INFLUENCE OF β-RADIATION ON OPTICAL ABSORPTION EDGE IN Cu_6PS_5I CRYSTALS

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Temperature studies of optical absorption edge in non-irradiated and β-irradiated Cu_6PS_5I crystals are performed. The effect of β-radiation upon Urbach absorption edge parameters, exciton-phonon interaction parameters and phase transitions in the crystals under investigation is studied.

Introduction

Cu_6PS_5I crystals belong to argyrodite family, being characterized by high concentration of disordered vacancies and known as fast-ion conductors and ferroelastics [1, 2]. Below room temperature they undergo two phase transitions (PTs), one of them being superionic at T_s=(165–175) K, the other – ferroelastic at T_c = (269±2) K [2]. At room temperature Cu_6PS_5I compound crystallizes in cubic syngony ($F\bar{4}3m$ space group) [1]. High ionic conductivity in these compounds is explained by the presence of Cu^+ ions characterized by high mobility, as well as the specific features of the crystal structure providing the favourable conditions for migration of copper ions [1].

Absorption edge studies in Cu_6PS_5I crystals have shown exciton absorption bands being observed in the range of direct optical transitions at low temperatures [3]. With the temperature increase a noticeable broadening of the exciton absorption bands is observed. In the vicinity of the superionic PT they undergo considerable changes: the band corresponding to the bound exciton is smeared; the one corresponding to free exciton sustains stepwise broadening and long-wavelength shift. At $T>T_s$ at the absorption edge the exponential parts appear, being described by the Urbach rule. The Urbach absorption edge is formed by absorption processes in which exciton-phonon interaction (EPI) plays the predominant role. The mechanism of the EPI is well explained in the framework of the Dow-Redfield theory [4].

Experimental

Cu_6PS_5I crystals were obtained by chemical transport reactions method. Cu_6PS_5I crystal samples were irradiated with the fluence of 10^{15} cm^2 7-MeV electrons. The spectral dependence of the absorption coefficient α was studied in the temperature range from 77 to 323 K. The transmittance and reflectance measurements were carried out for the samples oriented at room temperature in cubic phase, the light beam propagating along the [100] crystallographic direction. The experimental setup and technique are described in [2].

Results and discussion

The measurements have revealed the absorption edge in both non-irradiated and irradiated crystals at $T>T_s$ to be of Urbach shape, however, the Urbach edge convergency point coordinates increasing in the irradiated sample (Fig.1). The convergency point coordinates values α_0 and E_0 are presented in Table 1.

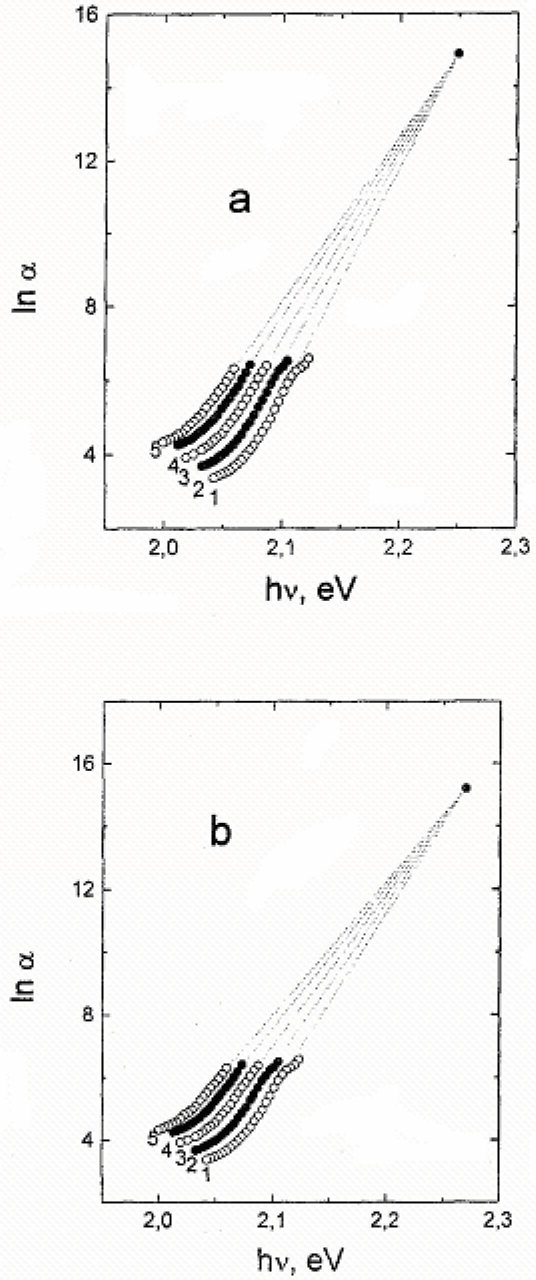

Fig.1. Spectral dependences of the absorption coefficient logarithm of non-irradiated (a) and irradiated (b) Cu_6PS_5I crystals at various temperatures (K): 1 – 215, 2 – 245, 3 – 273, 4 – 300, 5 – 323.

In the range of the second-order ferroelastic PT α_0 and E_0 parameters remain unchanged, only the temperature dependences of the steepness parameter σ and the absorption edge energy width w slowly vary at the paraelectric-to-ferroelastic PT (Fig. 2). The temperature dependences of σ and w can be described by the relations [5,6]:

$$\sigma(T) = \sigma_0 \cdot \left(\frac{2kT}{\hbar\omega_p}\right) \cdot th\left(\frac{\hbar\omega_p}{2kT}\right), \quad (1)$$

$$w = w_0 + w_1\left[\frac{1}{\exp(\theta_E / T) - 1}\right], \quad (2)$$

$\hbar\omega_p$ being the effective phonon energy in the single-oscillator model describing the EPI; σ_0 – a parameter related to the EPI constant g as $\sigma_0 = 2/3g$; w_0 and w_1 values being constant within the same phase; θ_E – the Einstein temperature corresponding to the mean frequency of phonon excitations of a non-interacting harmonic oscillator system. The obtained $\hbar\omega_p, \sigma_0$, w_0, w_1 and θ_E values are listed in Table 1. In both non-irradiated and irradiated Cu_6PS_5I crystals $\sigma_0 > 1$, this being the evidence for weak EPI [7].

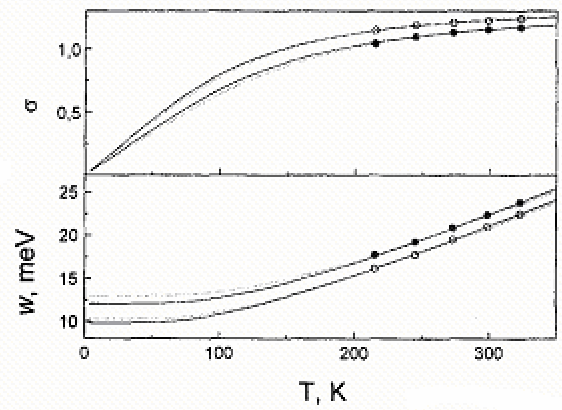

Fig.2. Temperature dependences of $\sigma = w/kT$ parameter and absorption edge energy width w of non-irradiated (open circles) and irradiated (dark circles) Cu_6PS_5I crystals. The calculated dependences, obtained according to Eqs. (1) and (2), for $T<T_c$ are shown by dashed lines, and for $T>T_c$ – by solid lines.

The irradiation is shown to result in the absorption edge blue shift by ≈ 0.003 eV (at T=300 K) and the absorption edge energy width increase from 21.2 meV to 22.5 meV (at T=300 K). Besides, a slight enhancement of the EPI is observed as well as the increase of the energy of effective phonon, participating in the absorption edge formation. Note that in the irradiated crystals the contribution of static structural disordering into the absorption edge energy width increases from 9.8 to 12.1 meV (Table 1).

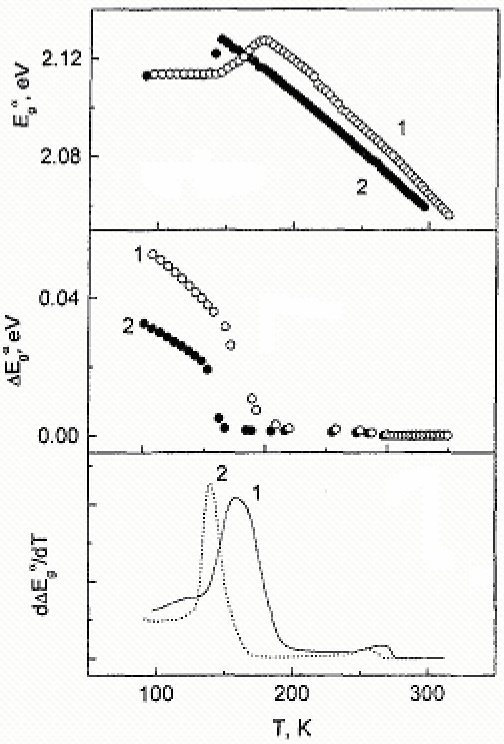

Fig.3. Temperature dependences of absorption edge energy position E_g^α (α=440 cm^{-1}), variation ΔE_g^α and derivative $d(\Delta E_g^\alpha)/dT$ for non-irradiated (1) and irradiated (2) Cu_6PS_5I crystals.

The isoabsorption mesurements have shown that in the range of the superionic PT, being of the first order, a step in E_g^α (*T*) behaviour is observed, while in the range of the ferroelastic PT, being of the second order, a typical change of the slope in the E_g^α (*T*) plot is revealed (Fig.3). Besides, Fig. 3 shows the absorption edge energy position variation ΔE_g^α at the PT determined as the increment of E_g^α in the low-temperature phase with respect to the high-temperature one:

$$\Delta E_g^\alpha(T) = E_{g,l}^\alpha(T) - E_{g,h}^\alpha(T), \qquad (3)$$

$E_{g,l}^\alpha(T)$ being the absorption edge energy position in the low-temperature phase, $E_{g,h}^\alpha(T)$ is obtained by extrapolation of the experimental values for the high-temperature phase to the low-temperature range. $E_{g,h}^\alpha(T)$ values in the low-temperature phase were calculated in accordance with the known relation [8]

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

where $E_g^\alpha(0)$ is the band gap at zero temperature, S_g is a dimensionless coupling constant.

Table 1. Urbach edge parameters and EPI parameters of non-irradiated and irradiated Cu_6PS_5I crystals.

Crystal	non-irradiated	Irradiated
α_0 (cm^{-1})	2.96×10^6	3.99×10^6
E_0 (eV)	2.250	2.270
Temperature range	$T>T_c$	$T>T_c$
$\hbar\omega_p$ (meV)	26.1	31.1
σ_0	1.328	1.288
θ_E (K)	303	361
w_0 (meV)	9.8	12.1
w_1 (meV)	19.7	24.2
E_g^* (300K) (eV)	2.081	2.084
w (300K) (meV)	21.2	22.5
T_s (K)	160	140
T_c (K)	271	261

The temperature dependences of the temperature derivative of the absorption edge energy position variation ΔE_g^α induced by the PT order parameter which follow the temperature behaviour of the anomalous part of the crystals specific heat, are as well presented in Fig.3. The temperature dependences of $d(\Delta E_g^\alpha)/dT$ reveal a maximum at the first-order PT (near T_s) and a step at the second-order PT (near T_c).

Irradiation results in the superionic and ferroelastic PT temperature shift to lower temperatures as well as the superionic PT smearing decrease.

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ВПЛИВ β-ВИПРОМІНЮВАННЯ НА КРАЙ ОПТИЧНОГО ПОГЛИНАННЯ В КРИСТАЛАХ Cu_6PS_5I

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Проведено температурні дослідження краю оптичного поглинання в неопромінених і β-опромінених кристалах Cu_6PS_5I. Вивчено вплив β-випромінювання на параметри урбахівського краю поглинання, параметри екситон-фононної взаємодії і фазові переходи в досліджуваних кристалах.