

High-frequency dielectric study of proustite crystals Ag_3AsS_3

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Abstract. The dielectric properties of the crystals proustite in the frequency of 10^6 - 10^9 Hz and a temperature range of 173 to 473 K were studied. The dispersion of the dielectric parameters indicates the existence of non-Debye relaxation mechanism correlates with structural changes in the phase transition region. The charge transfer is temperature activated with an activation energy of 2.40 ± 0.01 eV.

1. Introduction

Proustite monocrystal Ag_3AsS_3 is a ferroelectric material with a melting point 580 C. The crystal system is characterized by the high values of dielectric permittivity, which makes it challenging to use in nonlinear optic devices, electro-acoustic systems [1]. Dielectric study is a powerful tool in learning the effects of temperature and light factors on properties of wide class systems [1,2]. Currently, there are practically no data on the special features of polarization processes in proustite crystals in high frequency field.

Therefore, the aim of the work was to determine the special features of the dielectric relaxation mechanism in the proustite crystals Ag_3AsS_3 for frequencies $10^6 - 10^9$ Hz.

2. Experiment method

The measurements were taken with the spectrometer "Concept" 81 of the company NOVOCONTROL Technologies GmbH & Co. The samples consisted of monocrystal plate thickness of about 1 mm and an area of 1 cm^2 , with a flat surface perpendicular to the triad axis. Measurements of dielectric parameters (components of the complex dielectric permittivity (ϵ' , ϵ'')) of proustite crystals samples were done in a temperature range 173 to 473 K. Temperature measurement accuracy was 0.5°C . The measuring voltage on the sample was 1.0V.



3. Results and discussion

The study found that the dielectric permittivity frequency dependence is characterized by the presence of dispersion (figure 1). At higher frequencies the value ϵ' practically does not depend on the alternating field frequency. The main reason of it is the electronic polarization. As it is known, electronic polarization is a flexible displacement and deformation of the electron shells of atoms and ions. Electronic polarization is observed in all types of dielectrics and not associated with loss of energy up to the resonance frequencies. The polarizability of the particles under the electronic polarization does not depend of temperature, and the dielectric permittivity ϵ decreases with rise in temperature due to thermal expansion of the dielectric and the reduction of the number of particles per unit volume.

When you reduce the frequency in the whole temperature range you observe the rise of ϵ' , most likely due to the fact of dipole-relaxation polarization. It is known that if there are polar molecules in a dielectric and the relationship between them is small, they can relatively easily be rotated under the influence of the field. The thermal movement prevents from the orientation of the dipoles in the field. The result is a dipole polarization, which depends on the thermal movement. In the case of proustite, the silver ions can serve as dipoles and execute transition through the lattice, creating positively and negatively charged fields.

The dielectric permittivity temperature dependence reveals the existence of two zones: a monotonous dependence and a sharp increase of ϵ' under temperature increasing (figure 2). According to the literature the dependence mode change temperature $T \approx 420\text{K}$ (147°C) is the temperature at which the proustite executes of the first-order phase transition [2] due to the abrupt change of conductivity.

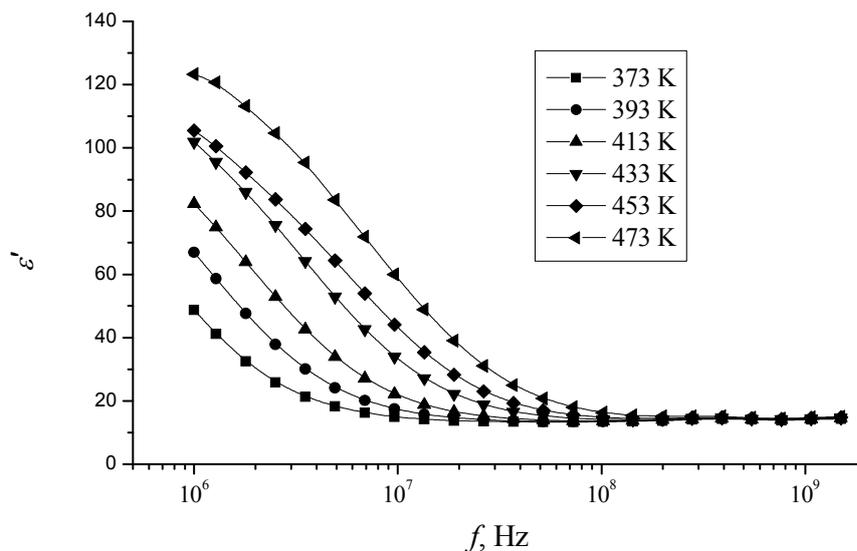


Figure 1. Frequency dependence of the dielectric permittivity ϵ' under different temperatures

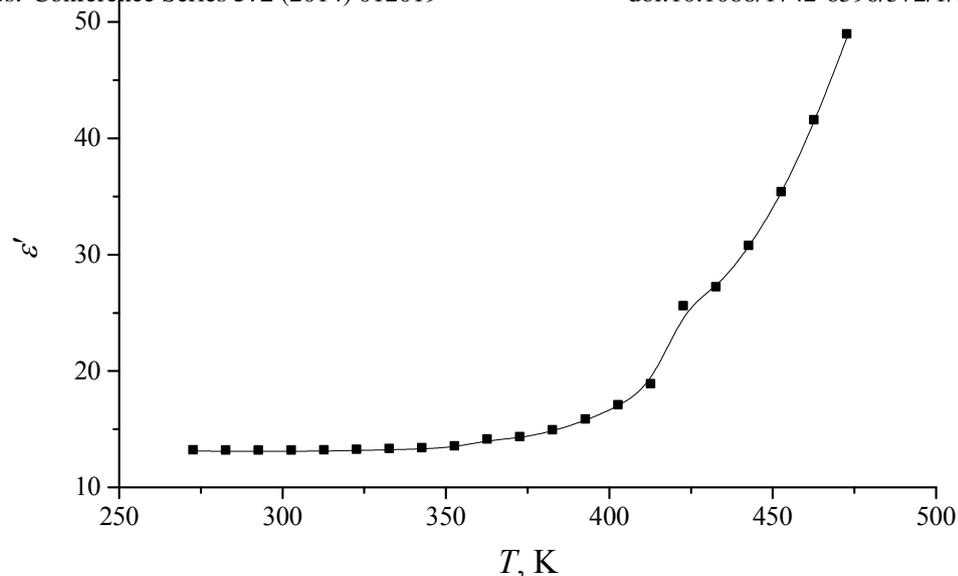


Figure 2. Temperature dependence of the dielectric permittivity under frequency $f=1.37 \cdot 10^7$ Hz.

Absence of evident relaxation processes under low temperatures (figure 3) may be due to fact that up to a certain temperature, the silver ions are placed in different lattice sites. At higher temperatures the silver ions gain sufficient energy to execute transition between unoccupied sites in the structure. In this case, we can speak about an effect of relaxation loss mechanism. Relaxation losses arise from active components of polarization currents. They are typical for dielectrics with slower types of polarization, and show themselves under very high frequencies when the polarization is behind the field change.

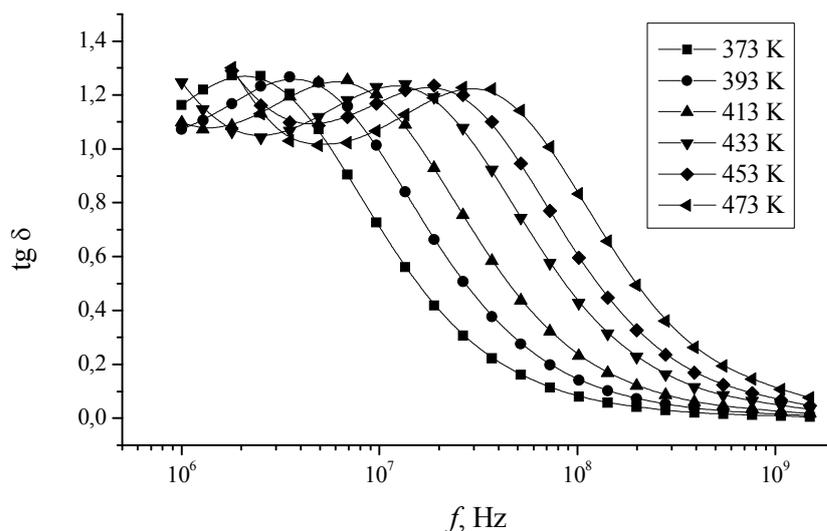


Figure 3. Frequency dependence of dielectric loss angle under different temperatures

In many dielectrics, relaxation processes are associated with the existence of not one relaxation time, but with a set of relaxation times. In this case we are dealing with the relaxation time distribution and consequently with the activation energies. This distribution can be attributed to a variety of relaxation processes according to their nature, or to distribution in accordance with concentration of dipoles in the

structure. In the case of ionic jump processes, such as in proustite, it is assumed that after each jump the potential energy is changed and you need some time to return to a minimum of potential energy. Taking into account the deposition of large numbers of moving defects, then we get a set of relaxation times [3].

Deviation from the classical model of relaxation by Debye for the case of one time of relaxation can be studied by using the Cole-Cole or Cole-Davidson model representation for the case of symmetric and asymmetric distribution of relaxation times respectively. If you build a Cole-Cole chart (characteristic curve $\varepsilon''=f(\varepsilon')$), then the existence of distribution of relaxation times will appear as a deviation from hemispherical dependence with the radius of the hemisphere $(\varepsilon_s-\varepsilon_\infty)/2$.

The existence of Non-Debye relaxation mechanism is confirmed by the estimation of parameter values in Havriliak-Negami two-parametric empirical function (HN) [4]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha_{HN}}]^{\beta_{HN}}}$$

where ε_∞ - the high-frequency limit of the real part of the dielectric permittivity, $\Delta\varepsilon$ – dielectric increment (difference between the low-frequency and high-frequency limits), $\omega=2\pi f$, α_{HN} and β_{HN} – form parameters that describe respectively the symmetric ($\beta = 1$ - Cole-Cole distribution) and asymmetric ($\alpha = 1$ - Cole-Davidson distribution) relaxation function extension [4]. Results of dielectric spectra measurements were approximated by using the software Novocontrol Winfit. Based on this approximation the positions of the dielectric loss peaks were emphasized and the parameters (HN) for the studied relaxation processes were defined:

Dielectric spectra of proustite samples have been measured in a wide temperature range, enabling the identification of the relaxation process existence in the range 90 to 200°C (figure 4). Uneven change of relaxation parameters with the temperature increasing was found. Their values are increased from a relatively constant value to higher values, against the background of the increasing intensity of the ions Ag^+ migration. Uneven change of relaxation parameters by temperature is attributed to the change in conductivity due to phase transition of the first kind and the second kind. Here the transfer jumping mechanism is replaced by the ion conductivity mechanism. The diagram of temperature against the most probable relaxation time τ_{\max} (figure 5) can be divided into three sections. The first and third sections correspond to the status of the system before and after a phase transition, respectively ($T=420$ K). At the second section dependence becomes complicated (not a simple exponential), that corresponds to the transition field. Activation energy of the third section of the dielectric relaxation process is 0.44eV (calculated according to the positions of dielectric losses peaks for different temperatures (figure 4)). The activation energy of a similar relaxation process observed in crystals Ag_3SbS_3 is a value of 0.40 that is close to the value of activation energy in proustite and may indicate that jumping mobility is stipulated by the movement of silver ions, but is not associated with the SbS_3 or AsS_3 groups. Throughout the temperature range investigated the charge transfer is also thermally activated process, the activation energy is equal to 2.40 ± 0.01 eV.

Thus, in view of the approximation error we can conclude that in the investigated range of frequencies and temperatures in proustite crystals a Debye vibration process is observed with the distribution of relaxation times according to the Cole-Cole model.

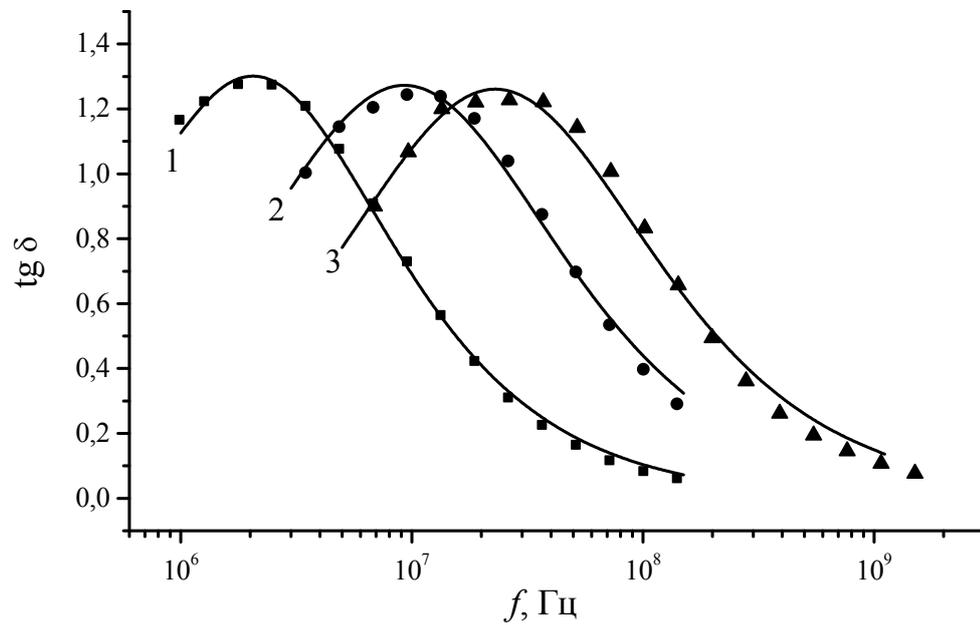


Figure 4. Frequency dependence of dielectric losses angle under different temperatures: 1 – 373 K, 2 – 423 K, 3 – 473 K. Solid lines – approximation by HN function.

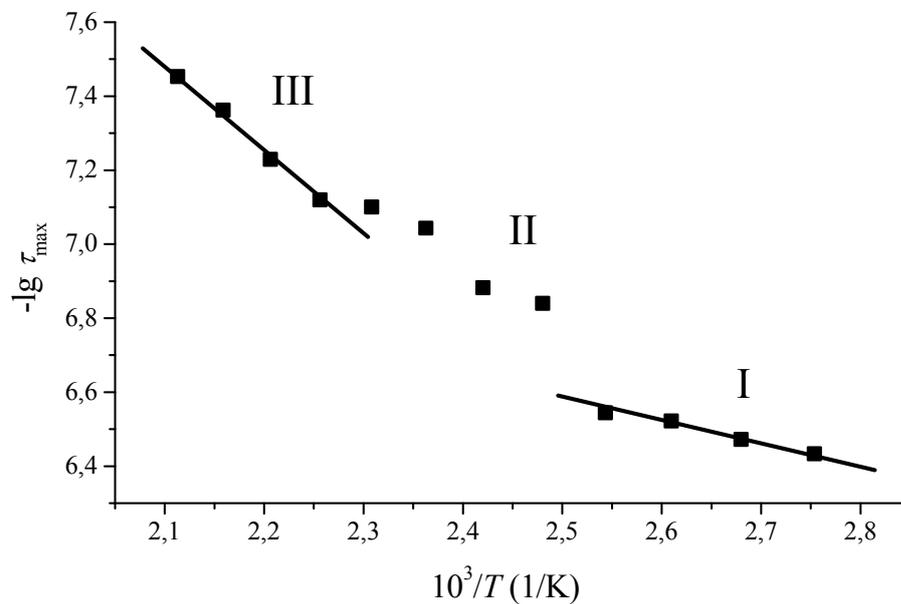


Figure 5. Temperature dependence of the most likely relaxation time for the high frequency field.

4. Conclusion

Thus, in the course of the executed study the following main results were obtained:

1. We have found, that in the high frequency area ($10^6 \dots 10^9$ Hz) the dielectric permittivity ϵ' practically does not depend on the alternating field frequency, and if the frequency is decreased in the whole temperature interval we observe that the value ϵ' is increased, most likely due to the start of dipole-relaxation polarization along with electronic polarization.
2. The dielectric permittivity temperature dependence reveals the existence of two sections: monotonous dependence and sharp increase of the value ϵ' under temperature increasing. The dependence nature change temperature $t \approx 420\text{K}$ (147°C) corresponds of the first-order phase transition, caused by a sharp change of the crystal conductivity.
3. The results of the dielectric spectra approximation by Havriliak-Negami function allow conclude, that at the studied field of high frequencies and temperatures Non-Debye relaxation process is observed in proustite crystals with symmetric distribution of relaxation times according to the Cole-Cole model.

5. Literature

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