

# Effect of additive coloring on the ionic conductivity of solid $\text{RbAg}_4\text{I}_5$ electrolytes

S. I. Bredikhin, N. N. Kovaleva and N. V. Lichkova

*Institute of Solid State Physics*

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The effect of additive coloring by iodine on the ionic conductivity of  $\text{RbAg}_4\text{I}_5$  crystals is investigated. It is discovered that insignificant changes in the stoichiometry of the specimens relative to silver of  $\leq 10^{-3}$  at % may cause substantial changes in the ionic conductivity  $\Delta\sigma_i/\sigma_0 \sim 0.1$ . The dependence of the ionic conductivity on the ratio of the total intensities of the primary bands in the photoluminescence spectrum of the  $\text{RbAg}_4\text{I}_5$   $\gamma$ -phase is established; these bands are produced by the luminescence centers containing the vacancies and interstitials of the silver cations. It is demonstrated that this effect is due to the change in mobility of the silver cations when their concentration is changed slightly.

Superionic crystals have been the subject of substantial attention due to their anomalously high ionic conductivity at comparatively low temperatures. Nonetheless, no information is currently available on the possible causes or mechanisms responsible for the ionic electrical conductivity in the superionic state. It is therefore useful to investigate the effect of stoichiometry with respect to the ions of the mobile subsystem on the ionic conductivity of solid electrolytes.

The present study analyzes the effect of additive coloring by iodine on the ionic conductivity  $\sigma_i$  and activation energy  $E_a$  of ionic migration in  $\text{RbAg}_4\text{I}_5$  crystals. The tests were performed on polycrystalline  $\text{RbAg}_4\text{I}_5$  specimens grown from the melt by the zone float technique.<sup>1</sup> Special cleaning techniques and optimum crystallization conditions made it possible to reduce the concentration of detectable heavy metal impurities in the specimens to  $10^{-4}$  wt %. The conductivity was measured by a four-contact a.c. technique. The silver point contacts were microwelded to the specimen immediately prior to the measurements. The contact quality was monitored by the frequency dependence of the electrical conductivity. The ionic electrical conductivity was measured at  $\approx 10^4$  Hz from the slope of the I-V characteristic with a measurement accuracy of better than  $\pm 5 \cdot 10^{-3}$   $(\Omega \cdot \text{cm})^{-1}$ . In order to measure the temperature dependence of the conductivity the specimen was placed in a thermostat in which temperature was maintained accurate to  $\pm 0.2$  K. The photoluminescence spectra were measured on the experimental set-up described in detail in Ref. 2. The photoluminescence was recorded from a freshly-cleaved surface of the specimen in a reflection geometry at  $T \approx 5$  K.

The additive coloring of  $\text{RbAg}_4\text{I}_5$  crystals in  $\text{I}_2$  vapors occurring at room temperature results from the time mobility of  $\text{Ag}^+$  ions. According to a simple model the iodine atoms are adsorbed on the crystal surface. Mobile silver ions that chemically combine with the ions adsorbed at the surface migrate from the crystal bulk to the surface. This forms holes that together with the silver vacancies  $[V]_{\text{Ag}}$  form  $V$ -centers in the  $\text{RbAg}_4\text{I}_5$  crystal that diffuse into the specimen bulk. Light absorption in iodine-colored  $\text{RbAg}_4\text{I}_5$  crystals was investigated in Refs. 3, 4; the data from these studies suggest that the concentration of the color centers was  $10^{16}$ – $10^{18}$   $\text{cm}^{-3}$ , which corresponds to a change in the stoichiometry with respect to the silver cations of  $10^{-4}$ – $10^{-2}$  at %. The additive coloring process is reversible, and the specimens lose their color after a few days.

Analyses of the effect of additive coloring on the ion conductivity of  $\text{RbAg}_4\text{I}_5$  solid electrolytes made it possible to establish that insignificant changes in the stoichiometry of the specimen with respect to the silver cations resulting from coloring ( $10^{-4}$ – $10^{-2}$  at %) will cause relative changes in conductivity  $\sim 10\%$ . Figure 1 provides measurement results for the conductivity of the  $\text{RbAg}_4\text{I}_5$  specimen after coloring in iodine vapors and subsequent complete loss of color ( $T \approx 300$  K). In this case the loss of ion conductivity from coloring is reversible and conductivity is nearly completely restored after decoloration of the specimen to its initial level.

Temperature measurements of the conductivity in the 300–380 K range were carried out in order to investigate the effect of additive coloring on ion conductivity. In classical ion crystals the ion migration process can be described by a simple jump model; the transport mechanism in superionic conductors has not yet been completely worked out. Formally the temperature dependence of the ionic conductivity in both cases has an Arrhenius nature and is described by the following formula:

$$\sigma_i = \frac{AD_0 \exp(-E_a/kT)}{kT}, \quad D(T) = D_0 \exp\left(-\frac{E_a}{kT}\right), \quad (1)$$

where  $E_a$  is the ion transport activation energy,  $AD_0$  is the preexponent. Taking the logarithm of this equation we obtain a straight line equation for the function  $\ln(\sigma_i kT) = f(1/kT)$ :

$$\ln(\sigma_i kT) = \ln(AD_0) - E_a/kT. \quad (2)$$

The solid circles in the left graph in Fig. 2 represent the

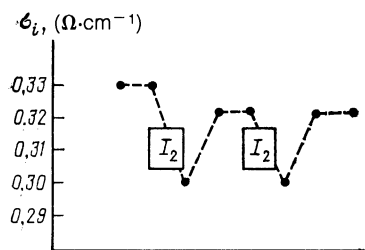


FIG. 1. Effect of additive coloring by iodine on the ionic conductivity of  $\text{RbAg}_4\text{I}_5$  crystals ( $T \approx 300$  K).

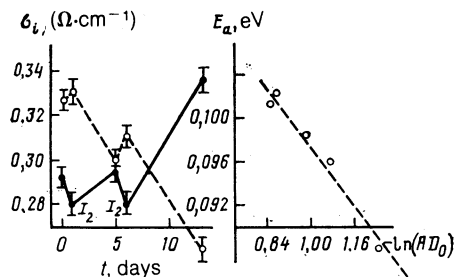


FIG. 2. Effect of additive coloring by iodine on the ionic conductivity ( $T \approx 300$  K) (solid curve) and activation energy (dashed curve) of  $\text{RbAg}_4\text{I}_5$  crystals.

ion conductivity measurement results for the  $\text{RbAg}_4\text{I}_5$  specimen at  $T \approx 300$  K. The first point on the graph corresponds to the initial specimen, while subsequent specimens are obtained after measuring either a colored or decolored specimen. The coloring process is represented in the figure by  $I_2$ . The time interval between measurements in units of days is plotted on the X-axis. The values of  $E_a \pm \Delta E_a$  and  $\ln(AD_0) \pm \delta$  corresponding to the activation energy are recovered from the temperature dependence of the ion conductivity using Eq. (2) by the least squares method; these are represented by the open circles in the graph. In this case a decreasing ion conductivity and a growing activation energy are observed after coloring of the  $\text{RbAg}_4\text{I}_5$  crystal in iodine vapors; the conductivity grows after decoloration, while the activation energy diminishes correspondingly. We know that when heterovalent impurities are introduced into ionic crystals the changes in  $E_a$  and  $\ln(AD_0)$  correlate<sup>5,6</sup>:

$$\ln(AD_0) = aE_a + b, \quad (3)$$

where  $a$  and  $b$  are constants. A relation of the form (3) is called a compensation law or Meyer-Neldel rule. A plot of the activation energy  $E_a$  as a function of the logarithm of the coefficient is shown on the right in Fig. 2; the experimental points lie on a straight line:

$$\ln(AD_0) = (28 \pm 3)E_a - (3.71 \pm 0.01).$$

Therefore additive coloring causes  $E_a$  and  $\ln(AD_0)$  to experience a correlated variation consistent with the compensation law, while the cation mobility  $\mu$  obeys the Einstein formula  $eD = \mu kT$ .

Previously<sup>2</sup> we established that the photoluminescence (PL) of the  $\gamma$ -phase of  $\text{RbAg}_4\text{I}_5$  crystals can be attributed to the color centers. Analyses of the PL spectra have revealed that the  $\lambda_{\text{PL1}} \approx 390$  nm band is due to centers which include the  $\text{Ag}^+$  cation vacancies, and the  $\lambda_{\text{PL3}} \approx 455$  nm band is due to centers including the interstitial silver cations, while the intensity ratio  $I_i/I_v$  of these bands correlates with stoichiometry with respect to the silver cations of the  $\text{RbAg}_4\text{I}_5$  crystals. Therefore additive coloring by iodine which is associated with an increase in the concentration of silver cation vacancies in the crystal bulk will serve to increase the intensity  $I_v$  of the  $\lambda_{\text{PL1}} \approx 390$  nm band and will decrease the intensity  $I_i$  of the  $\lambda_{\text{PL3}} \approx 455$  nm band. Parallel measurements of the electrical conductivity (at  $T \approx 300$  K) and PL spectra of the  $\gamma$ -phase made it possible to establish a correlation between the ion conductivity and the ratio  $I_i/I_v$  of the integral band intensities in the PL spectrum.

The open circles in Fig. 3 represent the measurement results for uncolored initial crystals, while the solid circles represent measurement results for crystals following coloring in the iodine vapors. The entire measurement range along the X-axis corresponds to a variation in the color center concentration ranging over  $10^{16}$ – $10^{18}$   $\text{cm}^{-3}$ , which amounts to  $10^{-4}$ – $10^{-2}$  at %. At the same time the amplitude of the variation in ionic conductivity amounts to approximately 27%. The figure clearly indicates that the decreasing relative fraction of vacancies is accompanied by a drop in the electrical conductivity, while the conductivity reaches a maximum as the relative fraction of defects associated with the interstitials increases, after which it again decreases. The optimum ratio between the concentrations of defects associated with the interstitials and the silver cation vacancies corresponds to the maximum of  $\sigma_i$  in the graph (Fig. 3) which in principle may correspond to stoichiometric composition of the  $\text{RbAg}_4\text{I}_5$  crystal. Deviation from stoichiometry is expressed as an excess concentration of defects associated with the vacancies or the interstitials and in this case a decreasing ion conductivity is observed experimentally. As we know the integral intensities of all the bands are proportional to the concentrations ( $n_i, n_v$ ) of the corresponding luminescence centers although each band has its own quantum efficiency. Hence  $\ln(n_i/n_v)$  may shift relative to  $\ln(I_i/I_v)$  by a magnitude corresponding to the constant. The derived  $\sigma_i = f(I_i/I_v)$  relation explains the ambiguous variation of  $\sigma_i$  resulting from the coloring of  $\text{RbAg}_4\text{I}_5$  specimens in the iodine vapors since the effect of additive coloring on the ion conductivity will depend on the initial stoichiometry of the specimens with respect to silver and on the concentration of the color centers. Hence an increase in the ion conductivity was observed together with a diminishing ion conductivity after coloring of several  $\text{RbAg}_4\text{I}_5$  specimens, while in many cases the conductivity remained virtually unchanged.

In the present study the dependence of the ionic conductivity on the color center concentration is investigated. For this purpose we carried out measurements of the time dependence of the ionic conductivity  $\sigma_i(t)$  during the decoloration of colored  $\text{RbAg}_4\text{I}_5$  crystals. Figure 4 provides the values of  $\sigma_i(t)$  for three  $\text{RbAg}_4\text{I}_5$  specimens. The variable nature of the  $\sigma_i(t)$  relations observed from the decoloration of the  $\text{RbAg}_4\text{I}_5$  specimens can evidently also be attributed to the nonmonotonic  $\sigma_i = f(n_i/n_v)$  relation identified here.

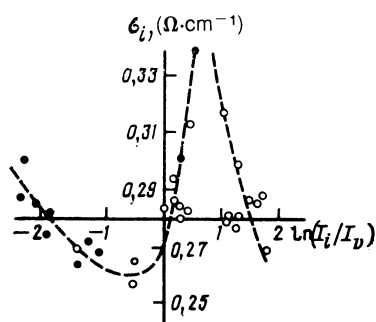


FIG. 3. The ionic conductivity ( $T \approx 300$  K) plotted as a function of the ratio  $I_i/I_v$  of the integral band intensities in the PL spectrum of the  $\gamma$ -phase of  $\text{RbAg}_4\text{I}_5$  related to the interstitials and vacancies of the silver cations.

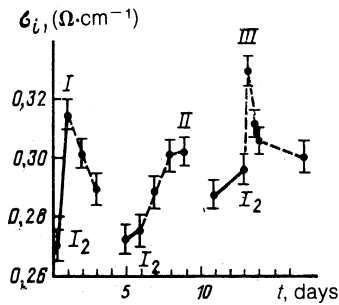
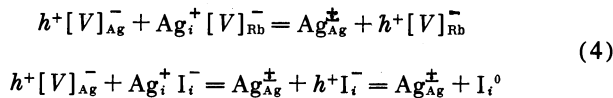


FIG. 4. Change in the ionic conductivity from decoloration of the  $\text{RbAg}_4\text{I}_5$  specimens at  $T = 300$  K (the numbers labeling the curves correspond to the number of the specimen).

We investigate the change in concentrations of optically active centers in the coloring process in order to explain the effect of additive coloring by iodine on the ionic conductivity and PL. One possible structure of the luminescence centers was analyzed in Ref. 7 in a study of the effect of ion implantation on the photoluminescence spectra of the  $\gamma$ -phase of  $\text{RbAg}_4\text{I}_5$ , where it was demonstrated that such centers may take the form of the following complexes containing interstitials and silver cation vacancies:  $\text{Ag}_i^+ [V]_{\text{Rb}}^-$ ,  $\text{Ag}_i^+ \text{I}_i^- [V]_{\text{Ag}}^- [V]_{\text{I}}^+$ ,  $[V]_{\text{Ag}}^- \text{Rb}_i^+$ . Additive coloring causes a diffuse flux of  $h^+ [V]_{\text{Ag}}^-$  color centers to appear in the specimen bulk, thereby reducing the concentration of defects associated with the silver cation interstitials:



and also serves to increase the concentration of defects associated with the vacancies:



It is also important to note that the  $h^+ [V]_{\text{Ag}}^-$  color center is a hole at the iodine ion next to the silver cation vacancy. According to reference data the iodine ion radius is  $2.2 \text{ \AA}$ , while atomic iodine  $\text{I}^0$  has a radius of  $1.33 \text{ \AA}$ . Consequently an elastic stress field arises around the color center. The changing concentration of optically active centers is

also accompanied by a change in the local elastic fields in the crystal consistent with (4), (5). We analyze the effect of the elastic stress fields around the luminescence and color centers on the  $\text{Ag}^+$  ion migration process in  $\text{RbAg}_4\text{I}_5$  crystals. The potential energy of the cation in the radial elastic stress field ( $\sigma_{rr} = P_0 a^3 / r^3$ ) takes the form  $U \approx \alpha a^3 / r^3$ , where  $a$  is the lattice constant,  $\alpha$  is the coefficient of 1 eV in ion crystals to within an order of magnitude.<sup>8,9</sup> It was discovered in the present study that additive coloring by iodine of  $\text{RbAg}_4\text{I}_5$  crystals serves to alter the migration energy  $\Delta E_a \approx 0.01$  eV. If we assume that the change in migration energy is due to the change in elastic fields around the color centers, this will occur at a distance  $r_0 \approx (\alpha a^3 / \Delta E_a)^{1/2} \approx 5a$  from the color center. Consequently for a color center concentration of  $N_0 \approx 10^{18} \text{ cm}^{-3}$  the change in activation energy occurs in the bulk of the  $\text{RbAg}_4\text{I}_5$  crystal

$$\Delta V \approx \frac{1}{2} \pi r_0^3 N_0 V_0 \approx 0.4 V_0.$$

These simple estimates suggest that the effect of additive coloring on ion conductivity and activation energy for cation motion identified in the present study may be due to the effect of the elastic stress fields around the color and luminescence centers on the potential barriers for  $\text{Ag}^+$  cation motion, which is responsible for the dependence of mobile cation mobility  $\mu$  on their concentration.

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