



## Electrical conductivity and optical absorption studies in superionic RbAg<sub>4</sub>I<sub>5</sub> thin films

S. Radhakrishna, K. Hariharan, and M. S. Jagadeesh

Citation: *Journal of Applied Physics* **50**, 4883 (1979); doi: 10.1063/1.325588

View online: <http://dx.doi.org/10.1063/1.325588>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/50/7?ver=pdfcov>

Published by the [AIP Publishing](#)

---



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



# Electrical conductivity and optical absorption studies in superionic $\text{RbAg}_4\text{I}_5$ thin films

S. Radhakrishna, K. Hariharan, and M. S. Jagadeesh

*Department of Physics, Indian Institute of Technology, Madras-600 036, India*

(Received 29 August 1978; accepted for publication 27 November 1978)

Electrical conductivity in thin films of the superionic conductor  $\text{RbAg}_4\text{I}_5$  was found to be in very good agreement with the best bulk value ( $0.27 \Omega^{-1} \text{cm}^{-1}$ ). From the conductivity data, the activation energy for  $\text{Ag}^+$ -ion conduction, and the free-ion-like parameters such as the mean free path and lifetime in the excited state have been deduced. The phase transition at  $210^\circ\text{K}$  has also been observed, and the activation energy for conduction before and after the phase transition has been evaluated. Optical absorption studies in these films reveal a well-defined exciton state at  $3750 \text{ \AA}$  at  $300^\circ\text{K}$ . Also, a weak band is observed at  $3350 \text{ \AA}$  on the higher-energy side of the exciton band which appears to be evidence for the existence of large-radius excitons. A broad band observed at  $4850 \text{ \AA}$  has been attributed to the existence of silver colloids in the films. A forbidden internal transition in the  $\text{Ag}^+$  ion has been observed at  $4250 \text{ \AA}$ .

PACS numbers: 73.90. + f, 78.65. - s, 66.90. + r, 85.80. - b

## INTRODUCTION

There is renewed basic as well as technological interest in the properties of solids of exceptionally high ionic conductivity because of their use as electrolytes in solid-electrolyte galvanic cells. The solid electrolytes belonging to the  $M\text{Ag}_4\text{I}_5$  family ( $M = \text{K}, \text{Rb}, \text{NH}_4$ , and to a limited extent Cs) have relatively high ionic conductivities.<sup>1,2</sup> The most serious shortcoming of the solid-state battery using the above compound as an electrolyte is the high value of the internal resistance, which has limited its practical utilization to micro-watt-power applications.<sup>3,4</sup> One way of achieving lower internal resistance is by using thin layers of the electrolyte. Optical absorption of the thin films coated on a transparent substrate can be studied easily. With these views in mind, electrical conductivity and optical absorption studies on the  $\text{RbAg}_4\text{I}_5$  compound have been carried out in thin films in the present investigation.

## EXPERIMENTAL

Specpure rubidium iodide (99.999%) and analar-grade silver iodide (99.95%) were used in the preparation of the  $\text{RbAg}_4\text{I}_5$  compound. The reactants ( $\text{AgI} : \text{RbI} = 80 : 20$ ) were vacuum sealed in a quartz tube, melted together, and then quenched. The product was ground and again annealed in vacuum at  $165^\circ\text{C}$  for 24 h. The stoichiometry of the compound  $\text{RbAg}_4\text{I}_5$  was verified by x-ray measurements. The compound thus prepared was used for thin-film evaporation. Films of different thicknesses were coated on thoroughly cleaned microscope glass slides with silver contacts on either ends. The vacuum during evaporation was  $3 \times 10^{-5}$  Torr, and the deposition rate was about  $50 \text{ \AA}/\text{sec}$ . The thickness of the film was measured using a quartz-crystal-thickness monitor. The coated films were annealed at  $165^\circ\text{C}$  for about 2 h *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 (between 1 and 50 V dc) and also because upon reversing the voltage polarity, no change in the current was observed. In order to establish that the film formed is indeed  $\text{RbAg}_4\text{I}_5$ , 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.

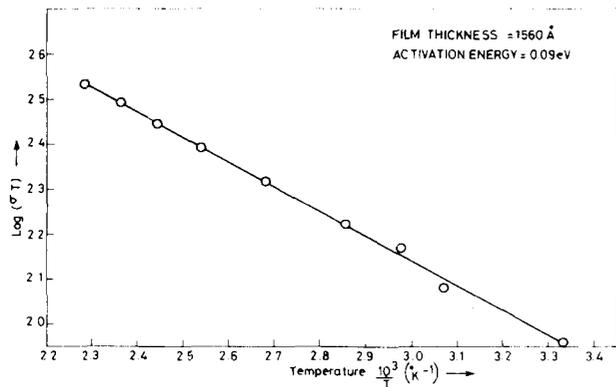
## RESULTS AND DISCUSSION

The x-ray diffraction pattern and the lattice parameter  $a$  ( $= 11.15 \text{ \AA}$ ) of the films in the present study agree well with those reported in the literature.<sup>5</sup>

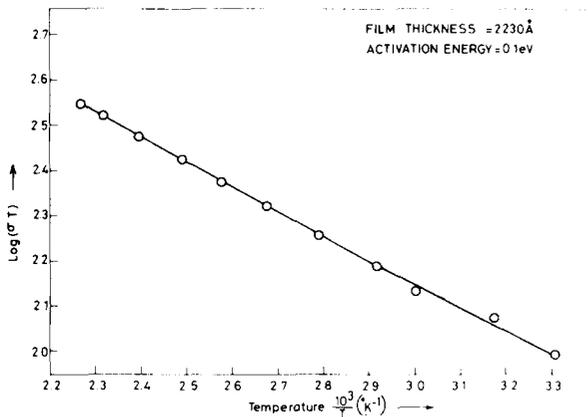
### Electrical conductivity

A conduction model for superionic conductors has been proposed by Rice and Roth,<sup>6</sup> according to which a plot of  $\log(\sigma T)$  against  $1/T$  (where  $\sigma$  is the conductivity and  $T$  is the temperature) yields the value of the activation energy for conduction. Some details for this model are given at a later stage. Figures 1(a), 1(b), and 1(c) show  $\log(\sigma T)$  versus  $10^3/T$  plots for films of thicknesses 1560, 2230, and 4230  $\text{ \AA}$ . The electrical conductivity values of the films of increasing orders of thicknesses were found to be 0.32, 0.31, and 0.32  $\Omega^{-1} \text{cm}^{-1}$  respectively at  $300^\circ\text{K}$ , the values being higher than the best value reported<sup>7</sup> for the compound in the bulk from ( $0.27 \Omega^{-1} \text{cm}^{-1}$ ). For one of the films (of thickness 4200  $\text{ \AA}$ ) the conductivity measurements were done down to  $140^\circ\text{K}$ , the plot of which is shown by curve 2 in Fig. 1(c).

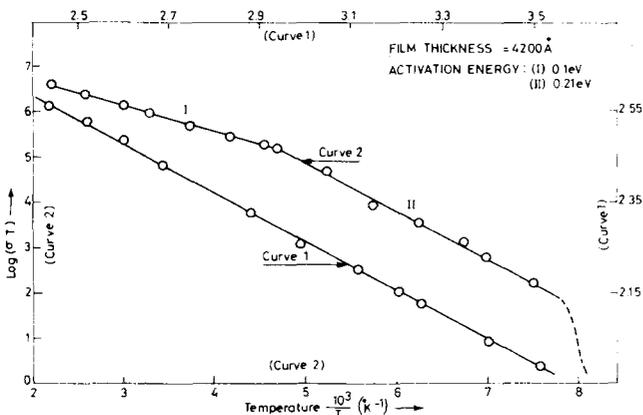
The density of the film is assumed to be that of the bulk<sup>3,7</sup> ( $5.38 \text{ g/cm}^3$ ) in the calculation of film thickness by the



(a)



(b)



(c)

FIG. 1. Conductivity-vs-temperature plots for  $\text{RbAg}_4\text{I}$ , Films. (a) Film thickness = 1560 Å, activation energy = 0.09 eV. (b) Film thickness = 2230 Å, activation energy = 0.1 eV. (c) In this figure is seen the conductivity variation below room temperature for the same film as in the second curve showing the phase transition around 210 °K.

quartz-oscillator method. However, it is likely that the density of the film may not be the same as that of bulk due to the very nature of thin films. The film-thickness measurement by Tolansky's multiple-beam interferometric (MBI) technique,<sup>8</sup> which is an absolute method, was found to be difficult to use since it was not possible to get a good reflecting film on the  $\text{RbAg}_4\text{I}$  film. Nevertheless, the film thickness was measured for one of the specimens. The film thickness by the MBI technique was found to be 1710 Å, whereas for the same specimen a quartz-crystal monitor gave a thickness

of 1560 Å. The estimated film thickness by a quartz-crystal monitor agrees with the value given by the MBI method, if one assumes the film density to be about 10% less than the bulk density. By using a film thickness of 1710 Å, the conductivity of the specimen was found to be  $0.27 \Omega^{-1} \text{ cm}^{-1}$ , which agrees with the best reported bulk value,<sup>7</sup> whereas the conductivity comes out to be  $0.32 \Omega^{-1} \text{ cm}^{-1}$  when the film thickness of 1560 Å is employed. Thus the conductivity values in the present work can be taken as agreeing well with the best bulk value.<sup>7</sup> It has been reported<sup>9</sup> that the conductivity reaches a value of  $0.25 \Omega^{-1} \text{ cm}^{-1}$  for films in the  $\text{AgI-RbI}$  system with 83–85 mole %  $\text{AgI}$ . But the authors have not given the method by which they determined the film thickness. It is reported in Ref. 10 that the conductivity of the  $\text{RbAg}_4\text{I}$  system is  $0.18 \Omega^{-1} \text{ cm}^{-1}$ . The thickness of the film used in the above study was of the order of 20–30 μ, whereas in the present case it is of the order of 0.15–0.5 μ. The final conductivity of the compound film depends on how accurately one can determine the film thickness apart from other possible changes due to structural variations. Also, the above authors have not annealed the film. Hence one can expect their films to have nonconducting-phase  $\text{Rb}_2\text{AgI}_3$  and  $\text{AgI}$  apart from the conducting-phase  $\text{RbAg}_4\text{I}_5$ . In the present case, the conductivity of the annealed film at 300 °K ( $0.32 \Omega^{-1} \text{ cm}^{-1}$ ) is found to be greater than the value for the unannealed film ( $0.29 \Omega^{-1} \text{ cm}^{-1}$ ).

The slope of the  $\log(\sigma T)$  versus  $10^3/T$  plot is found to be the same for films of different thicknesses and it represents the activation energy for  $\text{Ag}^+$ -ion conduction.<sup>2</sup> In the present investigation the activation energy turns out to be  $0.10 \pm 0.01$  eV, which is in good agreement with the reported value of 0.1 eV for the  $\text{RbAg}_4\text{I}_5$  compound.<sup>2</sup>

According to the theoretical model predicted by Rice and Roth<sup>6</sup> for ionic transport in superionic conductors, the expression for ionic conductivity is

$$\sigma = \frac{1}{3} \left( \frac{q^2}{KT} n V_0 l_0 \right) \exp\left( -\frac{\epsilon_0}{KT} \right)$$

$$= \frac{C}{T} \exp\left( -\frac{\epsilon_0}{KT} \right),$$

$$C = \frac{1}{3} \frac{q^2 n V_0 l_0}{K},$$

where  $l_0 = V_0 \tau_0$  and  $V_0 = (2\epsilon_0/M)^{1/2}$ . Here  $l_0$  and  $V_0$  represent the mean free path and velocity of the free ion-like state,  $\tau_0$  and  $n$  denote the lifetime of the excited state and the number of potentially mobile ionic species per unit volume, and  $q$  and  $M$  are the charge and mass of the free ion, respectively. The gap energy  $\epsilon_0$  denotes the energy difference between the localized ionic state and free-ion-like state of the mobile ion. The experimental plot of  $\log(\sigma T)$  versus  $10^3/T$  hence yields a straight line whose slope and intercept give respectively  $\epsilon_0$  and the preexponential factor  $C$  in the above equation. Thus the values of  $\epsilon_0$ ,  $\tau_0$ ,  $l_0$ , and  $V_0$  can be obtained from the observed conductivity if  $n$ ,  $q$ , and  $M$  are known. In the present calculation,  $n$  is assumed to be the total number of cations

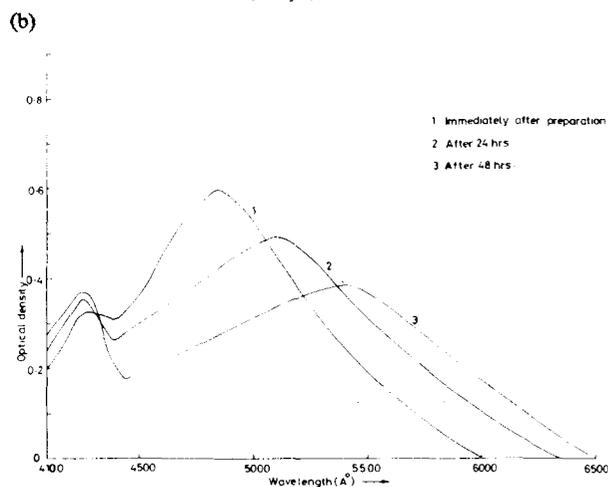
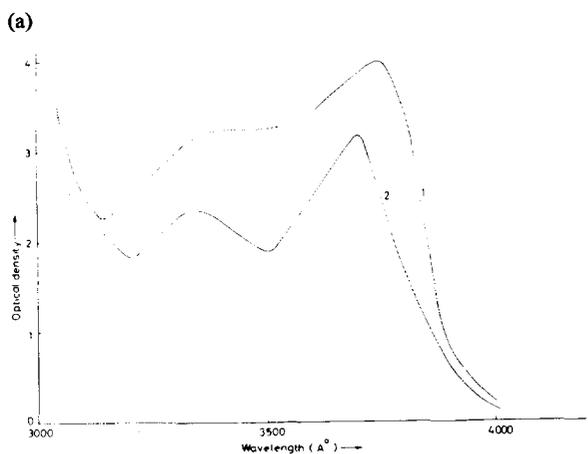
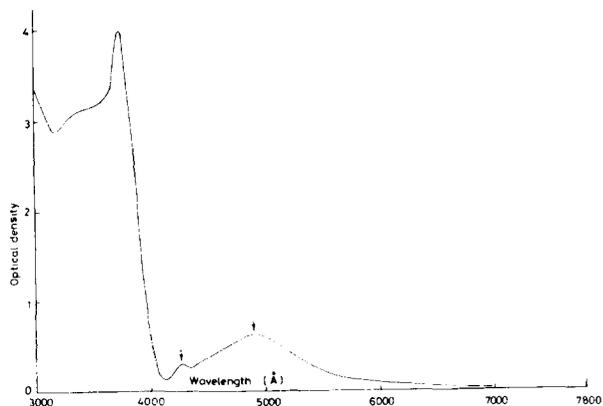


FIG. 2. (a) Optical absorption spectrum of  $\text{RbAg}_4\text{I}$  film at 300 °K. (b) Optical absorption spectrum of  $\text{RbAg}_4\text{I}$  thin film at 300 °K (curve 1) and at 80 °K (curve 2). (c) Effect of aging on 4850-Å band in  $\text{RbAg}_4\text{I}$  film.

per unit volume belonging to the disordered conducting species. For the values of  $q$ ,  $M$ , and  $n$  we have  $n = 1.13 \times 10^{22}/\text{cm}^3$ ,  $q = 1.602 \times 10^{-20}$  emu, and  $M = 107.88 \times 1.66 \times 10^{24}$  g. The values of the activation energy  $\epsilon_0$  and the constant  $C$  are obtained by the least-squares-fit method. Assuming the values of  $q$ ,  $n$ , and  $V_0$  [ $= (2\epsilon_0/M)^{1/2} = 0.42 \times 10^5$  cm sec $^{-1}$ ] given the mean free path  $l_0$  and the lifetime of the excited state  $\tau_0$  [ $= l_0/V_0$ ] turn out to be 0.25 Å and  $0.56 \times 10^{-13}$  sec, respectively.

The above values of  $l_0$  and  $\tau_0$  are found to be lower than

the corresponding values<sup>6</sup> 1.3 Å and  $3.1 \times 10^{-13}$  sec calculated from the conductivity plot of Owens and Argue.<sup>2</sup> It is to be noted that the deduced values of  $\tau_0$  and  $l_0$  are subject to an appreciable amount of uncertainty in the extraction of the preexponential factor from the observed conductivity. The values obtained in the present work represent the correct order of magnitude at least, as it was mentioned by Rice and Roth<sup>6</sup> that at best one can obtain the correct order of magnitude with the present knowledge of superionic solids.

Referring to curve 2 of Fig. 1(c), it is seen that the slope of the plot from 430 to 210 °K is different from the slope in the region between 210 and 140 K. It is known from the investigation on heat capacity<sup>11</sup> that  $\text{RbAg}_4\text{I}$  has two phase transitions at  $T_1 = 121.8$  °K and  $T_2 = 209$  °K. In the present investigation it is found that the point at which the slope of the graph changes (i.e., at 210 °K) lies at the second phase transition  $T_2$ . The activation energies before and after this phase transition are found respectively to be 0.1 and 0.2 eV. Similar features were also observed in the conductivity study performed on polycrystalline  $\text{RbAg}_4\text{I}$  specimens.<sup>7</sup> As seen from the curve, the transition at 210 °K is associated with a discontinuity in  $d\sigma/dT$  while  $\sigma$  is continuous. The transition is of the  $\lambda$  type, and crystals of  $\text{RbAg}_4\text{I}$ , which are optically isotropic at ambient temperatures become birefringent when cooled to 208 °K, which shows that this low-temperature phase is not really cubic. Geller<sup>12</sup> has reported that in  $\text{RbAg}_4\text{I}$ , domains are visible under a microscope at low temperatures. There are several unit cells in a microdomain where one or more of the three crystallographically inequivalent types of sites is fully occupied or completely empty.<sup>12</sup> Roth has made a similar suggestion for the two-dimensional superionic conductor  $\beta$ -alumina.<sup>13</sup> According to Pardee and Mahan,<sup>14</sup> the disintegration of ordered domains might be responsible for the above transition. Johnston *et al.*<sup>15</sup> interpret the above transition at 209 °K as the result of the interplay between changes in site-energy differences, in site occupations, and in concurrent lattice distortions.

Earlier conductivity studies on bulk specimens<sup>2</sup> reveal that the transition at 122 °K is a first order one with a discontinuous change in  $\sigma$  of two orders of magnitude. In the present study, the resistance of the film increased greatly on cooling below 140 °K, and it was difficult to measure the resistance values at different intervals of temperature. Hence the phase transition at 122 °K is shown by a dotted line. Although all superionic conductors belonging to the  $M\text{Ag}_4\text{I}$  family are thermodynamically unstable at subambient temperatures, the disproportionating reaction being  $2M\text{Ag}_4\text{I} \rightarrow 7\text{AgI} + M_2\text{AgI}_3$ , the transformation is sluggish, and  $\text{RbAg}_4\text{I}$ , particularly passes through these two phase transformations reversibly without disproportionation as indicated by the present as well as earlier studies.

## Optical absorption

The same films which were used in the conductivity studies were also used for optical absorption studies. Some optical studies were carried out for the films deposited on NaCl and fused-quartz substrates. In explaining the optical

absorption results for  $\text{RbAg}_4\text{I}_5$  thin films, it is worthwhile to compare the optical properties of  $\text{RbAg}_4\text{I}_5$  with those of  $\beta\text{-AgI}$ , since both the systems share a host of equivalent properties. Among them, the mean silver iodine distance is the same<sup>12,16</sup> and therefore their electronic structures are similar. The electronic states of  $\text{RbAg}_4\text{I}_5$  can be described in terms of a homogeneous solid solution of  $\text{RbI}(\text{AgI})_4$ .

Figure 2(a) shows the optical absorption spectrum of a film of  $\text{RbAg}_4\text{I}_5$  of thickness 4200 Å coated on a glass substrate. There are four bands at 4850, 4250, 3750, and 3350 Å. The observed bands are not due to interference effects because of the fact that for all thicknesses the bands appear at the same position irrespective of the substrate (glass, quartz, and NaCl crystal) on which the film is coated.

It is known<sup>17</sup> that silver halides possess a system of levels associated with the  $4d^9 5S$  state of the  $\text{Ag}^+$  ion which have the same parity as the ground state ( $4d^{10}$ ) in the free ion, and hence the transition  $4d^{10} \rightarrow 4d^9 5S$  is dipole forbidden. A band at 4230 Å has been reported<sup>18</sup> in the optical studies of  $\text{AgI}$  thin films. In the wurtzite lattice of  $\text{AgI}$ , each  $\text{Ag}^+$  ion is tetrahedrally surrounded by four  $\text{I}^-$  ions and there can be mixing of the states of opposite parity, namely, the states of  $\text{Ag}(4d^9)$  and  $\text{I}(5P^-)$ . Hence the forbidden transition  $4d^{10} \rightarrow 4d^9 5S$  becomes allowed because of the tetrahedral coordination of the  $\text{Ag}^+$  ion. In the crystal structure of  $\text{RbAg}_4\text{I}_5$ , also the arrangement of iodide ions provide 56 iodide tetrahedra sites per unit cell.<sup>12</sup> The 16  $\text{Ag}^+$  ions in the unit cell are distributed over 56 sites located in the centers of iodide tetrahedra. Hence, as in the case of  $\text{AgI}$ , the weak band at 4250 Å can be attributed to the forbidden internal transition in the  $\text{Ag}^+$  which becomes permitted because of the tetrahedral coordination of the  $\text{Ag}^+$  ion in  $\text{RbAg}_4\text{I}_5$ .

Now consider the well-defined band at 3750 Å (3.307 eV), with an absorption coefficient of  $8 \times 10^5 \text{ cm}^{-1}$ . At 80 °K the band shifts to 3700 Å (3.352 eV) as shown in Fig. 2(b). This band is attributed to the exciton state in the material with an energy of 3.307 eV at room temperature (300 °K). Bauer and Huberman<sup>19</sup> have reported a well-defined exciton state in the  $\text{RbAg}_4\text{I}_5$  single crystal at 3.338 eV (4.2 °K) and also that the temperature coefficient for  $\text{RbAg}_4\text{I}_5$  is  $-5.2 \times 10^{-4} \text{ eV/}^\circ\text{K}$  below 122 °K. Accordingly, the exciton state at 80 °K will go to 3.30 eV. In the present study, the exciton state is identified as 3.352 eV at 80 °K. The above band was quite sharp when the spectrum was taken immediately after removing the annealed film from the vacuum chamber. The band observed for the unannealed sample was broader. This is due to the fact that the defects get annealed out when the sample is annealed at 438 °K for 3 h. Again at 80 °K, the band was sharper than at 300 °K. The exciton moves in the field of fluctuating potential due to thermal vibration of the lattice, and these lattice vibrations are small when the temperature is lowered. Hence broadening of exciton states is due to the variation in exciton-phonon interaction<sup>20</sup> and due to the presence of defects in the film.

The band gap of the material can be defined as the energy of the first exciton peak plus the exciton binding (ionization) energy. The exciton binding energy in  $\text{RbAg}_4\text{I}_5$  is re-

ported to be  $\sim 0.08 \text{ eV}$ .<sup>19</sup> Hence the room-temperature band gap of the material becomes  $3.307 + 0.08 = 3.387 \text{ eV}$ . As already stated,  $\text{RbAg}_4\text{I}_5$  can be considered as a homogeneous solid solution of  $\text{RbI}(\text{AgI})_4$ . The band gap of  $\text{AgI}$  is  $\sim 3 \text{ eV}$ . Thus it is found that the band gap of  $\text{RbAg}_4\text{I}_5$  is about 0.387 eV greater than that of  $\text{AgI}$ . This is attributed to the addition of the high ionicity of  $\text{RbI}$  as compared to  $\text{AgI}$ , that is, the ionic nature of  $\text{RbAg}_4\text{I}_5$ , atomic bonding is more than that of  $\text{AgI}$ . Bauer and Huberman<sup>19</sup> have reported a tentative band picture of  $\text{RbAg}_4\text{I}_5$ , and the room-temperature band gap is said to be  $\sim 3.3 \text{ eV}$ .

A weak band is observed at about 3350 Å on the higher-energy side of the exciton peak, as shown in Figs. 2(a) and 2(b). This band becomes more prominent for films of higher thicknesses and for films coated at substrate temperatures different from room temperature. Similar bands with some structure on the higher-energy side of the first exciton peak of  $\text{RbI}$ ,  $\text{CsI}$ , and  $\text{KI}$  have been reported.<sup>21</sup> This band can be taken to be evidence for the existence of large-radius excitons because between the first exciton peak energy  $E_x$  and the band gap  $E_g$ , photons create bound hole-electron pairs of increasingly larger radius until a series limit is reached and free pairs are created. The additional structure above the band gap has led to extensive controversy, and several reasons are suggested for such structures.<sup>21</sup>

The following features have been observed in the band found at 4850 Å:

- (1) 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.
- (2) When the thickness of the film increases, there is a slight shift ( $\sim 100 \text{ Å}$ ) towards the longer-wavelength side in the position of the band.
- (3) Due to aging and subsequent annealing, the band intensity goes down and the band becomes broad. A slight shift in the peak position to the higher-wavelength side is observed.

From the above features, the band can apparently be attributed to the presence of silver colloids in the film. The above-mentioned features of the colloid centers agree well with those reported<sup>17,22-27</sup> on such centers in alkali and silver halides. Seitz<sup>17</sup> has suggested that the silver specks are likely to grow at a jog of an edge dislocation where an "incipient" halogen-ion vacancy exists. It can be shown that the vacancy will have an effective charge of  $+\frac{1}{2}e$ . If it captures an electron, the charge becomes  $-\frac{1}{2}e$ , which will attract a silver ion, and then the speck will grow by successive trappings of electrons and silver ions. Since the most frequently encountered defects in evaporated films are dislocations of  $10^{10}$ – $10^{11}$  lines/cm<sup>2</sup>, Seitz's mechanism for the formation of colloid centers may be applied to our case. It is reported<sup>9</sup> that the increase in thin-film cell resistance due to aging (on storage) can be attributed to coalescence of the  $\text{RbAg}_4\text{I}_5$  film which made it lose contact with the electrode film. This also may accelerate the process of colloid formation.

Light attenuation by a suspension of colloidal particles

is due to both absorption and scattering. The absorption and scattering of light occur in a resonant interaction of the electron plasma in the silver particles with the high-frequency electric field of the light.<sup>24</sup> In the present study, the position of the band is found to vary between 4800 and 5000 Å in the films of different thicknesses. This variation may be due to the difference in the colloid particle size in different films. 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 wavelengths as the particle size increases. Theoretical calculations<sup>22,24</sup> also establish the above fact. Again, the band at 4850 Å is found to be almost temperature independent when studied at 300 and 80 °K. This can be attributed to the fact that the colloidal particles should not be coupled with the lattice vibrations and hence the half-width and peak positions should not be affected by temperature variation.

The broadening of this absorption band has been said to be due to the growth of the particles. Thus, the observed characteristic of the band at 4850 Å in the present study can be accounted for by the features of the colloid centers in other alkali and silver halides.

## SUMMARY

The electrical conductivity studies done on vacuum-evaporated  $\text{RbAg}_4\text{I}_3$  thin films gave an activation energy of 0.1 eV for the  $\text{Ag}^+$ -ion conduction, which agreed with the earlier reported values. The activation energy deduced below the phase-transition temperature (210 °K) is 0.2 eV, which is twice the value obtained for conduction above the transition temperature. The mean free path of the  $\text{Ag}^+$  ion and the lifetime of the excited state calculated from the conductivity data are 0.25 Å and  $0.56 \times 10^{-13}$  sec, respectively, which agree with the theoretical calculations done earlier in order of magnitude.

Optical absorption studies in  $\text{RbAg}_4\text{I}_3$  films reveal some interesting phenomena. A well-defined exciton state at 3750 Å has been observed at 300 °K. The optical band gap of the material is calculated from the position of the exciton band to be 3.387 eV. The weak band observed on the higher-energy side of the exciton band (3750 Å) has been attributed as evidence for the existence of large-radius excitons. A broad band at 4850 Å has the characteristics of a colloidal band. A forbidden internal transition in free  $\text{Ag}^+$  ions becoming activated because of the structure of  $\text{RbAg}_4\text{I}_3$  has been observed at 4250 Å.

There have been some attempts to make silver halide thin-film electrolytic cells. Since the stability of the super-

ionic conductor  $\text{RbAg}_4\text{I}_3$ , is due to its crystal lattice structure, studies are required to examine the effect on the properties and composition of the above compound in the thin-film form. The present study indicates that the thin films of the above compound are very well formed and compare well with the reported best bulk characteristics. Hence, thin-film electrolytic cells using the above compound as an electrolyte can be prepared. Care should be taken in choosing the electrodes such that resistance of the electrochemical double layer at the electrode-electrolyte interface is as minimized as possible. An all-thin-film cell represents a goal in miniaturization and is useful in a variety of low-power applications in microelectronics.

- <sup>1</sup>J.N. Bradley and P.D. Greene, *Trans. Faraday Soc.* **62**, 2069 (1966); **63**, 425 (1967).
- <sup>2</sup>B.B. Owens and G.K. Argue, *Science* **157**, 308 (1967).
- <sup>3</sup>J.N. Murgudich, in *Encyclopedia of Electrochemistry*, edited by C.A. Hampel (Reinhold, New York, 1957).
- <sup>4</sup>M. De Rossi and B. Scrosati, *Electrotehnica* **54**, 779 (1967).
- <sup>5</sup>M.R. Manning, C.J. Venuto, and D.P. Boden, *J. electrochem. Soc.* **118**, 2031–2033 (1971).
- <sup>6</sup>M.J. Rice and W.L. Roth, *J. Solid State Chem.* **4**, 294 (1972).
- <sup>7</sup>B. Owens and R. Argue, *J. Electrochem. Soc.* **117**, 898 (1970).
- <sup>8</sup>S. Tolansky, *Multiple beam interferometry of surface and films* (Clarendon, Oxford, 1948).
- <sup>9</sup>John. H. Kennedy, Fred Chen, and James Hunter, *J. Electrochem. Soc.* **120**, 454 (1973).
- <sup>10</sup>V.S. Borovkov, A.K. Ivanov-Shits, and L.A. Tsvetnova, *Sov. Electrochem.* **11**, 624 (1975).
- <sup>11</sup>H. Wiedersich and W.V. Johnston, *J. Phys. Chem. Solids* **30**, 475 (1969).
- <sup>12</sup>S. Geller, *Science* **157**, 310 (1967).
- <sup>13</sup>W.L. Roth, *J. Solid State Chem.* **4**, 60 (1972).
- <sup>14</sup>W.J. Pardee and G.D. Mahan, *J. Chem. Phys.* **61**, 2173 (1974).
- <sup>15</sup>W.V. Johnston, H. Wiedersich, and G.W. Lindberg, *J. Chem. Phys.* **51**, 3739 (1969).
- <sup>16</sup>G. Burlev, *J. Chem. Phys.* **38**, 2807 (1963).
- <sup>17</sup>F. Seitz, *Rev. of Mod. Phys.* **23**, 328 (1951).
- <sup>18</sup>R.N. Kurdyumova and D.T. Sviridov, *Sov. Phys.-Crystallogr.* **12**, 643 (1968).
- <sup>19</sup>R.S. Bauer and B.A. Huberman, *Phys. Rev. B* **13**, 3344 (1976).
- <sup>20</sup>Hitoshi Sumi, *J. Phys. Soc. Jpn.* **32**, 616 (1972).
- <sup>21</sup>R.S. Knox and K.J. Teegarden, in *Physics of Color Centers*, edited by W.B. Fowler (Academic, New York, 1968), Chap. I.
- <sup>22</sup>W.D. Compton and J.H. Schulman, *Color Centers in Solids* (Pergamon, New York, 1962), Chap. IX, p. 256.
- <sup>23</sup>F.C. Brown and N. Wainfan, *Phys. Rev.* **105**, 93 (1957).
- <sup>24</sup>J.M. Worluck, *Phys. Rev.* **147**, 636 (1966).
- <sup>25</sup>N.F. Mott and R.W. Gurney, *Electronics Processes in Ionic Crystals* (Clarendon, Oxford, 1948), p. 227.
- <sup>26</sup>Allen B. Scott, William A. Smith, and Milton A. Thompson, *J. Phys. Chem.* **57**, 757 (1953).
- <sup>27</sup>W.T. Doyle, *Proc. Phys. Soc.* **75**, 649 (1960).