

Influence of structural disordering on phonon and electron spectra of $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ superionic crystals

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Raman scattering and optical absorption edge have been studied in $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals obtained at various technological conditions providing increased copper content and deviation from stoichiometry. The most noticeable changes of $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystal Raman spectra are revealed in the low-frequency range ($\nu < 100 \text{ cm}^{-1}$) where the modes are observed belonging to the diffusive-type vibrations of Cu atoms and Cu-Br bond vibrations. The temperature studies (77–325 K) of the optical absorption edge have shown that in the superionic phase it is characterized by Urbach shape, copper content increase resulting in the increase of its energy width. A correlation between the degree of static structural disorder and the deviation from stoichiometry in $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals is revealed.

Исследовано комбинационное рассеяние (КР) света и край оптического поглощения кристаллов $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$, полученных при различных технологических условиях, предусматривающих увеличение содержания меди и отклонение от стехиометрии. Наиболее заметные изменения спектров КР кристаллов $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ обнаружены в низкочастотной области ($\nu < 100 \text{ см}^{-1}$), в которой наблюдаются моды, относящиеся к диффузионному типу колебаний атомов Cu и колебаниям связей Cu-Br. Температурные исследования (77–325 K) края оптического поглощения показали, что в суперинионной фазе он имеет урбаховскую форму, причем увеличение содержания меди приводит к увеличению его энергетической ширины. Установлена корреляционная связь между степенью статического структурного разупорядочения и мерой отклонения от стехиометрии в кристаллах $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$.

$\text{Cu}_6\text{PS}_5\text{Br}$ single crystals are known as superionic and ferroelastic compounds [1, 2]. At room temperature, these crystals belong to cubic syngony (space group $F43m$) while at low temperatures, two phase transitions (PTs) are realized therein: a ferroelastic one at $T_c = (268 \pm 2) \text{ K}$ and a superionic one at $T_s = (166 \text{ to } 180) \text{ K}$ [1, 2]. Below the ferroelastic PT temperature, $\text{Cu}_6\text{PS}_5\text{Br}$ crystals belong to monoclinic syngony (Cc space group), and the superionic PT reveals the features of an isostructural transformation [3]. The results of electrical, dielectric, calorimetric, acoustic and optical properties of $\text{Cu}_6\text{PS}_5\text{Br}$ crystals were presented in [2, 4–10]. In these crystals, due to high concentration of vacancies, two sorts of structural disorder occur: (i) dynamic structural disorder

due to migration of Cu^+ ions in superionic phase; (ii) static structural disorder caused by the increased copper content resulting from differences in the crystal growth preparation procedure [8]. In this work, we consider the effect of structural disorder caused by deviation from the stoichiometric composition on the low-frequency range of phonon spectra and optical absorption edge parameters of $\text{Cu}_6\text{PS}_5\text{Br}$ crystals grown under various technological conditions.

$\text{Cu}_6\text{PS}_5\text{Br}$ single crystals were obtained by chemical transport reactions. For our studies, four types of samples obtained under different technological conditions were used: (a) grown from a stoichiometric mixture, halogen being used as a transport

agent (TA); (b) grown from a stoichiometric mixture, CuBr being used as a TA; (c) grown from the mixture with excessive CuBr+Cu₂S in the ratio of 3:1; (d) grown from the mixture with excessive CuBr+Cu₂S in the ratio of 1:3. Raman spectra were measured at 295 K in a 90° geometry using a DFS-24 double grating monochromator [7]. He-Ne ($\lambda = 632.8$ nm) laser was employed as the excitation source. The spectral dependences of absorption coefficient were studied in the temperature range 77–325 K by a technique described in [8]; a MDR-3 diffraction grating monochromator being used. The measurements were carried out for the samples oriented at room temperature in cubic phase, the light beam propagating along [100] crystallographic direction.

The variation of the technological procedures of Cu₆PS₅Br crystals growth in the sequence a→b→c→d resulted in obtaining crystals of larger size and with more perfect faces. However, this implied the increase of copper content and deviation from stoichiometry. As follows from the chemical analysis results, the formula of the compounds under investigation can be written as Cu_{6+ δ} PS₅Br, where the value δ is the measure of the deviation from stoichiometry. The δ value is shown to increase as the growth conditions vary in the sequence a→b→c→d.

Raman scattering studies of Cu_{6+ δ} PS₅Br crystals have shown that with the increase of δ , the most essential changes are revealed in the low-frequency range ($\nu < 100$ cm⁻¹)

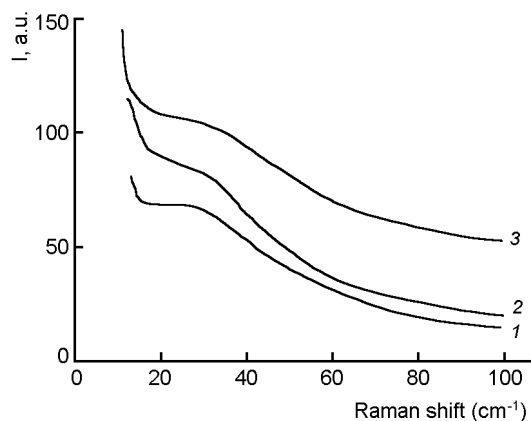


Fig. 1. Low-frequency part ($\nu < 100$ cm⁻¹) of the Raman spectra at $T = 295$ K for Cu_{6+ δ} PS₅Br crystals obtained at different technological conditions: a (1), b (2), c (3).

where the modes belonging to the diffusive-type vibrations of Cu atoms and Cu-Br bond vibrations are observed. The low-frequency range is characterized by strong light scattering at $\nu < 20$ cm⁻¹ (Fig. 1). Hence, the reconstruction of the true contours of the spectral bands, their position and halfwidth is strongly encumbered. Therefore, a procedure taking into account the Bose-Einstein statistical factor was applied. Such procedure is effectively used for other superionic conductors [11]. Raman scattering intensity with the account of the Bose-Einstein factor is given by

$$I_R(w) = I(w) \frac{w}{n(w, T) + 1}, \quad (1)$$

Table. Spectral position and halfwidth of the low-frequency Raman bands, parameters of the Urbach absorption edge and EPI of Cu_{6+ δ} PS₅Br crystals obtained at different technological conditions

Crystal	a	b	c	d
δ	-0.025	0.018	0.222	0.651
ν_1 (cm ⁻¹)	34.8	41.6	46.6	—
Γ_1 (cm ⁻¹)	26.3	33.0	36.4	—
ν_2 (cm ⁻¹)	59.9	74.2	77.2	—
Γ_2 (cm ⁻¹)	33.9	25.8	20.3	—
E_g^* (eV) 300 K	2.290	2.298	2.284	2.282
Ω (meV) 300 K	25.2	28.1	23.8	42.3
α_0 (cm ⁻¹)	$2.68 \cdot 10^5$	$2.63 \cdot 10^5$	$3.28 \cdot 10^5$	$4.65 \cdot 10^5$
E_0 (eV)	2.453	2.455	2.433	2.542
σ_0	1.04	0.94	1.24	0.75
$\hbar\omega_p$ (meV)	10.3	14.3	30.3	42.8

where $n(\omega, T) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the Bose-Einstein factor; $I(\omega)$, the experimentally observed intensity (Fig. 1). From the Raman spectra corrected for the Bose-Einstein factor (Fig. 2), the spectral positions and half-widths of two low-frequency bands were calculated (Table). As δ increases, a high-frequency shift of the bands is observed as well as the increase of intensity and halfwidth of the lower-frequency band corresponding to Cu atom vibrations. At that, intensity and halfwidth of the higher-frequency band corresponding to Cu-Br bond vibrations decrease.

Temperature studies of the optical absorption spectra have shown that in the superionic phase at $T \geq T_s$, in all $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals under investigation the absorption edge is of Urbach shape given by [12]

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

where ω is the Urbach absorption edge energy width; α_0 and E_0 , the convergence point coordinates. The comparative analysis of the absorption edge spectra shows the variation of α_0 and E_0 values as well as trends to slight long-wavelength shift of the absorption edge (decrease of the optical pseudogap E_g^*) and increase of its energy width under the variation of technological conditions in the sequence $a \rightarrow b \rightarrow c \rightarrow d$. The temperature dependences of ω and the absorption edge slope parameter $\tau = kT/\omega$ are well described by the Einstein relation [13]

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

and Mahr relation [14]

$$\sigma(T) = \sigma_0 \cdot \left(\frac{2kT}{\hbar w_p} \right) \cdot th \left(\frac{\hbar w_p}{2kT} \right), \quad (4)$$

where w_0 and w_1 are constant values; θ_E , the Einstein temperature corresponding to the average frequency of the phonon excitations in the system of uncoupled oscillators; $\hbar w_p$, the effective phonon energy in the single-oscillator model describing the exciton-phonon interaction (EPI); σ_0 , the parameter, related to the EPI constant g as $\tau_0 = (2/3)g^{-1}$. The obtained values of \hbar , σ_0 and the contri-

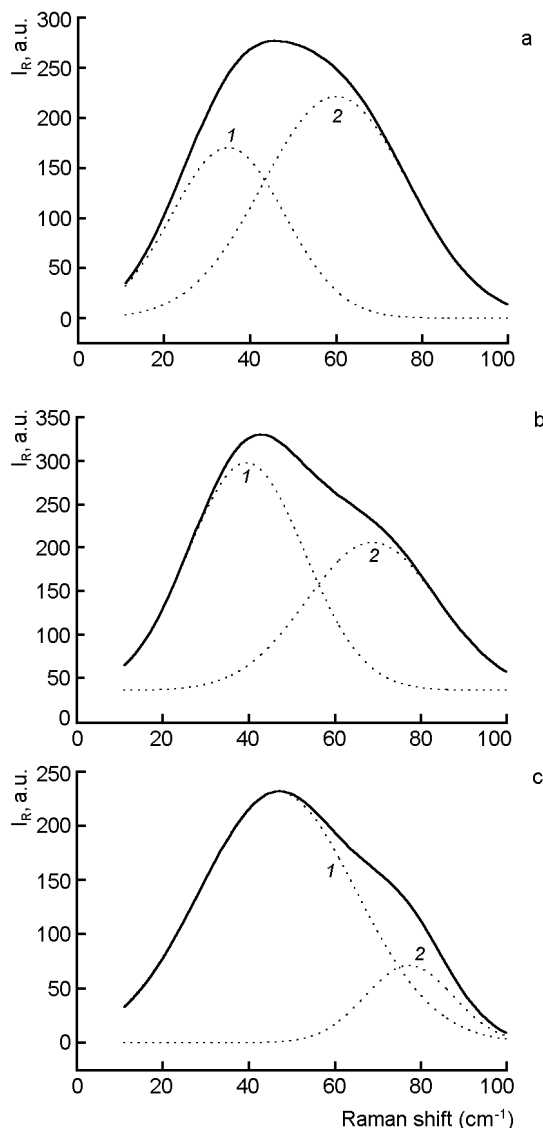


Fig. 2. Low-frequency part ($\nu < 100 \text{ cm}^{-1}$) of the Raman spectra at $T = 295 \text{ K}$, obtained with the account of the Bose-Einstein statistical factor for $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals, obtained at different technological conditions: a (1), b (2), c (3). The dotted lines denote the Gaussian contours simulating the experimental curve when being superimposed.

bution of static structural disorder into the absorption edge energy width $w_0 = w_x$ for the crystals under investigation are listed in Table 1. For all the crystals, the value σ_0 appeared to be higher than 1, what is the evidence of the weak EPI [15], though the variation of the growth conditions ($a \rightarrow b \rightarrow c \rightarrow d$) results in its considerable enhancement (Table). Besides, the value w_x , being the measure of static structural disorder is shown to increase with the

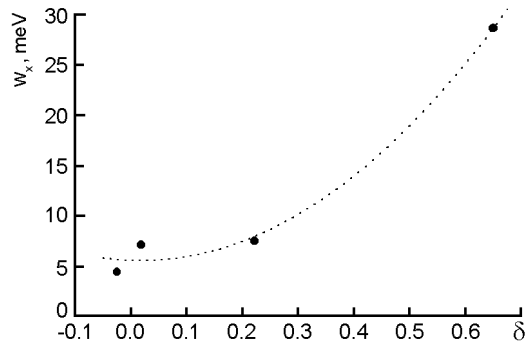


Fig. 3. Dependence of the value w_x determining the contribution of static structural disorder into the absorption edge smearing on the value δ being the measure of the deviation from stoichiometry for $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals.

copper content (δ value) in $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals (Fig. 3).

Thus, the most noticeable changes in the phonon spectra of $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals obtained under various technological conditions are revealed in the low-frequency range ($\nu < 100 \text{ cm}^{-1}$). The temperature studies of the absorption edge have shown that in the superionic phase it has the Urbach shape, the increase of copper content resulting in the increase of its energy width. A correlation between the measure of static structural disorder and the devia-

tion from stoichiometry in $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ crystals is revealed.

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Вплив структурного розупорядкування на фонові та електронні спектри суперіонних кристалів $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$

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Досліджено комбінаційне розсіювання (КР) світла і край оптичного поглинання кристалів $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$, отриманих у різних технологічних умовах, що передбачають збільшення вмісту міді та відхилення від стехіометрії. Найбільш помітні зміни спектрів КР кристалів $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$ виявлено у низькочастотній області ($\nu < 100 \text{ cm}^{-1}$), в якій спостерігаються моди, що належать до дифузійного типу коливань атомів Cu та коливань зв'язків Cu-Br. Температурні дослідження (77–325 К) краю оптичного поглинання показали, що у суперіонній фазі він має урбахівську форму, причому збільшення вмісту міді приводить до збільшення його енергетичної ширини. Встановлено кореляційний зв'язок між ступенем статичного структурного розупорядкування та мірою відхилення від стехіометрії у кристалах $\text{Cu}_{6+\delta}\text{PS}_5\text{Br}$.