

ANISOTROPY OF THE BLUE-COPPER LUMINESCENCE CENTERS IN ZnS:Cu(Cl, I) CRYSTALS

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Results concerning the polarization of blue-copper (B-Cu) luminescence in ZnS:Cu crystals grown in the presence of the coactivators Cl and I are presented in this paper. The calculated polarization diagrams fit the experimental results well. The absorption centers — rotators σ , emission centers — rotators σ and dipoles π are oriented along the symmetry three-fold axes of the crystal.

1. Introduction

Polarization measurements of luminescence are a very useful tool for investigating the nature of luminescence centers especially their symmetry and orientation. ZnS phosphors activated by copper emit various types of broad-band luminescences, depending on the species and on the relative concentrations of coactivators and also on the condition of the firing process. Lempicki [1] observed that the blue-copper luminescence in hexagonal ZnS:Cu crystals is polarized preferentially perpendicularly to the optical axes of the crystal, independent of whether the excitation light is polarized or not. Shionoya and coworkers [2] investigated in detail the polarization of B-Cu luminescence in regular ZnS:Cu(Cl, I) crystals. They have indicated that the center has its own characteristic symmetry which is lower than that of the host lattice and they constitute some kind of associated centers. From a comparison of the experimental diagrams with the theoretical ones for σ rotator and π dipole transitions one can find the C_{3V} and C_{2V} symmetry centers. An associated center is produced by the association of a Cu^+ ion at the substitutional site with another Cu^+ ion at the interstitial site. If one assumes that a coactivator is involved in the center, the C_s symmetry center is further produced. In the present paper we try to determine the orientation of the luminescence centers responsible for the blue-copper radiation of ZnS:Cu(Cl, I) crystals.

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2. Polarization diagrams of B-Cu luminescence in ZnS:Cu(Cl, I) crystals

For polarization studies the ZnS:Cu single crystals activated with Cu and coactivated with Cl were grown by the vapour phase method. To obtain the experimental polarization diagrams for the emission band at 2.66 eV equipment was used similar to that described in [3, 4]. The measurements have been carried out at the liquid nitrogen temperature. The crystals have been ground and polished along the $(11\bar{2}0)$ planes (the cleavage surface). Luminescence in the slab was excited by ultraviolet light linearly polarized (365 nm) directed perpendicularly to the optical axes of the crystal (electric vector is parallel to the $(11\bar{2}0)$ plane). Observation and measurements of glow is carried out along the excitation direction from the opposite side of the crystal. The two components of the glow intensity,

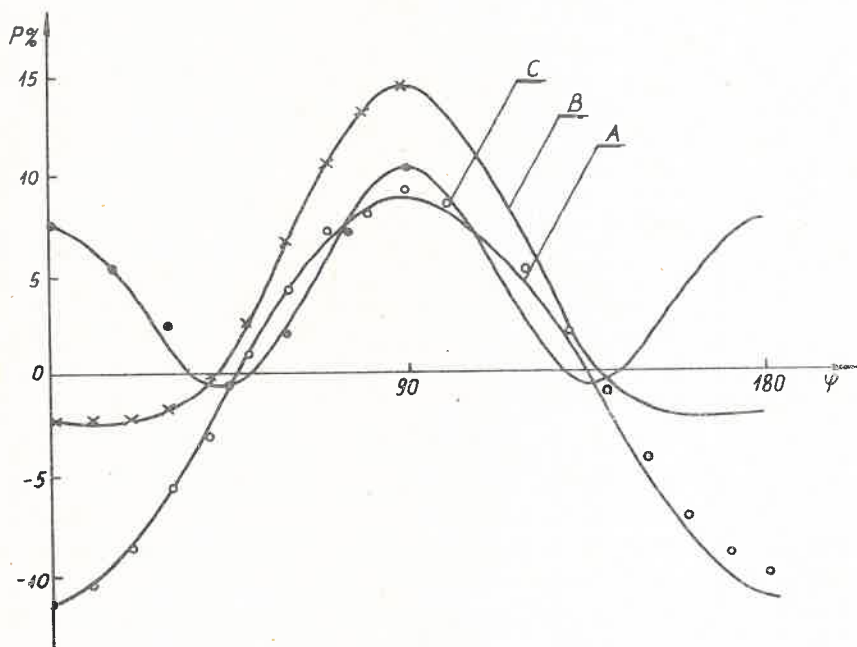


Fig. 1. Polarization diagrams of blue-copper luminescence in ZnS:Cu(Cl) and ZnS:Cu(I) crystals. The experimental values of polarization from [2, 5] are denoted by ● or ×, and from this paper — by ○. The calculated curves are shown by solid lines. Parameters p_j and $\cos \delta l$ take the following values: curve A: $p_1 = 0.660$, $p_2 = 0.100$, $p_3 = 0.437$, $\cos \delta l = -0.022$, curve B: $p_1 = 0.655$, $p_2 = 0.007$, $p_3 = 0.522$, $\cos \delta l = 0.017$, curve C: $p_1 = 0.570$, $p_2 = 0.150$, $p_3 = 0.350$, $\cos \delta l = 0.001$

parallel $I_{\parallel}(\varphi)$ and perpendicular $I_{\perp}(\varphi)$ are measured for the two positions of the analyzer with respect to the excitation vector. In Fig. 1 we have the polarization $P(\varphi)$ of the B-Cu luminescence in ZnS:Cu(Cl) and ZnS:Cu(I) crystals. The experimental values from [2, 5] are denoted by ● or ×. Points ○ denote the experimental value of polarization from this paper. Continuous curves represent the theoretical diagrams.

In [6] it was assumed that the role of the absorption centers is played only by rotator σ type oscillators oriented along the three-fold symmetry axes. As the emission centers one

can take both the σ rotator and dipole π type oscillators, which are also oriented along the three-fold symmetry axes.

The intensity of luminescence light emitted by the rotators and dipoles and passing through an analyzer located at an angle ψ with respect to the optical axis will be proportional to

$$I = \frac{1}{l} \int_0^l (a_x^2 \cos^2 \varphi + a_z^2 \sin^2 \varphi + a_y^2 - 2a_x a_z \cos \varphi \sin \varphi \cos \delta y) \\ \times \{ [a_x^2 \cos^2 \psi + a_z^2 \sin^2 \psi + a_y^2 - 2a_x a_z \cos \psi \sin \psi \cos \delta(l-y)] p_j \\ + [a_x^2 \sin^2 \psi + a_z^2 \cos^2 \psi + 2a_x a_z \cos \psi \sin \psi \cos \delta(l-y)] (1-p_j) \} dy,$$

where a_x, a_y, a_z are unit vector components, l — crystal thickness, δl — denote the phase shift between the components of the exciting vector and luminescence radiation.

The parameters p_j characterizing the contribution of the rotators in emission as well as the parameters $(1-p_j)$ are responsible for the dipole contribution. Values of the p_j and $(1-p_j)$ determine the anisotropy location of luminescence centers in the crystal lattices. Assuming $\psi = \varphi$ and $\psi = \varphi + 90^\circ$ we find the sum and difference of the components of the luminescence intensity which comes from the rotators and dipoles. Polarization $P(\varphi)$ resulting from j differently oriented and equivalent rotators and j differently oriented and equivalent dipoles has the form

$$P(\varphi) = \frac{\sum_j (I_{\parallel j} - I_{\perp j})}{\sum_j (I_{\parallel j} + I_{\perp j})}.$$

This polarization formula has been derived neglecting the dichroism of excitation and luminescent radiation as well as birefringence dispersion. Additionally, it has been assumed that δl has the same value for both excitation and luminescent radiation. For the case when the luminescence centers are oriented along the three-fold symmetry axis the polarization formula is as given in [6].

3. Final remarks

The calculated polarization diagrams presented in Fig. 1 fit the experimental results well. As seen in Fig. 1 the values of the polarization $P(\varphi)$ and shapes of the luminescence curves depend on the method and conditions under which ZnS:Cu crystals were obtained. The polarization luminescence is caused by anisotropic luminescence centers in the crystal and depends on the structure of the centers. The investigation of the polarization luminescence in the crystals [5] and the present ones, are characterized by their negative values $P(0^\circ)$, however the crystals investigated in [2] have positive values $P(0^\circ)$. Polarization $P(\varphi)$ for $\varphi = 90^\circ$ for all three crystals has positive and different values $P(90^\circ)$. Probably different values $P(\varphi)$ are caused by the different contribu-

tions p_j , $(1-p_j)$ of rotators σ and dipoles π to the emission energy. The parameter p_1 (characterizing contribution of the rotator σ_1 to the emission) has a relatively big value which is oriented along the optical axis of the crystal. Higher participation of the rotator σ_1 in the emission causes a decrease in the values $P(0^\circ)$ and determines the sign of the $P(\varphi)$ for $\varphi = 0^\circ$. For the three crystals the small contribution of the σ_2 rotator relative to the dipole π_2 is observed (axes of the oscillators are parallel to the tetrahedra symmetry plane). The oscillators $\pi_3, \pi_4, \sigma_3, \sigma_4$ oriented symmetrically along the direction of excitation have greater influence on the positive values of polarization $P(90^\circ)$ than that of σ_2 . Values of the polarization (except $\varphi = 0^\circ$ and $\varphi = 90^\circ$) and shape of the luminescence curves depend on the birefringence of the crystals.

In [2] a model was suggested for the associated center of luminescence in the ZnS:Cu crystals; we think that the results presented in this paper conform to the suggestions of [2]. It is possible that the Cu^+ ions which are located in the substitutional sites and interstitial ones are localized along the three-fold symmetry axes.

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