

## PHOTOCONDUCTIVITY AND LIGHT STIMULATED CONTACT POTENTIALS IN $\beta$ -RbAg<sub>4</sub>I<sub>5</sub>

V.G. MURAKHOVSKY † and W. VAN GOOL

*Inorganic Chemistry Department, State University of Utrecht,  
Croesestraat 77A, 3522 AD Utrecht, The Netherlands*

Received 9 January 1984

Revised manuscript received 29 June 1984

Photoconductivity and photoelectric effects have been established in thin polycrystalline films of  $\beta$ -RbAg<sub>4</sub>I<sub>5</sub>. The spectral and the temperature dependence of the phenomena have been studied. The results are interpreted using a model in which ionic processes dominate in the photoconductivity when the exciting photon energy less than 3.2 eV.

### 1. INTRODUCTION

The previous decade was marked by a sharp increase in the number of publications on ionic superconductors. RbAg<sub>4</sub>I<sub>5</sub> is a favourite among these. As a rule single crystals or polycrystalline tablets have been investigated, while the number of publications on physical properties of thin polycrystalline RbAg<sub>4</sub>I<sub>5</sub> films is scarce. This paper presents the results of investigations of photoconductivity and photoelectric voltage in RbAg<sub>4</sub>I<sub>5</sub> when exposed to light as a function of wavelenghts, light excitation and temperatures. The kinetic parameters of certain relaxation processes in polycrystalline RbAg<sub>4</sub>I<sub>5</sub> films have been measured.

### 2. EXPERIMENTAL

Photoconductivity and photoelectric contact voltage of polycrystalline RbAg<sub>4</sub>I<sub>5</sub> films have been measured. The films were obtained by thermal vacuum evaporation techniques (1). X-ray diffraction patterns of the films at ambient temperature showed that their composition corresponds to  $\alpha$ -RbAg<sub>4</sub>I<sub>5</sub>. The film thickness was 1  $\mu$ m. Silver contacts were applied by thermal vacuum deposition. Both planar and "sandwich" geometries were used for the electrodes. The thermal resistance at 120 K was 10<sup>6</sup> Ohm. All experiments were performed in a low-temperature optical cryostat under 10<sup>-7</sup> Torr pressure. The samples were excited by a high-power LOMO-lamp in combination with monochromator, or a set of light filters.

† Permanent address: Technological Institute of Refrigerating Industry, 1/3 Petra Velikogo St, 270000 Odessa, USSR.

### 3. RESULTS AND DISCUSSION

Figs.1 and 2 represent the spectral dependence of the photoconductivity in  $\beta$ -RbAg<sub>4</sub>I<sub>5</sub> films at 120 K.

The two curves correspond to the planar and the sandwich configuration. The peak photoconductivity is at 386 nm which is in good agreement with values found for the optical absorption edge in thin layers of  $\beta$ -RbAg<sub>4</sub>I<sub>5</sub> (2). Fig.2 shows that a large difference in photoconductivity is found as a function of the contact type in the region of 500 - 700 nm. We assume that a great number of surface defect states is present with the planar arrangement of the contacts. This leads to the formation of active clusters in the surface film layer when exposed to light. We assume that the excitation of the carriers from these centers leads to the peak of the photoconductivity curve at 520 nm. Ionic

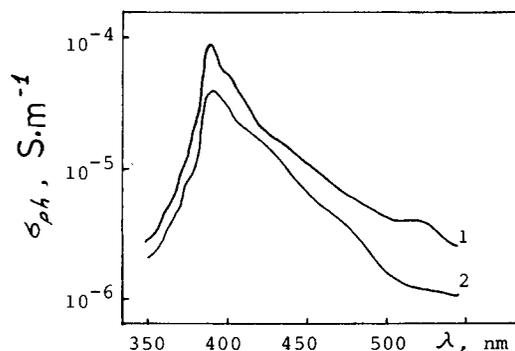


Fig.1. Spectral dependence of photoconductivity in  $\beta$ -RbAg<sub>4</sub>I<sub>5</sub> absorption edge region: 1-planar contact geometry; 2-sandwich contact geometry.

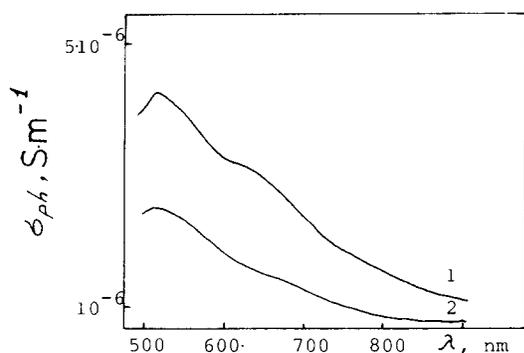


Fig. 2. Photoconductivity in the impurity region: 1-planar contact geometry; 2-sandwich contact geometry.

$\text{MAg}_4\text{I}_5$  type superconductors are known for the formation of quasimetallic centers (clusters) (3).

Fig. 3 present the photoconductivity vs temperature curve at different excitation energies. Interesting is the discrepancy in temperature dependence of the peak values of the photocurrent in the regions of 390 and 520 nm. While the super ionic conductors in the region of 390 nm behave as usual (compared to  $\beta\text{-AgI}$  (4)) the behaviour in the region of 520 nm is far from being standard. This is demonstrated by the fact that in the temperature region of 125 - 200 K the photoconductivity peak values at 520 nm increase with increasing temperature.

The above behaviour of the photoconductivity strengthens our assumption that the relevant defects exists of quasimetallic silver centers in polycrystalline  $\text{RbAg}_4\text{I}_5$  layers. The photoconductivity relaxation kinetics at various temperatures and wavelengths of the excitation light

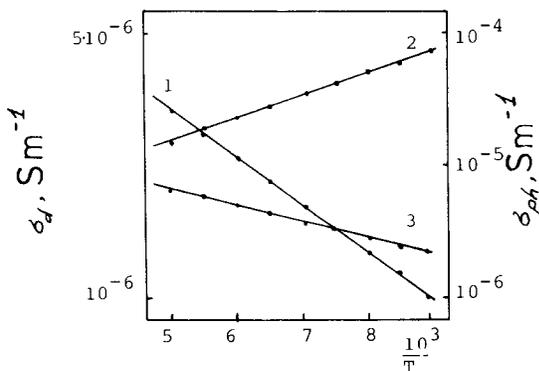


Fig. 3. Photoconductivity versus temperature at different wavelengths of excitation light: 1- dark conductivity; 2-  $\lambda = 390$  nm; 3-  $\lambda = 520$  nm.

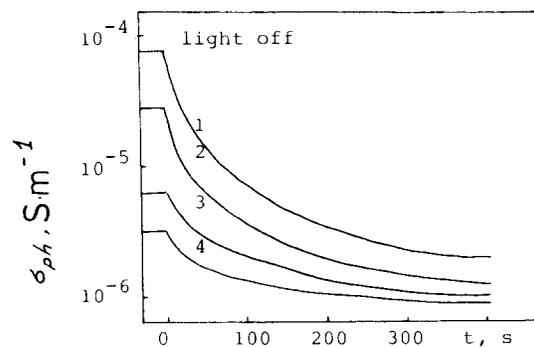


Fig. 4. Kinetics of photoconductivity relaxation: 1,2 - of exciting light 390 nm, temperature 120 and 160 K, respectively; 3,4-  $\lambda = 520$  nm, temperature 120 and 160 K, respectively.

(fig. 4) shows two different types of relaxation processes which suggest the presence of several excitation and recombination paths in  $\beta\text{-RbAg}_4\text{I}_5$ . For one type of relaxation process the characteristic time is  $t_1 = 50$  s; it is most eminent when excitation takes place with  $\lambda < 410$  nm. A second type of decay with  $t_2 > 50$  s takes place over the whole spectral range.

The investigation of thin films of  $\text{RbAg}_4\text{I}_5$  leads to another interesting result, viz. a contact voltage of the order 0.15 - 0.25 V when the layer is exposed to light. Such voltage must in fact be the result of different contact potential barriers in the electrode regions of the films. The spectral dependence of this contact photoelectric voltage is presented in fig. 5; measurements were conducted on samples with planar contact geometry only. An inversion of the sign of the contact voltage was observed for all samples when the excitation takes place in the

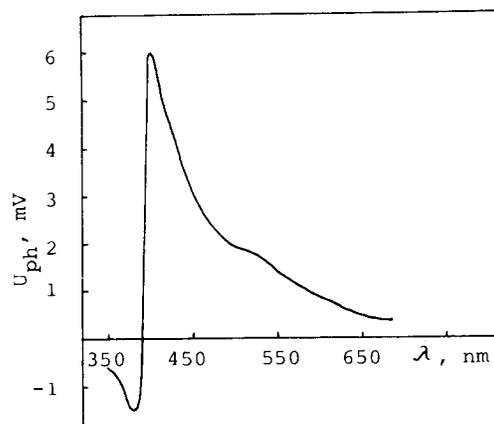


Fig. 5. Spectral dependence of contact photoelectric voltage in  $\beta\text{-RbAg}_4\text{I}_5$ .

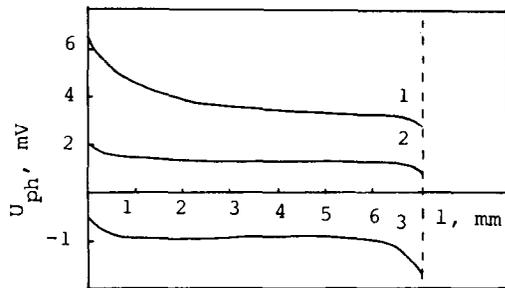


Fig.6. Photoelectric contact voltage versus location and wavelength of light probe: 1-  $\lambda = 390$  nm; 2-  $\lambda = 520$  nm; 3-  $\lambda = 375$  nm.

region of fundamental absorption. The contact photoelectric voltage value depends on the location of the light probe on the film. In order to excite the sample an optical probe (0.5 mm in diameter) with wavelengths 350, 390 and 520 nm (fig.6) was used. The internal field distribution is in good agreement with that described in (5). Such a distribution is characteristic for silver - containing superionic photoelectrets using a weak excitation. The value of contact voltage decreases with increasing temperature.

The results described above lead us to the following conclusions. The mechanism of the physical processes which take place in thin

polycrystalline films of the  $\beta$  - RbAg<sub>4</sub>I<sub>5</sub> superionic conductors when exposed to light does not vary in the wavelength range  $\lambda > 400$  nm. In this spectral region the photoelectric contact voltage changes in the same way as the dark voltage. To our opinion this supports the assumption that exposure of  $\beta$  - RbAg<sub>4</sub>I<sub>5</sub> to light produces Ag "photo" ions. Photoionisation of silver atoms localized in the lattice or on quasimetallic centers may serve as a basis for the emergence of such carriers. In the absorption edge region a change takes place from electronic conduction to predominantly ion conduction with increasing wavelength, which leads to the inversion of photoelectric voltage.

Our conclusion is that the photoconductivity in thin films of  $\beta$  - RbAg<sub>4</sub>I<sub>5</sub> ionic superconductor is due to the production of silver ions by light.

#### 1. REFERENCES

- (1) V.Borzim, E.Vasilkovskaj, I.Pzola, in Sbornic Nauchnyh Trudov IPM (1975) 27 (in Russian)
- (2) V.Murakhovsky, Inorganic Materials 9 (1983) 123 (in Russian).
- (3) V.Drozdov, V.Murakhovsky, Solid State Phys. 21 (1979) 275 (in Russian).
- (4) L.Konstantinov, I.Kostadinov, E.Popov, Solid State Ionics 8 (1983) 127.
- (5) V.Drozdov, P.Kovalsky, V.Murakhovsky, Phys. Semiconductors and Microelectronics (1980) 32 (in Russian).