Dielectric spectroscopy of Ag_2S nanowires synthesized in porous silicate glasses

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Abstract. We have studied the frequency dielectric spectra of silver sulfide nanowires synthesized in porous silicate glasses. A possible mechanism of the thermal superionic phase transition in the samples is discussed. In this work, based on the analysis of the DS, the following conclusion was made. After the superionic phase transition occurs, the octa coordinated Ag^+ ions become mobile, representing the elements of a "viscous liquid", while the tetra-coordinated Ag^+ ions, remaining immobile (up to phonon vibrations), stabilize the crystal lattice of the material.

Keywords: superionic phase transition, nanowires silver iodide, nanoporous silicate glasses, dielectric spectroscopy

Диэлектрическая спектроскопия нанонитей, синтезированных в пористых силикатных стеклах

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Аннотация. В работе изучены частотные диэлектрические спектры нанонитей сульфида серебра, синтезированных в пористых силикатных стеклах. Обсуждается возможный механизм термического суперионного фазового перехода в таких образцах. На базе анализа ДС сделан следующий вывод. После совершения суперионного ФП окта координированные ионы Ag^+ становятся подвижными, представляя собой элементы «вязкой жидкости», а тетра-координированные ионы Ag^+, оставаясь неподвижными (с точностью до фононных колебаний), стабилизируют кристаллическую решетку материала.

Introduction

Superionic materials, in particular silver sulfide, are used as the working medium of various sensors with combined electron-ion conductivity, as miniature capacitors of ultrahigh capacitance [1]. Along with applied research, it is also important to study the fundamental physical properties of superionics and, in particular, the semiconductor superionic phase transition, which expands the possibilities of superionic materials application [2].

Silver sulfide has two types of phase transitions: $\alpha \to \beta$ transition with the transition temperature $T_c = 176$ °C and $\beta \to \gamma$ transition (transition temperature $T_c = 592$ °C) [3]. The dielectric spectroscopy (DS) research method, presented in this paper, opens up new possibilities for studying the physical properties of Ag_2S nanocrystallites embedded in nanoporous silicate glasses (NSG). The purpose of this work is to demonstrate the peculiarities of the semiconductor-superionic phase transition mechanism in Ag_2S nanowires synthesized inside NSG channels.

Materials and Methods

NSG samples were made at the National Research University ITMO in St. Petersburg. They were silicon dioxide structures with branched through filamentous tubes 17 nm in diameter. The sample size was $10 \times 10 \times 1$ mm. The inner space of the tubes was half filled with Ag_2S nanocrystals. The samples were warmed up to 110 °C immediately before measurements of the DS to remove water that penetrated into the pores of the NSG during long-term storage of the samples in air.

The impedance measurements were performed on a Concept 81 dielectric spectrometer from Novocontrol Technologies. The sample was placed in the spectrometer cell between flat electrodes. The electrical capacitance of the empty cell was $C_0 = 1.7$ pF. DS were measured in the frequency range $10^{-1}-10^6$ Hz. The sample temperature T was varied with a step of 10 °C in the range of $0-250$ °C.

Results and Discussion

The frequency dependences of the $tg\delta(f)$ (dielectric loss tangent) and the Cole-Cole diagrams $\varepsilon''(\varepsilon')$ of the NSG + Ag_2S samples are shown in Figure 1. Here $\varepsilon'(f)$ is the real part of the permittivity ε, and $\varepsilon''(f)$ is its imaginary part. The maximum of the function $tg\delta(f)$ was located by $T = 0$ °C at a frequency 0.5 Hz, and its value was $tg\delta(f_{max}) = 0.35$. The maximum of the $tg\delta(f)$ function shifted with increasing temperature towards higher frequencies, while its value increased from 0.35 to 0.6. At $T > 160$ °C the frequency shift stopped. With a temperature decreasing, the frequency position of this maximum on the frequency scale was reproduced within the measurement error, that is, the temperature hysteresis of the frequency position of the maximum was not recorded.

Nevertheless, the temperature hysteresis of the numerical value of $tg\delta(f)$ at the frequency $f = 0.1$ Hz was registered (Fig. 2). The point is that at such a low frequency, with increasing T, a "slope" of the second, even lower frequency, maximum of the function $tg\delta(f)$ began to appear, the position of which at low temperatures went beyond the frequency range of the spectrometer measurements. The temperature hysteresis loop was located in the region of $160-220$ °C and had a width of 60 °C. This indicates that in this temperature range a phase transition occurs, which has a thermal hysteresis.

Since there are two maxima $tg\delta(f)$ in the DS and also two semicircles on the Cole-Cole diagram take place, the 2-circuit equivalent electrical circuit of the sample should be used to simulate

the physical processes under study (inset in Fig. 1). Calculations of circuit parameters were performed with such modeling by the symbolic method.

At temperatures of $0-110$ °C the Ag_2S nanowires, filling the filamentous tubes of the NSG sample, are in the semiconductor phase. Therefore, it was sufficient to use one electrical circuit to simulate the DS. In it, in parallel with the resistance R_I of the semiconductor Ag_2S, the capacitance C_I is included the capacitance of the NSG. Capacitance C_{II} was the capacitance of a thin dielectric layer between the cell electrodes and the NPS sample. The thermal variation of the frequency position of the first maximum of the function tgδ(f) in the temperature range $0-110$ °C is determined from general physical considerations mainly only by changing the resistance value R_I with temperature because the thermal constancy of the capacitance.

At temperatures of $110-250$ °C in Ag_2S nanowires the semiconductor superionic phase transition occurs. Therefore, to describe the DS at temperatures above T_c, but in the immediate vicinity of it, the simulation requires the use of both electrical circuits, although at higher temperatures far from the phase transition, only the second circuit can be used for modeling. Significant differences in the parameters of electrical circuits come down to the fact that $C_{IV} \gg C_{II}$ and $R_{II} \gg R_I$. The point is that at high temperatures after the phase transition, free Ag^+ ions appear which increase the conductivity of the sample at low frequencies. In this case, the former high value of the ohmic resistance R_{II} decreases. A thin layer of metallic silver with a high electric capacitance appears inside the NSG sample in the region close to the electrodes. This contributes to the appearance of the second maximum of the function tgδ(f) in the DS at low frequencies. The results of the calculation of the equivalent electrical circuit are shown in Fig. 1 by dotted lines. The calculated curves are in good agreement with the experimental data.
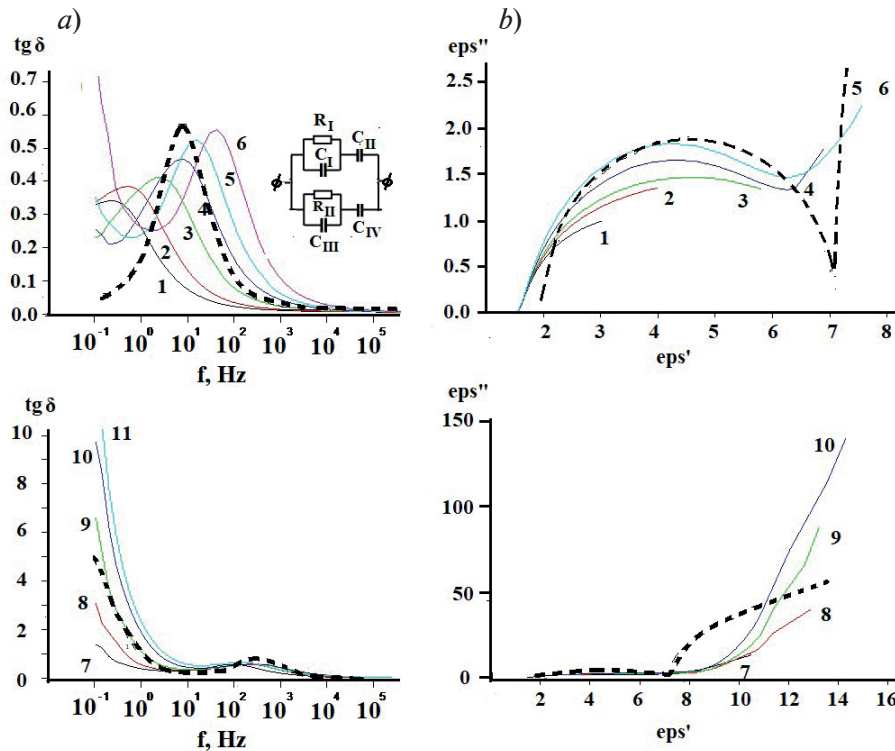

Fig. 1. Frequency dependences tgδ(f) (*a*), and Cole-Cole diagrams (*b*), obtained experimentally at temperatures $T = 0$ (1), 20 (2), 40 (3), 60 (4), 80 (5), 100 (6), 120 (7), 140 (8), 160 (9), 180 (10) °C for NSG samples with pores, filled with Ag_2S. Dashed curves are calculation results

With an increase in T, the tgδ maximum first moves towards high frequencies (curves $1-6$, *a*), then at $T > 100$ °C the second maximum tgδ appears in the low-frequency region (curves $7-11$, *a*). At the same time, a semicircle is formed in the region of high frequencies (curves $1-6$, *b*), then at $T > 100$ °C a second semicircle appears in the region of low frequencies (curves $7-10$, *b*).

The shift of the maximum of the dielectric loss tangent towards higher frequencies with increasing T is explained by a decrease in the resistance of the Ag_2S semiconductor nanowire

due to an increase in the rate of thermal generation of free electrons. In addition, since a phase transition ($\alpha \rightarrow \beta$) occurs at high temperature at $T_c = 176$ °C, a "liquid" fraction of Ag^+ ions appears, and the electrical conductivity acquires a predominantly ionic character. As a result, the total electrical resistance of the NSG sample decreases significantly and the numerical value of tgδ(f) increases many times over. The semiconductor superionic phase transition demonstrates the presence of temperature hysteresis, which is shown in Fig. 2, where the temperature hysteresis loop of tgδ at frequency of 0.1 Hz can be seen.

To explain the results obtained, we propose the following microscopic model of the superionic phase transition. Ag_2S undergoes a transition from the monoclinic crystalline α modification to the cubic β-modification at $T_c = 176$ °C. The details of the phase transition are explained with the help of Fig. 3, which shows a fragment of the Ag_2S crystal lattice [4].

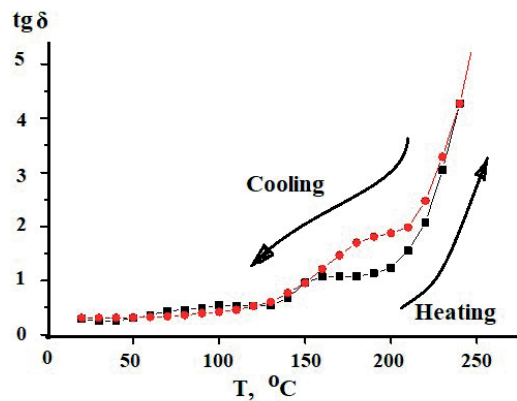Fig.2. Temperature hysteresis of the tgδ value for dehydrated NSG + Ag_2S samples at frequency $f = 0.1$ Hz
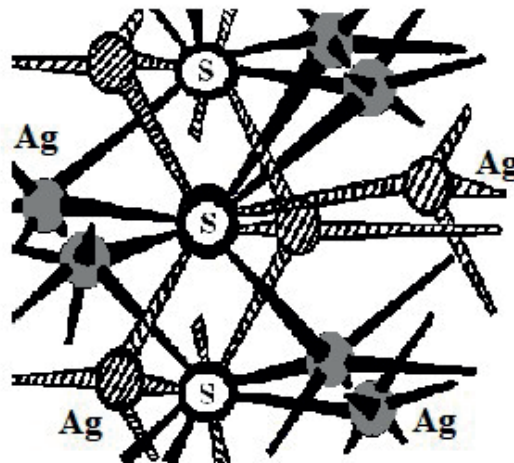

Fig.3. Fragment of the Ag_2S lattice with tetra-coordinated (shaded circles) and octa-coordinated (shaded circles) Ag^+ ions

As the temperature rises, the bonds of the octa-coordinated Ag^+ ions break, while the tetra coordinated Ag^+ ions retain their integrity, remaining unaffected by heating. The released octa-coordinated Ag^+ ions behave like a liquid with a high degree of viscosity [3]. When the critical concentration of broken bonds is reached, the symmetry of the crystal lattice changes from monoclinic to cubic and a structural superionic phase transition of the first order occurs, which has a temperature hysteresis. At the same time, the crystal lattice itself remains stable due to the preservation of the integrity of strong tetra-Ag-S-σ-bonds.

The band gap of the low-temperature semiconductor phase is $E_g = 0.9$ eV [5]. We point out that at $T_c = 176$ °C the thermal energy is much less than this value: $kT = 40$ meV. In spite of this, octa-coordinated Ag^+ ions still break, as was mentioned above. The reason for this is that

the band gap sharply decreases as the conduction band is thermally populated by electrons as T_c is approached. This means that the Ag_2S semiconductor inherits the strong correlation properties of the neutral silver atom. This process leads to a strong "metallization" of the crystal immediately before the structural superionic phase transition. Thus, before the superionic structural phase transition, a purely electronic Mott transition of the second order, which is extended in temperature, takes place. From what has been said, it follows that the temperature-extended Mott correlation transition [6] initiates a structural phase transition (superionic in the case of Ag_2S).

Conclusion

Thus, in this work, based on the analysis of the DS, the following conclusion was made. After the superionic phase transition occurs, the octa-coordinated Ag^+ ions become mobile, representing the elements of a "viscous liquid", while the tetra-coordinated Ag^+ ions, remaining immobile (up to phonon vibrations), stabilize the crystal lattice of the material.

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