03

Investigation of the system AgBr-AgI optical materials volt-ampere characteristics

© A. Turabi, N.N. Akif'eva, A.S. Korsakov, L.V. Zhukova¶, A.A. Yuzhakova, D.D. Salimgareev, J.O. Zelenkova

Ural Federal University after the first President of Russia B.N. Yeltsin,
620002 Yekaterinburg, Russia

¶e-mail: l.v.zhukova@urfu.ru

Received February 22, 2022
Revised June 22, 2022
Accepted July 15, 2022

IR light guides based on crystals and ceramics of the AgBr−AgI system are transparent in the mid-infrared range from 2 to 25 μm, which is in demand for thermal imaging, laser technology and spectroscopy. High photo- and radiation resistance makes these materials particularly attractive. For the design of optical equipment, information is needed on the electrical properties of the material, which are most fully characterized by the current-voltage characteristic (VAC). In this work, the dependence of VAC of the studied materials in the range of compositions from 5 to 80 mol.% AgI in the system AgBr−AgI on the composition of the material and temperature in the range of 298-453 K. It has been established that an increase in the iodine content for crystalline materials of AgBr−AgI systems leads to a decrease in electrical conductivity. The values of specific conductivity under equal conditions (the same temperature and the same applied voltage) for ceramics of the AgBr−AgI system are two to three orders of magnitude higher than for crystals. The values of specific conductivity for ceramics are at the level of conductivity of solid electrolytes. At the temperature of the β-AgI−α-AgI phase transition in ceramics of the AgBr-AgI systems, a jump in conductivity is observed, which is explained by the β-AgI−α-AgI phase transition.

Keywords: Solid solutions of the AgBr-AgI system, current-voltage characteristic, specific conductivity

DOI: 10.21883/EOS.2022.10.54864.3311-22

Introduction

For today, crystals and ceramics based on the AgBr−AgI [1,2] system are promising optical materials for the manufacture of IR light guides, windows, lenses, and other optical products. Such crystals and optical ceramics are transparent in the spectral band from 0.46 to 50 μm [1]. The light guides obtained on the basis of these materials are transparent in the wavelength band from 3 to 26 μm [3,4], which, according to Planck's law, corresponds to temperatures from 966 to 188 K. Thus, the considered optical materials can become widely used in various fields of science and technology, including laser, endoscopic and diagnostic medicine, remote thermal & spectral control of technological equipment. Materials of the AgBr−AgI system have a high photo [5], which makes it possible to use these materials without special protective filters. High stability at radiation exposure makes it possible to use these crystalline materials and IR waveguide from them under conditions of increased ionizing radiation up to doses of 500 kGy, which offers exciting possibilities for the introduction of such optical materials in nuclear energy technologies [6,7] and astronautic ones [8].

The purpose of present work is to study the electrical properties, knowledge of which is necessary for the practical application of crystalline materials of the AgBr−AgI system in optical and electrical devices. Such devices are designed to operate in electromagnetic fields, in particular as temperature sensors instead of thermoelectric converters on high-voltage equipment.

As a result of accidents, adverse natural phenomena (lightning), etc. induced voltage may appear on products made of materials under study during their operation on high-voltage equipment (voltage from 10 to 500 ,kV)/. Induced voltage on products made of materials with ionic conductivity can be created by conductors under high voltage, as well as any by high-voltage electrical installations, located near devices using crystalline materials of the AgBr−AgI [9–11] system.

In these cases, it is important to know the level of impressed voltage values that cause deterioration in the transmission properties of IR waves in order to correctly design the device and its protection, as well as correctly formulate the parameters of the main and additional operating conditions of the sensors in terms of influencing values.

The results of studies of the electrical properties of silver halide samples are presented in the works of the authors of this article [1], as well as other authors [12–14].. In these works, the electrical properties of silver halides were studied in in the direction of assessing of conduction type, the current-voltage characteristics (VACs) themselves were not given upon that.

The most complete characteristic of the electrical properties is VAC. VAC demonstrates the nature of the conductivity (conductor, semiconductor, dielectric, material with ionic conductivity) and the destruction potential for the

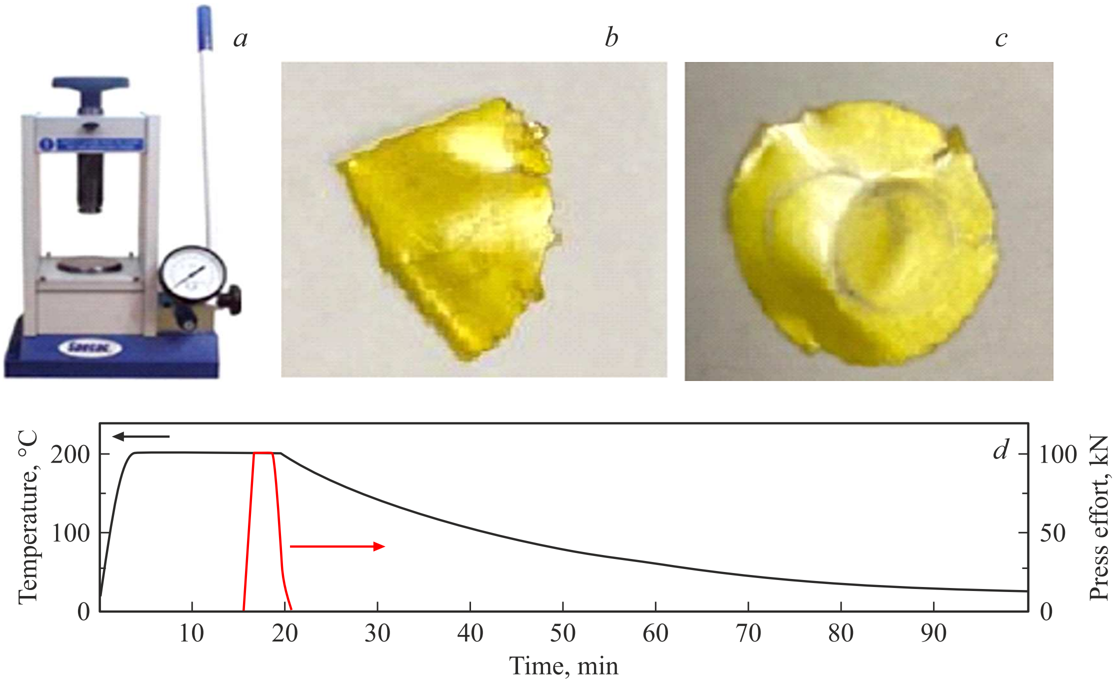

Figure 1. Hand-operated hydraulic press by Specac 15 Ton: (*a*) installation appearance; (*b*) sample of a polycrystalline $AgBr_{0.96}I_{0.04}$ 0.5 mm thick plate before and (*c*) after electrical breakdown; (*d*) temperature conditions and load conditions for plate pressing.

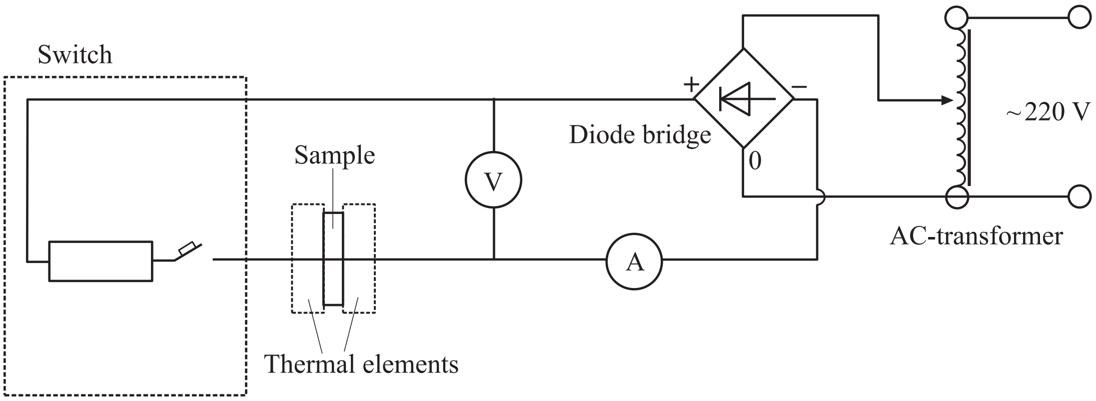

Figure 2. Scheme for measuring the VAC of crystals and ceramics.

material (breakdown voltage). Using the VACs, one can study the dependence of conductivity on various factors: the purity and composition of the material, the phase state, temperature, etc. These data may be required, for example, when manufacturing of spectral fiber-optic sensors operating in wide wavelength band from 3 to 26 μm and allowing you to control the chemical composition of transformer oil, as well as fiber temperature sensors for monitoring the condition high-voltage transformers, generators of power plants etc., when operating near which, under certain conditions, electromagnetic interference occurs with an induced voltage value that can be tens of volts [9–11].

In this work, optical materials with compositions from 4 to 76 mol.% AgI in the AgBr−AgI system were studied. The dependence of the current-voltage characteristics of materials on the composition and on temperature for thin plates with a thickness of 0.5 and 1.7 mm was studied. Also in recent years, in the scientific laboratory „Fiber Technologies and Photonics" of UrFU, the authoring team have studied in detail the phase diagrams of the materials of the AgBr−AgI system (the results of studying the phase state of these systems are given in the work [1]). Therefore, it was of interest in the framework of this work for the AgBr−AgI system to compare the results of the study of the VAC with the results of the study of the phase diagram. The specific conductivity of materials of the AgBr−AgI system was also determined in comparison with the specific conductivity of superionic materials α-Ag-I [12,13].

Materials and methods

To study the VACs, samples of optical materials in the form of plates of optical materials were obtained by hot pressing on a hand-operated hydraulic press by Specac 15 Ton (Fig. 1, *a*), that is used to create flat polycrystalline plates. The loading on the sample with area $\sim 78\,mm^2$ was 6 t [15]. For pressing, the samples were clamped between polished stainless steel plates, and the tooling itself was heated. The plate pressing mode is shown in Fig. 1, *d*.

In the process of pressing, the sample under study was heated to a temperature of 393 K and held for 20 min (plateau in Fig. 1, *d*). This was necessary so that the sample had time to heat up, since insufficient heatup leads to cracking when a loading is applied. At the end of the heatup, a loading of 6ṫ was applied, which was maintained for one minute. Then the resulting plate was cooled to room temperature. To measure the electrical characteristics of crystals and ceramics of the AgBr–AgI system, we used a two-electrode (two-contact) circuit shown in Fig. 2.

In this method, a voltage is impressed to a sample placed between two electrodes. To create an electrical circuit in this experiment, reversible electrodes were used, the reversibility of which is determined in relation to current-conducting ionic (in solid electrolytes) and electron carriers, i.e., the electrode itself „contains" a conducting ion. For the AgBr–AgI system, the material of reversible electrodes is silver.

The measuring circuit contains a rectifier, protective and measuring elements necessary to protect the equipment and ensure multiple repetition of the experiment. During the experiment, a constant current [15] was passed through the plate. The current parameters, namely the current strength and the applied voltage, were recorded using a B7-58 microammeter with a wide measurement range from $1\,\mu A$ to 10 A and a voltmeter by Mastech with a measurement range from $1\,\mu V$ up to 600 V, connected to the circuit as shown in Fig. 2. A preliminary test of this experimental unit is described by the authors in a previous article [15]. The tests were performed using samples of the $AgCl_{0.25}Br_{0.75}$ system. The measurement results obtained on these samples were correlated with the known experimental data of the authors [14], the correlation of the data arrays presented in Fig. 3 was 0.96.

The heating elements shown in Fig. 2 were used to study the temperature VAC. The testing material was clamped by ring electrodes placed between two heating elements of the 15 Ton-press by Specac. Thus, the plate and electrodes were heated to the same temperature, which was maintained with an accuracy of $\pm 1\,^\circ C$ using an heating plate controller of Atlas series. VACs were measured at sample temperatures in the range of 298–503 K. The choice of temperatures is due to the following factors: firstly, the possible applications of these materials, such as spectral and temperature sensors of electrical and thermal equipment; secondly, the interest in the nature of alternating current

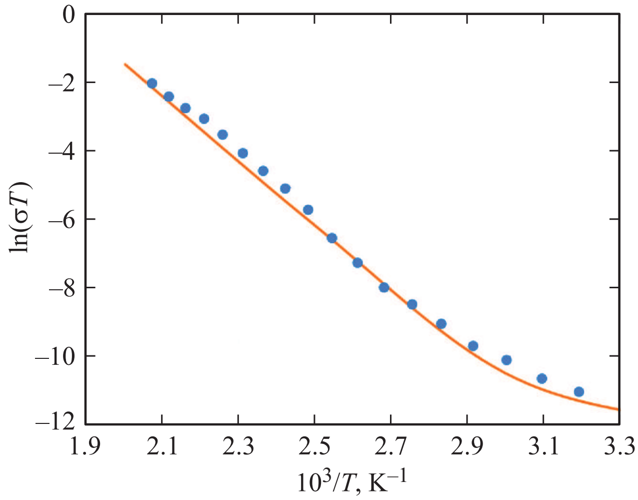

Figure 3. Comparison of the data of the authoring team (points) obtained by the two-electrode method with the known data [15] (line) for the $AgCl_xBr_{1-x}$ solid solution.

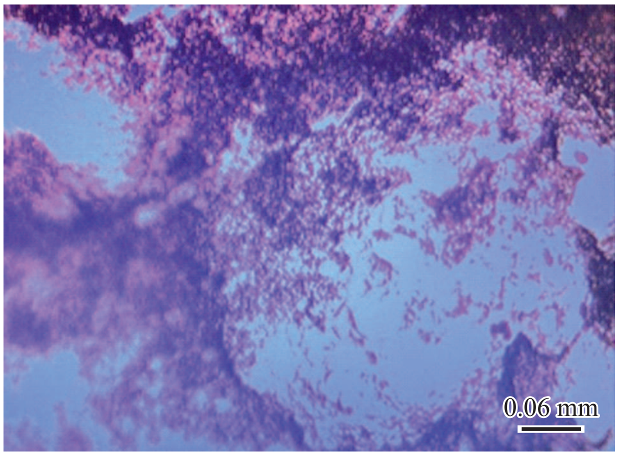

Figure 4. Photo of a plate with the composition $AgBr_{0.76}I_{0.24}$ after electrical breakdown, obtained on optical microscope with a magnification of 200x

in the region of the β-AgI to α-AgI phase transition for ceramics [1]. The thicknesses of the plates under study were 1.7, 0.5, and 0.1 mm. For samples of crystalline plates (the principle of classifying materials of the AgBr–AgI system into crystal and ceramics will be explained later in this work), at each of the chosen temperatures, a voltage was impressed from 0.6 V to voltage at which a breakdown of this plate was observed with the formation „of a silver trace". Example of surface degradation of the plate after electrical breakdown is shown in the photo in Fig. 4.

A voltage was impressed to the ceramic samples at each of the chosen temperatures, from the minimum voltage at which the current was stably fixed (for various compositions and sample thicknesses, this is from 0.02 to 0.6 V), to the voltage at which the current began to increase sharply with virtually no increase in impressed voltage. It should be noted that after a sharp increase in current, the ceramic plates remained intact, and the characteristic was reproduced after repeating the experiment.

When studying the dependence of the VACs of materials on temperature, the voltage was impressed to the plates in steps, with an exposure of at least 2 min at each stage and a subsequent pause of 10–15 min, which is necessary to establish a new temperature mode. Fig. 5 shows the mode of voltage impressing.

The spectral characteristics of crystalline plates based on solid solutions of the AgBr–AgI system were measured using a IRPrestige-21 IR Fourier spectrometer by Shimadzu. The operating parameters of the spectrometer were as follows: operating spectral band from 1.28 to 28.5 μm, divider KBr, detector DLaTGS (deuterated triglycine sulfate doped with L-alanine), resolution 4 cm^{-1}; the number of background and sample scans is 20 scans.

Results and discussion

As already noted in the introduction, in this work, the VACs of materials of the AgBr–AgI system were studied in both crystalline and ceramic forms. The authors attribute the material to crystals if the AgI content in the AgBr–AgI system is in the range 0–30 mol.%, which corresponds to the homogeneity region in the AgBr–AgI phase diagram. At a higher AgI content, the material belongs to optical ceramics, since two phases exist in the solid state (cubic one and rhombic one). This classification is based on the phase diagram obtained in the same laboratory, which carried out the studies of the VACs described in the work [1]. Thus, samples containing AgI 4 and 24 mol.% in AgBr–AgI are crystalline, and samples containing AgI 65–76 mol.% in AgBr– AgI were attributed to ceramics.

Fig. 6, *a–c* shows the VACs obtained for plates made of crystals of the AgBr–AgI system 0.5 and 1.7 mm thick

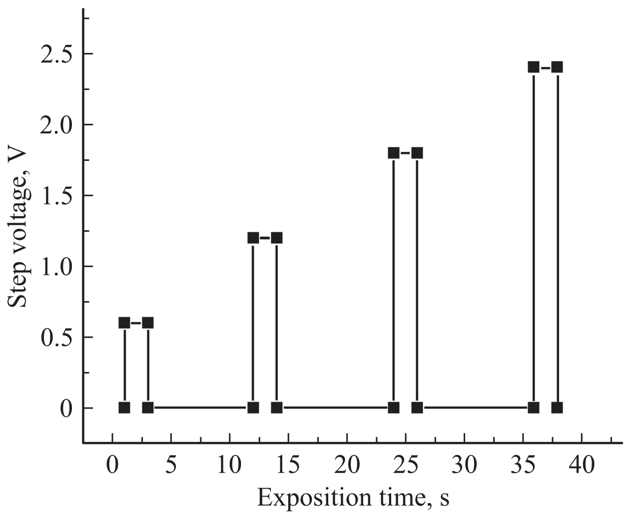

Figure 5. The mode of impressing voltage to the plates under study.

and 10 ± 1 mm in diameter. The dependence of current on voltage is linear up to the breakdown voltage. When approaching the breakdown voltage, a sharp inflection is observed on the diagram. As the temperature of the material increases, the breakdown voltage decreases, and the VAC is smoothed over. The values of the breakdown voltage for plates of the AgBr–AgI system lie in the range of 2–34 V depending on the composition, thickness, and temperature. Fig. 7 shows VACs obtained for AgBr–AgI ceramic plates 0.5 mm thick. As can be seen from the curves, the breakdown voltage for ceramics at the same temperatures is an order of magnitude lower than the breakdown voltage for plates of crystals (Fig. 6).

Fig. 8 and 9 show the transmission characteristics of IR radiation measured for crystalline plates before and after electrical breakdown in the wavelength band from 1.3 to 25.0 μm on IRPrestige IR Fourier spectrometer 21 . It can be seen that electrical breakdown leads to a decrease in transmission over the entire spectral band, so for plates with a thickness of 0.5mm, the decrease in transmission is about 20%; for plates with a thickness of 1.7 mm — about 40%, and this decrease in transmission is more significant in short waves than in long ones. Photographic images of a polycrystalline $AgBr_{0.96}I_{0.04}$ plate 0.5 mm thick before (Fig. 1, *b*) and after (Fig. 1, *c*) of electrical breakdown show the external change of the plates after exposure to an eclectic current in the event of electrical breakdown.

Fig. 10 shows the characteristics of the transient current when the voltage is impressed stepwise (Figure 5) to a plate of composition $AgBr_{0.96}I_{0.04}$ made of crystalline material. The characteristic was obtained at a temperature of 298 K. It is noted that, starting from a certain value of the impressed step voltage, the current characteristic becomes similar to the transient characteristic of a self-leveling oscillatory element. With a further increase in the value of the impressed step voltage and approaching this value to the breakdown voltage, the current characteristic becomes similar to the periodic transient characteristic of an element at the stability boundary.

Fig. 11 and 12 show the specific conductivity of crystals and ceramics at different temperatures. Specific conductivity was calculated by the formula [16]

$$\sigma = L/SR,$$

where L is sample thickness (cm), S is electrode area (cm^2), and R is sample resistance at a given temperature (Ω).

The results obtained are consistent with the data given in the works of other authors. Namely:

• at a phase transition temperature of 463 K, a jump in conductivity is observed in ceramics of the AgBr–AgI system (curves *4* — $T = 453$ K; *5* — $T = 503$ K in Fig. 12), explained by the β-AgI–α-AgI phase transition, which coincides in values with authors' results [12,13];

• the temperature dependences of the conductivity of the AgBr–AgI system, obtained in the temperature range

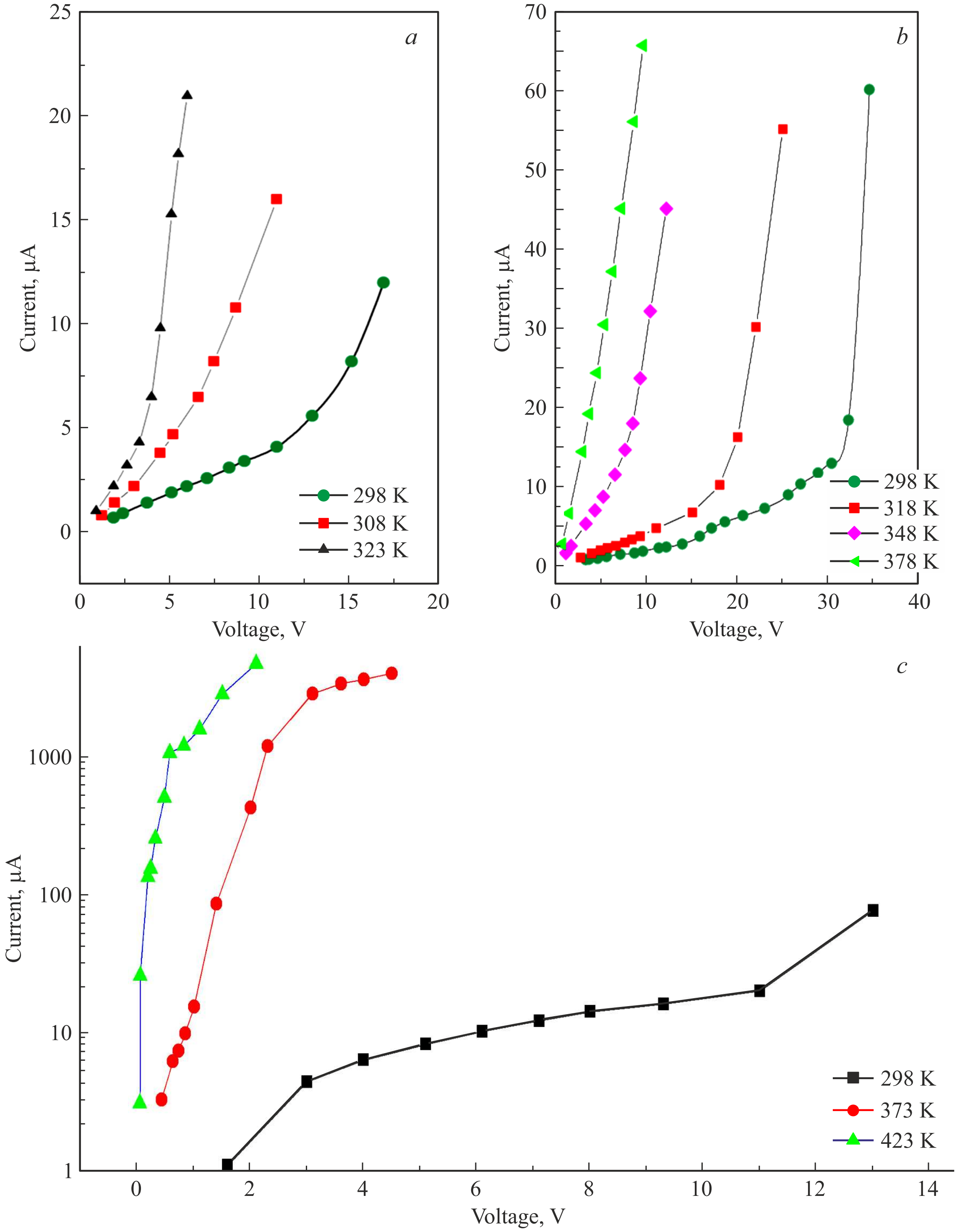

Figure 6. VACs for plates made of crystals of the AgBr–AgI systems: (*a*) $AgBr_{0.76}I_{0.24}$ 0.5 mm thick, (*b*) $AgBr_{0.76}I_{0.24}$ thickness 1.7 mm, (*c*) $AgBr_{0.96}I_{0.04}$ 0.5 mm thick, at various temperatures.

from 298 to 373 K, coincide with the data of other publications [13];

• for temperatures above 373 K data for comparison in the in public sources was not found;

• trends show that the conductivity values for ceramics are at the level of the conductivity values of solid electrolytes [17–19]; these values amount from 0.001 to 100 $\Omega^{-1} \cdot \mathrm{cm}^{-1}$.

An increase in the content of AgI for crystalline materials of the AgBr–AgI system leads to a decrease in electrical conductivity. This can be explained by strengthening the bonds of ionic carriers (Ag^{+}) with the crystal lattice sites

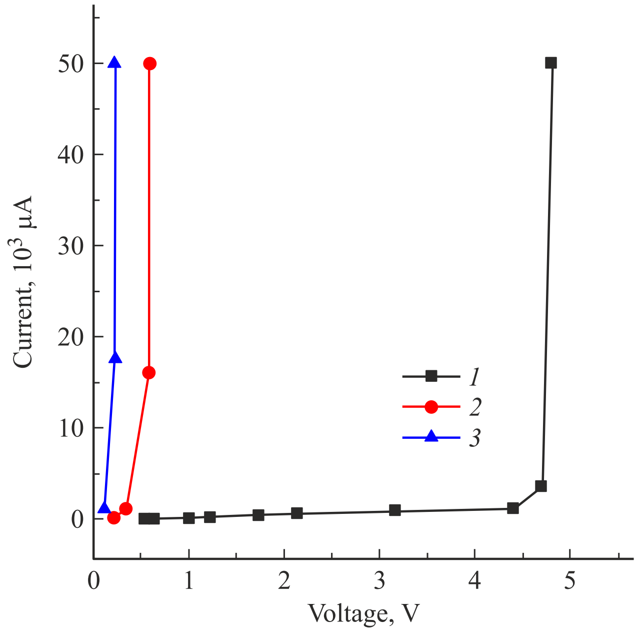

Figure 7. VACs for $AgBr_{0.24}I_{0.76}$ ceramic plates 0.5 mm thick: *1* — 298 K; *2* — 373 K; *3* — 423 K.

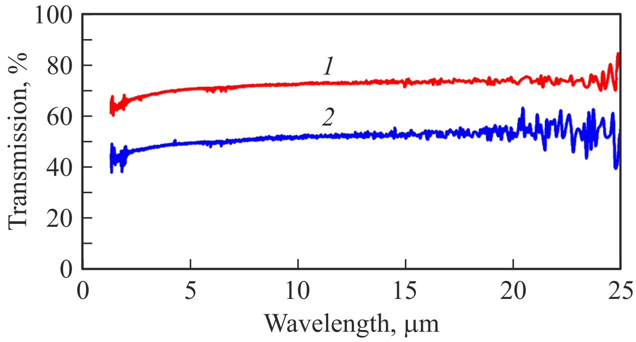

Figure 8. Transmission spectrum of a crystalline plate $AgBr_{0.96}I_{0.04}$ 0.5 mm thick: *1* — before breakdown, *2* — after breakdown.

Ceramic materials of the AgBr−AgI system at the same values are characterized by a higher level of conductivity than crystalline materials. The values of specific conductivity at similar temperatures and applied voltages for optical ceramics are by 2−3 orders of magnitude higher than for crystals. The values of specific conductivity for ceramics are formed by iodine ions, which are heavier and less mobile than bromine ions. For crystalline materials, an increase in the temperature of the material leads to decrease in the breakdown voltage.

Conclusions

It has been found that electrical breakdown leads to a significant deterioration in the transmission characteristics of IR radiation in the entire studied wavelength band from 1.5 to 25.0 μm. These data, as well as the values of the breakdown voltage for crystalline materials containing AgI 4 and 24 mol.% in AgBr−AgI, are important for designing devices using optical materials, in particular, automation devices designed to operate in electrical equipment.

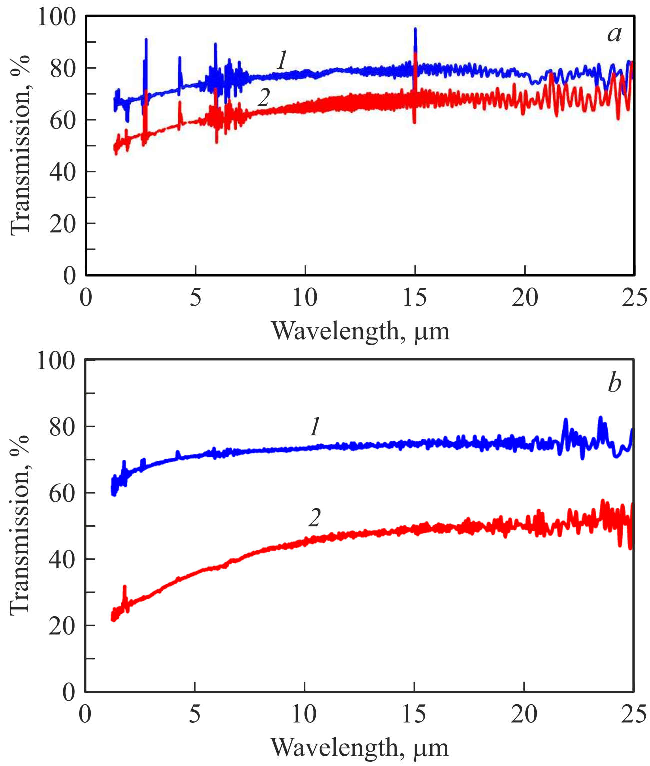

Figure 9. Transmission spectrum of crystalline plates: (*a*) $AgBr_{0.76}I_{0.24}$ 0.5 mm thick, (*b*) $AgBr_{0.76}I_{0.24}$ thickness 1.7 mm; *1* — before breakdown, *2* — after breakdown.

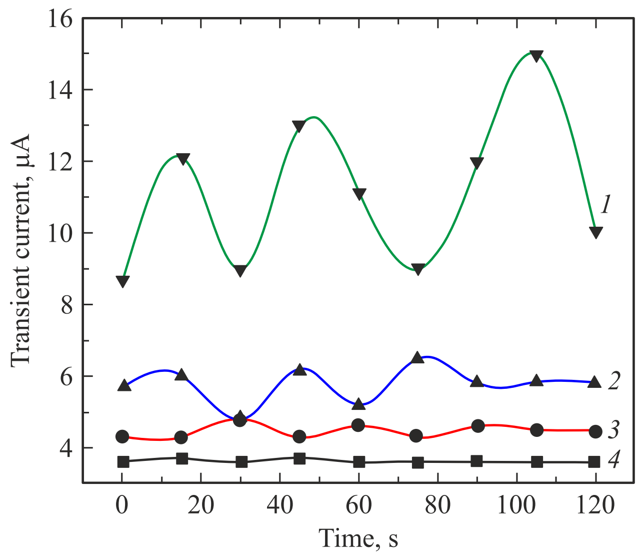

Figure 10. Transient characteristics of the current at a step voltage on a 0.5 mm thick $AgBr_{0.96}I_{0.04}$ plate at a temperature of 298 K: *1* — 8.7 V; *2* — 5.7 V; *3* — 4.3 V; *4* — 3.6 V.

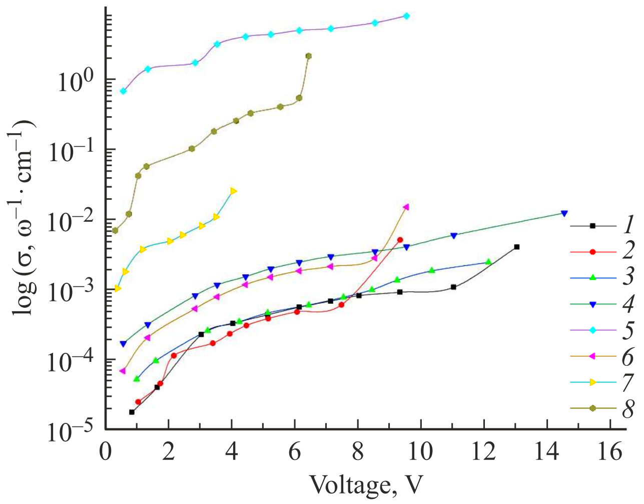

Figure 11. Specific conductivity for crystalline samples of the AgBr–AgI system at different temperatures: *1* — $AgBr_{0.76}I_{0.24}$, $t = 298$ K, thickness = 0.1 mm; *2* — $AgBr_{0.76}I_{0.24}$, $t = 318$ K, thickness = 0.1 mm; *3* — $AgBr_{0.96}I_{0.04}$, $t = 298$ K, thickness = 0.5 mm; *4* — $AgBr_{0.76}I_{0.24}$, $t = 358$ K, thickness = 1.7 mm; *5* — $AgBr_{0.76}I_{0.24}$, $t = 373$ K, thickness = 0.1 mm; *6* — $AgBr_{0.76}I_{0.24}$, $t = 373$ K, thickness = 1.7 mm; *7* — $AgBr_{0.76}I_{0.24}$, $t = 423$ K, thickness = 0.1 mm; *8* — $AgBr_{0.76}I_{0.24}$, $t = 503$ K, thickness = 1.7 mm.

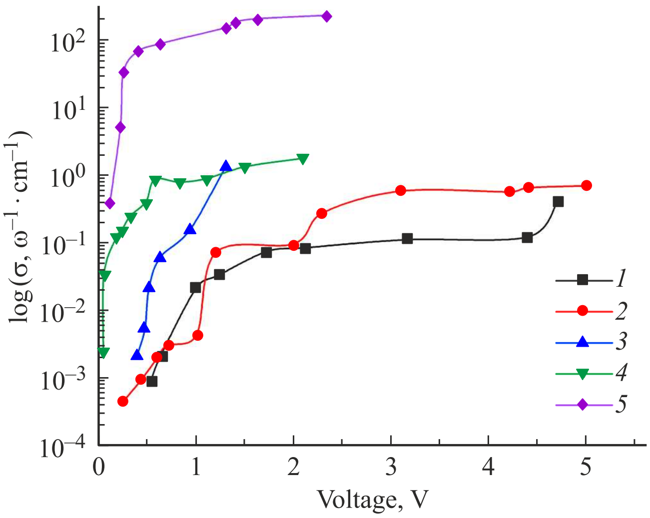

Figure 12. Specific conductivity for ceramic samples of the AgBr–AgI system 0.5 mm thick at different temperatures: *1* — $AgBr_{0.24}I_{0.76}$, $t = 298$ K; *2* — $AgBr_{0.24}I_{0.76}$, $t = 373$ K; *3* — $AgBr_{0.24}I_{0.76}$, $t = 423$ K; *4* — $AgBr_{0.35}I_{0.65}$, $t = 453$ K; *5* — $AgBr_{0.35}I_{0.65}$, $t = 503$ K.

at the level of conductivity of solid electrolytes. This can be explained by weaker bonds of ionic carriers (Ag^+) with iodine ions in ceramics than in a crystal.

VACs of crystals of the AgBr–AgI system, measured by applying voltage to plates 0.5 and 1.7 mm thick from these materials, up to a certain voltage (about 2–3 V) demonstrate a linear dependence of the current on the applied voltage . Further, a nonlinear dependence of the current on voltage is observed, and a periodic section is observed in the characteristics of the transient current. VACs of ceramics, measured by impressing a voltage to plates with a thickness of 0.5 mm from these materials, demonstrate a nonlinear dependence of the current on the applied voltage.

Funding

The study was supported by a grant from the Russian Science Foundation № 21-73-10108, https://rscf.ru/project/21-73-10108/.

References

[1] D. Salimgareev, A. Lvov, L. Zhukova, D. Belousov, A. Yuzhakova, D. Shatunova, A. Korsakov, A. Ishchenko. Optics and Laser Technology, **149**, 107825 (2022). DOI: 10.1016/j.optlastec.2021.107825

[2] D. Salimgareev, A. Lvov, A. Yuzhakova, D. Shatunova, D. Belousov, A. Korsakov, L. Zhukova. Optical Materials, **125**, 112124 (2022).

[3] D.D. Salimgareev, A.A. Yuzhakova, A.E. Lvov, L.V. Zhukova, A.S. Korsakov. Foton-ekspress, **6** (174), 80–81 (2021) (in Russian). DOI: 10.24412/2308-6920-2021-6-80-81

[4] A.A. Yuzhakova, D.D. Salimgareyev, A.Ye. L'vov, A.S. Korsakov, L.V. Zhukova. *Lazerno-informatsionnyye tekhnologii: trudy XXIX Mezhdunarodnoy nauchnoy konferentsii* (BGTU, Novorossiysk, 2021), p. 126–127 (in Russian).

[5] L.V. Zhukova, A.E. Lvov, D.D. Salimgareev, V.S. Korsakov. Opt. Spectrosc. **125** (6), 933–943 (2018). DOI: 10.1134/S0030400X18120238

[6] M.P. Kharain, V.S. Kostarev, N.N. Akif'eva, A.A. Yuzhakova, L.V. Zhukova, A.S. Korsakov. Containment. 2021 In: IOP Conf. Ser.: Mater. Sci. Eng., **1089**, 012048 (2021). DOI: 10.1088/1757-899X/1089/1/012048

[7] A. Turabi, A.S. Korsakov, L.V. Zhukova, B.P Zhilkin. Optical Materials, **109** (4), 110215 (2020). DOI: 10.1016/j.optmat.2020.110215

[8] E. Korsakova, A. Lvov, D. Salimgareev, A. Korsakov, S. Markham, A. Mani, C. Silien, T.A.M. Syed, L. Zhukova. Infrared Physics and Technology, **93**, 171–177 (2018). DOI: 10.1016/j.infrared.2018.07.031".2018.07.031

[9] National standard of the Russian Federation „Facilities for measuring side electromagnetic radiation and pickup parameters.GOST R 53112-2008. [Electronic resource]. URL: https://docs.cntd.ru/document/1200075567

[10] Standard of the company JSC „FGC UES", „Guidelines for determining the induced voltage on disconnected overhead lines located near operating OHLs", STO 56947007-29.240.55.018-2009 [Electronic resource]. URL: https://www.fsk-ees.ru/upload/docs/STO-56947007-29.240.55.018-2009.pdf

[11] J. Wang, S. Wang, L. Cai, D. Lu, Q. Li, M. Zhou, Y. Fan. IEEE transactions on power delivery, **35** (4), 1968–1976 (2020). DOI: 10.1109/TPWRD.2019.2958182

[12] A.K. Ivanov-Shits, I.V. Murin. Ionika tverdogo tela. V1 (SPbGU, Sankt-Peterburg, 2000) (in Russian).

[13] V.V. Tomaev, Y.S. Tver'yanovich, M.D. Bal'makov. Crystallography Rep., **57** (7), 948–954 (2012).

[14] L.S. Cain, L.M. Slifkin. J. Phys. Chem. Solids, **41**, 173–178 (1978).

[15] A. Yuzhakova, D. Salimgareev, A. Turabi, A. Korsakov, L. Zhukova. Optics and Laser Technology, **139**, 106995 (2021). DOI: 10.1016/j.optlastec.2021.106995

[16] *Elementarnyy uchebnik fiziki. Ed. G.S. Landsberg. V. II. Elektrichestvo i magnetizm* (Nauka, Moskva, 1985) 479 p (in Russian).

[17] A.K. Ivanov-Shits, I.V. Murin. *Ionika tverdogo tela. V2* (SPbGU, Sankt-Peterburg, 2000) (in Russian)

[18] S. Ono, R. Tomizawa, T. Nagai, Phase Transitions, **93** (9), 856–864 (2020). DOI: 10.1080/01411594.2020.1798956

[19] T. Tani, H. Mifune, S. Yamashita, S. Aiba, T. Ohzeki, K. Yamane, J. Imaging Sci. Technol., **51** (3), 202–206 (2007) DOI: 10.2352/J.ImagingSci.Technol.(2007)51:3(202)