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Dispersion of dielectric permittivity and electrical modulus in Ag_xHfS_2 compounds with a layered structure

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According to the impedance spectroscopy data, a significant frequency dispersion of the real and imaginary components of the permittivity was found in the intercalated Ag_xHfS_2 samples. Using the modular formalism, the dielectric relaxation times were determined, which decrease in magnitude with an increase in the silver content in the samples. Their coincidence with the relaxation times determined from the frequency dependences of the imaginary parts of the complex impedance was shown.

Keywords: Intercalates, impedance, hafnium disulfide, silver, dielectric permittivity, electrical module.

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1. Introduction

Recently, many publications have been devoted the investigation of transition metal dichalcogenide with a general formula TX_2 ($T = 3d$ metal, $X = \mathrm{S, Se, Te}$). These materials feature quasi-two-dimensional crystal structure that enables their properties to be modified by introducing (intercalation) atoms of other elements between layers TX_2 [1–4]. By its crystal structure, hafnium disulfide also belongs to this group of compounds. Its structure is a set of structural fragments S-Hf-S interconnected by means of weak Van der Waals (VdW) interaction.

Electrical properties of intercalated Ag_xHfS_2 in direct and alternating current have been investigated earlier and activation nature of conductivity and its frequency dispersion were finally determined [5]. It was assumed that a significant contribution may be also made by mobile silver ions during charge transfer processes. Such assumption is quite probable because existence of ion conductivity in other silver-containing titanium and hafnium compounds is reported [6,7]). Thus, for example, in $Ag_4Hf_3S_8$ compound which also has a lamellar structure, the silver ion transfer number is close to unity and the ion conductivity is about 10^{-3} S/cm [7]. Investigations of Ag_xHfSe_2 showed the presence of polarization phenomena in them. The occurrence of difference in silver concentration in metal electrode (Ag) and Ag_xHfSe_2 specimens resulted in EMF initiation in electrochemical cells using the specimens as solid electrolyte [8].

Mobile ion redistribution in the electric field leading to polarization processes simultaneously induces dielectric response to an external electric field. Dielectric performance of such silver-containing intercalated compounds has not been investigated before and are investigated herein.

2. Experiment

Production of initial hafnium disulfide as intercalation matrix and synthesis of Ag_xHfS_2 ($x = 0.1; 0.2$) polycrystalline specimens were carried out by solid-state reaction method in full-vacuum quartz vials in a two-stage process. Such process has been used multiple times before for synthesizing intercalated materials and described in detail in [4,5,8]. From our experience, this allowed to avoid direct interaction between free sulfur and silver metal which is enabled when specimens are synthesized from initial elements. For homogenization, synthesized specimens were subjected to repeated grinding, compacting and annealing. X-ray qualification of the obtained intercalated compounds has shown that their crystal structure, like the original HfS_2, corresponds to the CdI_2 structure type. AC impedance measurements were carried out at various temperatures using Solartron 1260A multi-purpose frequency response analyzer in linear frequency range (f) 1 Hz–5 MHz. The exciting signal was the same in all experiments and was equal to 0.2 V. The analysis was carried out within an equivalent scheme with resistor and capacitor connected in parallel. Real and imaginary parts of permittivity were determined from impedance data and geometrical capacity of the utilized cell [9]. Due to the fact that intercalated specimens had high resistance, all measurements were carried out using two point probe method.

3. Rezults

The investigations detected significant frequency dispersion of real (ε') and imaginary (ε'') parts of the complex permittivity. Thus, Figures 1 and 2 show such dependences for $Ag_{0.1}HfS_2$ and $Ag_{0.2}HfS_2$ specimens. ε'

and ε'' steadily decrease with increase in frequency and demonstrate inverse proportion to frequency. High ε' and ε'' at low frequencies may be caused by polarization effects as it is in ion-conducting materials [10]. This is indicative of the existing dielectric relaxation in these specimens. Such type of dependences was also detected in titanium diselenide intercalated with copper atoms [11]. Complex-place permittivity spectrum in the studied frequency range shown in Figure 3 has a linear character and shows no peak typical of the Cole-Cole diagrams. Such diagrams with linear dielectric spectrum are also detected for other materials, including silver-containing compounds [12,13]. The type of the presented dependences does not allow to use them for quantitative determination of dielectric relaxation. In such cases, data may be represented in the form of electrical modulus [14,15] whose complex quantity is inverse to complex permittivity $M^* = 1/\varepsilon^* = M' + i \cdot M''$. In this case, according to [16], the contribution of electrode and other interphase effects may be minimized. This allows to identify the inherent dielectric behavior of the studied materials. In this case the imaginary part of electrical modulus transforms the low-frequency growth of permittivity into a relaxation peak whose position allows to determine the relaxation time.

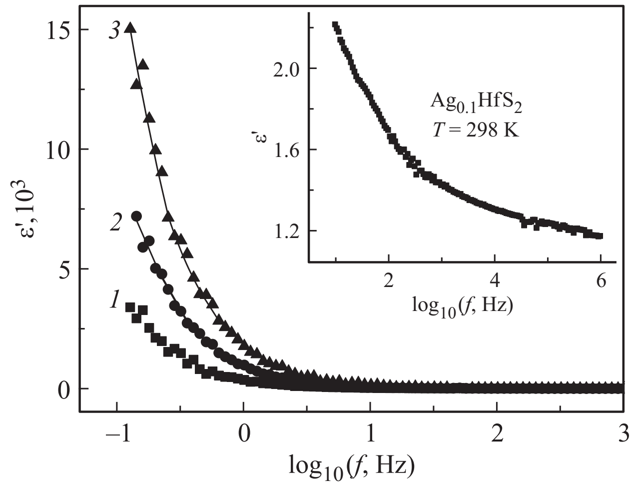

Figure 1. Frequency dependences of the real part of permittivity $Ag_{0.1}HfS_2$ at $T = 298$ K (see the detail) and $Ag_{0.2}HfS_2$ at different temperatures 275 K (*1*) 298 K (*2*), 330 K (*3*).

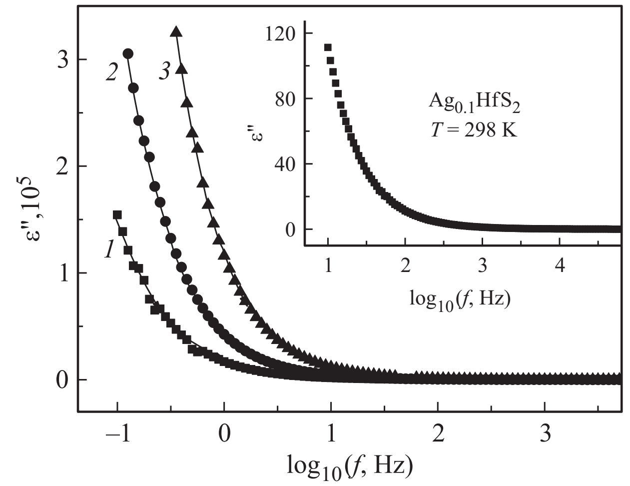

Figure 2. Frequency dependences of the imaginary part of permittivity $Ag_{0.1}HfS_2$ at $T = 298$ K (see the detail) and $Ag_{0.2}HfS_2$ at different temperatures 275 K (*1*) 298 K (*2*), 330 K (*3*).

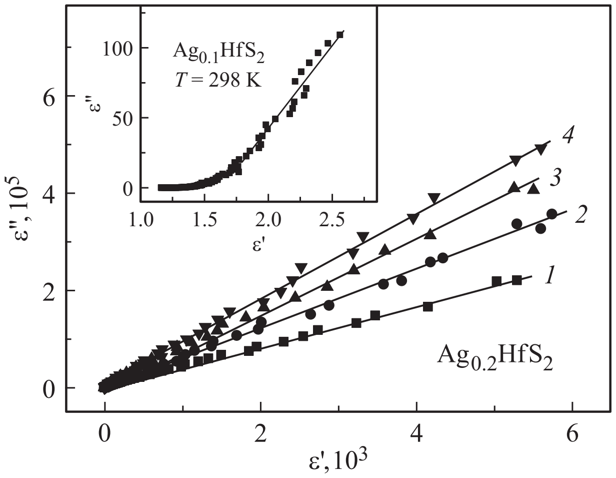

Figure 3. Permittivity hodographs $Ag_{0.1}HfS_2$ at $T = 298$ K (see the detail) and $Ag_{0.2}HfS_2$ at different temperatures 298 K (*1*), 330 K (*2*), 340 K (*3*), 350 K (*4*).

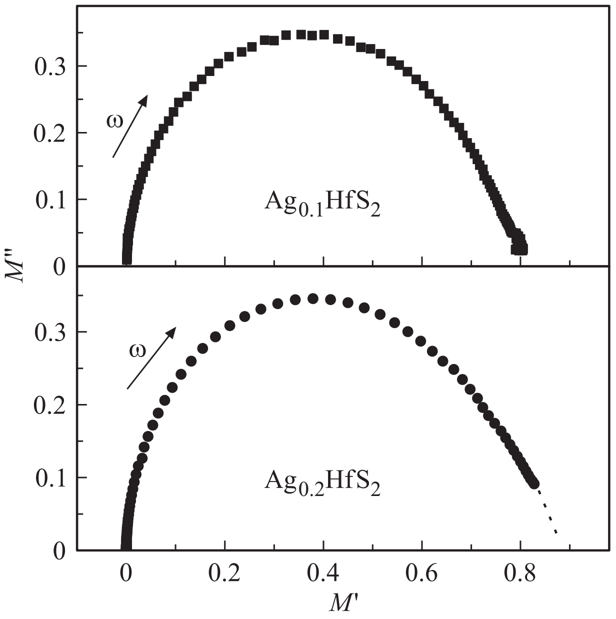

Figure 4. Electrical modulus spectra for $Ag_{0.1}HfS_2$ and $Ag_{0.2}HfS_2$ spectra at $T = 298$ K.

Actually, such transformations gave the complex-plane electrical modulus spectra in the form of the arc of a circle (Figure 4). Since this figure shows no explicit frequency dependences of the module components, Figure 5 shows

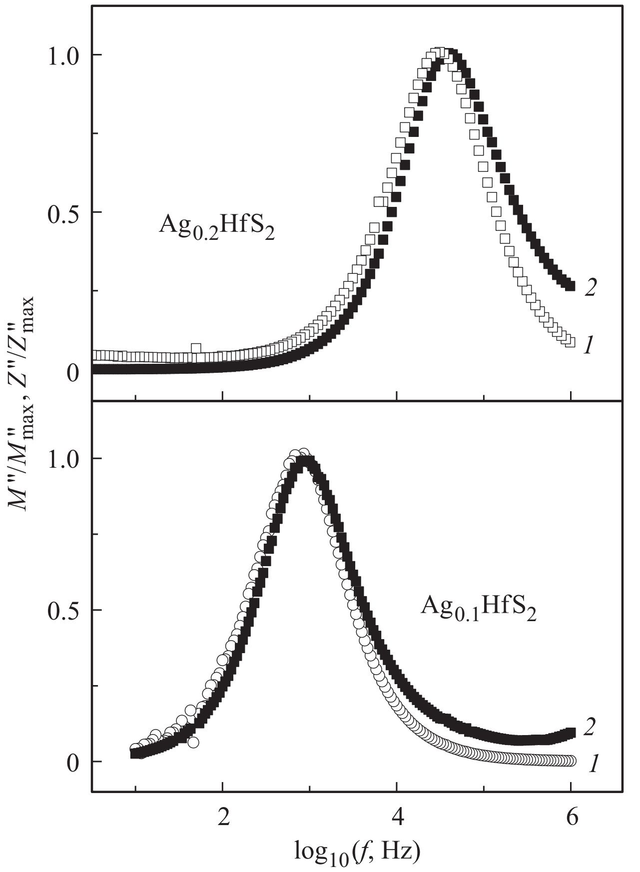

Figure 5. Frequency dependences of specified imaginary parts of impedance (1) and electrical modulus (2) Ag_xHfS_2 at $T = 298$ K.

dependences of specified values $M''/M''_{\max}$ vs. frequency that feature strongly pronounced peaks at certain frequencies $f_{\max}$. It is apparent that increased silver content in the compounds results in displacement to $M''_{\max}$ position into the higher frequency area which is indicative of decrease in relaxation time $\tau_r = (2\pi \cdot f_{\max})^{-1}$ from $1.85 \cdot 10^{-4}$ s for $Ag_{0.1}HfS_2$ to $4 \cdot 10^{-6}$ s for $Ag_{0.2}HfS_2$. This figure also shows frequency dependences of the imaginary parts of the complex impedance as $Z''/Z''_{\max}$ for these specimens. Data in Figure 5 shows that the relaxation times during charge transfer almost coincide with dielectric relaxation times. This may be indicative of the fact that the polarization process kinetics is primarily governed by the charge transfer kinetics. Moreover, this is proved by the fact that frequency values $f_{\max}$ at which maximum M'' values are reached are close to the frequencies at which frequency dependence of ac-conductivity shows transition towards the dispersion region described by the power law $\sigma_{ac} \sim \omega^n$ [5]. According to [16], this frequency separates two hopping conductivity processes. At $f < f_{\max}$ — long-range hops prevail, and at $f > f_{\max}$ — hops into adjacent, closely-spaced positions.

4. Conclusion

Investigations od dielectric properties of hafnium disulfide intercalated with silver atoms were carried out for the first time. Dielectric properties were analyzed in the permittivity presentation and in electrical modulus presentation. The complex-plane permittivity spectra show no peak typical of the Cole-Cole diagrams and represent a linear dependence. It is shown that the modular formalism in this case is more informative for quantitative determination of relaxation characteristics of these materials. Such presentation allowed to define relaxation times which decrease with the increase in silver content in the specimens. Frequencies at which the imaginary part of the electrical modulus has its maximum value are close to the frequencies at which ac-conductivity frequency dispersion segment starts. This segment is specific to the hopping conductivity mechanism.

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Conflict of interest

The author declares that he has no conflict of interest.

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