Photovoltage in crystals of the solid electrolyte $RbAg_4I_5$

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A current has been observed to flow when regions of $RbAg_4I_5$ crystals near the contacts are exposed to light. The spectral and temperature characteristics of this current has been studied. A method is proposed for studying the spectrum of electronic states in the α phase of the $RbAg_4I_5$ crystal.

Studying the electron subsystem and electronic transport processes in solid electrolytes is more complicated than corresponding studies in ordinary crystals because of effects which stem from the disordering of one of the ion sublattices and also the flow of an ion current. All these difficulties complicate a study of the electronic states and introduce ambiguities in the interpretation of electronic transport phenomena.[1,2]

In this letter we report a study of the effect of illumination on the electrical characteristics of junctions of graphite with a solid electrolyte and of silver with a solid electrolyte, carried out in an effort to learn about the spectrum of electronic states of

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the crystals of the solid electrolyte $RbAg_4I_5$. For the study we used polycrystalline samples of $RbAg_4I_5$ grown from the melt by zone melting.[3] Samples 6 mm long with a cross section of 2×4 mm^2 were cut from the ingots just before an experiment. Electrodes were deposited on the end faces of the samples; the electrodes were fabricated from fine powders of silver and graphite. During the measurements, the sample was in an optical helium constant-temperature chamber.

The study revealed that a current arises in the external circuit when the contact region of the $RbAg_4I_5$ crystal is exposed to light. The direction of this current corresponds to a transport of electrons toward the exposed electrode. The current density is on the order of 10^{-9} A/cm^2. When the light is scanned along the length of the sample, the photocurrent decreases; it changes sign when the middle of the sample is crossed. To determine the mechanism for the appearance of this photostimulated current, we studied its spectral and temperature characteristics. At room temperature the spectrum of the photocurrent (Fig. 1) has four main bands, peaking at 3.31, 2.85, 2.64, and 2.35 eV. As the temperature is lowered to 260 K, the band at 3.31 eV disappears from the spectra of the photostimulated current. Figure 2 shows the temperature dependence of the photostimulated current for the lines at 2.85 and 2.64 eV. At the temperature ($T_c \approx 209$ K) of the phase transition of the $RbAg_4I_5$ crystal from the α phase to the β phase, which is also superionic, the photostimulated current decreases abruptly, and measurements in the β phase become impossible.

Our measurements of the position of the peaks of the lines in the spectra of the photostimulated current showed that the spectral positions of the lines at 2.64 and 2.35 eV do not change as the temperature is lowered. On the other hand, the line which peaks at 2.85 eV at room temperature shifts in the short-wavelength direction. The coefficient of this thermal shift turns out to be $-7.0\pm0.8\times10^{-4}$ ev/K, in good correlation with the temperature-induced changes in the band gap of $RbAg_4I_5$ crystals.[4]

When materials with various (electron) work functions were used as electrodes

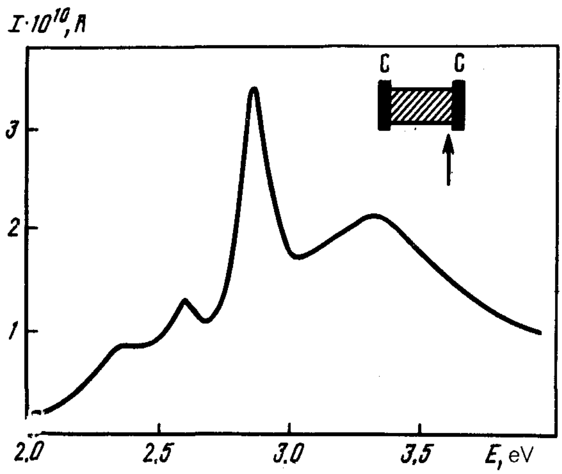

FIG. 1. Spectrum of the photostimulated current during illumination of a region of a $RbAg_4I_5$ crystal near a contact ($T = 300$ K).

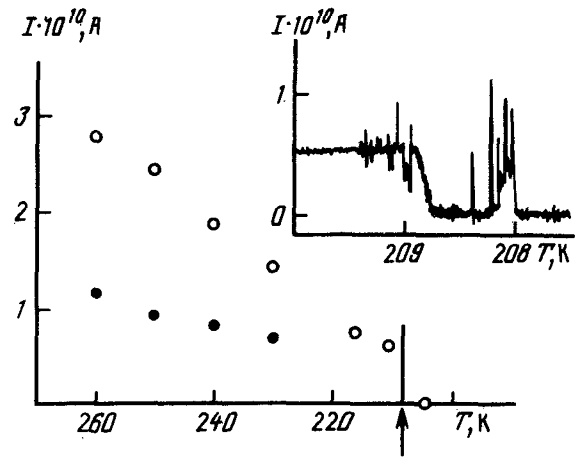

FIG. 2. Temperature dependence of the magnitude of the photostimulated current for bands peaking at (○) 2.85 eV and (●) 2.64 eV (the arrow shows the temperature of the phase transition $T_c \approx 209$ K).

($A_{Ag} \approx 4.5$ eV, $A_C \approx 4.7$ eV; Ref. 5), we observed that the magnitude and spectral characteristics of the photostimulated current depend on the particular region of the sample which is exposed to the light. The direction of the current corresponds to a transport of electrons in the external field toward the electrode which has the higher work function. Figure 3 shows spectra of the photostimulated current which arises during exposure of various regions of a $RbAg_4I_5$ crystal with silver and graphite electrodes. During illumination of the region of a $RbAg_4I_5$ crystal bordering the graphite electrode, the spectra are dominated by the band at 2.85 eV (curve 3 in Fig. 3). In the spectra recorded during exposure of the central part of the crystal we observed a redistribution of the intensities between this band and the band at 2.64 eV. As the light was subsequently scanned along the length of the $RbAg_4I_5$ crystal, from the graphite

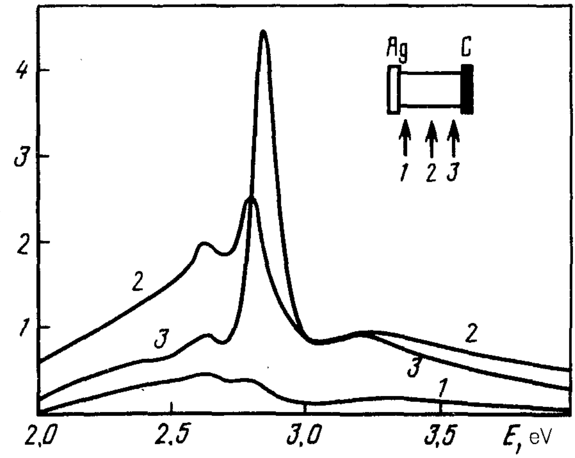

FIG. 3. Spectra of the photostimulated current found during the exposure to light of various parts of a $RbAg_4I_5$ crystal with silver and graphite electrodes ($T = 300$ K).

electrode to the silver electrode, the amplitude of the signal of the photostimulated current decreased rapidly. As the region of the sample being exposed shifts from the graphite electrode to the silver electrode, the spectrum of the photostimulated current reveals a relative decrease in the intensity of the band at 2.85 eV.

Note that all of the lines in the spectra of the photostimulated current correlate with bands in the spectra observed in a study of the optical characteristics of $RbAg_4I_5$ crystals. The line at 3.31 eV coincides with a maximum at the optical absorption edge of thin films and an exciton reflection line of $RbAg_4I_5$ crystals.[4,6] The band at 2.8 eV (435 nm), apparently coincides with a line ($\lambda_{LE} \approx 426$ nm) in the luminescence excitation spectrum of the low-temperature γ phase of the $RbAg_4I_5$ crystals.[7] The broad band with a maximum at 2.4–2.5 eV has been observed previously[8] in the optical absorption spectra of ion-implanted $RbAg_4I_5$ crystals.

The mechanism for the appearance of the photostimulated current is similar to the mechanism for the appearance of a photovoltage during illumination of *p-n* junctions in semiconductors. In this case the nonequilibrium electrons and holes generated by the light are separated by the electric field of the *p-n* junction. According to a simple model involving the diffusion of nonequilibrium carriers, their density falls off in accordance with $\Delta n(x) = \Delta n_0 \exp(-x/L)$ with distance from the illumination region, where $L = \sqrt{D\tau}$ is the diffusion length (D is the diffusion coefficient, and τ is the lifetime of the minority carriers). We see that the decrease in the photocurrent as the light is scanned along the length of the sample and also the change in the sign of the photocurrent when the middle of the sample is crossed result from changes in the fluxes of nonequilibrium carriers which are arriving in the regions of the $RbAg_4I_5$ crystal near the electrodes. It might also be suggested that the absence of a photocurrent in the superionic β phase of the $RbAg_4I_5$ crystal is a consequence of a decrease in the diffusion length L at the transition from the α phase to the β phase.

The correlation between the bands in the spectra of the photostimulate current observed in this study, on the one hand, and the bands which have been observed in a study of the optical characteristics of $RbAg_4I_5$ crystals, on the other, suggests that the spectral and temperature dependence of the photostimulated current can be used to analyze the spectrum of electronic states in the band gap of the superionic α phase of the $RbAg_4I_5$ crystals. The fact that the magnitude and spectral characteristics of the current depend on the particular part of the $RbAg_4I_5$ crystal which is exposed to the light means that one can analyze the variations in the distribution of defects along the length of the sample and the processes which occur near the electrode-(solid electrolyte) junctions.

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