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Synthesis and improved photoluminescence of Eu:ZnO phosphor

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Abstract Zinc oxide doped with europium has been prepared by high temperature calcination method using ZnO, Eu_2O_3, and LiOH. Structural characterization by X-ray diffraction and optical studies by photoluminescence spectroscopy together give evidence that Eu^{3+} is going to the substitutional site of Zn^{2+}. The concentration of chemicals used, sintering temperature, and time are optimized with photoluminescence excitation spectroscopy for a sharp and intense red signal which is a signature of Eu^{3+}. Characteristic red emission at 607 nm is observed using high-energy excitation along with the native deep center emission of ZnO peaking around 525 nm.

Introduction

Semiconductors doped with rare earth ions are excellent phosphors of high efficiency and low degradation in addition to their unique physical and chemical properties [1]. II–VI compound semiconductors have been found to be unique host materials for doping of optically active impurities, which exhibit efficient luminescence at room temperature [2]. Zinc oxide is one of the most promising wide-band gap semiconducting phosphor materials, which show excellent luminescent properties under electron beam and UV excitation. It has a bulk band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature. ZnO is also known for its chemical stability and n-type conductivity [3–6].

Human eyes are more sensitive to monochromatic colors than to broadband spectrum colors. Thus rare earth ions are better luminescent materials because of the sharp and intense emission due to their 4f intra shell transitions. Among the lanthanides Eu^{3+} has attracted significant attention due to its enormous potential in various applications. Although there are a few reports in literature on rare earth doped compounds, as bulk and nanostructures [7–11] but their structural and luminescence properties are not very clear due to the difficulties in doping procedures. Further optimization of the procedures is needed for the development of complete understanding of doping processes. Present work is one such attempt in this direction. In this work, we are successful in doping Eu in ZnO with augmented luminescence characteristics. Doping in ZnO is done using solid-state reaction method. Compared to the conventional preparation methods, the solid-state reaction or calcination method has advantage of its low cost, high yield, and ability to achieve high purity in making oxide powders [12].

X-ray diffraction (XRD) and scanning electron microscopic studies were done for structural characterization. Photoluminescence excitation spectroscopy and photoluminescence spectroscopy were carried out to study its luminescence properties.

Experimental

Zinc oxide powder doped with Eu^{3+} is prepared by high temperature calcination to study their structural and optical

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properties. The chemicals used in the experiment are ZnO bought from Qualigens, Analytical reagent grade, 99.9% pure; Eu_2O_3 bought from Indian Rare Earth Company which is 99.9% pure and $LiOH.H_2O$ bought from Aldrich, 99.995% pure. The samples are prepared by thoroughly mixing Eu_2O_3 and ZnO powders. Slurry is made with LiOH solution and ethanol in a beaker and dried in an oven. After drying, the mixture is ground for more than half an hour and then sintered in air. Samples are made in batches of approximately 10 g. X-ray diffraction is carried out using Bruker X-ray diffractometer. Measurements for all the samples are carried out at the same time and in the same setting of the instrument. Photoluminescence excitation spectroscopy and photoluminescence spectroscopy is done using Perkin Elmer (LS-55) spectrometer. The excitation source is a xenon flash lamp, which produces an intense short duration pulse of radiation over the spectral range of the instrument. The Eu^{3+} concentration in ZnO is kept constant at 1% and other parameters, e.g., firing ambiance, time, and temperature are changed, in order to optimize the preparation conditions by analyzing photoluminescence spectra. Concentration of Li^+ is varied from 0 to 0.6%, and 0.3% is found to be the optimum concentration with which a sharp intense peak at 607 nm could be obtained when excited by wavelengths between 225 and 260 nm. Firing temperature is varied from 800 to 1,200 °C and time is varied from 1 to 8 h. Samples are named from ZnO 2 to ZnO 12. For ZnO 2–ZnO 5, firing temperature, time and ambiance are kept as 1,000 °C, 1 h and air, respectively, and only Li^+ concentration is changed. Concentration of Li^+ is kept at 0.3% for ZnO 2, 0.6% for ZnO 3, 0.1% for ZnO 4 and ZnO 5 are prepared without Li^+. Eu^{3+} concentration is kept constant at 1% for all the samples except for ZnO 11 which is prepared in extreme conditions. Concentration of ZnO has been adjusted as to keep the total amount 100%. ZnO 6 and ZnO 7 has Li^+ concentrations as 0.1% and 0% respectively and is sintered in air at 1,000 °C for 3 h. Concentration of Li^+ ions in the following samples is fixed at 0.3% as it has been found to be optimum. ZnO 8 is sintered in N_2 ambiance at 1,000 °C for 1 h. Sintering is done at 800 °C in air for ZnO 9. The next three samples ZnO 10, ZnO 11 and ZnO 12 are sintered at 1,200 °C for 1, 8 and 3 h, respectively. Tabular form of the preparation conditions for all the samples is given in Table 1.

Scanning Electron Microscopy gives an evidence of the fact that the composition which is sintered at 1,000 °C for 1 h has smaller grains of similar size, but the one which is sintered at 1,200 °C for 3 h consists of bigger grains as a result of agglomeration which break down when the sintered material is powdered.

Results and discussion

X-ray diffraction spectra show peaks corresponding to polycrystalline ZnO and no extra phase related to other compounds like Eu_2O_3 is found (Fig. 1). Peaks at 31.791°, 34.453°, 36.298°, 47.576°, 56.623°, 62.910°, 66.409°, 67.986°, and 69.127° correspond to reflections from 100, 002, 101, 102, 110, 103, 200, 112, and 201 crystal planes, respectively (JCPDS Card file No. 36-1451). Structurally there is no significant change in any composition which was sintered in air at 1,000 °C and XRD spectra shows well defined phases of polycrystalline ZnO. The composition which was sintered in N_2 ambiance (ZnO 8) has comparatively weak intensity for most of the peaks of ZnO indicating its poor quality. Comparison of the XRD spectra suggests that the composition which is sintered at 800 °C for 1 h (ZnO 9) is structurally better than the one sintered at 1,200 °C for 1 h (ZnO 10). When the same composition is subjected to prolong sintering at 1,200 °C

Table 1 Samples of ZnO doped with Eu^{3+} prepared with different Li^+ concentration, sintering time, temperature and ambiance

Sample	ZnO %	Li %	Eu %	Time (h)	Temp. (°C)	Ambiance
ZnO 2	98.7	0.3	1	1	1,000	Air
ZnO 3	98.4	0.6	1	1	1,000	Air
ZnO 4	98.9	0.1	1	1	1,000	Air
ZnO 5	99	0	1	1	1,000	Air
ZnO 6	98.9	0.1	1	3	1,000	Air
ZnO 7	99	0	1	3	1,000	Air
ZnO 8	98.7	0.3	1	1	1,000	N_2
ZnO 9	98.7	0.3	1	1	800	Air
ZnO 10	98.7	0.3	1	1	1,200	Air
ZnO 11	94.7	0.3	5	8	1,200	Air
ZnO 12	98.7	0.3	1	3	1,200	Air
ZnO	100	0	0	1	1,000	Air

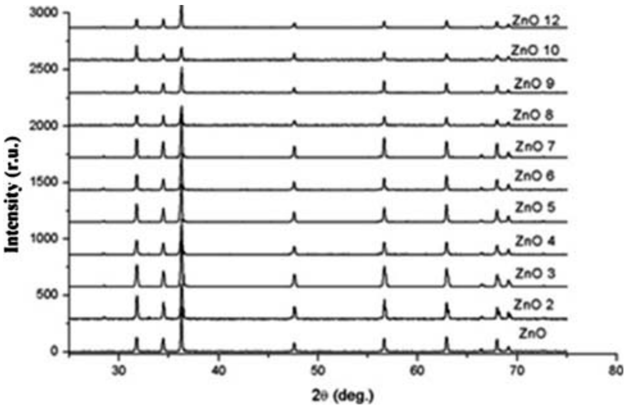

Fig. 1 XRD spectra of Eu doped ZnO prepared different Li^+ concentration, sintering time, temperature and ambiance

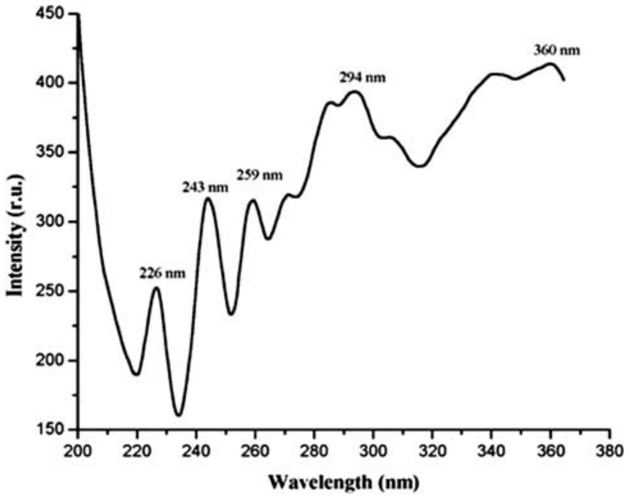

Fig. 2 Excitation spectra of Eu doped ZnO prepared in optimum conditions (ZnO 12)

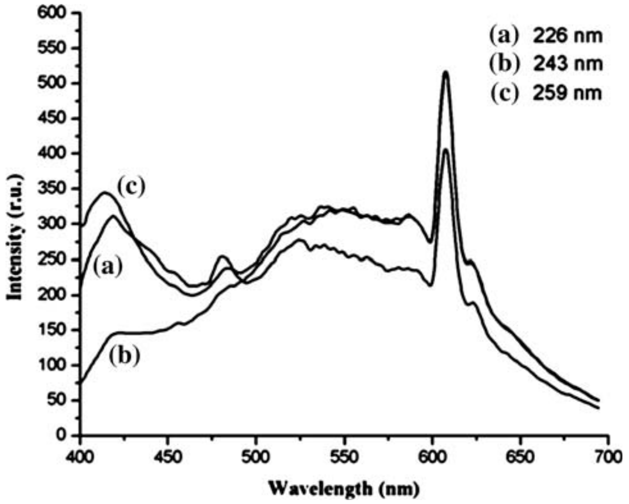

Fig. 3 Emission spectra of Eu doped ZnO (ZnO 12) for excitations (**a**) 225 nm, (**b**) 248 nm and (**c**) 259 nm

(ZnO 12) an improvement in the structural quality has been observed which can be attributed to the better incorporation of Eu^{3+} at the substitutional site and annealing of most of the defects created in the process.

It has already been established that Li^+ ions as a dopant play an important role in increasing the luminescence efficiency of phosphors [13–15]. Role of Li^+ as a co dopant and charge compensator has been extensively studied for various phosphor host lattices [14–17]. Gu et al. have explained the contribution of Li^+ ions in ZnO doped with Dy^{3+} ions [11]. As the ionic radius of the Li^+ ion (0.76 Å) is similar to that of the Zn^{2+} ion (0.75 Å), it is assumed that the Li^+ ion can easily substitute for the Zn^{2+} ion. Upon excitation of the $ZnO:Eu^{3+}$ co-doped with Li^+, more holes can be trapped at the Li_{Zn} defects. This causes an increase in the recombination probability of electrons and trapped holes leading to high emission intensity of Eu^{3+}. It can also be assumed that the incorporation of Li^+ ions create oxygen vacancies, which act as the sensitizer for the energy transfer to the rare earth ion, due to the strong mixing of charge transfer states resulting in the strong luminescence.

The results of photoluminescence excitation spectroscopy for ZnO 12 are shown in Fig. 2. Excitation peaks are found at 226, 244, 259, 294, and 360 nm. Excitations by 226, 244, and 259 nm wavelengths in UV range show similar spectrum with a broad emission peaking at 524 nm and an intense sharp emission at 607 nm (Fig. 3). Emission spectra for excitations 294 and 360 nm consists of only broad emission at 524 nm (Fig. 4).

Peaks at 418 and 480 nm are due to some defects, which are created when the sample is subjected to high temperature treatment. These peaks are also found in pure ZnO powder sintered at 1,000 °C for 1 h. Broad emission peaking at 524 nm can be ascribed to transitions mediated by defect levels in the band gap such as oxygen vacancies which is a native defect of ZnO [18]. Oxygen vacancy acts as radiative center in luminescence process. The emission at about 590 nm originates from magnetic dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition [4]. Sharp peak at 607 nm is due to the $^5D_0 \rightarrow {}^7F_2$ transition.

The characteristic emission peaks of Eu^{3+} at 590 and 607 nm are sensitive to the site symmetry. If the site symmetry of Eu^{3+} belongs to the O_h group, the emission at 590 nm is dominant. If the site symmetry of Eu^{3+} reduces, the intensity of emission at 607 nm increases. High intensity of 607-nm transition indicates that Eu^{3+} occupies a low symmetry site [4].

Several experiments have been carried out in order to obtain the optimum preparation conditions for Eu doping in ZnO phosphor. Optimization is done with photoluminescence excitation spectroscopy. The ratio of intensities of emission at 607 nm and corresponding excitation (243 nm)

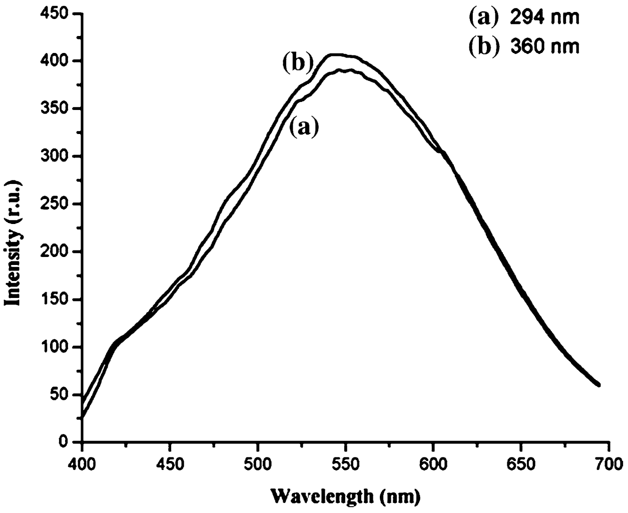

Fig. 4 Emission spectra of Eu doped ZnO (ZnO 12) for excitations (**a**) 294 nm and (**b**) 360 nm

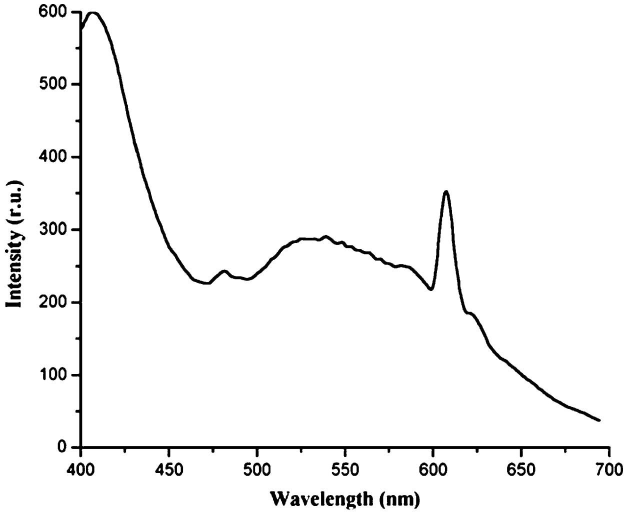

Fig. 6 Emission spectra of Eu doped ZnO prepared without Li^+ (excitation by 242 nm)

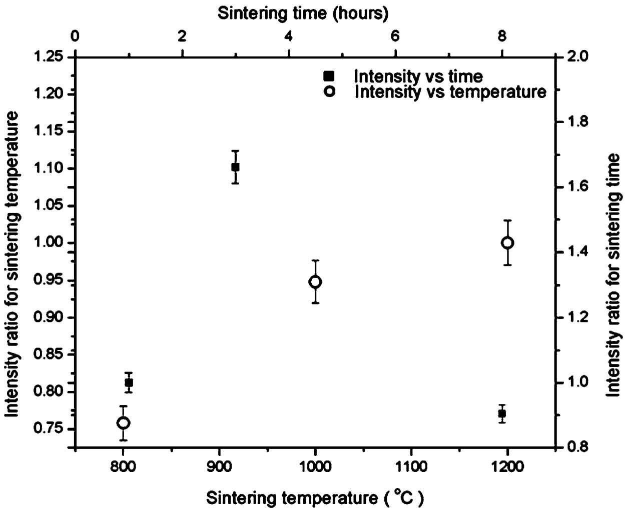

Fig. 5 Variation of intensity ratio (emission/excitation) with sintering temperature and time

has been plotted against sintering time and temperature (Fig. 5). Temperature has been kept constant as 1,200 °C for time versus intensity plot and similarly time has been kept constant as 1 h for temperature versus intensity plot. The curves thus obtained show that the intensity ratio is maximum for the sample which is sintered at temperature 1,200 °C for 3 h of sintering time.

In order to confirm that Li^+ ions do not contribute to the sharp red emission at 607 nm, a composition was made containing 1% Eu_2O_3 and 99% ZnO only and fired at 1,000 °C for 1 h in air (ZnO 5). The powder thus obtained is excited by 242 nm. Corresponding emission spectrum (Fig. 6) also shows broad hump peaking at 526 nm and strong sharp transition at 607 nm. This eliminates the possibility of Li^+ having a role in the red emission and confirms the fact that it is only due to Eu^{3+}.

Scanning electron micrographs (Fig. 7) help in estimating the size of the grains thus formed. Big and very big grains observed for ZnO 12 can be attributed to the agglomeration due to prolonged sintering at very high temperature.

Conclusion

Preparation of zinc oxide doped with europium by high temperature calcinations with optimum reaction conditions

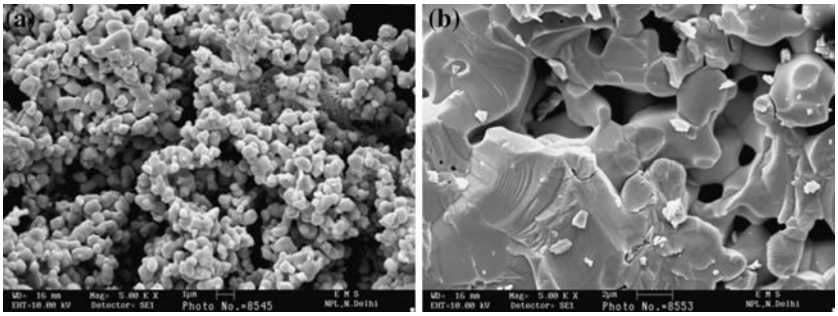

Fig. 7 Scanning Electron Micrograph of Eu doped ZnO (**a**) ZnO 2 sintered at 1,000 °C for 1 h (**b**) ZnO 12 sintered at 1,200°C for 3 h

seems to be an efficient, inexpensive and easy method. Prolong sintering of the composition at high temperature ensures better incorporation of Eu^{3+} which results in sharp and intense transition. This is achieved at the cost of grain size because high temperature leads to agglomeration. Incorporation of Eu^{3+} in the structure of ZnO has been confirmed by the strong and sharp red emission at 607 nm along with deep center emission of zinc oxide around 525 nm.

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