

# LOW-TEMPERATURE LUMINESCENCE IN *Cu<sub>6</sub>PS<sub>5</sub>Br* SUPERIONIC CRYSTALS

I.P.Studenyak, M.Kranjcec<sup>1</sup>, V.V.Bunda<sup>2</sup>, Yu.M.Azhniuk<sup>3</sup>,  
Gy.S.Kovacs, V.V.Panko

Uzhhorod State University, 54 Voloshyna str., 294000 Uzhhorod, Ukraine

<sup>1</sup> Ruder Boskovic Institute, PO Box 1016, 10000 Zagreb, Croatia

<sup>2</sup> Institute of CSEL, 85 Zankovetskoj str., 294000 Uzhhorod, Ukraine,

<sup>3</sup> Institute of Electron Physics, 21 Universytetska str., 294016 Uzhhorod, Ukraine

Photoluminescence (PL) spectra of *Cu<sub>6</sub>PS<sub>5</sub>Br* crystals are studied in a broad spectral range (0.5–2 μm) at 77 K, under various excitation conditions. In the PL spectra a number of bands of different origin is revealed. The computer processing of the spectrum is carried out and the mechanisms of the radiative recombination resulting in the band appearance, are discussed. The comparative analysis of the PL and optical absorption spectra is performed.

## INTRODUCTION

*Cu<sub>6</sub>PS<sub>5</sub>Br* crystals of argyrodite type are known as fast-ion conductors and ferroelastics [1]. The fundamental absorption edge of these crystals was studied in detail in a broad spectral and temperature range [2–4]. At low absorption levels ( $\alpha < 150 \text{ cm}^{-1}$ ) the absorption edge is formed by indirect electron-phonon transitions [2], and at high absorption levels ( $200 \text{ cm}^{-1} < \alpha < 2000 \text{ cm}^{-1}$ ) and low temperatures in the range of direct optical transitions exciton bands are observed, exhibiting the series of “allowed” *s*-excitons of Wannier-Mott type [3]. The increase of temperature results in the exciton bands smearing and at  $T \geq 200 \text{ K}$  at the absorption edge only exponential parts are observed, their temperature and spectral behaviour being described by Urbach’s rule. In [4] the exciton luminescence at 77 K was reported, correlating well with the exciton absorption spectrum. However, no detailed PL studies in a broad spectral range were performed.

## EXPERIMENTAL

For the experimental studies *Cu<sub>6</sub>PS<sub>5</sub>Br* single crystals, obtained by chemical vapour transport [1], were used. It should be noted that at room temperature the crystals belong to the cubic syngony (space

group *F43m*) and at  $T < 102 \text{ K}$  – to the monoclinic syngony (space group *C<sub>2</sub>*) [1]. The PL spectra were studied at various excitation conditions, using an *Ar<sup>+</sup>* ( $\lambda = 476.5 \text{ nm}$ ), *He-Cd* ( $\lambda = 440.7 \text{ nm}$ ) and a nitrogen pulsed ( $\lambda = 337 \text{ nm}$ ) lasers. The spectra were measured by SDL-1, DFS-24 and MDR-3 diffraction spectrometers. The crystal was mounted in a UTREX cryostat, providing the temperature stabilizing within 0.1 K.

## RESULTS AND DISCUSSION

In the PL spectra of *Cu<sub>6</sub>PS<sub>5</sub>Br*, shown in Figs. 1 and 2, at 77 K a number of bands of different intensities and widths is observed as sharp peaks and shoulders. The PL spectrum, obtained under pulsed laser excitation, looks rather complicated. After the necessary computer processing and fitting it revealed to be a superimposition of seven bands whose energy positions, widths, relative intensities and contour areas are listed in the general Table. The observed bands can be divided into several groups depending on the mechanism of the radiative recombination. The long-wavelength group of *E<sub>1</sub>* to *E<sub>6</sub>* (the notions of the bands in Figs. 1 and 2 correspond to those in the Table) broad bands results from the recombination of free and bound

to a local centre charge carriers ("band-to-local centre" transitions). The narrowest  $E_9$  band corresponds to the annihilation of the

free exciton in the ground state ( $n = 1$ ). Accordingly, the exciton absorption band is located at 2.327 eV [4].

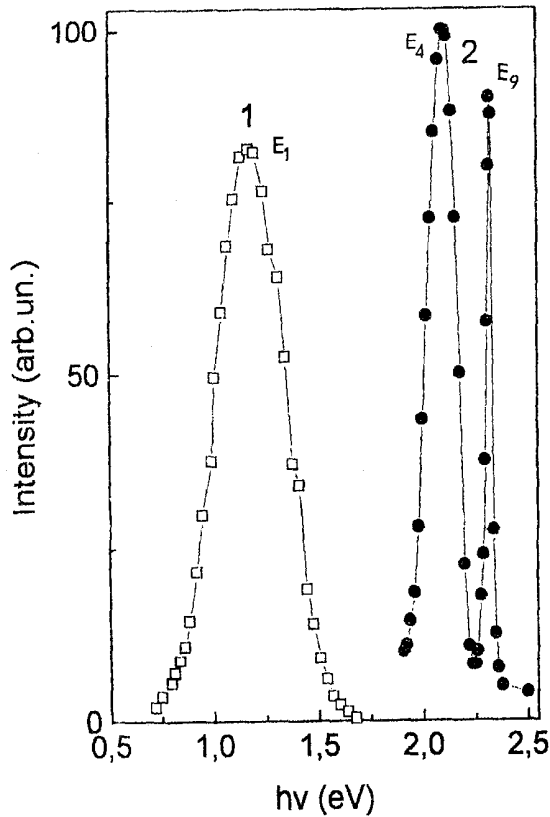


Fig. 1. Unpolarized PL spectra of  $Cu_6PS_5Br$  crystal at 77 K obtained under the excitation by  $He-Cd$  ( $\lambda=440.7$  nm) (1) and  $Ar^+$  ( $\lambda=476.5$  nm) (2) lasers.

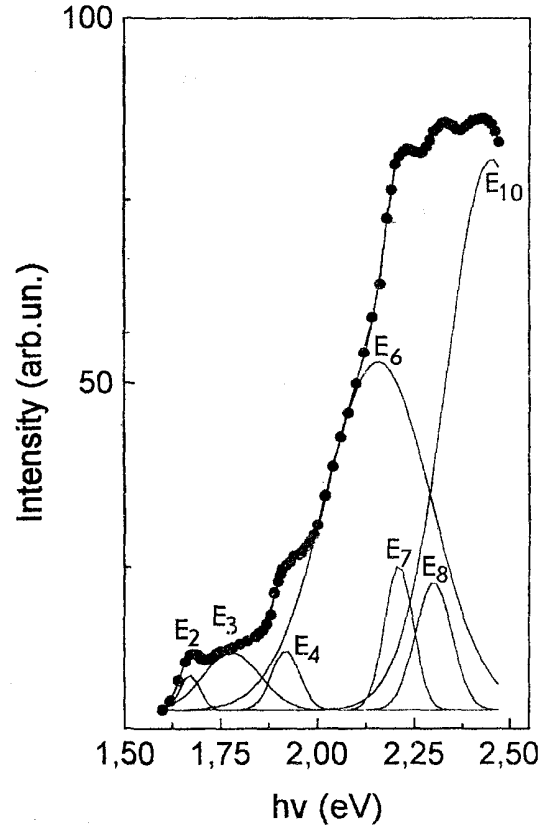


Fig. 2. Unpolarized PL spectra of  $Cu_6PS_5Br$  crystal at 77 K obtained under the excitation by pulsed nitrogen laser ( $\lambda=337$  nm).

Now consider the origin of  $E_7$ ,  $E_8$  and  $E_{10}$  bands, being revealed under pulsed nitrogen laser excitation. The energy position of the  $E_7$  band correlates well with the indirect gap value  $E_g^i = 2.193$  eV [2], therefore it corresponds to the indirect interband transition. The  $E_8$  band is of the same nature as the  $E_9$  band. The stronger Stokes shift of the  $E_8$  band relatively to that of the  $E_9$  can be the result of the higher excitation power provided by the pulsed nitrogen laser ( $(3-5) \times 10^9$  W/pulse). The

mechanism leading to the  $E_{10} > E_g^d$  band appearance is probably related to the surface recombination of free electrons and holes as well as free copper atoms. It should be also noted that no bands corresponding to the direct interband transition, have been observed in the PL spectra (the direct gap width, determined from the exciton absorption spectrum, is given in the Table and equals to 2.341 eV [4]).

Table. Energy positions, widths, relative intensities and contour areas of the PL spectrum bands of  $Cu_6PS_5Br$  crystals.

Peak	Transition	Luminescence				Excitonic absorption $E_{exc}$ (eV)	$E_g^i$ (eV)	$E_g^d$ (eV)
		Center (eV)	Height (a.u.)	Area (a.u.)	Width (eV)			
$E_1$	$E_1 \rightarrow E_v$ $E_c \rightarrow E_1$	1.179	84.11	34.11	0.324	-	-	-
$E_2$	$E_2 \rightarrow E_v$	1.671	3.78	0.312	0.052	-	-	-
$E_3$	$E_3 \rightarrow E_v$	1.779	6.21	1.44	0.148	-	-	-
$E_4$	$E_4 \rightarrow E_v$	1.919	6.43	0.73	0.072	-	-	-
$E_5$	$E_5 \rightarrow E_v$	2.095	7.93	16.27	0.133	-	-	-
$E_6$	$E_6 \rightarrow E_v$	2.157	37.8	16.29	0.274	-	-	-
$E_7$	$E_c^i \rightarrow E_v$	2.210	15.77	1.83	0.074	-	2.193	-
$E_8$	$E_{exc} \rightarrow E_v$	2.300	13.93	2.07	0.095	-	-	-
$E_9$	$E_{exc} \rightarrow E_v$	2.322	79.17	2.56	0.026	2.327	-	-
								2.341
$E_{10}$	$E_{10} \rightarrow E_v$	2.450	59.90	22.01	0.234			

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## НИЗКОТЕМПЕРАТУРНА ЛЮМІНЕСЦЕНЦІЯ СУПЕРІОННИХ КРИСТАЛІВ $Cu_6PS_5Br$

І.П.Студеняк, М.Краньчец<sup>1</sup>, В.В.Бунда<sup>2</sup>, Ю.М.Ажнюк<sup>3</sup>,  
Д.Ш.Ковач, В.В.Панько

Ужгородський державний університет, 294000, Ужгород, вул.Волошина, 54,

<sup>1</sup> Інститут Руджера Бошковича, Хорватія, 10000, Загреб, п/с 1016,

<sup>2</sup> Інститут інформатики, економіки і права, 294000, Ужгород, вул. Заньковецької, 85,

<sup>3</sup> Інститут електронної фізики, 294016, Ужгород, вул.Університетська, 21

Досліджені спектри фотолюмінесценції кристалів  $Cu_6PS_5Br$  в широкому спектральному діапазоні (0.5 – 2 мкм) при температурі 77 К та різних умовах збудження. Обговорюються механізми випромінювальної рекомбінації, що приводять до виникнення смуг різної природи, виявлених у спектрах фотолюмінесценції. Проведено порівняльний аналіз спектрів фотолюмінесценції та оптичного поглинання.