Features of the phase transition in thin films of AgI superionic semiconductor

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The paper considers the features of relaxation processes that characterize the phase transition in the superionic semiconductor AgI. Two maxima correspond to the relaxation of arrays of free electrons and positively charged silver ions were found on the spectra of the dielectric loss tangent and on the Cole−Cole diagrams. It is shown that the material under study is characterized by a temperature hysteresis, which is expressed in the lag in temperature of the reverse phase transition from the superionic phase to the semiconductor one.

Keywords: phase transition, superionic, silver iodide, relaxation processes.

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In recent years, research into solid-state materials with ionic conductivity, which are called „superionics" [1–3], has attracted great interest. A promising feature of such materials for practical use is that they have high values of ionic conductivity in the solid state after a superionic phase transition (PT). The study of phase transitions in solids is the subject of numerous studies, and one of the highly informative methods in this direction is the method of dielectric spectroscopy (DS) [4,5]. The DS method is extremely sensitive to even minor changes in the structure and properties of materials, and the analysis of experimental results significantly expands the understanding of the mechanism of phase transformations in the samples under study. Silver iodide AgI is of great interest for studying — semiconductor phase transitions. Silver iodide has applications in photography [6], photocatalytic reactions, optoelectronics and photonics; in addition, it is used in the design of miniature capacitors with ultra-high electrical capacity [7–10]. In this work, attention is paid to identifying the features of relaxation processes in an array of free charge carriers (electrons and silver ions) in AgI in the region of superionic PT temperatures.

The AgI samples were thin (100 nm) crystalline films synthesized on mica substrates. The half-width of the AgI grain size distribution histogram was 40 nm with a maximum at 96 nm. The first stage of the synthesis consisted of depositing a thin layer of silver onto high-quality (optical) mica 40 μm thick by evaporation in a vacuum, after which the mica heated to 150°C was placed for 45 μm in an atmosphere of iodine vapor. The vapors were created by the sublimation of crystalline iodine at a temperature of 110°C. A monolayer nanocrystalline film AgI was synthesized on mica in the result of the chemical interaction of iodine with silver. Monolayering was confirmed by examining a film section using atomic-force microscopy.

Dielectric spectra were measured using a Novocontrol concept 41 spectrometer at the Center for Collective Use of the Russian State Pedagogical University named after A.I. Herzen. Conductivity spectra were measured in the frequency range $10^{-1}-10^{7}$ Hz. The sample temperature T was varied in the range 140−250°C.

Figures 1, *a* and *b* show the frequency spectra of the dielectric loss tangent $\mathrm{tg}\,\delta(f)$ and Cole−Cole diagram $\varepsilon''(\varepsilon')$ (CC diagram) of a silver iodide (AgI) sample at temperatures near the PT. In this case, the sample was first heated from 140 to 164°C in increments of 3°, and then cooled to the initial temperature. Thus, PT was studied in both the forward and reverse directions. Figure 1, *c* shows the temperature hysteresis loop for $\log(\tau_1)$, where $\tau_1 = 1/(2\pi f_1)$ was the frequency position of the maximum of the function $\mathrm{tg}\,\delta(f)$.

Analysis of Figure 1, *a* shows that with increasing temperature, the frequency f_1 of the location of the maximum $\mathrm{tg}\,\delta(f)$ gradually increases, and the numerical value of its value practically does not change with a change in frequency. In the temperature range 140−160°C, the maximum shifts abruptly towards high frequencies. At high temperatures ($T > 170$°C) a second weak maximum of the $\mathrm{tg}\,\delta(f)$ function appears in the low-frequency area (the curve at $T = 230$°C in Figure 1, *a*). The value of the $\mathrm{tg}\,\delta(f)$ function at the second maximum is small: $\mathrm{tg}\,\delta(f_2) = 0.05$, $f_2 \approx 1$ Hz.

Figure 1, *b* shows Cole−Cole diagrams $\varepsilon''(\varepsilon')$ constructed from the dielectric spectra of the AgI film. They comprise semicircles, the appearance of which weakly depends on temperature in the entire temperature range, with the exception of the high temperature region: at $t > 160$°C,

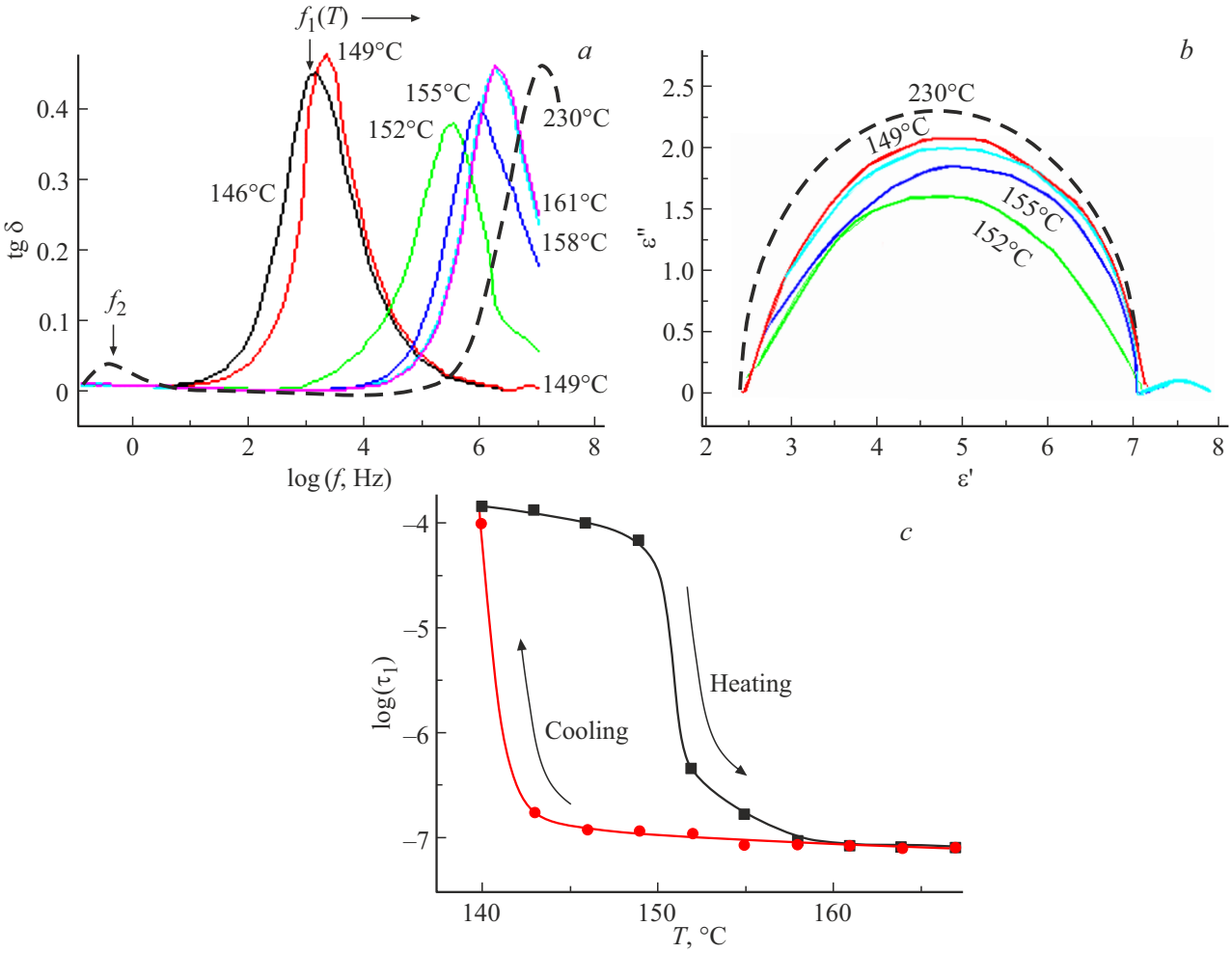

Figure 1. Frequency spectra $\mathrm{tg}\,\delta(f)$ (a) and Cole–Cole diagram $\varepsilon''(\varepsilon')$ for film AgI; (c) temperature hysteresis loop $\log(\tau_1)$. (The colored version of the figure is available on-line).

a part of an additional second semicircle of small radius appears in the right part of Figure 1, b, which corresponds to low frequencies. A careful measurement of the dielectric spectra in the temperature range 140–160°C detects small changes of the form of the main semicircle. It has an irregular shape (compared to the ideal shape of the „Debye" semicircle: the dotted curve in Figure 1, b), and its center is located below the abscissa axis. But with $T = 152$°C the main semicircle takes on the correct shape, but its center ($\Delta\varepsilon'' = 0.5$)) drops even lower.

A detailed study of the temperature dependences of the frequency position $f_1(T)$ of the maximum $\mathrm{tg}\,\delta(f)$ in the temperature range (140–155)°C reveals thermal hysteresis (see Figure 1, c). Temperature hysteresis, expressed in a lag in temperature of the reverse PT from the superionic phase to the semiconductor phase, is characteristic of the entire class of similar materials. The authors of the work [4] when studying the PT in Ag_2S believe that the presence of hysteresis is associated with a change in the symmetry of the crystal lattice, accompanied by a jump in the geometric parameters of the lattice cell, which in turn dictates the need to deviate from the phase equilibrium temperature to ensure the movement of ions gratings into new stable positions. Moreover, such a deviation occurs for both the heating and cooling branches of thermal hysteresis.

In this work, calculations of the dielectric spectra of the AgI film were performed within the framework of the Debye theory. Calculations were carried out for two types of relaxers with characteristic times τ_1 and τ_2, which allows to write the complex dielectric constant ε^* in the form

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1 + (i\omega\tau_1)} + \frac{\Delta\varepsilon_2}{1 + (i\omega\tau_2)}, \qquad (1)$$

where ε_∞ — the high-frequency limit of the real part of the dielectric constant ε^*, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ — the heights of the steps of the real par ε^*, $\omega = 2\pi f$ — angular frequency.

Figure 2 shows the $\mathrm{tg}\,\delta(f)$ graph calculated according to formula (1) and the corresponding Cole–Cole diagram.

The $\mathrm{tg}\,\delta(f)$ dependence has two maxima at the frequencies f_1 and f_2, the $\varepsilon''(\varepsilon')$ CC diagram has the form of regular semicircles of different diameters. Formula parameters (1) are selected in such a way that the calculated

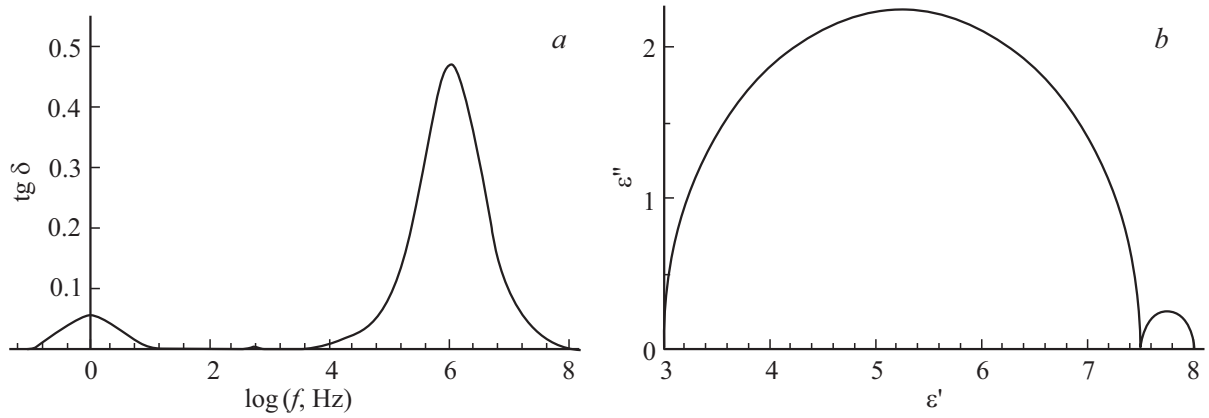

Figure 2. Frequency dependences $\mathrm{tg}\,\delta(f)$ calculated using formula (1) and CC diagram — dependence $\varepsilon''(\varepsilon')$.

curves constructed correspond to the experimental curves obtained at a temperature of 180°C, i. e. at the temperature at which there are simultaneously high-frequency and low-frequency dielectric spectra features in the experiment. A comparison of the graphs in Figures 1 and 2 shows that the Debye theory qualitatively explains the appearance of the dielectric spectrum of silver iodide.

Analysis of the results demonstrates that in our case, the values of the parameters of the dielectric spectra (frequency position of the maxima $\mathrm{tg}\,\delta(f)$, shape and position of the centers of semicircles on the CC diagrams) are determined by a specific type of relaxers, namely, high-frequency features are determined by the relaxation time of the array of free electrons, and low-frequency features — an array of positively charged free silver ions. For both arrays, the characteristic relaxation time is the Maxwellian relaxation time $\tau_{\mathrm{M}} = \varepsilon\varepsilon_0/\delta$, where σ — specific electrical conductivity of the material.

Let us pay attention to the fact that with $t = 140-150$°C, i. e. in the PT area, the Maxwellian time in a narrow temperature interval decreases by 3 order: from $\tau_{\mathrm{M1}} = \tau_1 = 1.6 \cdot 10^{-4}$ to $1.6 \cdot 10^{-7}$ s, respectively ($f_1 = 10^3$ and 10^6 Hz — see curves for $T = 140$ and 152°C in Figure 1, *a*). In other words, the electronic conductivity of the semiconductor layer increases by orders of magnitude. However, in the area of high temperatures, when the semiconductor-superionic phase transition occurred, i. e. with $T > T_c$, a second maximum $\mathrm{tg}\,\delta(f)$ and a second semicircle appear in the low-frequency region on the CC diagram. Such changes in the dielectric spectra in the low-frequency region are associated with additional screening of the external field by the slow drift of an array of positively charged silver ions. The Maxwellian relaxation time is a very large value for free silver ions at $T = 230$°C, i. e. in the temperature range significantly exceeding the temperature of the superionic PT: $\tau_{\mathrm{M2}} = \tau_2 = 1.6 \cdot 10^{-1}$ s ($f_2 = 1$ Hz).

The mechanism for the difference between the times τ_{M1} and τ_{M2} ($\tau_{\mathrm{M1}} \ll \tau_{\mathrm{M2}}$) is associated with the nature of the electrical conductivity of the AgI film. Thus, if the magnitude of the charges and the concentrations of positive and negative charge carriers are practically the same at a given temperature, then the mobility of free electrons is several orders of magnitude higher than the mobility of free but massive silver ions. Assuming, for example, that the mobility of microparticles in a rough approximation is inversely proportional to their mass, and comparing the masses of the Ag ion and the electron, we obtain the value $\tau_{\mathrm{M1}}/\tau_{\mathrm{M2}} \sim 10^5$ observed experimentally (Figure 1).

The presented results demonstrate the important fact that the DS method allows to separately study the electronic and ionic processes occurring during superionic PT. This separation revealed and allowed to determine the characteristic times of Maxwellian relaxation of free charge carriers (electrons and silver ions) in the temperature range of the superionic phase transition in AgI.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] T.Yu. Vergentyev, E.Yu. Koroleva, D.A. Kurdyukov, A.A. Naberezhnov, A.V. Filimonov. FTT, **55** (1), 157 (2013). (in Russian). http://journals.ioffe.ru/articles/viewPDF/907

[2] R.R. Abdulgafarov, L.V. Tsygankova, D.N. Bukharbaev. Sb. tezisov: *Mater. Dvadtsat' shestoy Vseross. nauch. konf. studentov-fizikov i molodykh uchenykh (VNKSF-26, Ufa, Bashkortostan)* („Al'tair LLC", Ufa, 2020) s. 321. (in Russian). https://elar.urfu.ru/bitstream/10995/103805/1/978-5-91951-593-7_2020_225.pdf

[3] N.N. Bikkulova, Yu.M. Stepanov, L.V. Bikkulova, A.R. Kurbangulov, A.Kh. Kutov, R.F. Karagulov. Crystallografiya, **58** (4), 603 (2013). (in Russian). DOI: 10.7868/S0023476113040061

[4] A.V. Ilinsky, R.A. Kastro, M.E. Pashkevich, I.O. Popova, E.B. Shadrin. FTT, **62** (12), 2138 (2020). (in Russian). DOI: 10.61011/FTP.2023.08.56956.5097C
[5] A.A. Kononov, R.A. Castro, Y. Saito, P. Fons, G.A. Bordovsky, N.I. Anisimova, A.V. Kolobov. J. Mater. Sci. Mater. Electron., **32** (10), 14072 (2021). DOI: 10.1007/s10854-021-05986-4
[6] T.KH. Dzheyms. *Teoriya fotograficheskogo protsessa* (L., Khimiya, 1980). (in Russian).
[7] A.V. Dotsenko, L.B. Glebov, V.A. Tsekhomsky. *Physics and Chemistry of Photochromic Glasses* (CRC Press LLC, 1998). DOI: 10.1201/9781003067986
[8] A.I. Gavrilyuk. Phys. Rev. B, **75**, 195412 (2007). DOI: 10.1103/PhysRevB.75.195412
[9] R. Khaton, S. Kashiwagi, T. Iimori, N. Ohta. Appl. Phys. Lett., **93** (23), 234102 (2008). DOI: 10.1063/1.3044385
[10] N.V. Nikonorov, A.I. Sidorov, V.A. Tsekhomsky. Optichesky Zhurnal, **75** (12), 61 (2008). (in Russian).

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