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Features of the dielectric spectra of silver iodide films doped with copper

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In this work, the fine structure of dielectric spectra in the temperature range corresponding to the superionic phase transition (PT) of AgI:Cu nanocrystallites from the β-phase to the α-phase is discovered and analyzed. The effect of doping with Cu ions on the PT temperature and the shape of the thermal hysteresis loop is studied. Keywords: dielectric spectroscopy, silver iodide, semiconductor-superionic phase transition, AgI films, copper doping.

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1. Introduction

Solid-state ion conductors, in particular silver iodide (AgI), are being actively studied due to the prospects of their practical application. An example is the currently very relevant process of creating energy-intensive electric batteries, as well as capacitors with a high specific electrical capacity [1,2]. It is known that in an undoped AgI film, the phase transition (PT) occurs near $T_c = 147\,^{\circ}\mathrm{C}$ and is a complex Mott-Peierls semiconductor — superionic PT [3,4]. Silver iodide, as it is known [4] exists in three different crystal modifications, namely, in α-, β- and γ-phases: γ-phase has a face-centered cubic structure of the crystal lattice, for which the corresponding scheme of hybridization of atomic orbitals of silver and iodine ions ensures the stability of the crystal lattice due to σ-bonds between ions Ag^+ and I^- having different energy levels [5]. The electronic configurations of the ions Ag^+ and I^- determine the physical properties of the β- and α-phases, taking into account that the thermal PT of the β-phases in α-phase is a semiconductor-superionic PT, in contrast to the transition temperature preceding it $\gamma \rightarrow \beta$, which is a standard PT of the first kind of the semiconductor type–a semiconductor with a change in lattice symmetry, but without adding a new type of conductivity as a result of PT. The following physical properties of silver iodide single crystals are of fundamental importance for the analysis of subsequent experimental material: 1) the absence of ion-conducting channels in the β-phase after the semiconductor-semiconductor type PT ($\gamma \rightarrow \beta$) and the presence of ion-conducting channels in the α-phase after the semiconductor-superionic type PT ($\beta \rightarrow \alpha$); 2) the formation of coexisting electronic and ionic types of conductivity of various phases; 3) the stability of the crystal lattice structure of the α-phase, which persists during the occurrence of superionic conductivity after PT, despite the temperature destabilization of part of the chemical bonds of silver ions with iodine ions. This work is a continuation of the authors' cycle of work on the study of the features of the PT mechanism in AgI films and is devoted to the study of the effect of Cu doping on the PT mechanism of AgI crystalline grains from the hexagonal β-phase to the cubic volume-centered α-phase.

2. Experimental procedure

The AgI and AgI:Cu films studied were thin ($0.2-0.8\,\mu$m) polycrystalline films synthesized by evaporation in vacuum on optical mica substrates with a thickness of $40\,\mu$m of either an Ag layer or a layer of a mixture of Ag and 5 vol.% Cu. After this process, the metal film, heated to $150\,^{\circ}$C, was placed for 45 min in an atmosphere of iodine vapor (sublimation of crystalline iodine at a temperature of $110\,^{\circ}$C). As a result of the interaction of iodine vapor with metal grains, nanocrystalline films of AgI or AgI:Cu were synthesized. Monolayer was confirmed by atomic force microscopy (AFM) on an NT-MDT Solver device by monitoring the topography of the film surface, conducted at the AFM Center for Collective Use of Microscopy and Vacuum Spraying at the Herzen Russian State Pedagogical University. DS studies were performed in the temperature range of $40-190\,^{\circ}$C using Novocontrol concept 41 spectrometer of the Herzen Russian State Pedagogical University's Center for Collective Use. It is important that the measuring cell of the dielectric spectrometer consisted of two flat metal electrodes, between which a sample was

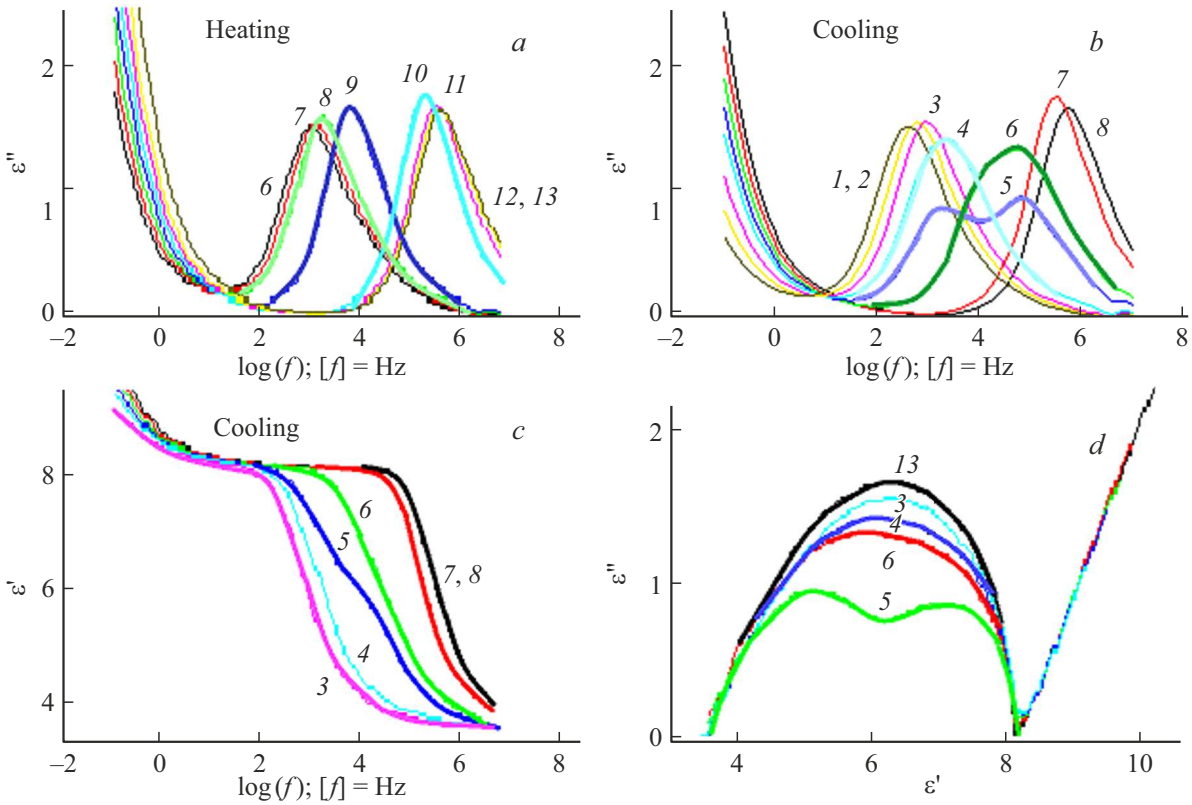

Figure 1. Dielectric spectra of the AgCuI film ($\varepsilon''(f)$when the sample is heated (a), $\varepsilon''(f)$ — (b), $\varepsilon'(f)$ — (c) and the Cole diagram–Cole — (d) during its cooling), demonstrating a fine structure in the temperature range of the superionic PT from β-phase to α-phase: $T(^\circ\mathrm{C}) = 100$ (*1*), 110 (*2*), 120 (*3*), 130 (*4*), 135 (*5*), 140 (*6*), 145 (*7*), 150 (*8*), 155 (*9*), 160 (*10*), 165 (*11*), 170 (*12*), 180 (*13*).

placed in the form of a polycrystalline film with an average thickness of about 250 nm, synthesized on a relatively thick substrate of optical mica with a thickness of 40 μm. In the process of measuring DS, an alternating voltage with an amplitude of 1 V was applied to the cell, the frequency of which varied within the range of $10^{-1}-10^{7}$ Hz.

3. Experimental results

A comparison of the AFM images obtained in the study shows that during iodination, the crystalline grains of silver iodide become larger: from 0.1 μm (for undoped AgI) to 0.8 μm (for AgI:Cu), the smallest grains disappear, and the film itself becomes more homogeneous. The processes of grain enlargement, as well as the analysis of the physical causes and consequences of such changes in the texture of nanocrystalline grains, are of undoubted interest for further study, planned as a development of the present research.

Figure 1 shows the frequency dependences of the imaginary part of the complex permittivity $\varepsilon''(f)$ of AgI:Cu films. A single maximum of the frequency dependence function $\varepsilon''(f)$ is observed for all temperatures, with the exception of the PT region 130–160 °C. This DS feature in the form of a maximum $\varepsilon''(f)$ monotonously shifts with increasing temperature towards high frequencies. However, in the temperature range of 140–160 °C in the frequency range of $10^{3}-10^{6}$ Hz, accelerated thermal displacement of this maximum occurs. It is noteworthy that with an increase in temperature in the low-frequency region of the spectrum $10^{-1}-1$ Hz, the second maximum of the function $\varepsilon''(f)$ appears. As the sample cools, these DS features shift to the low-frequency side of the spectrum, with a temperature delay of approximately 10 °C, i.e. thermal hysteresis of the frequency position of the maxima occurs. A more detailed measurement of the DS in the temperature range of 130–160 °C demonstrates the appearance of a fine structure of the spectra. It manifests itself in the appearance of two maxima of the function $\varepsilon''(f)$, two steps of the function $\varepsilon'(f)$ and two semicircles in the Cole–Cole diagrams (fig. 1). This structure is most clearly manifested when the sample is cooled to a temperature of $T = 135\,^\circ$C — curves *5*. The position of the maxima of the fine structure components was determined more precisely by decomposing the maxima into Gaussian components — Figure 2.

The measured DS are adequately described by the Debye formula. In this case, all the reference points of the Debye formula can be associated with elements of a relatively simple equivalent scheme (Figure 3, a). Thus, C_s represents

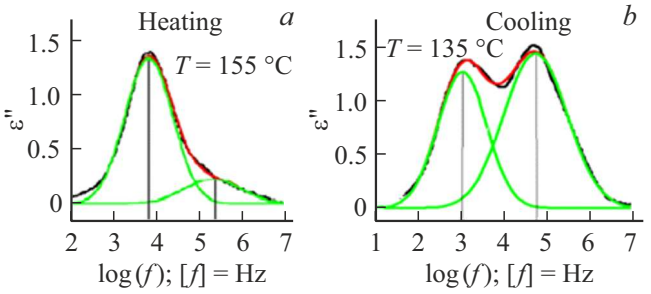

Figure 2. Decomposition of the fine structure of DS into Gaussian components upon heating (a) and cooling (b) of the sample AgI:Cu.

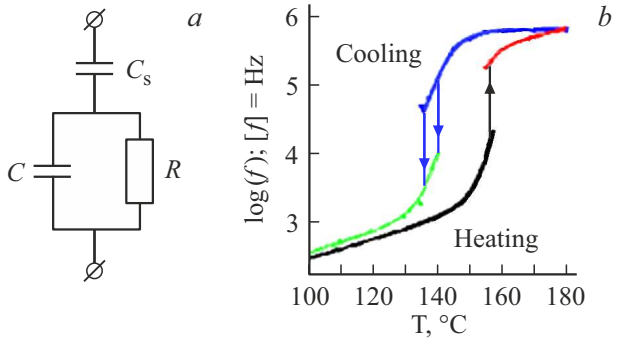

Figure 3. (a) Equivalent scheme of AgI:Cu films; (b) The loop of thermal hysteresis of the frequency position of the maxima $\varepsilon''(f)$.

the electrical capacitance of the insulating mica substrate, the electrical capacity C and the resistance R are the characteristics of the AgI:Cu film. In particular, the maximum of the function $\varepsilon''(f)$ in such an equivalent circuit is achieved at the frequency f_0:

$$f_0 = \frac{1}{2\pi RICI\sqrt{\frac{C_sI}{CI}+1}},$$

and after the transformation we have:

$$f_0 = 1/(2\pi\tau_m) = \sigma/(2\pi\varepsilon\varepsilon_0),$$

where τ_m is the Maxwellian relaxation time, σ is the specific conductivity of the crystalline grain material. That is, the frequency position of the DS features is directly proportional to the value of the specific conductivity of the nanocrystallites of the film and does not depend on their total ohmic resistance.

Based on experimental data, a loop of temperature hysteresis of the frequency position of the maximum $\varepsilon''(f)$ was constructed for the studied samples (AgI:Cu) (Figure 3, b). Detailed analysis reveals its fine structure, which manifests itself when the sample is heated in the presence of two characteristic frequencies for each fixed temperature of $T = 145\,^\circ$C, $150\,^\circ$C — Figure 2, a, and when it is cooled for temperatures of $T = 140\,^\circ$C, $135\,^\circ$C — Figure 2, b. Pairs of points corresponding to one fixed temperature in Figure 2 are connected by vertical arrows pointing up when the sample is heated and down when it is cooled.

The following differences between AgI and AgI:Cu are observed: the PT temperature of doped AgI:Cu films is $5\,^\circ$C higher than that of undoped films, and is $T_c = 155\,^\circ$C; the resonant frequency of DS features decreases during doping, but the amplitude of these features increases. This indicates a decrease in the specific conductivity of the material during Cu doping, while increasing the concentration of free equilibrium electrons. It can be argued that it is caused by a decrease in the mobility of free equilibrium electrons with an increase in the degree of doping of the Cu sample. Doping also increases the range of ε'' at its maximum (for undoped 0–0.3; for doped 0–2.0) and ε' at its maximum (for undoped 0–4.5; for doped 0–13.0); in addition, the maximum position of the doped sample is shifted to the low frequency region.

4. Discussion of the results

As already noted in the introduction, the PT in silver iodide has a complex character, characterized by the fact that the structural semiconductor-superionic PT is preceded by the electronic Mott transition, which occurs in the temperature range. With increasing temperature, a set of the least durable crystalline bonds (coordination σ-Ag–I bonds) is destroyed, the concentration of free electrons in the semiconductor conduction band increases, the specific conductivity of nanocrystallites increases, and the observed features of DS monotonously shift towards high frequencies. When a critical degree of bond destruction is reached, a structural PT occurs from the β-phase to the α-phase. In the low-frequency region of the spectrum (10^{-1}–1 Hz), a second maximum $\varepsilon''(f)$ and a second step $\varepsilon'(f)$ appear, which are caused by low mobility and therefore slow drift in the external electric field of silver ions released as a result of the occurrence of PT. In the high-frequency range of the spectrum (10^3–10^6 Hz), as the temperature increases, a rather sharp increase in the specific conductivity of crystalline grains occurs, and a fine spectral structure is observed for silver iodide films doped with copper. These changes are due to the characteristic physical features of the semiconductor-superionic PT. Let's look at them in more detail. Doping of the AgI crystal with Cu atoms with the final electronic configuration $3p^6(3)3d^{10}(5)4s^1(1)$ during the formation of the AgI:Cu compound leads to the replacement of the iodine ion in the center of the cube of α-phase by the ion Cu^-. The copper ion is also capable, like the iodine ion, of delegating seven electrons to four hybrid orbitals $3d^2_{xy}(1)3d^2_{xz}(1)3d^2_{yz}(1)4s^1(1)$ in the β-phase. However, it is fundamentally important that the copper ion, occupying the 29th cell of the Periodic Table (and not 53, like the iodine ion), forms at least twice as strong bonds as the iodine ion, since the Cu^- ion has significantly less shielding compared to the iodine ion. of the outer electron

shell by its inner shells. According to the theory of valence bonds [6], such bonds are several times stronger than the bonds created by elements with strong shielding of the outer shell by internal electron shells. The result of this position is an increase by 5 °C in the temperature T_c of superionic PT from β-phase to α-phase in the AgI : Cu crystal compared to T_c in an AgI crystal.

5. Conclusion

In conclusion, we would like to point out that the superionic PT in AgI : Cu films demonstrates both the possibility of measuring DS and the fine structure of the branches of the thermal hysteresis loop of the frequency position of the DS features. The reason for the splitting of the branches is that this transition, like the semiconductor-metal transition in VO_2 [7], has a martensitic nature. Namely, the Laplace pressure of the nanocrystallite surface of the AgI film widens the elementary loop of each nanocrystallite by an amount ΔT inversely proportional to the square root of its average diameter [7]. Therefore, both the heating and cooling branches of the loop in the PT area contain information about both aggregates of AgI grains that have performed PT and aggregates of grains that have not performed it. And since, with superionic PT, the specific conductivity of each grain increases, as indicated above, by almost 2 orders of magnitude, both branches of the loop split, simultaneously containing information about both sets of grains. This circumstance leads to splitting of the maxima of the $\varepsilon''(f)$ function in DS (Figure 1), since the frequency position of the DS features depends on the specific conductivity of the grains. We especially point out that the branches of the hysteresis loops, being very steep in temperature, each occupy a temperature range of no more than 10 °C (Figure 3). Therefore, the fixation of DS recorded with a temperature range of 2.5 °C makes it possible to obtain no more than two spectra with a pronounced fine structure (Figure 2).

Thus, the novelty of the presented results is reduced to the establishment of: the fact of an eightfold increase in the grain size of the Ag : Cu film during their iodination; the fact of an increase by 5 °C in the temperature of the PT during doping of the AgI film with Cu ions; the fact of the appearance of a fine DS structure and a thermal hysteresis loop.

Conflict of interest

The authors declare that they have no conflict of interest.

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