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Structural and optical studies of Cu_6PSe_5I-based thin film deposited by magnetron sputtering

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Abstract. $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film was deposited onto silicate glass substrate by non-reactive radio frequency magnetron sputtering. Structural studies were carried out using X-ray diffraction and SEM techniques. Spectrometric studies of transmission spectra of $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film in the temperature interval 77 to 300 K were investigated. It is shown that the temperature behaviour of optical absorption edge is described by the Urbach rule. Temperature dependences of optical parameters of the Urbach absorption edge and refractive index have been analyzed. The influence of temperature and structural disordering on the Urbach tail has been studied. The comparison of optical parameters of Cu_6PSe_5I crystal and $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film has been performed.

Keywords: thin film, magnetron sputtering, optical absorption, Urbach rule, refractive index.

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1. Introduction

Cu_6PSe_5I crystals belong to an argyrodite family of tetrahedrally close-packed structures [1]. These materials are known as superionic conductors or solid electrolytes. They have attracted great interest not only in the view of the possibility to apply them in a high-energy-density batteries and sensors, but also due to their remarkable properties.

Cu_6PSe_5I crystals, by analogy with Cu_6PS_5I, have the cubic syngony (space group $F\bar{4}3m$) at room temperature [1]. The stepwise change of the total electrical conductivity in Cu_6PSe_5I crystals, a sudden increase in ionic conductivity as well as a decrease of the activation energy have shown the existence of the superionic first-order phase transition (PT), which occurs within the temperature range $T_s = 260…268$ K [2]. This PT is related with the structural topological disorder of copper-cation sublattice, resulting in copper-ion migration and drastic growth of the ionic component in the electric conductivity. Temperature behaviour of the dielectric permeability and absorption edge of Cu_6PSe_5I crystal in the vicinity of the superionic PT has been presented in Ref. [3].

Temperature behaviour of optical properties of Cu_6PSe_5I crystals were studied in Refs. [4-6]. The long-wave side of absorption edge in Cu_6PSe_5I crystal in the non-superionic ($T < T_s$) and superionic ($T > T_s$) phases exhibits exponential dependence on photon energy. The temperature studies have shown that the exponential parts obey the Urbach rule in both phases, though the convergence point coordinates of the Urbach edge are different for the two phases. In the temperature range of superionic PT, a stepwise behaviour of the optical parameters are observed. The temperature dependence of the optical pseudogap and Urbach energy were described in the framework of the Einstein single oscillator model.

Thus, the physical properties of Cu_6PSe_5I single crystals are well known, while the investigation of physical properties of thin films on their basis only begins. It should be noted that Cu_6PS_5I thin films for the first time were obtained and studied in Ref. [7]. The influence of annealing on the optical absorption edge parameters of Cu_6PS_5I thin films was investigated in Ref. [8]. Electrical and optical studies of Cu_6PS_5I-based thin films with a different copper atoms content were performed in Ref. [9].

Here, we report on the deposition, structural investigation, and spectrometric studies of the transmission spectra in Cu_6PSe_5I-based thin film. Besides, we would like to analyze the temperature behaviour of the Urbach absorption edge, to study disordering processes in Cu_6PSe_5I-based thin film as well as to compare the optical parameters of Cu_6PSe_5I single crystal and thin films under investigation.

2. Experimental

Thin films were deposited from synthesized polycrystalline Cu_6PSe_5I onto silicate glass substrate by non-reactive radio-frequency magnetron sputtering; the film growth rate was close to 3 nm/min. Deposition was carried out at room temperature in Ar atmosphere. The structure of the deposited film was analyzed using X-ray diffraction; the diffraction pattern obtained using DRON-3 diffractometer (conventional θ–2θ scanning technique, Bragg angle $2\theta \cong 10$–$60°$, Cu K_α, Ni filtered radiation) shows the films to be amorphous. Structural studies were performed for the thin film (Fig. 1) by using the scanning electron microscopy (SEM) technique (Hitachi S-4300); the thin film chemical composition ($Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$) was determined using energy-dispersive X-ray spectroscopy (EDX) studies, which enabled us to check the chemical composition in different points of the film surface. The deposited thin films were observed to be depleted by copper and enriched with phosphorous and iodine.

Optical transmission spectra of $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin films were studied in the interval of temperatures 77…300 K by an MDR-3 grating monochromator, a UTREX cryostat was used for low-temperature studies. From the temperature studies of interferential transmission spectra, the spectral dependences of the absorption coefficient as well as dispersion dependences of the refractive index were derived [10].

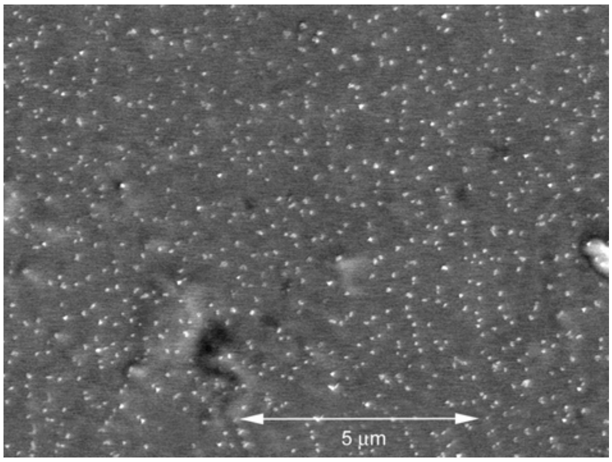

Fig. 1. SEM image of $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film.

3. Results and discussion

The interferential transmission spectra of $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin films at various temperatures are shown in Fig. 2. With temperature, a red shift of both the short-wave part of the absorption spectrum (related to the temperature behaviour of the absorption edge) and the interferential maxima are observed. Besides, Fig. 2 presents the temperature isoabsorption dependence of the characteristic energy E_g^α from the short-wave part of the absorption spectrum, corresponding to the fixed absorption coefficient value $\alpha = 4200$ cm^{-1}. No anomalies in the isoabsorption dependence within the temperature interval 77…300 K were revealed, which is the evidence of the absence of PTs in this temperature range.

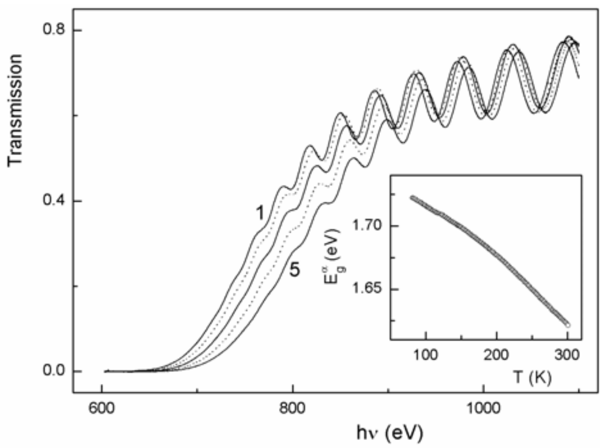

Fig. 2. Spectral dependences of transmission coefficient for $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film at various temperatures: (*1*) 77, (*2*) 150, (*3*) 200, (*4*) 250, (*5*) 300 K. The inset shows the temperature dependences of the absorption edge energy position E_g^α ($\alpha = 4200$ cm^{-1}) obtained in the heating mode.

It is seen (Fig. 3) that the optical absorption edge spectra within the range of their exponential behaviour in amorphous $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin films, similarly to those in the Cu_6PSe_5I single crystal, are described by the Urbach rule [11]

$$\alpha(h\nu,T)=\alpha_0\exp\left[\frac{\sigma(h\nu-E_0)}{kT}\right]=\alpha_0\exp\left[\frac{h\nu-E_0}{E_U(T)}\right],\quad(1)$$

where E_U is the Urbach energy, σ is the absorption edge steepness parameter, α_0 and E_0 are the convergence point coordinates of the Urbach bundle. The coordinates of the Urbach bundle convergence point α_0 and E_0 for the $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin films are given in Table. The latter also presents the α_0 and E_0 values for Cu_6PSe_5I single crystal.

The temperature behaviour of the Urbach absorption edge in $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film is explained by electron-phonon interaction (EPI) that is strong in the thin films under investigation. The EPI parameters were obtained from the temperature dependence of absorption edge steepness parameter (Fig. 3) using the Mahr formula [12]

$$\sigma(T)=\sigma_0\cdot\left(\frac{2kT}{\hbar\omega_p}\right)\cdot\tanh\left(\frac{\hbar\omega_p}{2kT}\right),\quad(2)$$

where $\hbar\omega_p$ is the effective phonon energy in a single oscillator model, describing the EPI, and σ_0 – parameter related to the EPI constant g as $\sigma_0=(2/3)g^{-1}$ (parameters $\hbar\omega_p$ and σ_0 are given in Table). For the $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film $\sigma_0<1$, which is the evidence for the strong EPI [13]. It should be noted that in the thin film, as compared to the single crystal, the EPI is substantially enhanced (it corresponds to a decrease of the σ_0 parameter) and the energy $\hbar\omega_p$ of the effective phonon, taking part in absorption edge formation, increases (Table).

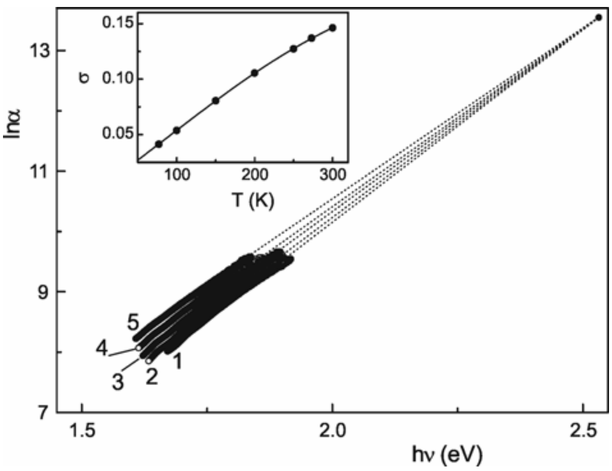

Fig. 3. Spectral dependences of the absorption coefficient for $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film at various temperatures: (*1*) 77, (*2*) 150, (*3*) 200, (*4*) 250, (*5*) 300 K. The insert shows the temperature dependence of the steepness parameter σ.

Table. The parameters of Urbach absorption edge and EPI for Cu_6PSe_5I single crystal and $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film.

Material	Single crystal	Thin film
α_0 (cm^{-1})	2.78×10^5	7.65×10^5
E_0 (eV)	1.211	2.532
E_g^α (eV)	1.059 ($\alpha=10^3$ cm^{-1})	2.053 ($\alpha=5\times10^4$ cm^{-1})
E_U (meV)	27.1	175.6
σ_0	1.359	0.243
$\hbar\omega_p$ (meV)	60.3	77.6
θ_E (K)	700	900
$(E_U)_0$ (meV)	22.2	156.3
$(E_U)_1$ (meV)	44.1	312.2
$E_g^\alpha(0)$ (eV)	1.089	2.105
S_g^α	4.61	4.11

For the spectral characterization of the Urbach absorption edge in $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film, we use their energy position E_g^α at a fixed absorption coefficient $\alpha=5\times10^4$ cm^{-1} (Table). The temperature dependences of E_g^α and the Urbach energy E_U for $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film are summarized in Fig. 4. The temperature behaviour of E_g^α and E_U can be described in the Einstein model by the following relations [14, 15]

$$E_g^\alpha(T)=E_g^\alpha(0)-S_g^\alpha k\theta_E\left[\frac{1}{\exp(\theta_E/T)-1}\right],\quad(3)$$

$$E_U=(E_U)_0+(E_U)_1\left[\frac{1}{\exp(\theta_E/T)-1}\right],\quad(4)$$

where $E_g^\alpha(0)$ and S_g^α are the energy gap at 0 K and a dimensionless constant, respectively; θ_E is the Einstein temperature, corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators, $(E_U)_0$ and $(E_U)_1$ are constants. The obtained $E_g^\alpha(0)$, S_g^α, θ_E, $(E_U)_0$, and $(E_U)_1$ parameters for the thin film are given in Table, and the temperature dependences of E_g^α and the Urbach energy E_U for the $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film calculated from Eqs. (3) and (4) are shown in Fig. 5 as solid and dashed lines, respectively. Besides, in Table we listed the values of $E_g^\alpha(0)$, S_g^α, θ_E, $(E_U)_0$, and $(E_U)_1$ parameters for Cu_6PSe_5I single crystal.

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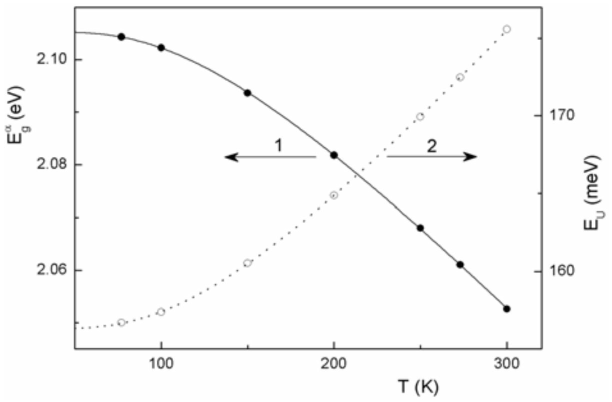

Fig. 4. Temperature dependences of the absorption edge energy position E_g^{α} at $\alpha = 5\times10^4\ cm^{-1}$ (*1*) and the Urbach energy E_U (2) for $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film.

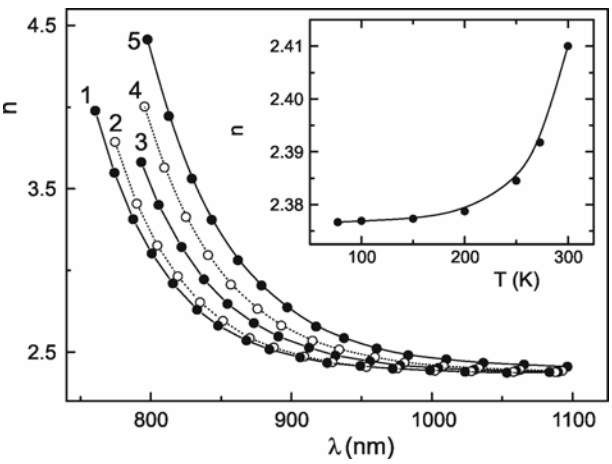

Fig. 5. Refractive index dispersions for $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film at various temperatures: (*1*) 77, (*2*) 150, (*3*) 200, (*4*) 250 and (*5*) 300 K. The inset shows the temperature dependence of refractive index.

It should be noted that in $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film the Urbach behaviour of the absorption edge is observed in the whole temperature interval under investigation, while in the single crystal it is observed in non-superionic and superionic phases separately. An essential characteristic of the absorption edge spectra inherent to the thin films under investigation is a lengthy Urbach tail, which results in the Urbach energy E_U increase by the factor over than 6 in comparison with that of the single crystal.

In Ref. [16], it was shown that both temperature and structural disordering affect the Urbach absorption edge shape, *i.e.*, the Urbach energy E_U is described by the equation

$$E_U = (E_U)_T + (E_U)_X = (E_U)_T + (E_U)_{X,stat} + (E_U)_{X,dyn}, \quad (5)$$

where $(E_U)_T$ and $(E_U)_X$ are the contributions of temperature and structural disordering to E_U, respectively; $(E_U)_{X,stat}$ and $(E_U)_{X,dyn}$ – contributions of static structural disordering and dynamic structural disordering to $(E_U)_X$, respectively. It should be noted that the first term in the right-hand side of Eq. (4) represents static structural disordering, and the second one represents temperature-related types of disordering: temperature disordering due to thermal lattice vibrations and dynamic structural disordering due to the presence of mobile ions in the superionic conductor.

The static structural disordering $(E_U)_{X,stat}$ in $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film as well as in Cu_6PSe_5I single crystal is caused by structural imperfectness due to the high concentration of disordered copper vacancies. Moreover, the static structural disordering in $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film, unlike to that in Cu_6PSe_5I single crystal, increases due to: (1) the absence of long-range order in the atomic arrangement and chemical bond breakdown; (2) lower density of the atomic structure packing due to the presence of pores; (3) the transition from the three-dimensional bulk structure to the two-dimensional planar structure. Thus, the absolute value of contribution of static structural disordering into the thin film Urbach energy increases by the factor over than 7 in comparison with that in the single crystal, while its relative value grows from 82% in the single crystal to 89% in the thin film.

The dynamic structural disordering $(E_U)_{X,dyn}$ is related to the intense motion of mobile copper ions, participating in ion transport, and is responsible for the ionic conductivity. Preliminary electrical studies have shown that the total electric conductivity of the thin film at $T = 295$ K is $\sigma_t = 3.9\times10^{-3}$ S/cm at the frequency close to 1 MHz, while the total electric conductivity for the single crystal is $\sigma_t = 5.6\times10^{-2}$ S/cm at 1 kHz [2].

The dispersion dependences of the refractive index for the $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film were obtained from the interferential transmission spectra (Fig. 5). The slight dispersion of the refractive index is observed in the transparency region, but it increases when approaching to the optical absorption edge region. With temperature increase, the nonlinear growth of the refractive index in $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film has been revealed.

4. Conclusions

$Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin films were deposited onto silicate glass substrate by non-reactive radio frequency magnetron sputtering. X-ray diffraction pattern shows the films to be amorphous. Structural studies were performed using SEM technique, which gives the evidence for the formation of a homogeneous two-dimensional structure. Temperature variation of the transmission spectra as well as the temperature variation of the absorption edge spectra within the range of its exponential behaviour have been studied. A typical Urbach bundle has been observed, temperature dependences of the optical parameters of the Urbach absorption edge have been analyzed. In two-dimensional $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin films, the Urbach absorption edge is formed by strong EPI. The influence of temperature and structural disordering on the Urbach tail is studied and a comparative analysis of the Urbach absorption edge parameters for Cu_6PSe_5I single crystal and $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film has been performed. It should be noted that the transfer from Cu_6PSe_5I single crystal to $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film causes the substantial increase of the Urbach energy E_U, enhances EPI (decrease of σ_0 parameter) and increases the effective phonon energy $\hbar\omega_p$ as well as the relative contribution of static structural disordering into E_U from 82% to 89%. The dispersion dependences of the refractive index for the $Cu_{5.5}P_{1.2}Se_{5.0}I_{1.3}$ thin film have been obtained from the interferential transmission spectra; the nonlinear increase of refractive index with temperature increase has been revealed.

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