Charge transport processes in proustite crystals Ag₃AsS₃

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Abstract. Structural characteristics and charge transfer processes in Ag₃AsS₃ crystals were studied by dielectric spectroscopy and scanning electron microscopy methods; the relaxation parameters of the system were evaluated.

1. Introduction

Proustite (light red silver ore) Ag₃AsS₃ single crystal is a ferroelectric with a melting point of 580 °C. This crystal system is characterized by high values of dielectric permittivity, advantageous for its application in nonlinear optical devices and electron acoustic systems [1]. Currently, proustite crystals are used for the development of infrared emission transducers. At the moment, there are practically no data on the characteristics of polarization processes in the high frequency range and the effects of such factors as illumination, introduction of admixtures of various metals, etc. on dielectric properties of this class of materials. The study of electric and dielectric properties is of particular importance both for specifying the electronic processes in different materials and for understanding the nature of their fundamental properties [2, 3]. In this regard, the objective of this work was to define the specific features of charge transfer mechanisms in proustite crystals Ag₃AsS₃ using dielectric spectroscopy method.

2. Experimental methodology

Measurements were taken with a “Concept 81” spectrometer, NOVOCONTROL Technologies GmbH & Co. The samples were single-crystal wafers of about 1 mm thick and 1 cm² in area, with an even surface perpendicular to the third-order axis. Measurements of dielectric spectra (components of the complex conductivity ϵ*) in proustite crystal samples were taken in the temperature range T = 173 ... 473 K. Temperature precision was ±0.5°C. The measuring voltage applied to the sample was 1.0 V. Investigation of the film surface structures and the elemental composition of the samples was performed with a Carl Zeiss EVO 40 scanning electron microscope (SEM). The table 1 presents the data on the weight % and atomic % content of chemical elements in proustite crystal samples.
Table 1. Elemental composition of Ag₃AsS₃ samples.

| Element | Nominal concentration | Mass fraction | Weight % | Weight % Sigma | Atomic fraction % |
|---------|-----------------------|---------------|----------|----------------|------------------|
| S       | 4.11                  | 0.9846        | 18.53    | 0.21           | 41.76            |
| As      | 2.64                  | 0.9432        | 12.43    | 0.28           | 11.99            |
| Ag      | 13.23                 | 0.8513        | 69.04    | 0.31           | 46.25            |
| Total   |                       |               | 100      |                |                  |

3. Results and discussion

In the low frequency range, we observe a continuous increase in conductivity with an increase in frequency, i.e., the dispersion of type $\sigma \sim \omega^{s} T^{L}$ is detected, which, in general, is typical of solids, where transport processes are caused by the jumps of charge carriers (figure 1). This transfer mechanism was first proposed by Pollack [4] for chalcogenide glasses and later was applied to a wide class of materials by other authors [5, 6]. We can assume the existence of a hopping transfer mechanism for charge carriers in proustite crystals, in which silver ions make thermally activated jumps through the lattice. The correctness of this assumption stems from the more pronounced dispersion $\varepsilon'$ in low frequency range, observed with increasing temperature. The changing pattern of dielectric permittivity response on the frequency change can result from the increasing pace of thermal excitation of silver ions. It should be noted that the ion hopping transport contributes to both components of the complex dielectric permittivity, since silver ions can oscillate in the lattice sites as dipoles and can move along the lattice sites thus creating quasi dipoles; they can also move across the lattice and perform hopping charge transport. The exponent $s$ of the frequency dependence decreases with increasing temperature and takes values in the range ($s = 0.45 \ldots 0.70$), which is also indicative of a hopping mechanism of conductivity.

![Figure 1](image-url)
We have revealed an exponential temperature dependence of specific conductivity with two regions (figure 2) with activation energy $E_1 = 0.10 \pm 0.01$ eV and $E_2 = 0.30 \pm 0.01$ eV, respectively. It can be assumed that the charge transport is a thermally activated process; the activation energy on alternating current ($E_a(\omega)$) for various frequencies is part of the well-known Arrhenius expression [7]:

$$\sigma_\infty(\omega) = \sigma_0 \exp\left(\frac{E_a(\omega)}{k_B T}\right),$$

(1)

where $\sigma_0$ is a constant.

Changes in the temperature dependence pattern can be associated either with the presence of impurities and defects in the structure, or with the transition from the mixed to the ionic conductivity.

Figure 2. Temperature dependence of the specific conductivity of proustite crystal samples at frequency $f = 10^2$ Hz.

At higher frequencies, the specific conductivity depends weakly on the frequency over the entire temperature interval (figure 3). At low temperatures, a decrease in conductivity is even observed at the higher frequency range. This can be associated with the fact that the rapid change in the field polarity prevents the ordered motion of silver ions, which are, as noted earlier, primary charge carriers. As the temperature increases, there comes a point when carriers take on enough energy to perform jumps, which in combination with possible phase transitions leads to the changing nature of dispersion $\sigma'$. The temperature dependence of $\sigma'$ is presented in figure 4, which shows that the specific conductivity also increases exponentially with the absolute temperature. The value of activation energy $E_a$ at $f = 10^8$ Hz was calculated and found to be $2.40 \pm 0.01$ eV.
4. Conclusions
A continuous increase in specific conductivity with increasing frequency has been observed in the low frequency range, i.e., the dispersion of type $\sigma \propto \omega^s T^\ell$ is detected, which in general is typical of solids, where transport processes are caused by hopping mechanism of charge transport. The exponent $s$ of the frequency dependence decreases with increasing temperature and takes values in the range ($s = 0.45 \ldots 0.70$). An exponential temperature dependence of specific conductivity with two plots with activation energy $E_1 = 0.10 \pm 0.01$ eV and $E_2 = 0.30 \pm 0.01$ eV, respectively, has been revealed.
Changes in the temperature dependence pattern can be associated either with the presence of impurities and defects in the structure, or with the transition from the mixed to the ionic conductivity. In the frequency range $f = 10^6 \ldots 10^9$ Hz, the specific conductivity is virtually independent of frequency; at low temperatures, a certain decrease in conductivity is observed with an increase in frequency, which can be associated with the fact that a rapid change in the field polarity prevents the ordered motion of silver ions.

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