Exciton-phonon interaction and disordering processes in Cu$_6$P(Si$_{1-x}$Se$_x$)$_5$J fast-ion conductors

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Abstract

Absorption edge of Cu$_6$P(Si$_{1-x}$Se$_x$)$_5$J fast-ion conductors is studied in a broad temperature range. The effect of anionic substitution on the position and shape of the absorption edge as well as parameters of exciton-phonon interaction are analysed.

Key words: Fast-ion conductors; ferroelastic; phase transition; absorption edge; Urbach rule; compositional disorder.

Cu$_6$PS$_5$J crystals belong to argyrodite family, characterized by high concentration of disordered vacancies and known as fast-ion conductors and ferroelastics [1]. They undergo two phase transitions (PT) below room temperature, one of which being superionic ($T_s = (165\text{-}175)$K), the other - ferroelastic ($T_c = (269\pm2)$ K). In Cu$_6$PS$_5$J crystals only one PT~ superionic at $T_s=(260\text{-}268)$K - is observed [1]. At room temperature Cu$_6$PS$_5$J and Cu$_6$PSe$_5$J are crystallized in cubic syngony ($F\ \overline{4}3m$ space group), Cu$_6$PS$_5$J bellow the temperature of superionic PT belongs to monoclinic syngony (Cc space group) [2]. The intermediate phase (between the superionic and ferroelastic PT temperatures) symmetry for Cu$_6$PS$_5$J and dielectric phase (bellow the temperature of superionic PT) symmetry for Cu$_6$PS$_5$J has not yet been determined. 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 [2]. Substitution of

sulphur atoms by selenium results in a considerable increase of total conductivity by more than an order of magnitude [3].

The present paper is aimed at studying the effect of anionic substitution of S atoms by Se on the excitonic absorption spectra, Urbach absorption edge parameters and exciton-phonon interaction parameters in Cu$_6$P(S$_{1-x}$Se$_x$)$_5$J mixed crystals.

Mixed Cu$_6$P(S$_{1-x}$Se$_x$)$_5$J single crystals were obtained by chemical vapour transport method [3]. The crystals were grown from mixture, enriched with CuI+Cu$_2$Se(S), CuI serving as a transport agent. The temperature at the hot end of the vessel was kept at 550 to 750°C, and at the cool end - 500 to 650°C, depending on the crystal composition. The temperature measurements of the absorption coefficient a were done on the samples of different thickness (d = 1 1-200 μm), oriented at room temperature in cubic phase, the light beam propagating along the [100] crystallographic direction. The measurements technique and the experimental setup are described in [1].

In pure Cu_6PS_5J crystals at low temperatures in the spectral range of the fundamental absorption edge three absorption bands are observed (at $T = 77K$ their energy positions are $E_1 = 2.135$ eV, $E_2 = 2.177$ eV and $E_3 = 2.385$ eV) [4]. The analysis of their spectral position and temperature behaviour has shown the E_1 band to correspond to light absorption with the formation of a bound exciton being a Wannier-Mott exciton localized on a charged copper impurity. The E_2 band corresponds to the light absorption with the formation of a free exciton, and the high-energy E_3 band - to the interband Van Hove-Phillips singularity. With the temperature increase a noticeable broadening of the exciton absorption bands and long-wavelength shift of the E_3 band are observed. In the vicinity of the superionic PT the bound exciton breaks down, the E_1 band is smeared, and the stepwise broadening and long-wavelength shift of the free exciton band E_2 occurs. This anomalous behaviour of the exciton absorption at the superionic PT is caused by the dynamic structural disordering of copper cation sublattice [4]. At $T>T_s$ at the absorption edge the exponential parts appear, being described by the Urbach rule [4].

The absorption edge studies of $Cu_6P(S_{1-x}Se_x)_5J$ solid solutions in a broad temperature range have shown the substitution of S atoms by Se to result in the long-wavelength shift and broadening of all the absorption bands [5]. The absorption bands are completely smeared at $x \geq 0.15$, and the shape of absorption edge in the whole temperature interval under investigation is exponential. The smearing of the exciton bands with S→Se substitution at low temperature is related to the effect of compositional disordering in solid solutions and can be explained by the interaction of excitons with increasing local fluctuations of the crystal lattice field in the mixed crystals [6].

Substitution of S atoms by Se results not only in the excitonic absorption band smearing, but also in the changes of the Urbach edge

parameters – optical pseudogap E_g^* (E_g^* is the energy position of the exponential absorption edge at fixed absorption level $a = 10^3$ cm^{-1}) and the absorption edge energy width w. With the increase of x from 0 to 1 in $Cu_6P(S_{1-x}Se_x)_5J$ crystals the following features are observed: (i) the absorption edge long-wavelength shift and non-linear decrease of optical pseudogap at $T = 300$ K from 2.079 eV for Cu_6PS_5J to 1.059 eV for Cu_6Pse_5J (fig.1); (ii) the increase of the energy width $-w$ of the exponential absorption edge at $T = 300$ K from 19.3meV for Cu_6PS_5J to 39.3 meV for $Cu_6P(S_{0.6}Se_{0.4})_5J$ and its subsequent decrease to 27.1 meV for Cu_6PSe_5J (fig.1).

The Urbach behaviour of the absorption edge is usually related to the exciton-phonon interaction (EPI) [7]. It should be noted that the temperature dependence of the parameter $\sigma = kT/w$ in the superionc phase (for x=0.8, 0.9, 1.0 in the dielectric phase as well) is described by the known Mahr relation [7]:

$$\sigma(T) = \sigma_0 \cdot \left(\frac{2kT}{\hbar\omega_p} \right) \cdot \tanh\left(\frac{\hbar\omega_p}{2kT} \right) \qquad (1)$$

σ_0 is a constant independent of temperature within the same phase and related to the EPI constant g as $\sigma_0 = 2/3g$, $\hbar\omega_p$ is the effective average phonon energy in a single-oscillator model, describing the EPI [8]. The obtained values of effective phonon energy $\hbar\omega_p$ and σ_0 parameter are listed in Table 1. With x increasing from 0 to 1 in $Cu_6P(S_{1-x}Se_x)_5J$ the following features are observed: (i) a trend to the effective phonon energy increase in the interval $0<x<0.6$ and its subsequent decrease in the range $0.6<x<1$; (ii) EPI enhancement in the range $0<x<0.6$ and its subsequent weakening at $0.6<x<1$. In $Cu_6P(S_{1-x}Se_x)_5J$ crystals for $0.15<x<0.6$ $\sigma_0<1$ what is the evidence for strong EPI [8].

Besides, the optical studies (isoabsorption measurements, measurements of optical transmission of polarizer–crystal–analyzer system) in 77-300K temperature range have shown that the substitution of S atoms by Se

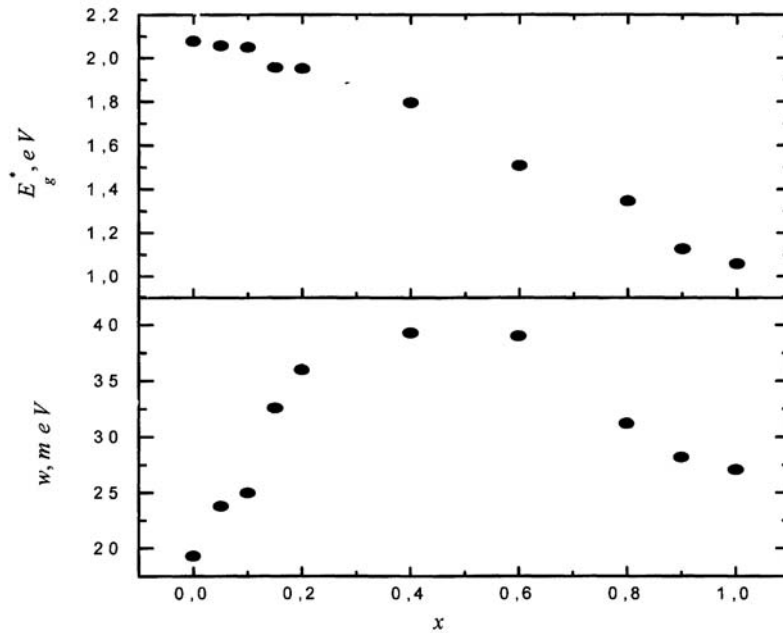**Fig.1.** Compositional dependences of the optical pseudogap E_g and the absorption edge energy width w at T = 300 K for $Cu_6P(S_{1-x}Se_x)_5J$ mixed crystals.

leads to sharp decrease of ferroelastic and superionic phase transition temperatures for $0 < x < 0.15$, the absence of ferroelastic phase transition in the interval of concentrations $0.2 \leq x \leq 1.0$ and the absence of the superionic PT at $0.15 \leq x \leq 0.8$ as well as the increase of the superionic phase transition for $0.8 \leq x \leq 1.0$ (see Table 1).

One should note that temperature and compositional variation of the absorption edge in $Cu_6P(S_{1-x}Se_x)_5J$ crystals are determined not only by the effect of compositional, but also of temperature and structural disordering. The temperature disordering in these materials is

realized mostly by means of exciton-phonon interaction while the contribution of the lattice temperature expansion can be neglected. The family of materials under investigation is characterized by two types of structural disordering: (i) dynamic structural disordering arising from disordering in cation sublattice and copper ion migration, and (ii) static structural disordering due to the difference in the technological conditions of the crystal growth [9]. The dynamic structural disordering is temperature-dependent and especially essential for such materials as fast-ion conductors.

Table 1.

Phase transition temperatures and exciton-phonon interaction parameters for $Cu_6P(S_{1-x}Se_x)_5J$ crystals

Crystal	T_s(K)	T_c(K)	$\hbar\omega_p$ (meV)	σ_0
Cu_6PS_5J	165-175	269±2	32.0	1.550
$Cu_6P(S_{0.95}Se_{0.05})_5J$	120-138	244±2	42.1	1.307
$Cu_6P(S_{0.9}Se_{0.1})_5J$	80-120	199±2	31.0	1.163
$Cu_6P(S_{0.85}Se_{0.15})_5J$	–	145±5	43.7	0.962
$Cu_6P(S_{0.8}Se_{0.2})_5J$	–	–	48.2	0.914
$Cu_6P(S_{0.6}Se_{0.4})_5J$	–	–	58.3	0.915
$Cu_6P(S_{0.4}Se_{0.6})_5J$	–	–	65.7	0.983
$Cu_6P(S_{0.2}Se_{0.8})_5J$	104-208	–	47.6	1.038
$Cu_6P(S_{0.1}Se_{0.9})_5J$	218-230	–	36.3	1.057
Cu_6PSe_5J	260-268	–	60.3	1.359

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