Photo- and Roentgenoluminescence of ZnSe

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Abstract—The photoluminescence (PL), roentgenoluminescence (RL), and optical absorption of ZnSe were measured near the fundamental edge in the temperature range from 80 to 400 K. Because of the much smaller absorption coefficient for x-rays as compared to visible light, the contribution to RL from emitting centers located deeper in the sample is higher. The quality of ZnSe can be assessed by correlating its near-edge PL and RL spectra. The temperature dependences of the peak positions of the blue PL and RL bands indicate that these emissions are due to the same center. The blue RL band is redshifted by 18 meV in comparison with PL, and its intensity is lower than that of the longer wavelength bands. The different positions of the PL and RL bands are interpreted in terms of thermal spike formation under x-ray excitation and reabsorption of the emitted light.

Precise knowledge of the spatial distribution of the excitations produced in a crystal phosphor by highenergy photons or particles is of prime importance in radioluminescence studies. The mechanisms and spectral distribution of radioluminescence in alkali halide crystals are a field of intense research [1], because these crystals are widely used in scintillation detectors. The use of tungstates in roentgenoluminescent screens has reduced the interest in cathodo- and roentgenoluminescence (RL) of II–VI semiconductors, in particular ZnSe; nevertheless, they continue to be leading infrared materials and are candidate media for electron-beampumped lasers [2]. The quality of ZnSe can be assessed by correlating its near-edge photoluminescence (PL) and RL spectra.

In this work, we focus on the near-edge PL and RL of nominally undoped single-crystal and polycrystalline ZnSe.

The RL spectra were excited with a BSV-8 x-ray tube (Mo anode, 15–45 kV, 20 mA), and PL was excited with the 337-nm nitrogen laser line through a UFS-2 light filter. In both cases, band-to-band excitation was provided. We also measured the near-edge absorption spectra. The luminescence spectra were corrected for the spectral response of the recording unit.

The 4.2-K near-edge PL spectrum of polycrystalline ZnSe shows the E_x , I_2 , I_1^x , and I_1^d lines associated with free and bound excitons; phonon replicas I_1 ; and the Q_0 , R_0 , and Y lines due to donor-acceptor pair recombination [3-5]. This indicates a high structural perfection of the samples studied and a low level of impurities.

As the temperature rises, the PL spectrum becomes structureless owing to the thermal broadening of lines. Above 80 K, the spectrum contains only one, excitonic band centered at 445.0 nm, which persists to 400 K. The RL spectra recorded above 80 K show a blue band peaked at 448.8 nm and several weak lines, whose intensity decreases rapidly with increasing temperature. It should be stressed that the blue bands in the RL and PL spectra of ZnSe differ in peak energy position (Fig. 1a). Note also that the positions of these bands vary with temperature in a similar way, with a nearly constant temperature difference ΔT , and are identical for all the samples studied. Thus, the differences between the band gap E_g and the PL and RL peak energies remain unchanged in the range from 80 to 400 K, indicating that the blue bands in the PL and RL spectra are due to the same center.

The different positions of the PL and RL peaks can be interpreted in terms of two processes accompanying x-ray excitation: thermal spike formation and reabsorption of the emitted light. When ZnSe is excited at 337 nm, the photon energy slightly exceeds E_{o} , and, therefore, the absorption coefficient is very high, k > k10⁴ cm⁻¹. Electron-hole pairs are generated in a surface layer less than 1 μ m thick. Most of the photon energy is reemitted $(hv_{lum}/hv_{exc} = 0.757)$, and the rest of the energy goes into heating. Absorption of an x-ray photon gives rise to generation of electron-hole pairs in a microregion [1, 6]. At the power density of x-ray excitation used in this work, there is little or no overlap between such microregions. The absorption coefficient of x-rays ($\sim 100 \text{ cm}^{-1}$) is much less than that of visible light, and x-ray photons penetrate deeper into the sample. The energy required to create an electron-hole pair is about $3E_g$ [7], and most of the deposited energy $(\approx 65\%)$ evolves into a thermal spike. There are no other fundamental differences between the mechanisms of PL and RL.

The temperature distribution in a spherical thermal spike can be determined using a simple model: All the heat is released at time $\tau = 0$ in an infinitely small volume at point r = 0; that is, the initial temperature distri-



Fig. 1. (a) 85-K (1, 2) PL and (3, 4) RL spectra of the ZnSe recorded in two different geometries. (b) 85-K PL spectra recorded in a 90° geometry: (1) maximum PL intensity; (2) laser spot displaced from the sample face; (3) exciting beam apertured on the side facing the photodetector.

bution is described by a delta function. Solving the heat equation gives the temperature distribution at time τ :

$$\Delta T(r,\tau) = \frac{\Delta Q}{\left(4a^2\pi\tau\right)^{3/2}C\rho} \exp\left(-\frac{r^2}{4a^2\tau}\right), \qquad (1)$$

where $\Delta Q = C\rho\Delta V\Delta T = \frac{2}{3}\frac{2}{3}eV_0$ is the spike energy (e is

the electron charge, and V_0 is the voltage applied to the x-ray tube), a^2 is the thermal diffusivity, C is the specific heat, and ρ is the mass density. The radial temperature profiles calculated for a thermal spike in ZnSe are shown in Fig. 2. In reality, during thermalization of a hot electron, heat is released randomly in a finite volume. The avalanche generation of electron-hole pairs lasts ~10⁻¹³ s, and the thermalization of hot carriers

takes ~10⁻¹² s [1, 7]. We believe that, for $\tau \ge 10^{-12}$ s, the calculated $\Delta T(r, \tau)$ distribution adequately describes the actual distribution. Note that the cooling rate of thermal spikes is determined by thermal diffusivity. Since the a^2 values for II-VI compounds and oxides fall in the narrow range from 3×10^{-6} to 1.2×10^{-5} m²/s [8], the $\Delta T(r, \tau)$ distributions must be similar for these materials. Thus, our estimates indicate that the spike lifetime is several tens of picoseconds. In the general case, spike formation reveals itself in luminescence data if the emission centers involved satisfy the following conditions: (1) both PL and RL should be well-observed over a wide temperature range; (2) the shapes of the emission bands should vary with temperature rapidly enough for a temperature difference of about 5 K to be detectable; (3) the radiative lifetime of the emission centers should be short ($\leq 10^{-11}$ s) compared to the spike lifetime.

To assess the possible effect of reabsorption on the position of the blue luminescence peak, we measured the optical absorption spectrum of polycrystalline ZnSe (Fig. 3). A strong absorption (~10 cm⁻¹) was observed in the spectral range of the near-edge PL and RL. In line with this finding, the luminescence intensity was found to depend on the experimental geometry (Fig. 1a), whereas the shape of the spectra remained virtually unchanged. When the luminescence was recorded in an on-axis geometry, no near-edge PL or RL was detected for sample thicknesses above 1 mm. In addition, without changing the observation geometry, we varied the path length of the emitted light (Fig. 1b). When the laser-beam spot was slightly displaced from the sample face along the lateral surface (Fig. 1b, inset), the intensity of near-edge emission decreased drastically (Fig. 1b, curves 1, 2), whereas the intensity of the longer wavelength bands remained unchanged. Also, when the exciting beam was apertured on the side closer to the photodetector, the intensity of near-edge luminescence decreased more strongly than that of the longer wavelength bands. The shape of the PL spectrum was strongly dependent on the experimental geometry (Figs. 1a, 1b). When PL was recorded in a 90° geometry, the band at 448.8 nm, typical of RL, was much more pronounced. This strong effect of experimental geometry on the PL spectrum provides clear evidence that the near-edge luminescence in ZnSe is reabsorbed, as in the case of CdS [9].

In summary, the different positions of the near-edge PL and RL bands can be accounted for by reabsorption of the shortest wavelength emission in RL. Since the absorption coefficient of x-rays is well below that of visible light, luminescence is excited at a greater depth than in the case of photoexcitation. The effect of thermal spike formation under x-ray excitation is only sig-



Fig. 2. Radial temperature distribution in a thermal spike $(V_0 = 35 \text{ kV})$ at $\tau = (1) 2 \times 10^{-12}$, (2) 5×10^{-12} , (3) 10^{-11} , and (4) 5×10^{-11} s. Inset: time variation of temperature at point r = 0.



Fig. 3. (1) 85- and (2) 295-K near-edge absorption spectra of polycrystalline ZnSe.

nificant for centers with a radiative lifetime shorter than 10^{-11} s.

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