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Polarization processes in silver iodide films near the superionic phase transition temperature

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Abstract. The article reports the results of dielectric spectroscopy analysis exploring polarization processes in silver iodide nanocrystalline films in the region of thermal superionic phase transition. It also provides calculations of the system's relaxation and energy parameters. The abrupt change of parameters at the transition point is demonstrated by activation energy of semiconductor conduction and commit phases, indicator of the degree of frequency dependence of conductivity, and the maximum value of the function of the tangent of the dielectric loss angle. The article proposes a model of the micro-mechanism of the thermal phase transition from a semiconductor to a superionic state. It is shown that, along with the superionic phase transition, films undergo a percolation phase transition with the formation of a two-dimensional percolation cluster.

Keywords: superionic phase transition, silver iodide, dielectric spectroscopy, polarization processes, relaxation processes

Introduction

Solid-state ionic conductors, which include silver iodide, are being actively studied in connection with the prospects of their application. They are used in energy conservation devices, heavy-duty micro-data storage systems, as part of fiber-optic communication lines, etc. (Fokina et al. 2016; Makiura et al. 2009; Naik, Rabinal 2022; Sidorov et al. 2021).

Along with this, it is still of interest to study the mechanism of the thermal phase transition (PT) from a semiconductor to a superionic state at Tc = 440 K (147 °C) (Amrani et al. 2008; Johan et al. 2011), an issue that still remains unexplored.

According to (Vergent'eva et al. 2013), silver iodide exists in three different crystal forms. At T = 293 K (20 °C), AgI is a two-phase mixture of a cubic gamma phase with a zinc blende structure (F43m, a = 6.495 Å, Z = 4) and a hexagonal beta phase with a wurtzite structure (P63mc, a = 4.592 Å, c = 7.510 Å, Z = 2). The predominant phase at T = 293 K is the AgI gamma phase with a zinc blende structure (face-centered cubic structure F43m). However, about 2% β-AgI with a hexagonal wurtzite structure P63mc are also present.

β-AgI becomes a stable phase above 384 K (111 °C). During the thermal phase transition it turns into a body-centered cubic α-AgI at 420 K (147 °C). This phase becomes stable above 420 K and is a superionic phase.

In the high-temperature superionic phase, iodine anions I form cubic cells with a cube edge equal to a = 5.062 Å at 453 K (180 °C) (Wright, Fender 1977). Each Ag$^+$ cation is able to move along the crystal lattice, occupying 21 possible positions in succession. There are three different types of positions in total. There are 6 tetrahedral, 12 trigonal and 3 octahedral positions in a crystal cell. These three types of positions are crystallographically and energetically nonequivalent. Silver cations occupy such positions with different probabilities.

Analysis of the electron density distribution (Ivanov-Shits, Murin 2000) showed that mobile Ag$^+$ cations move freely throughout the crystal, except for the zones occupied by immobile Ag$^+$ and I anions, which stabilize the crystal lattice. This indicates the existence of conducting channels in the alpha phase of the AgI crystal, which interconnect the most probable spatial positions of Ag$^+$.

Thus, the physical cause of the superionic PT is the thermal rearrangement of the crystal lattice structure upon reaching the PT temperature. This rearrangement creates the possibility of the appearance of positions free of silver ions. In this case, almost free migration of silver ions through the crystal lattice becomes possible under the action of an external electric field (Gurevich, Kharkats 1987). From this point of view, silver iodide (AgI) is a model system for studying the superionic phase transition.

Thus, it was shown in (Makiura et al. 2009) that silver iodide nanoparticles 11 nm in size coated with poly-N-vinyl-2-pyrrolidone (PVP) exhibit a decrease in the PT temperature to Tc = 393 K (120 °C) compared to single crystals, in which Tc = 420 K (147 °C). At room temperature, the conductivity of AgI with iodine-coated nanoparticles reaches 1.5×10^{-2} Ω^{-1}cm^{-1}. This is a record for ionic conductivity at T = 293 K for a binary compound.

The authors of (Vergent'eva et al. 2013) studied the behavior of the conduction property of an AgI-based composite embedded in porous glasses (average pore size about 7 nm) and opal (pore size 40–100 nm). They found that the temperature of the phase transition of nanoparticles in porous glasses and AgI opals decreases by 20 K, and the width of the temperature hysteresis loop of the phase transition doubles compared to free nanoparticles. The temperature dependence of the conductivity in this case has a thermally activated character.

Near the phase transition, the parameters of the function σ (1/T) change, which indicates a change in the activation energy of conduction during the superionic phase transition. Thus, in the low temperature phase, the activation energy is 450–470 meV, while in the high temperature phase it is 100 meV.

It was also found that the effect of an anomalous increase in ionic conductivity can be observed when mixing two ionic conductors with the same cation, for example, in AgCl-AgI or AgBr-AgI systems. It was also found that the effect of an anomalous increase in ionic conductivity can be observed when mixing two ionic conductors with the same cation, for example, in AgCl-AgI or AgBr-AgI systems. The reason for this effect is that the common mobile ion, upon transition to the region with a lower chemical potential, increases the number of anion vacancies in the region of the space charge of one of the phases. At the same time, the number of interstitial cations increases in the other phase. This phenomenon is similar to the phenomenon of a sharp increase in ion transport in the near-contact region of two electronic conductors differing in chemical potentials (Ivanov-Shits, Murin 2000).

The above information formed the purpose of this work, which is to use dielectric spectroscopy to study polarization processes in nanocrystalline silver iodide films in the region of thermal superionic phase transition.

Experimental technique

Thin films of silver iodide were synthesized by thermal iodization (at 300 °C) of a layer of metallic silver 180 nm thick and 1 cm^2 in area, which was previously deposited on a glass substrate.

Silver contacts were deposited on the film surface, which ensured the planar geometry of the conductivity study.

The dielectric spectra of the layers under study (temperature-frequency dependence of the complex electrical impedance components) were obtained on a Concept-81 spectrometer (Novocontrol Technologies GmbH) in a wide range of frequencies ($f = 10^0 - 10^6$ Hz) and temperatures (T = 293–473 K).

In this case, the values of the real and imaginary parts of the complex impedance of the cell with the measured sample were measured:

$$Z^*(\omega) = R + \frac{1}{i\omega C} = Z' + iZ'' = \frac{U_0}{I^*(\omega)} \tag{1}$$

On this basis, the frequency spectra of the complex permittivity and complex conductivity were calculated:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{-i}{\omega Z^*(\omega)} \frac{1}{C_0} \tag{2}$$

$$\sigma^* = \sigma' - i\sigma'' = \frac{-i}{\omega Z^*(\omega)} \frac{S}{d} \tag{3}$$

where $C_0 = \frac{\varepsilon_0 S}{d}$ is the capacity of the cell without a sample. The relative error of the experiment did not exceed 5 %.

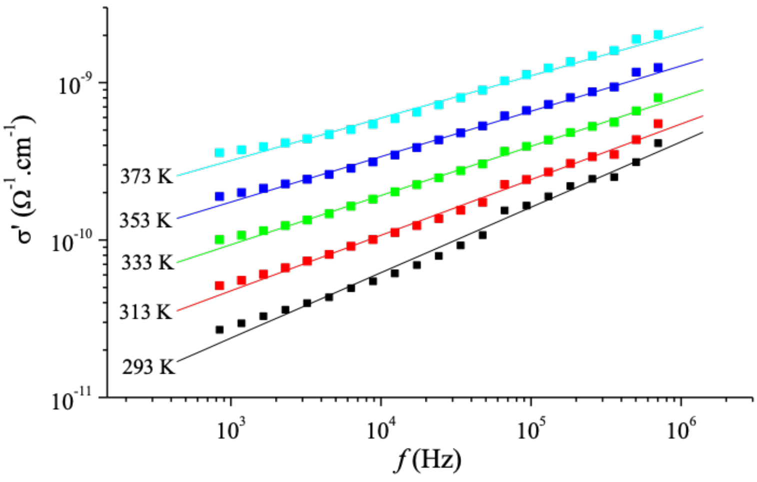
To calculate the values of the relaxation parameters of the system, the obtained dielectric spectra were approximated by the three-parameter Havriliak—Negami function (Kremer, Schonhals 2003). In this case, the computer programs of the Novocontrol Winfit spectrometer were used.

Experimental results with their preliminary analysis

The experiment showed that the frequency dependence of the specific conductivity σ' of thin AgI films increases with increasing frequency of the probing field (Fig. 1). This occurs at all temperatures. It is known (Mott, Davis 1982) that such a dependence of the conductivity on frequency is typical for many crystalline semiconductors and most amorphous semiconductors, for which the frequency dependence of the conductivity obeys the power law of growth:

$$\sigma(\omega) = A\omega^s, \tag{4}$$

where s is the exponent, A is a temperature-dependent constant, $\omega = 2\pi f$ is cyclic frequency.



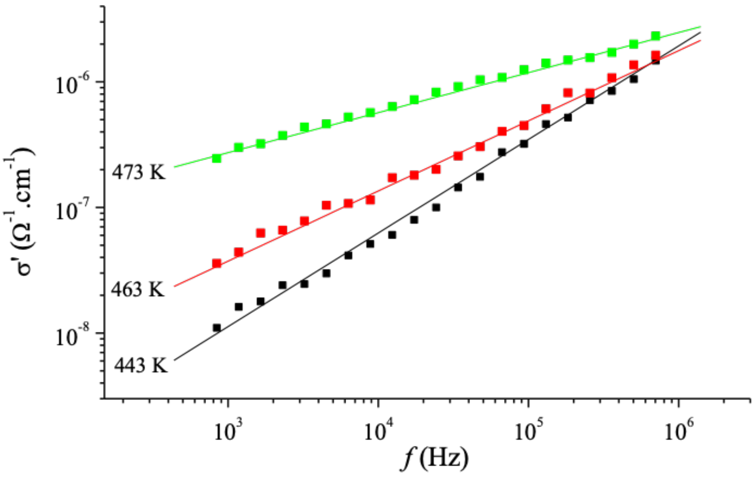


Fig. 1. Frequency dependence of specific conductivity σ' at different temperatures

The presence of Dependence (4) corresponds to the existence of a wide range of relaxators in the system, which have different relaxation times and create different mechanisms of dielectric losses.

The temperature dependence of the exponent *s* can be used to elucidate the features of the charge transfer mechanisms in the low-frequency range at temperatures of 293–473 K (Castro-Arata et al. 2021; Farid et al. 2005; Ulutas et al. 2013). This circumstance forced us to study the temperature dependence of the exponent *s*, which is shown in Fig. 2. This figure demonstrates the existence of two temperature regions: region I in the range $T = 293–433$ K and region II at $T = 433–473$ K. As noted above, at a temperature of $T = 420$ K silver iodide undergoes a structural change with a transition from the beta phase to the alpha phase. It can be argued with a high degree of probability that regions I and II correspond to the state of the system before and after the superionic phase transition, respectively.

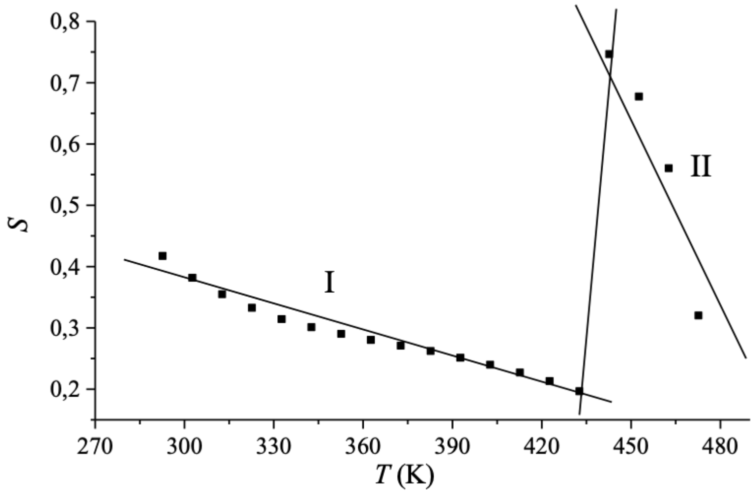


Fig. 2. Temperature dependence of the exponent s of the function *σ*(*ω*) for thin films of silver iodide

The found power Dependence (4) of the conductivity on frequency and the change in the value of the parameter *s* with increasing temperature allow us to assert the existence of a hopping mechanism of conductivity. In this case, charge carriers (ions, electrons) make thermally activated jumps through potential barriers in the structures of the semiconductor system.

The decrease in the exponent s in both phases with increasing temperature indicates the classical case of overcoming the energy barrier by charge carriers, according to the CBH model (correlated barrier hopping model) (Gurevich, Kharkats 1987). In this case, the expression for the conductivity on alternating current at a specific fixed temperature has the form (Makiura et al. 2009):

$$\sigma(\omega) = \frac{\pi^3 N^2 \varepsilon\varepsilon_0 \omega R_\omega^6}{24}, \tag{5}$$

here N is the density of states between which charge carriers jump, R_ω is jump length.

The relationship between the jump length R_ω and the height of the potential barrier is expressed by the relationship:

$$R_\omega = \frac{e^2}{\pi\varepsilon\varepsilon_0}\left[W_M - kT\ln\left(\frac{1}{\omega\tau_0}\right)\right]^{-1}, \tag{6}$$

where τ_0 is the characteristic relaxation time, the reciprocal of the phonon frequency ν_{ph}. On the other hand, the exponent s is related to the barrier height W_M by:

$$s = 1 - \frac{6kT}{W_M}, \tag{7}$$

As was shown in (Amrani et al. 2008), based on the obtained experimental data using Equations (5)–(7), it is possible to calculate the values of the conductivity parameters of the system N, R_ω and W_M at different temperatures. The results of the calculations are presented in Table 1.

Table 1. Values of the charge transfer parameters in thin films of silver iodide before (region I) and after (region II) the superionic phase transition

T (K)	s	N (m^{-3})	R_ω (m)	W_M (eV)
Region I				
293	0.41	1.08E22	2.46E-9	0.25
313	0.35	2.38E22	2.32E-9	0.24
333	0.31	4.77E22	2.17E-9	0.25
353	0.29	8.82E22	2.00E-9	0.26
373	0.28	1.57E23	1.85E-9	0.27
Region II				
443	0.75	1.54E25	7.72E-11	0.92
463	0.55	3.99E27	4.27E-11	0.53
473	0.32	7.46E28	3.17E-11	0.36

Figure 3 shows the temperature dependence of the conductivity of silver iodide films in the coordinates ln[$\sigma(\omega)$]=$\zeta(10^3/T)$. It shows that charge transfer is a thermally activated process. The existence of two temperature regions was found, at the temperature boundary between which a change in the slope of the graphs is observed at T = 428 K. This coincides to within 2% with Tc = 420 K (147 °C) of the superionic phase transition. Before and after the PT, the conduction activation energies are as follows: E_1 = 0.34 eV before the transition and E_2 = 1.63 eV after the transition, respectively.

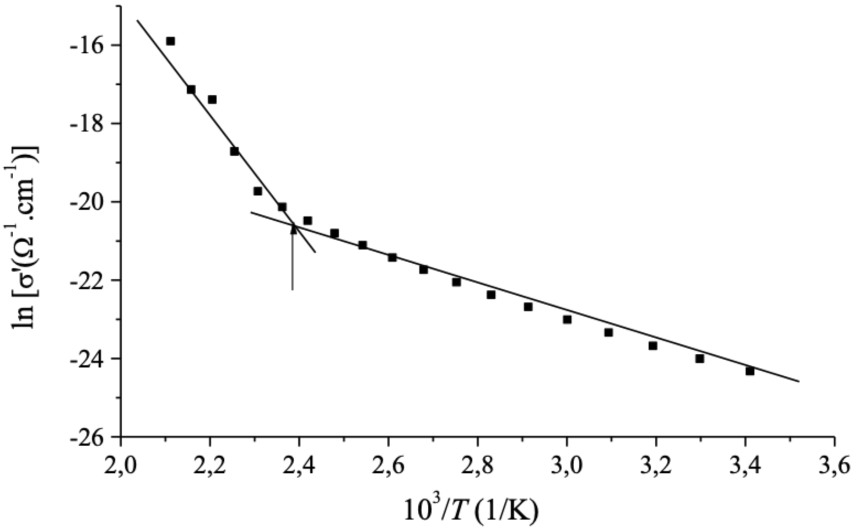


Fig. 3. Temperature dependence of specific conductivity σ' of thin films of silver iodide at frequency $f = 10^3$ Hz

Measurement of the dielectric loss tangent tgδ in AgI films at different temperatures (Fig. 4) revealed the existence of a loss maximum, which shifts to high frequencies with increasing temperature. In this case, the absolute value of the maximum of the function tgδ(ω) at a temperature Tc = 420 K (this is a temperature of the transition of the AgI film to the superionic state) is halved.

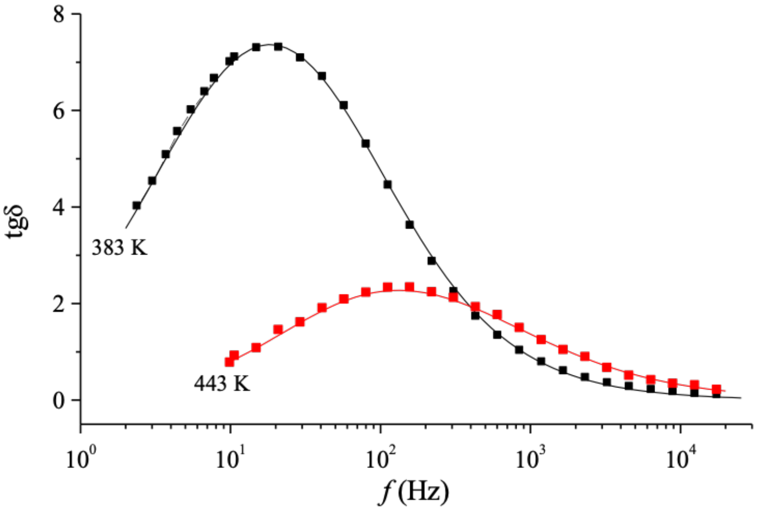


Fig. 4. Frequency dependence of the dielectric loss tangent tgδ = ε''/ε' at temperatures of 383 and 443 K. Solid lines are the approximation of the experiment by Function (8) taking into account the Havriliak—Negami Function (9). After the PT is completed, the temperature rises with a jump in the parameters of Function (9): $\tau = 0{,}08$ s $\rightarrow \tau = 0{,}009$ s, $\alpha = 0.98 \rightarrow \alpha = 97$, $\beta = 0.97 \rightarrow \beta = 0{,}93$

As an approximating function in the calculations, the Havriliak—Negami function was used (Volkov et al. 2018) in the form (8).

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\int_0^\infty \frac{G(\tau)}{1+i\omega\tau}\,d\tau, \tag{8}$$

where ε_s is the permittivity at extremely low frequencies, τ is the relaxation time. This function contains three variable parameters (τ_{HN}, α_{HN} and β_{HN}) for each type of grain and has the form:

$$G(\tau) = \frac{1}{\pi} \times \frac{\left(\tau/\tau_{HN}\right)^{\beta(1-\alpha)} \sin\left(\beta\varphi\right)}{\left[\left(\tau/\tau_{HN}\right)^{2(1-\alpha)} + 2\left(\tau/\tau_{HN}\right)^{(1-\alpha)} \cos\left(\pi\left[1-\alpha\right]\right) + 1\right]^{\beta/2}}, \tag{9}$$

where

$$\varphi = arctg\left[\frac{\sin\left(\pi\left[1-\alpha\right]\right)}{\left(\tau/\tau_{HN}\right) + \cos\left(\pi\left[1-\alpha\right]\right)}\right].$$

Expression (8) together with expression (9) allow using the Havriliak—Negami function to approximate the frequency dependence function tgδ(ω).

Conversely, empirical data on the frequency dependence of the function tgδ(ω) make it possible to determine the parameters of the distribution function of relaxers from their relaxation times. The computer built into the spectrometer allows the fitting procedure and calculations to be carried out automatically.

Namely, in the first case, the value τ_{HNmax} is fixed, ω is a variable, and the theoretical curve is fitted to the experimental results, as shown in Fig. 4. At the same time, for $f_{\max}$ = 20 Hz, the values $\alpha_{HN} = 0.98$ ($T = 383$ K) and $\beta_{HN} = 0.97$ ($T = 383$ K) were obtained. For $f_{\max}$ = 200 Hz, the value $\alpha_{HN} = 0.97$ ($T = 383$ K) and $\beta_{HN} = 0.93$ ($T = 383$ K).

In the second case, the value $\omega_{\max}$ is fixed in expression (8), and the parameter τ is a variable.

The parameters of the HN function reflect the average position of relaxers on the time scale (τ_{HN}), the degree of spread (α_{HN}), and the inhomogeneity (asymmetry) of the distribution of relaxers (β_{HN}) over relaxation times. The software of modern spectrometers makes it possible, as indicated, to obtain the HN function with coefficients τ_{HN} at their output. α_{HN} and β_{HN} are adjusted to the measurement results.

Table 2. Values of the relaxation parameters of thin films of silver iodide in the temperature region of the phase transition

Temp. [K]	**Tau-Max [s]**	**Alpha []**	**Beta []**
403	3.040e-01	1.0000e+00	9.4140e-01
413	7.272e-01	1.0000e+00	9.1930e-01
423	1.847e-01	1.0000e+00	9.1270e-01
433	2.093e+00	1.0000e+00	8.7950e-01
443	1.526e-02	9.7780e-01	8.3950e-01
453	8.530e-02	9.8060e-01	8.0000e-01
463	2.516e-02	9.8970e-01	6.7490e-01

The values of the relaxation parameters of AgI thin films obtained by approximating the experimental curves with a two-parameter empirical Havriliak—Negami function are presented in Table 2.

The analysis of data in Table 2 allows us to conclude that there are non-Debye mechanisms of dielectric relaxation in the region of the PT from a semiconductor to a superionic conductor. Attention is drawn to the maximum value of the most probable relaxation time located near $T = 433$ K, which is close to Tc = 420 K of the superionic phase transition.

As noted, the power-law dependence of the conductivity on frequency is a sign of the existence of a hopping mechanism of charge transfer in the studied frequency and temperature ranges. This corresponds to the presence of a wide range of relaxators in the system, which have different relaxation times and provide different dielectric loss mechanisms.

In this regard, we have studied the behavior of the distribution function of relaxators over relaxation times $G(\tau)$. The value of $G(\tau)$ can be obtained, as indicated, from Expression (8) as a result of solving the inverse problem.

Fig. 5 shows the temperature dependence of the maximum value of the function $G(\tau)_{\text{max}}$, which has a maximum height at a temperature $T = 425$ K. This temperature is also close to the temperature of the superionic phase transition (PT).

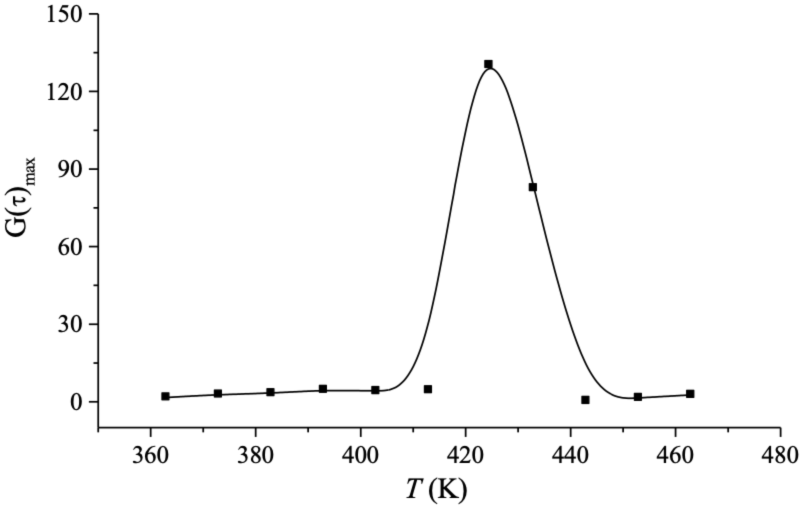


Fig. 5. Temperature dependence of the maximum value of the relaxation time distribution function $G(\tau)_{\text{max}}$ for AgI films

Discussion: A Phenomenological model

The behavior of silver iodide AgI during the thermal phase transition from a semiconductor to a superionic state can be explained by the phenomenological concepts described below.

During the synthesis, the iodination of the metallic silver layer was carried out from the surface of the grains. Therefore, all grains turned out to be covered with a thin layer of crystalline iodine, which has a conductivity an order of magnitude lower than the conductivity of AgI nanocrystallites in the superionic state.

The iodine film played the role of a blocking electrode for the contacts deposited to study the frequency dependence of electrical conductivity in plane geometry. We point out that in the semiconductor state the conductivity of AgI is purely electronic.

When a thermal phase transition to the superionic state occurs as the temperature increases, individual AgI crystallites pass into the state of a superionic conductor at different temperatures. This is due to the martensitic nature of the transition. That is, the deviation from the phase equilibrium temperature necessary for the completion of the phase transition (PT) differs for different grains (Elliott 1987; Kobayashi et al. 2004; Long 1982; Popova et al. 2005).

These differences arise due to the variation in the sizes of crystallites, which are distributed, as shown by AFM studies, in a wide range of values (Popova et al. 2005).

In addition, the amount of deviation required to complete the transition is affected by the elastic energy of adhesion of AgI crystallites to the substrate, the value of which also depends on the size of the crystallites, i. e., on the contact area of the grain with the substrate.

The combination of the described factors leads to a thermal increase in the conductivity of the entire mass of nanocrystallites composing the film according to the percolation law, which is well studied for the case of dc conduction (Farid et al. 2005).

In this case, the single-layer arrangement of grains on the substrate surface corresponds to the simplest case of two-dimensional percolation, if each grain has a conductive contact with only four nearest neighbors. This is indicated by AFM studies. For two-dimensional percolation, it is also necessary that all the grains of the film undergo the same jump in conductivity during the phase transformation. This takes place in the first approximation in the AgI film.

From what has been said, it follows that even in the simplest case of two-dimensional percolation, two phase transitions take place, one of which is a transition in each grain from a low-conducting semiconductor to a high-conducting superionic state.

Another, purely geometric, phase transition is a jump-like transition of the entire mass of film grains to a highly conductive state during the formation of an infinite percolation cluster and is designated as a percolation phase transition.

In AgI, the described case is the case of a square percolation grating with the number of measurements equal to half the number of contacts of each grain (Ivanskoi 2008). This situation is similarly well known for superionic conductors.

It is known (Barman et al. 1995) that in the case of silver sulfide, the primary process that initiates the phase transition to the superionic state is down to two factors: the interaction between the vacancies of Ag^+ ions and the interaction of the “interstitial silver ion–vacancy” dipoles, which reduce the energy of the ion exit from nanocrystal silver. This is further facilitated by the high Laplacian pressure produced by the high surface tension of the nanocrystals.

A similar situation occurs in silver iodide films, where mobile silver ions can occupy several different positions in the unit cell with different probabilities. They are able to migrate between these positions, that is, move along the conductive channels of the crystal lattice, as described in the introduction.

On the whole, the motion of silver ions in a superionic crystal is complex and combines phonon oscillations of ions at potential energy minima and diffusion hops of silver ions from one equilibrium position to another during hopping conduction (Ivanov-Shits 2007).

A change in the crystal structure of the material as a result of the breaking of chemical bonds during superionic (PT) leads to a change, in addition to the ionic, in the electronic structure of the material and is accompanied by an abrupt change in the electronic part of the conductance (PT) (Barman et al. 1995).

Micromechanism of superionic phase transition in AgI

Silver iodide exists in three different crystalline phases.

At room temperature, the dominant phase is γ-AgI with a zinc blende structure (face-centered cubic structure of F43m symmetry), although 2% of β-AgI with a hexagonal wurtzite structure of P63mc symmetry is present. β-AgI becomes a stable phase above 384 K (111 °C).

Both phases transform into a body-centered cubic α-AgI phase at 420 K (147 °C), which is stable above this temperature and is a superionic phase. Alpha silver iodide is only stable above 147 °C and enters the beta phase when cooled to room temperature.

Hybridization of iodine (I) in the β-AgI lattice is (spf):

$$5p_{xy}{}^{2}(1)4f_{x(3x2-y2)}{}^{0}(1)5s^{1}(1).$$

All three orbitals are located almost in the same plane of the hexagon with a slight bend in the bonds (Pauling 1974) (see Fig. 6). Each hybrid orbital contains one electron.

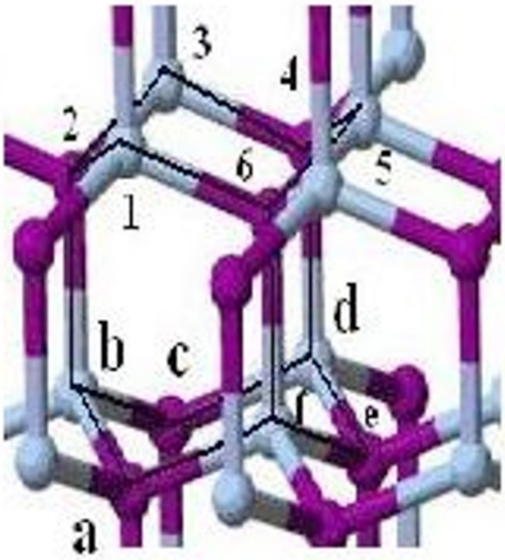


Fig. 6. Fragment of the crystal structure of β-AgI (Binner et al. 2006)

These hybrid orbitals of the Ag and I atoms, containing one electron each, form stable sigma bonds between themselves in the hexagon plane (Fig. 6).

In addition, each iodine (I) atom has two p-orbitals not involved in hybridization: $5p_y^2\ 5p_z^2$, each of which contains two electrons. Therefore, two of the three bonds of each atom (Ag and I) in the hexagon plane are double: along with the usual sigma bonds 2 p-orbitals $5p_y^2\ 5p_z^2$ of the I atom not used in hybridization form 2 coordination π-bonds with empty *f*-orbitals of the Ag atom. This additionally strengthens the bonds of the Ag and I atoms in the hexagon plane (bonds 1–2, 2–3, 3–4, 4–5, and 5–6 in Fig. 6).

The connection of the hexagon planes with each other is carried out due to the coordination sigma bonds between the $4d_{z2}^2$ orbitals of the Ag atom, containing two electrons each, and the empty $4f_{z3}^0$ orbitals of the I atom (bonds 2-b, 4-d, and 6-f in Fig. 6). Recall that the energy of coordination bonds is an order of magnitude less than the energy of double bonds 1–2, 2–3, 3–4, 4–5 and 5–6 (Davydov 1973).

It follows from this that the coordination bonds connecting the planes of hexagons are destroyed first of all with an increase in temperature near the point of the superionic phase transition. This leads to a rearrangement of the crystal structure from a hexagonal to a body-centered cubic structure (β-AgI goes over α-AgI).

The body-centered crystal structure that appears above *T*c = 147 °C (420 K) after superionic PT has been made retains its integrity due to the usual sigma bonds between iodine ions and silver ions. Each ion is located in the center of a cube made up of ions of the sign opposite to the given ion. The hybrid orbitals needed to create 8 sigma bonds with 16 electrons on them are formed like this. The Ag atom donates 8 $4f^0(7)5s^1$ orbitals for hybridization with one electron on them. Atom I donates 8 orbitals for hybridization $4d_{xy}^2 4d_{xz}^2 4d_{yz}^2 4d_{x2\text{-}y2}^2 5s^2\ 5p_x^1\ 5p_y^2\ 5p_z^2$ with 15 electrons on them. In total, we have 8 bonds with 16 electrons.

It should be said that, according to the theory, with such a large number of orbitals used in hybridization which inevitably differ in energy, a full-fledged hybridization process is hardly possible (Murrell et al. 1965).

So, most likely, 7 out of 8 bonds are low-energy coordination (donor-acceptor) bonds between the d-orbitals of the Ag^+ ion, containing two electrons each, and the empty f-orbitals of the I- ion. The exceptions are a full-fledged sigma bond between $5p_x^1$, the orbital of the I atom, and $5s^1$, the orbital of the Ag atom.

The presence of low-energy coordination bonds provides a low energy barrier between the positions of ions of adjacent crystal cells. This contributes to the emergence of high mobility in Ag^+ ions in comparison with the mobility of I⁻, i. e., it provides an effective hopping mechanism of ionic conduction and forms the superionic properties of the material.

The ionic radius of silver ions (0.074 nm) is significantly smaller than that of iodine ions, 0.137 nm, which creates an additional advantage of the drift of metallic Ag^+ ions along the lattice when an external electric field is applied. The drift is carried out along the corresponding ion-conducting channels, as described in the Introduction.

Conclusion

Thus, in this work, the dielectric spectra of thin films of iodized silver AgI have been studied. Dielectric spectroscopy methods have shown that a thermal phase transition from a semiconductor to a superionic state occurs in AgI films at 420 K (147 °C).

The abrupt change of parameters at the transition point is demonstrated by:

- activation energy of semiconductor conduction and commit phases;
- indicator of the degree of frequency dependence of conductivity;
- parameters of the Havriliak-Negami function,
- numerical values of the frequency position and the maximum value of the function of the tangent of the dielectric loss angle.

A model of the micro-mechanism of the thermal phase transition from a semiconductor to a superionic state is proposed.

It is shown that, along with the superionic phase transition, films undergo a percolation phase transition with the formation of a two-dimensional percolation cluster.

Conflict of interest

The authors declare that there is no conflict of interest, either existing or potential.

Author contributions

The authors have made an equal contribution to the preparation of the text.

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