Electrical and optical absorption studies of Cu_7GeS_5I fast-ion conductor

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Abstract

Electrical conductivity and fundamental absorption spectra of monocrystalline Cu_7GeS_5I were measured in the temperature ranges 95–370 and 77–373 K, respectively. A rather high electrical conductivity ($\sigma_t = 6.98 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 300 K) and low activation energy ($\Delta E_a = 0.183$ eV) was found. The influence of different types of disordering on the Urbach absorption edge and electron–phonon interaction parameters were calculated, discussed and compared with the same parameters in Cu_7GeS_5I, Cu_6PX_5I ($X =$ S,Se) and Ag_7GeX_5I ($X =$ S,Se) compounds. We have concluded that the P $\rightarrow$ Ge and Cu $\rightarrow$ Ag cation substitution results in an increase of the electrical conductivity and a decrease of the activation energy. Besides, P $\rightarrow$ Ge substitution, results in complete smearing and disappearance of the exciton absorption bands and in blue shift of the Urbach absorption edge, an increase of the edge energy width and an electron–phonon-interaction enhancement. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Through the recent decades, fast-ion conductors were considered as basic materials in a number of applications: such as high-energy-density batteries, capacitors and sensors. Hence, the search for new materials and their studies are of particular interest. Though the Cu_7GeS_5I crystals were synthesized rather a long time ago [1], they have been scarcely studied, except for some electrochemical properties [2]. Christallographically Cu_7GeS_5I compounds belong to argyrodite family with the general formula $A_{(12-n-x)/m}^{m+}B^{n+}X_{6-x}^{2-}Y_x^{1-}$, where A: Cu, Ag, Cd, Hg; B: Ga, Si, Ge, Sn, P, As; X: S, Se, Te; Y: Cl, Br, I; $0 \leq x \leq 1$ [1]. The most extensively studied among the compounds of this family is Cu_6PS_5I, which, besides high ionic conductivity, exhibits ferroelastic and nonlinear optical properties [1], and two phase transitions (PTs) at low temperatures; one super-

ionic, and the other ferroelastic [3,4]. Silver-containing analogue, Ag_7GeS_5I fast-ion conductor, shows pure ionic conductivity, and has no structural PTs [5]. At room temperature Cu_7GeS_5I as well as Cu_6PS_5I and Ag_7GeS_5I, belong to cubic syngony [1]. In this paper electrical and optical absorption edge studies in Cu_7GeS_5I crystals are presented. Detailed comparison with analogous properties of Cu_6PS_5I and electrical properties of Ag_7GeS_5I crystals has been performed and analyzed comparing both static and dynamic structural disorder in these materials.

2. Experimental

Cu_7GeS_5I single crystals were grown by using the chemical transport reaction method. Cu_7GeS_5I compound was synthesized from extra pure Cu_4GeS and CuI compounds, additionally purified by distillation in vacuum. Maximal synthesis temperature was 1020–1070 K. To avoid contamination and the deviations from stoichiometry the single crystals were synthesized and grown in the same evacuated

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(down to 0.13 Pa) quartz ampoules. The evaporation temperature zone was kept within 973–1073 K, that of the crystallization zone, within 873–1023 K. Ten to 20 mg of CuI per 1 cm^3 of the ampoule free volume was used as a transport agent. Thus, the as-grown crystals had the shape of a plane-parallel platelets or distorted tetrahedron $5 \times 3 \times 3(2.5)$ mm^3 of dark-red colour.

Spectral dependence of the linear optical absorption coefficient α for monocrystalline Cu$_7$GeS$_5$I was studied in the temperature range 77–373 K using the setup described in Ref. [4]. Transmittance, T, and reflectance of the surface, R, were measured by unpolarized light along the [100] crystallographic direction. The reflectance measurements were performed on samples with laped back end so that the reflection from the rear surface could be neglected. The absorption coefficient α was calculated using the well known formula, which takes into account multiple internal reflections,

$$\alpha = \frac{1}{d}\ln\left\{ \frac{(1-R)^2}{2T} + \sqrt{\left[\frac{(1-R)^2}{2T}\right]^2 + R^2} \right\} \qquad (1)$$

where d denotes the thickness of the plane-parallel sample. The product $\alpha \cdot d$ has been kept between 1 and 3 in order to remain within the accepted level of accuracy of $\Delta\alpha/\alpha < 8\%$ [6]. This means that samples ranging in thickness from 17 to 200 μm enabled measurements of α in the range from 150 to 1800 cm^{-1}. Iso-absorption temperature studies consisted in measuring the absorption edge energy position at the fixed absorption level.

The temperature dependence of electrical conductivity was measured by a system described previously [7], with a heating rate ~0.1 K/min and 50 mV applied voltage. The specimen had the dimensions of approximately 0.2 cm$^2 \times$ 0.1 cm. Measurements were performed in the dark, over the frequency range 100 Hz–10 kHz. Prior to the measurement the sample was annealed at 700 K for 1 h. The accuracy of the measurements was 0.1%.

3. Results

The as grown crystals were identified by X-ray diffraction, and their composition was verified by chemical analysis. At room temperature Cu$_7$GeS$_5$I crystallize in cubic syngony (space group $F\bar{4}3m$). The calculated lattice parameters correspond to the reference data [1], and the chemical composition corresponds to Cu$_7$GeS$_5$I formula within the margin of the experimental error.

Fig. 1(a) shows the total conductivity $\log\sigma_t$ for Cu$_7$GeS$_5$I single crystal as a function of the inverse temperature $10^3/T$. In the temperature range 140–370 K the $\log\sigma_t$ vs $10^3/T$ dependence is linear, with activation energy $\Delta E_a = 0.183$ eV. At lower temperatures ($T < 140$ K) a non-linear behaviour is observed. There are no singularities, which would indicate a PT in the temperature range under investigation.

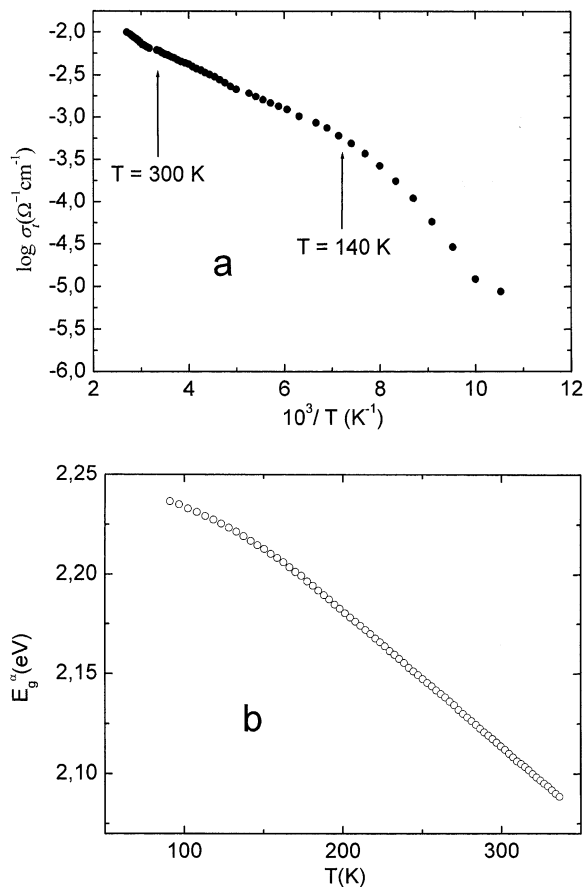In Fig. 1(b), the results of the iso-absorption temperature

Fig. 1. (a) Electrical conductivity versus temperature for Cu$_7$GeS$_5$I crystal, measured at frequency 100 Hz; (b) the temperature dependence of the absorption edge energy position E_g^α ($\alpha = 800$ cm^{-1}), obtained from the iso-absorption studies.

studies are shown. The temperature dependence of the optical absorption edge energy position E_g^α obtained at the absorption level $\alpha = 800$ cm^{-1} in the temperature range 77–373 K does not exhibit any singularities, thus confirming the absence of PTs in the temperature interval under investigation.

Fig. 2 depicts spectral dependence of the optical absorption coefficient α in Cu$_7$GeS$_5$I crystals measured at different temperatures in the temperature range 77–373 K. It can be seen that, in contrast to Cu$_6$PS$_5$I [8], the optical absorption edge temperature studies in Cu$_7$GeS$_5$I did not reveal exciton bands at the absorption edge. The absorption edge in the spectral range of direct optical transitions has exponential shape following the Urbach rule [9]:

$$\alpha(h\nu, T) = \alpha_0 \cdot \exp\left[\frac{h\nu - E_0}{w(T)}\right], \qquad (2)$$

where $w(T)$ is a characteristic Urbach energy, or the width of the exponential absorption edge, while $h\nu$ and T are the
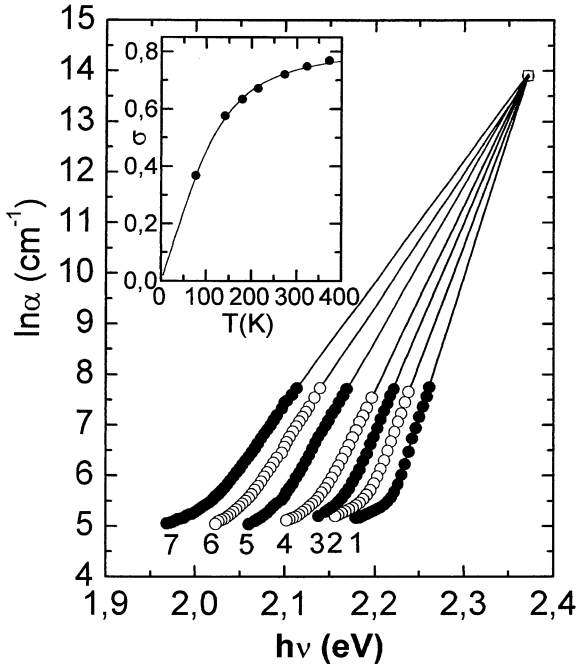
Fig. 2. Spectral dependencies of Cu_7GeS_5I crystal absorption coefficient at various temperatures: (1) 77 K, (2) 142 K, (3) 180 K, (4) 215 K, (5) 273 K, (6) 323 K, (7) 373 K. The insert shows the temperature dependence of $\sigma = RT/w$ parameter: dark circles, experimental values, solid line, fitting of Eq. (5) on experimental data.

Table 1
Urbach edge parameters and electron-phonon-interaction parameters of Cu_7GeS_5I and Cu_6PS_5I crystals

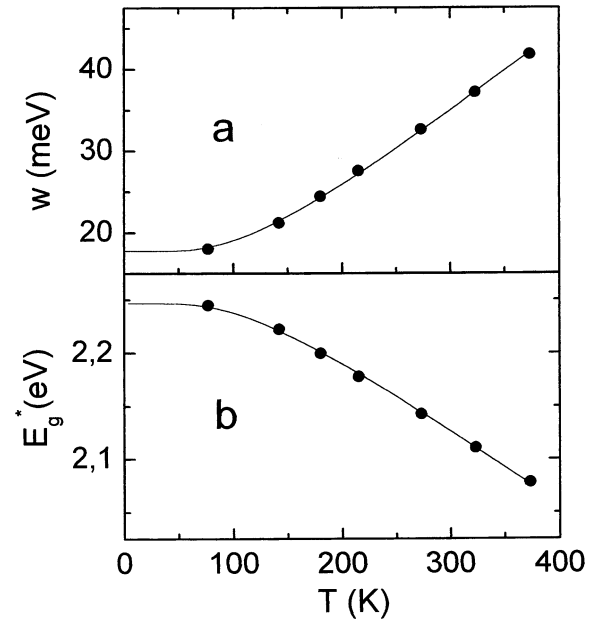| Crystal	Cu_7GeS_5I	Cu_6PS_5I	
Temperature range	77–373 K	$T < T_c$	$T > T_c$
α_0 (cm^{-1})	1.10×10^6	2.96×10^6	
E_0 (eV)	2.371	2.230	
$\hbar\omega_p$ (eV)	0.029	0.027	0.032
σ_0	0.81	1.52	1.55
θ_E (K)	333	313	371
w_0 (meV)	17.8	9.9	9.6
w_1 (meV)	35.1	15.8	23.2
E_g^* (300 K) (eV)	2.125	2.079	
w (300 K) (meV)	35	19.3	
$E_g^*(0)$ (eV)	2.247	2.157	2.152
S_g^*	8.54	5.35	5.39

Fig. 3. Temperature dependence of absorption edge energy width w (a) and optical pseudo-gap E_g^*; (b) of Cu_7GeS_5I crystal: dark circles, experimental values; solid lines, fitting of Eqs. (3) and (10) on experimental data.

photon energy and temperature, respectively. Constants α_0 and E_0, which are independent of temperature and represent the coordinates of the convergence point of the Urbach bundle, were obtained from the fit of Eq. (2) to the experimental data. Coordinates α_0 and E_0 for Cu_7GeS_5I are given in Table 1. For comparison the Table 1 contains the corresponding parameters of Cu_6PS_5I.

From the analysis of the temperature dependence of the optical absorption edge, the width w of the edge as a function of temperature was determined [Fig. 3(a)]. In the Einstein model w is described as [10]:

$$w = w_0 + w_1\left[\frac{1}{\exp(\theta_E/T) - 1}\right] \tag{3}$$

where θ_E is the Einstein temperature, corresponding to the mean frequency of phonon excitations of a system of non-interacting harmonic oscillators, w_0 and w_1 are constants. The values of w_0, w_1 and θ_E (listed in Table 1) were obtained by fitting the Eq. (3) to the experimental data of the temperature dependence of w.

Since possible direct optical transitions in Cu_7GeS_5I crystals were completely masked by Urbach tails we could not determine direct energy gap $E_g^d(T)$ from the measured absorption edge spectra (Fig. 2). Therefore, in order to describe temperature shift of the absorption edge, we have

used an approximated value, optical pseudo-gap $E_g^*(T)$, determined at a certain absorption level $\alpha^* = 1000 \text{ cm}^{-1}$ [11,12]:

$$E_g^*(T) = E_0 - w(T)\ln\left(\frac{\alpha_0}{\alpha^*}\right). \tag{4}$$

Although E_g^* is close to E_g^d [13], values of the pseudo-gap $E_g^*(T)$ are related to the empirical parameters of the Urbach rule only, and do not correspond to the direct gap E_g^d in the one-electron approximation. The temperature dependence of the optical pseudogap E_g^* is given in Fig. 3(b).

4. Discussion

Contrary to what is observed in Cu_6PS_5I [14], in which anomalies in the temperature range of PT were detected, for Cu_7GeS_5I the $\log\sigma_t$ vs $10^3/T$ plot smoothly changes the trend from linear to nonlinear [Fig. 1(a)]. This behaviour rather resembles the behaviour of $\log\sigma_t$ vs $10^3/T$ in Ag_7GeS_5I, where two domains are distinguished: the 'high-temperature domain' ($T > 243$ K), characterized by a smaller activation energy ($\Delta E_a = 0.139$ eV) and the 'low-temperature domain' ($T < 213$ K; $\Delta E_a = 0.264$ eV) [5]. The transition from a domain with low activation energy to the domain with high activation energy was found to be related to the partial ordering of the Ag^+ ions, which is occurring progressively without affecting the crystal lattice [5]. The values of σ_t and ΔE_a for Cu_6PX_5I ($X = $ S,Se) [3], Ag_7GeX_5I ($X = $ S,Se) [5] and Cu_7GeS_5I crystals, listed in Table 2, show the increase of the electrical conductivity and a decrease of the activation energy with the P → Ge and Cu → Ag cation substitution.

The exponential form of the long-wavelength side of the optical absorption edge is usually associated with exciton (electron)-phonon interaction (EPI) [15]. The width of the edge, $w(T)$, is related to another characteristic materials parameter, the slope of the Urbach edge, $\sigma(T)$, as $w(T) = kT/\sigma(T)$, k being the Boltzmann constant. In the whole temperature interval 77–373 K, Cu_7GeS_5I crystals follow the temperature dependence of $\sigma(T)$ described by the Mahr relation [15]:

$$\sigma(T) = \sigma_0 \cdot \left(\frac{2kT}{\hbar\omega_p}\right) \cdot \tanh\left(\frac{\hbar\omega_p}{2kT}\right) \tag{5}$$

depicted as an insert in Fig. 2. σ_0 is a constant independent of temperature and related to the EPI constant g via $\sigma_0 = 2/3g$, while $\hbar\omega_p$ is the effective average phonon energy in a single-oscillator model, describing the EPI [15]. The values of $\hbar\omega_p$ and σ_0 parameter are also given in Table 2. Note that σ_0 is <1, which indicates a strong EPI [16].

It has been shown in Ref. [17] that both temperature and structural disordering affect Urbach absorption edge shape, i.e. the energy position of the Urbach absorption edge $E_g(T)$ and its width w are described by equations:

$$E_g = E_{g,0} - k_g(W_T^2 + W_S^2), \tag{6}$$

$$w = k_0(W_T^2 + W_S^2), \tag{7}$$

where k_0 and k_g are constants, $E_{g,0}$ is the energy gap of a perfect crystal without disordering and W_T^2, W_S^2 are mean-quadratic deviations from the electrical potential of the ideally ordered structure due to thermal vibrations and structural disorder, respectively. In Eqs. (6) and (7) the equivalence, independence and additivity of two types of disorder on the absorption edge has been obviously assumed. Hence, the mean-quadratic deviation W_S^2 can also be written as a superposition of two independent terms: of the $(W_S^2)_{dyn}$, due to dynamic, temperature-dependent disordering and,

Table 2
Electrical conductivity σ_t and activation energy ΔE_a of Cu_7GeS_5I and some other argyrodite-type fast-ion conductors: Cu_6PX_5I ($X = $ S, Se) [3], Ag_7GeX_5I ($X = $ S, Se) [5]

Compound	σ_t (Ω^{-1} cm^{-1})	ΔE_a (eV)
Cu_7GeS_5I[a]	6.98×10^{-3}	0.183
Cu_6PS_5I[a]	1.30×10^{-3}	0.220
Cu_6PSe_5I[a]	5.60×10^{-2}	0.100
Ag_7GeS_5I[b]	2.77×10^{-2}	0.139
Ag_7GeSe_5I[b]	7.96×10^{-2}	–

[a] At temperature 300 K and frequency 10^2 Hz.
[b] At temperature 298 K and frequencies 5–10^7 Hz.

$(W_S^2)_{stat}$, due to static, temperature-independent disordering [4]:

$$W_S^2 = (W_S^2)_{dyn} + (W_S^2)_{stat}. \tag{8}$$

However, since the dynamic structural disordering term $(W_S^2)_{dyn}$ can be, instead, included into the temperature-related term in Eq. (5):

$$W_T^2 = W_{TV}^2 + (W_S^2)_{dyn}, \tag{9}$$

where W_{TV}^2 corresponds to the contribution of thermal lattice vibrations, i.e. to the contribution of phonons interacting with electrons—EPI. Through the analysis of the disorder in Cu_6PS_5I it was shown that the static structural disordering in copper-containing argyrodites stems from the high concentration of disordered copper vacancies [4]. Hence, the static structural disordering $(W_S^2)_{stat}$ in Cu_7GeS_5I, is also caused by the vacancy-related structural imperfectness. This results in the formation of local non-uniform electric fields which, in turn, lead to additional smearing of the energy band edges. The dynamic structural disordering $(W_S^2)_{dyn}$ in Cu_7GeS_5I, like in the case of Cu_6PS_5I, is caused by the presence of mobile copper ions, which participate in ion transfer and are responsible for ionic conductivity. By comparing Eqs. (7) and (3), it could be seen that the first term in the right-hand side of Eq. (3) represents static structural disordering, and the second one represents temperature-dependent types of disordering: temperature disordering due to thermal lattice vibrations W_{TV}^2 and dynamic structural disordering $(W_S^2)_{dyn}$ due to the presence of mobile ions in fast-ion conductors.

The temperature variation of the energy gap in semiconductors is affected, basicaly, by two contributions—thermal expansion and the EPI [18]. The temperature behaviour of the E_g^* due to the EPI can be described in the Einstein model by a relation [19]:

$$E_g^*(T) = E_g^*(0) - S_g^* k\theta_E \left[\frac{1}{\exp(\theta_E/T) - 1}\right], \tag{10}$$

where $E_g^*(0)$ and S_g^* are the energy gap at 0 K, and a dimensionless coupling constant, respectively. Parameters $E_g^*(0)$ and S_g^* obtained from the fit are given in Table 1. The temperature dependence of the optical pseudogap E_g^* in

Cu_7GeS_5I, calculated from the Eq. (10), is shown in Fig. 3(b) as a solid line. The performed calculations show that in the whole temperature range the experimental values of E_g^* are well described by Eq. (10) confirming that EPI contribution strongly dominates over the thermal expansion term. The dominant role of EPI in the energy gap temperature variation of Cu_7GeS_5I is consistent with the results obtained on Cu_6PS_5I where the thermal expansion contribution was found to be lower by almost an order of magnitude than that of EPI [4].

5. Summary and conclusions

Electrical conductivity and optical absorption edge studies of Cu_7GeS_5I were carried out in the temperature ranges 95–370 and 77–373 K, respectively. The total electrical conductivity at room temperature was found to be rather high, as expected and typical for the fast-ion conductors. The dependence of $\log \sigma_t$ vs $10^3/T$ in the temperature range 140–370 K is linear, with activation energy $\Delta E_a = 0.183$ eV, whereas at low temperatures ($T < 140$ K) the plot becomes nonlinear.

Absorption edge studies have shown that the edge exhibits Urbach shape which can be related to the strong EPI. The width w of the optical absorption edge is determined by the effect of both temperature-dependent (thermal vibrations of lattice and dynamic structural disordering in the cation sublattice) and static structural disordering. Temperature dependences of the optical pseudo-gap and the energy width of the absorption edge are well described in the framework of Einstein model. No phase transitions were revealed in the temperature range 77–373 K.

Comparative analysis of the electrical and the absorption edge parameters of Cu_6PS_5I and Cu_7GeS_5I shows that the heterovalent cationic substitution P → Ge results in: (i) the absence of the PT in the 77–373 K temperature range [Fig. 1(a) and (b)]; (ii) an increase of the electrical conductivity σ_t and a decrease of the activation energy ΔE_a (Table 2); (iii) the absence of the exciton bands (Fig. 2); (iv) blue shift of the absorption edge by approximately 0.05 eV and an almost doubled energy width at 300 K (Table 1); (v) the EPI enhancement (almost twice smaller σ_0) and the increase of the effective phonon energy (Table 1); (vi) the increase of the absolute contribution of static structural disordering to the increase of the absorption edge energy width w (9.6 → 17.8 meV, Table 1). Thus, both the electrical and optical studies lead to the same conclusion: the ion transfer in Cu_7GeS_5I is considerably larger than in Cu_6PS_5I which manifests in the increase of the electrical conductivity and the smearing of the optical absorption edge in Cu_7GeS_5I.

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