Raman scattering and optical absorption edge studies of $CuInP_2S_6$ and $CuInP_2(S_{0.95}Se_{0.05})_6$ layered ferrielectrics

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Abstract

Raman scattering spectra at room temperatrure and optical absorption edge spectra in the temperatrure range 77-373 K in $CuInP_2(S_{0.95}Se_{0.05})_6$ crystal are investigated. The comparative analyzis of the obtained spectra with the similar spectra for pure $CuInP_2S_6$ crystal is performed. The anionic substitution of S atoms by Se results in the red shift of the Urbach absorption edge, its additional smearing and sharp decrease of the ferrielectric phase transition.

Introduction

$CuInP_2S_6$ layered crystals belong to the collinear two-sublattice ferrielectric system [1]. Here a first-order phase transition (PT) of the order-disorder type from paraelectric to ferrielectric phase is realized (T_c=315 K). The symmetry reduction at the PT (C2/c $\rightarrow$ Cc) occurs due to ordering in copper sublattice and displacement of cations from centrosymmetric positions in indium sublattice. Spontaneous polarization, arising at the PT to the ferrielectric phase, is perpendicular to the layer planes.

Raman spectra of $CuInP_2S_6$ crystals were studied in [2]. The analysis has shown the bands corresponding to internal vibrations of $[P_2S_6]^{4-}$ anions to be observed in the frequency range 160-600 cm^{-1}, the bands corresponding to external vibrations of $[P_2S_6]^{4-}$ anions – in the range 40-120 cm^{-1}, and those, corresponding to Cu^+ and In^{3+} cation translations – in the range $20-70$ cm^{-1}. The increase of temperature and transition to the paraelectric phase are accompanied by essential changes in the external and internal vibrations of $[P_2S_6]^{4-}$ anions, consisting in variation of S–P–S and S–P–P angles. At the transition to the paraelectric phase the width and intensity of the bands, corresponding to internal stretching vibrations of anions, change as well. Besides, in the PT range the frequencies of the translational vibrations of anions are changed.

In the ferrielectric phase of $CuInP_2S_6$ the absorption edge shape corresponds to direct allowed interband transitions [3], while in the paraelectric phase ($T>T_c$) the exponential Urbach shape is observed. In the PT range the Urbach absorption edge parameters change, being determined by the influence of various types of temperature and structural disorder. The exponential Urbach tails, appearing in $CuInP_2S_6$ crystals, can be related to the essential effect of dynamical structural disorder, occurring in copper cation sublattice.

The present paper is aimed to the investigation of the effect of anionic substitution in mixed $CuInP_2(S_{1-x}Se_x)_6$ crystals (at small x values in sulphur-rich region) upon Raman spectra, optical absorption edge and ferrielectric PT.

Experimental

$CuInP_2S_6$ and $CuInP_2(S_{0.95}Se_{0.05})_6$ single crystals were obtained by chemical transport reactions. Raman measurements of $CuInP_2(S_{0.95}Se_{0.5})_6$ layered crystals were performed at room temperature for ZZ–components of scattering tensor. Raman spectra were measured using a DFS-24 monochromator equipped with a FEU-79 phototube and photon counting system. He-Ne (λ=632.8 nm) laser was employed as the excitation source. The spectral slit did not exceed 2 cm^{-1}.

The absorption edge studies were carried out for the samples of different thickness (d = 20– 100 μm) in a broad temperature range (77 – 373 K). The light beam was propagated along the normal to the layer plane. The temperature studies of the absorption edge were performed for the $E \parallel Y$ polarization. A MDR-3 diffraction monochromator was used for transmittance and reflectance measurements. A UTREX cryostat was applied, the temperature being stabilized within 0.1 K. The absorbance values were calculated according to the known formula [3], the relative error in the absorbance measurements $\Delta\alpha/\alpha$ not exceeding 10% at $0.3 \le \alpha d \le 3$.

Results and discussion

Raman spectrum of $CuInP_2(S_{0.95}Se_{0.05})_6$ crystal, obtained at room temperature for ZZ-component of the scattering tensor, is shown in Fig. 1. Considerable smearing of all bands is observed in comparison with $CuInP_2S_6$ crystal Raman spectrum. In the frequency range 20–70 cm^{-1} the bands, corresponding to Cu^+ and In^{3+} cation translations, are revealed. Besides, the characteristic feature of the obtained spectrum is the presence of additional bands (for example, at $\omega \approx 346$ cm^{-1}), which is not observed in $CuInP_2S_6$ spectrum [2] and corresponds to PS_2Se-PS_3 structural pyramid vibrations [4]. This resembles the situation observed in $Sn_2P_2(Se_xS_{1-x})_6$ mixed "three-dimensional" crystals [4], and is the evidence for the multi-mode character of Raman spectrum transformation in $CuInP_2(S_{0.95}Se_{0.5})_6$ mixed crystal. In mixed "two-

dimensional" hypothio(seleno)diphosphates, similarly to "three–dimensional" $Sn_2P_2(Se_xS_{1-x})_6$ [4], statistical distribution of atoms over crystal lattice sites can be assumed.
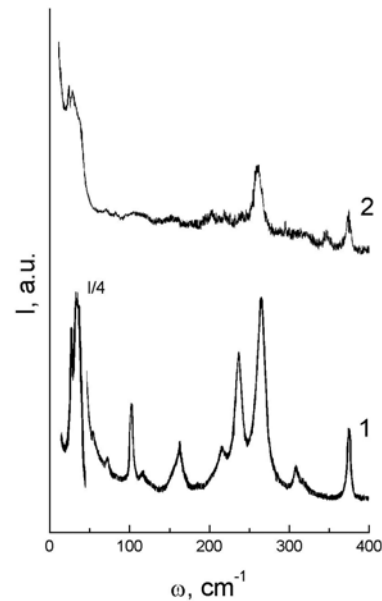

Fig.1. Raman spectra of $CuInP_2S_6$(1) [2] and $CuInP_2(S_{0.95}Se_{0.05})_6$(2) single crystals at room temperature for ZZ-components of the scattering tensor.

Optical absorption edge spectra of $CuInP_2(S_{0.95}Se_{0.5})_6$ crystals were studied in the temperature interval T=77–373 K (Fig. 2). In case 5 mol.% Se are being introduced into $CuInP_2S_6$ crystal $(\alpha \cdot h\nu)^2 = f(h\nu)$ spectral dependen-ces, typical for direct transitions, are smeared, and Urbach absorption tails appear in the ferrielectric phase ($T < T_c$), which are described by Urbach rule:

$$\alpha(h\nu, T) = \alpha_0 \cdot \exp\left[\frac{h\nu - E_0}{w(T)}\right], \qquad (1)$$

where $w(T)$ is the characteristic Urbach energy or the width of the exponential absorption edge, $h\nu$ and T are the photon energy and temperature, respectively. Constants α_0 and E_0, which represent the coordinates of the convergence point of the Urbach bundle, were obtained from the fit of Eq. (1) to the experimental data. Coordinates α_0 and E_0 for $CuInP_2(S_{0.95}Se_{0.5})_6$ crystal are given in Table 1.
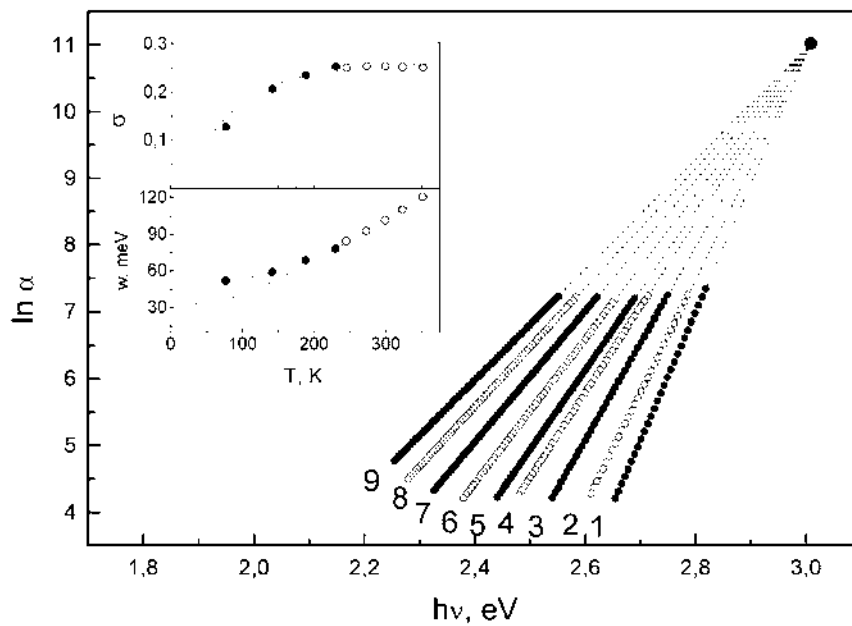
Fig.2. Spectral dependences of $CuInP_2(S_{0.95}Se_{0.05})_6$ crystal absorbance logarithm at various temperatures (K): 1—77 , 2—142 , 3—188 , 4 – 230, 5 – 245, 6 – 273, 7 – 299, 8 – 323, 9 – 352. The insert shows the temperature dependences of the absorption edge energy width w and $\sigma = kT/w$ parameter: the experimental values for $T<T_c$ are presented by dark circles, and those calculated according to Eqs. (1) and (2) – by solid curves, for $T>T_c$ – by open circles and dashed curves, respectively.

Table 1. The absorption edge energy position E_g^α at α =800 cm^{-1} and the exponential absorption edge energy width w at T = 325 K; the Urbach absorption edge parameters α_o and E_0, EPI parameters $\hbar\omega_p$ and σ_0 as well as θ_E, w_0 and w_1 parameters, obtained while describing the experimental results by Eqs. (1)-(3) for $CuInP_2S_6$ and $CuInP_2(S_{0.95}Se_{0.05})_6$ crystals.

Crystal	$CuInP_2S_6$	$CuInP_2(S_{0.95}Se_{0.05})_6$	
E_g^α (eV)	2.623	2.521	
w (meV)	107.5	112.2	
Temperature interval (K)	315-573	77-235	245-360
α_0 (cm^{-1})	1.66×10^5	6.11×10^4	
E_0 (eV)	3.195	3.009	
σ_0	0.269	0.301	0.269
$\hbar\omega_p$ (meV)	17.5	30.4	22.5
θ_E (K)	203	353	261
w_0 (meV)	32.3	50.5	33.3
w_1 (meV)	65.1	99.0	95.6
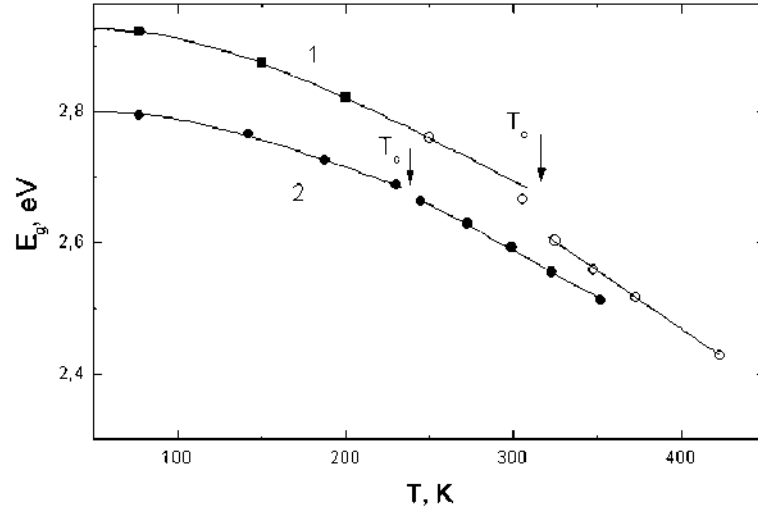
Fig.3. Temperature dependences of CuInP$_2$S$_6$ crystal energy gap (1) [3] and optical pseudogap E_g^* of CuInP$_2$(S$_{0.95}$Se$_{0.05}$)$_6$ crystal (2). For CuInP$_2$S$_6$ the experimental values of E_g^d are represented by dark rectangles, and E_g^α (α=640 cm^{-1}) – by open circles; for CuInP$_2$(S$_{0.95}$Se$_{0.05}$)$_6$ E_g^* values are represented by dark circles, and those calculated from Eq. (3) – by solid lines.

Besides, the absorption edge red shift is observed as well as its energy width w increases and the change of Urbach convergency point coordinates (see Table 1), caused by the influence of compositional disorder at S→Se anionic substitution in CuInP$_2$(S$_{0.95}$Se$_{0.5}$)$_6$ mixed crystal.

In the insert to Fig. 2 the temperature behaviour of $\sigma = kT / w$ parameter is shown, which is described by the known formula [5]:

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

$\hbar\omega_p$ being the effective phonon energy in the single-oscillator model describing the electron(exciton)-phonon interaction (EPI); σ_0 – a parameter related to the EPI constant g as $\sigma_0 = 2/3g$ [5]. The obtained $\hbar\omega_p$ and σ_0 values are listed in Table 1. In CuInP$_2$(S$_{0.95}$Se$_{0.5}$)$_6$ crystals $\sigma_0 < 1$, this is the evidence for strong EPI [6]. The comparative analysis of CuInP$_2$S$_6$ and CuInP$_2$(S$_{0.95}$Se$_{0.05}$)$_6$ crystals absorption edge have also shown the electron-phonon constant to remain unchanged

at slight increase of the effective phonon energy participating in the absorption edge formation in CuInP$_2$(S$_{0.95}$Se$_{0.05}$)$_6$ crystal.

The temperature dependences (see Figs.2,3) of the absorption edge energy width w and the optical pseudogap energy E_g^*, being the absorption edge energy position at the absorption level α=10^3 cm^{-1}, in the Einstein model can be described by the relations [7,8]

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

$$E_g^*(T) = E_g^*(0) - S_g^* k\theta_E \left[\frac{1}{\exp(\theta_E / T) - 1}\right], \qquad (4)$$

w_0 and w_1 values being constant within the same phase, $E_g^*(0)$ being the energy gap at 0 K, S_g^* – a constant number, θ_E – the Einstein temperature corresponding to the mean frequency of phonon excitations of a non-interacting harmonic oscillator system. w_0, w_1 and θ_E parameter values, obtained while describing the experimental temperature dependences of w by Eq. (3), are listed in

Table 1. In the PT range the change of the absorption edge energy width w is observed.

It should be noted that even small (5 mol.%) substitution of S atoms by Se results in the sharp decrease of the PT temperature from 315 K to 240 K and strong smearing of the anomaly in the temperature behaviour of optical pseudogap is typical for the first-order PT (Fig.3). The smearing is also explained by the effect of compositional disorder.

Conclusions

The results of optical studies (Raman spectroscopy, optical absorption) give the evidence for essential disorder of crystal lattice at the transition from $CuInP_2S_6$ to $CuInP_2(S_{0.95}Se_{0.5})_6$. The atomic substitution in the anionic sublattice of $CuInP_2(S_{0.95}Se_{0.5})_6$ mixed crystal drastically affects the structural PT. This is evidently determined by the pre-sence of a morphotropic phase boundary at the temperature-composition diagram for $CuInP_2(S_{1-x}Se_x)_6$ solid solutions. Such boundary separates monoclinic and trigonal phases, namely centrosymmetric $C2/c$ ($CuInP_2S_6$) and $R\bar{3}$ ($CuInP_2Se_6$) and noncentrosymmetric Cc ($CuInP_2S_6$) and $R3$ ($CuInP_2Se_6$) phases. In thisview further studies of optical properties of other mixed $CuInP_2(S_{1-x}Se_x)_6$ crystals near the morphotropic phase boundary seem promising.

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