\text{RbI}(\text{AgI})_{4-x}(\text{CuI})_x$ , the shift in the peak positions to higher wavelength (low energy) can be attributed to the addition of  $\text{CuI}$  to the system. The band at  $3800 \text{ \AA}$  which is well defined and sharp in the spectrum taken for the sample annealed at  $438 \text{ K}$ , becomes broad and reduced in intensity due to aging (see Fig. 3). Also, there is a reduction in the electrical conductivity of these films with time. This may be due to the copper ions serving as centers for the phase transition from the high-conductivity modification to the low-conductivity phase.

### Summary

Electrical ionic conductivity studies on thin films of superionic compound  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  ( $x = 0$  to  $0.4$ ) show that the conductivity decreases as the concentration of copper increases whereas the activation energy for cation conduction is not affected much and is found to be  $0.10 \pm 0.01$  eV. A phase transition at 210 K has been observed. The activation energies before and after the above phase transition were found to be 0.1 and 0.2 eV. Electronic absorption spectrum curves of  $\text{RbAg}_4\text{I}_5$  and  $\text{RbAg}_{4-x}\text{Cu}_x\text{I}_5$  films have similar features but for the fact that the peak positions were slightly shifted to the low-energy side in the latter case due to the addition of CuI to the system.

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