ZnO: Eu RED PHOSPHOR GROWN FROM $Na_2B_4O_7$ MELT

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Abstract

A ZnO-based red phosphor was grown from a $Na_2B_4O_7$ melt and the efficiency of Eu^{3+} ion excitation was demonstrated. The analysis of the emission related to the Eu^{3+} 4f-4f intrashell transitions suggests that the phosphor represents a nanocomposite consisting of ZnO and $Na_2B_4O_7$ nanoparticles, a part of Eu^{3+} ions being incorporated into ZnO and another part into $Na_2B_4O_7$ constituent.

Zinc oxide (ZnO) is a promising material for manufacturing UV light emitters, spin functional devices, gas sensors, transparent electronics, and surface acoustic wave devices (see for instance Ref. 1 and references therein). Another perspective area of application for ZnO is the elaboration of field emission displays (FEDs). The main element of a FED is the “cold cathode” material or structure that emits the electrons with relative easy into the vacuum. Recently, ZnO nanowires and nanoneedles were demonstrated to be excellent field emitters [2,3]. Opposite each field emitter pixel in a FED is a similar sized area of phosphor material patterned over a transparent and conducting substrate forming the anode. ZnO transparent conducting films are nowadays fabricated using a number of technological approaches (see for instance Ref. 4 and references therein). Nowadays, ZnS doped with different impurities is a most common phosphor. One problem of this phosphor is the accelerated degradation, since its surface can degrade to non-luminescent ZnO. Therefore, the elaboration of ZnO based phosphors, which are superior in chemical stability and electrical conductivity to conventional zinc sulfide materials is a challenge towards the fully integrated ZnO FEDs.

The emission wavelengths of a phosphor can be varied by changing the rare earth (RE) impurity dopants, and red, green, and blue colors can be realized in a single host phosphor. The radiative transition from the $^5D_0$ excited state to the $^7F_2$ level in Eu^{3+} ions is well known to produce a deep red color which is suitable for display applications. Efforts have recently been made to prepare efficient, reproducible red ZnO phosphors by incorporating RE elements [5]. However, there is still controversy concerning the possible mechanism of Eu^{3+} ion excitation when it is incorporated into ZnO lattice. Some investigations suggested that there is no energy transfer between ZnO and Eu^{3+} ion [6], while according to Park et al. [7] the $^5D_0 \rightarrow {}^7F_2$ red emission of Eu^{3+} around 620 nm in a red ZnO:$EuCl_3$ powder phosphor is caused by energy-transfer excitation through UV-pumped ZnO. On the other hand, Fujihara et al. [8] suggested that the phosphors prepared by Park et al. are indeed a mixture of ZnO and EuOCl, and the red emission comes from EuOCl crystals. Respectively, Fujihara et al. [8] fabricated red thin-film phosphors based on a ZnO:(La,Eu)OF nanocomposite structure where (La,Eu)OF nanoparticles were dispersed in a ZnO film matrix. According to Fujihara et al., the Eu^{3+} ion in this nanocoposite is incorporated into the LaOF lattice, and the excitation is a charge transfer process between the Eu^{3+} and O^{2-} ions.

In the present study ZnO-based red phosphor was grown from a $Na_2B_4O_7$ melt and the efficiency of Eu^{3+} ion excitation was demonstrated.

The $Na_2B_4O_7$ melt with 20 M % of B_2O_3, 70 – 75 M % of ZnO, and 1 – 2 M % of Eu_2O_3 was heated up to 1100 ^oC and cooled down to 850 ^oC at a rate of 10 – 25 ^oC/hour.

The photoluminescence (PL) was excited by the 351.1 nm line of an Ar^+ SpectraPhysics laser and analyzed in a quasi-backscattering geometry through a double spectrometer with 1200 grooves/mm gratings assuring a linear dispersion of 0.8 nm/mm. The signal from a FEU-106 photomultiplier with SbKNaCs photocathode working in a photon counting mode was introduced in an IBM computer. The resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 optical cryogenic system. The excitation laser beam at the power of 30 mW was about 2 mm in diameter.

Figure 1 shows the PL spectra in the ultraviolet (UV) spectral range of as prepared ZnO:Eu phosphor. The PL spectrum consists of four PL bands at 3.376; 3. 363; 3.309, and 3.290 eV labelled as X_A, D^0X, FB, and DA as well as of LO phonon replicas of the FB, and DA bands. The temperature dependence of the X_A and D^0X PL bands suggests their connection with the recombination of free and donor bound excitons, respectively. The intensity of the D^0X luminescence sharply decreases exhibiting an activation quenching with increasing temperature. The activation energy deduced from the insert of Fig. 2 equals 17 meV. This behavior suggests that the D^0X peak is related to the recombination of neutral donor bound excitons [9]. At temperatures higher than 100 K, the luminescence related to the recombination of free X_A exciton becomes stronger than the luminescence related to the recombination of D^0X exciton. The temperature dependence of the position of X_A and D^0X lines is presented in Fig. 3. The solid curve in Fig. 3 represents the fit to the experimental data by the phenomenological Varshni formula [10]:

$$E(T) = E_0 - \alpha T^2/(T+\beta)$$

with E_0 = 3.377 eV, $\alpha = 1x10^{-3}$ eV K^{-1}, and β = 900 K parameters.

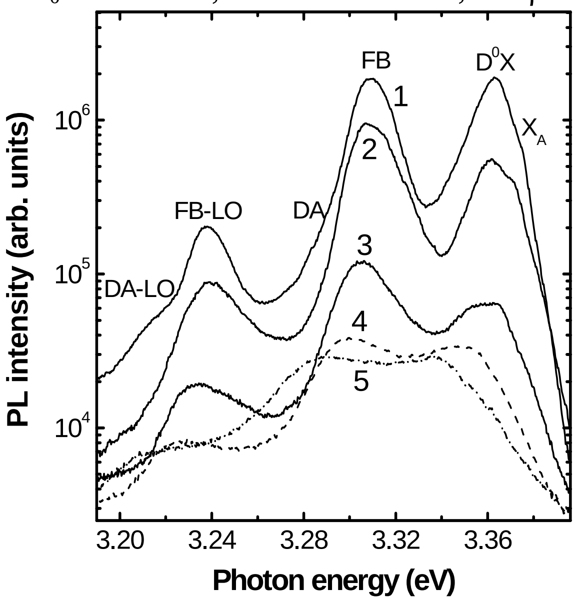

Fig. 1. PL spectra in the UV spectral range of as prepared ZnO:Eu phosphor measured at different temperatures as follows: 1 – 10 K;2–50 K; 3 – 100 K; 4 – 150 K; 5 – 200 K.

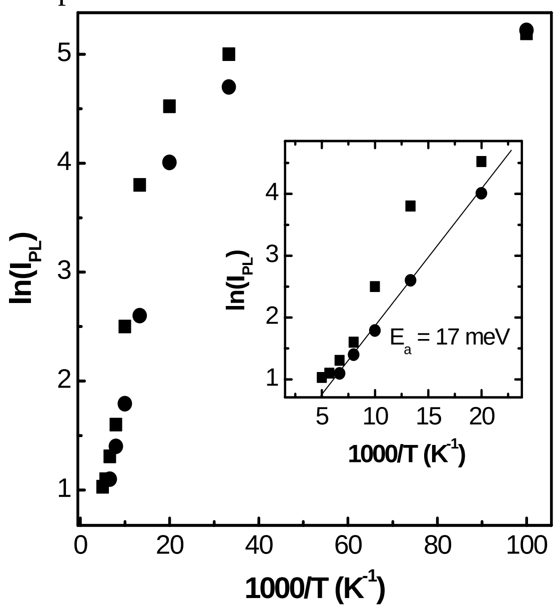

Fig. 2. Temperature dependence of the intensity of D^0X (circles) and FB (squares) PL bands.

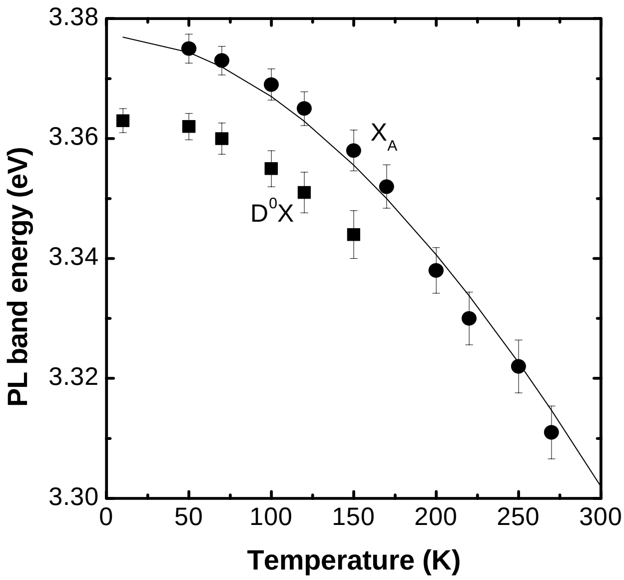

Fig. 3. Temperature dependence of the X_A (circles) and D^0X (squares) energy peaks. The solid curve represents the fit to the experimental data by the Varshni formula.

The temperature dependence of the FB and DA PL bands suggests free to bound and donor acceptor nature of electron transitions responsible for these PL bands, respectively. The intensity of the DA band decreases considerably with the temperature increase (see Fig. 1), since the impurity with smaller binding energy involved in DAP transitions (most probably the donor impurity) is ionized with increasing temperature.

The intense donor bound exciton luminescence and the observation of free exciton luminescence is indicative of good optical quality of the material. This is also supported by the analysis of the visible luminescence (see Fig. 4). The PL spectrum in the visible spectral range consists of a series of PL bands related to the Eu^{3+} 4f-4f intrashell transitions superimposed on a broad PL band with the maximum at 670 nm. This broad PL band in ZnO is commonly believed to come from structural defects, and the relative PL intensity ratio of the UV near-band edge emission to the visible emission is used as a parameter for estimation of the quality of the material. This parameter equals 100 for our phosphor, thus confirming the good quality of the material.

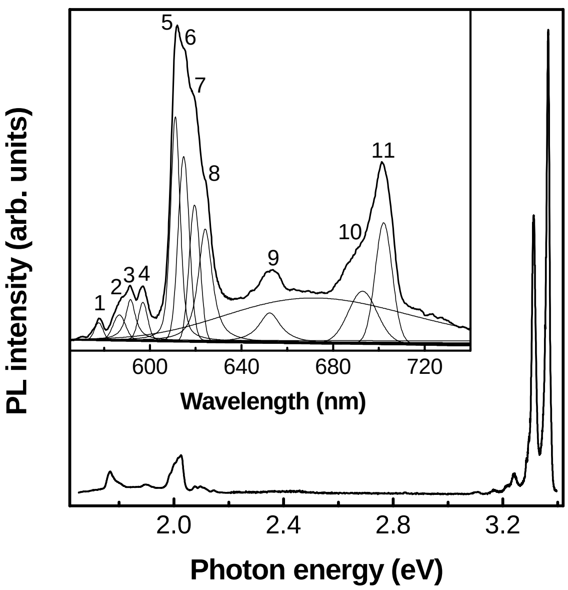

Fig. 4. PL spectrum of ZnO:Eu phosphor related to the Eu^{3+} 4f-4f intrashell transitions.

The intensity of the emission related to the Eu^{3+} 4f-4f intrashell transitions depends on the Eu concentration, the highest efficiency being achieved for the doping concentration of 2 at %. All the observed lines summarized in Table 1 are consistent with Eu^{3+}-related emission from ${}^5D_0 \rightarrow {}^7F_j$ (J = 1,2,3,4) transitions. It is well documented that Eu^{3+} ions are usually incorporated in II-VI compounds by substitution on the metal sublattice with C_{3v} site symmetry. The C_{3v} site symmetry splits ground ${}^7F_{2-5}$ levels. Theoretically, the ${}^7F_2$ level gives three crystal field levels of A_1 and 2E with C_{3v} symmetry [8]. The presence of four lines related to ${}^5D_0 \rightarrow {}^7F_2$ transitions instead of three, along with two additional lines related to ${}^5D_0 \rightarrow {}^7F_1$ transitions, suggests that in our phosphor a part of Eu^{3+} ion is incorporated into sites with the symmetry different from C_{3v}. This observation suggests that the phosphor represents actually a nanocomposite consisting of ZnO and $Na_2B_4O_7$ nanoparticles, a part of Eu^{3+} ions being incorporated into ZnO and another part into $Na_2B_4O_7$ constituent.

Table 1. The PL bands related to the Eu^{3+} 4f-4f intrashell transitions.

Band label	1	2	3	4	5	6	7	8	9	10	11
Wavelength, nm	578	587	591	597	611	614	620	624	653	693	702
Transition	${}^5D_0 \rightarrow {}^7F_0$	${}^5D_0 \rightarrow {}^7F_1$			${}^5D_0 \rightarrow {}^7F_2$				${}^5D_0 \rightarrow {}^7F_3$	${}^5D_0 \rightarrow {}^7F_4$	

In conclusion, the results of this study demonstrate the possibility to fabricate ZnO:Eu phosphors, in which the Eu^{3+} ions are efficiently excited by the UV radiation resulting in intense red emission with good color purity.

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