Fluorescence behaviour of Eu doped Gd_2O_3 nanosheets via CuO incorporation

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Abstract. The present research deals with the variation in fluorescence emission of Eu doped Gd_2O_3 phosphor in the presence of different CuO concentrations. Sheet-like phosphor materials have been successfully synthesized by a simple solution combustion route. The crystalline nature, phase formation and presence of elements in the prepared materials were identified by X-ray diffraction and energy dispersive X-ray spectroscopy, respectively. Microstructure analysis has been performed by scanning electron microscopy. The photoluminescence emission spectra have been recorded to observe the fluorescence behaviour upon 325 nm laser excitation and the corresponding colour coordinates were also calculated.

1. Introduction

Lanthanide activated phosphors have been studied extensively since the last few decades owing to their strong luminescence behaviour useful in multifunctional applications e.g. fluorescent lamps, display devices, solar cells, light emitting diodes, optical and temperature sensing, etc. [1-3]. The selection of materials (host and dopants) andthe synthesis technique play a crucial role in the development of such phosphors. Gadolinium oxide(Gd_2O_3) is an interesting material for luminescence investigation due to its characteristics of serving both as host as well as doping elements for different applications purposes. It gives a suitable environment for doping elements as a host because of its high band gap, low phonon frequency,and good thermal and chemical stability [2, 4, 5]. Numerous studies have been performed by researchers with lanthanide doped/codoped gadolinium oxide for strong multicolor emissions via both the upconversion and downconversion processes [2, 5-7]. Europium (Eu) is very popular as doping element among the lanthanides for its strong red emission through 4f-4f transitions and the Eu^{3+} to O^{2-} charge transfer excitation band [8].Several articles have been reported on Eudoped Gd_2O_3 nano-phosphor/crystals for optical/structural investigations [5, 7, 9].Incorporation of transition metals may affect the structural and optical properties of the materials. CuO is one of these materials containing transition metals that can be considered. Severalphosphors have been reported via codoping ofcopper and lanthanide combinations[10, 11] but no such report is available with Cu/Eucodoping.Therefore, it is interesting to see the effect of the incorporation of CuO into the Gd_2O_3:Eusystem. Control over shape and size of the phosphors makes it more advantageous from an applications point of view and influences the optical, electrical and magnetic properties of the materials [9].Various synthesis techniques have been reported for producing materials of different size and shapes but the solution combustion method is found to be betterdue to its low processing temperature, homogeneous mixing and smaller particle formation [12].

The formation of sheet-like structuresand the influence on the luminescence emission upon adding CuO to the Gd_2O_3:Eusystemwas the aim of the present study. The structural and optical characterizations wereperformed by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and photoluminescence (PL)measurementsand explained in detail.

2. Material synthesis and characterization

Eudoped Gd_2O_3 phosphor powder has been prepared by the low temperature solution combustion route [12]. Gd_2O_3,Eu_2O_3 and CuO were used as starting materials, HNO_3 as solvent and urea as organic fuel. All the chemicals were of highly pure (99.90-99.99%) analytical grade purchased from Sigma Aldrich. A number of samples have been prepared according to the following composition

$$(100\text{-}x\text{-}y)\ Gd_2O_3 + x\ Eu_2O_3 + y\ CuO \qquad (1)$$

where$x$ = 5.0 mol% and y =0.0, 1.0, 3.0, 5.0 mol%.

The oxide materialswere dissolved in concentrated HNO_3 to convert them to the form of nitrates. The nitrate forms of the host and dopants were mixed together and dissolved until transparent. Then the urea (organic fuel) was added to the final transparent solution and stirred about an hour at 60 ^{0}C till a transparent gel was obtained. The formed gel-like solution was taken in an alumina crucible and placed inside an electrical furnace preheated to 500 ^{0}C where combustion took place. The obtained samples were grounded to obtain fine and homogeneous powders and then annealed at 800 ^{0}C for 2 h. The heat-treated samples have been used for further characterization.

The XRD patterns were measured by a Bruker-D8 Advance diffractometer with a Cu-target radiation (λ= 0.154 nm), SEM and EDS images have been taken by using a JSM-7800F analytical field emission scanning electron microscope.A325 nm He-Cd laser was used to excite the samples and the emission was measured using an Ocean Optics USB2000+ spectrometer. The colour coordinates were calculated by using the 1931 Commission Internationale de L'Eclairage (CIE) software.

3. Results and discussion

3.1. Structural analysis

The XRD spectra of the Gd_2O_3:Eu/CuOnanosheets recorded in the 15 to 65 degree range are shown in Fig. 1. The patterns matched suitably with JCPDS card no. 12-0797 of the cubic Gd_2O_3 with space group Ia3. All the observed peaks were well indexed and the sharp diffraction peaks indicating the crystalline nature of the prepared phosphors. Interestingly, some extra peaks were detected on incorporation of the CuO and seemed to increase on increasing the concentration of CuO.These impurity peaks were identified for different orientation of pure monoclinic CuO (as assigned in Fig. 1) JCPDS card no. 48-1548. The crystallite size of the developed phosphors has been calculated by using the Scherrer equation [13]

$$D = \frac{k\lambda}{\beta Cos\theta} \qquad (2)$$

where$D$ is the crystallite size,k is the shape factor (assumed to be 0.9),λ is wavelength of the X-ray radiation (0.154056 nm for Cu Ka radiation).$\theta$is Bragg diffraction angle and β is the full width of the diffraction peak measured at half of its maximum intensity (in radians).The values of the average crystallite size were found to be 34 nm and did not changed significantly on incorporation of CuO (from 37 to 41 nm).

To observe the surface morphology of the prepared phosphors, the SEM images of the Gd_2O_3:Euwithout and with 3 mol% CuO codoped samples have been obtained (Fig. 2). Fig. 2(a) shows the SEM image of Gd_2O_3:Euat1µm scale. The image displays a sheet-like particle structure of different sizes. The SEM image with CuO incorporated into the sample also demonstrates a sheet like structure as observed from Fig. 2(b). The thickness of the sheets was found to be about 100 nm as indicated by the red circles of Fig. 2(c). Thus the formation of sheet-like structures with nano thicknesses (i.e. nano-sheets) was confirmed by the SEM characterization.

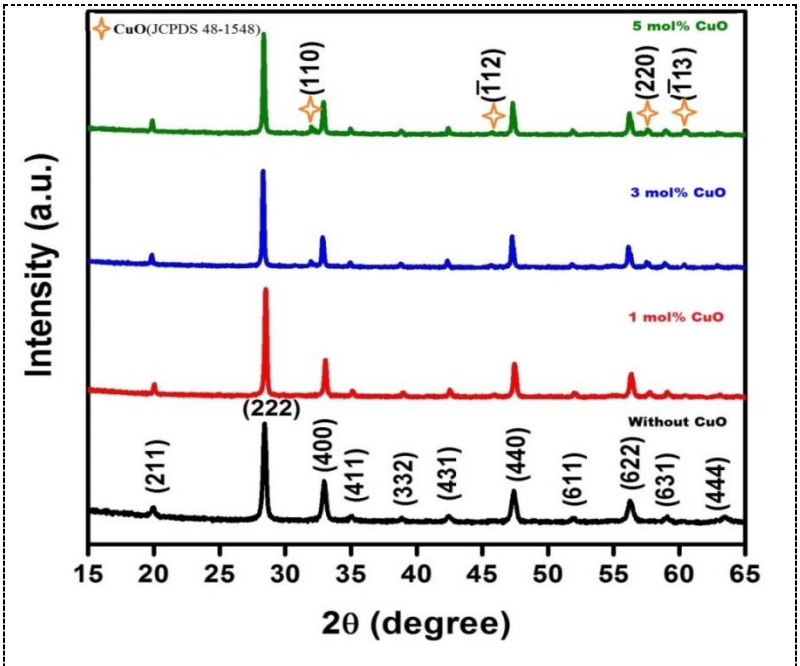

Figure 1. XRD patterns of the Gd_2O_3:Eunanosheets with different CuO concentrations.

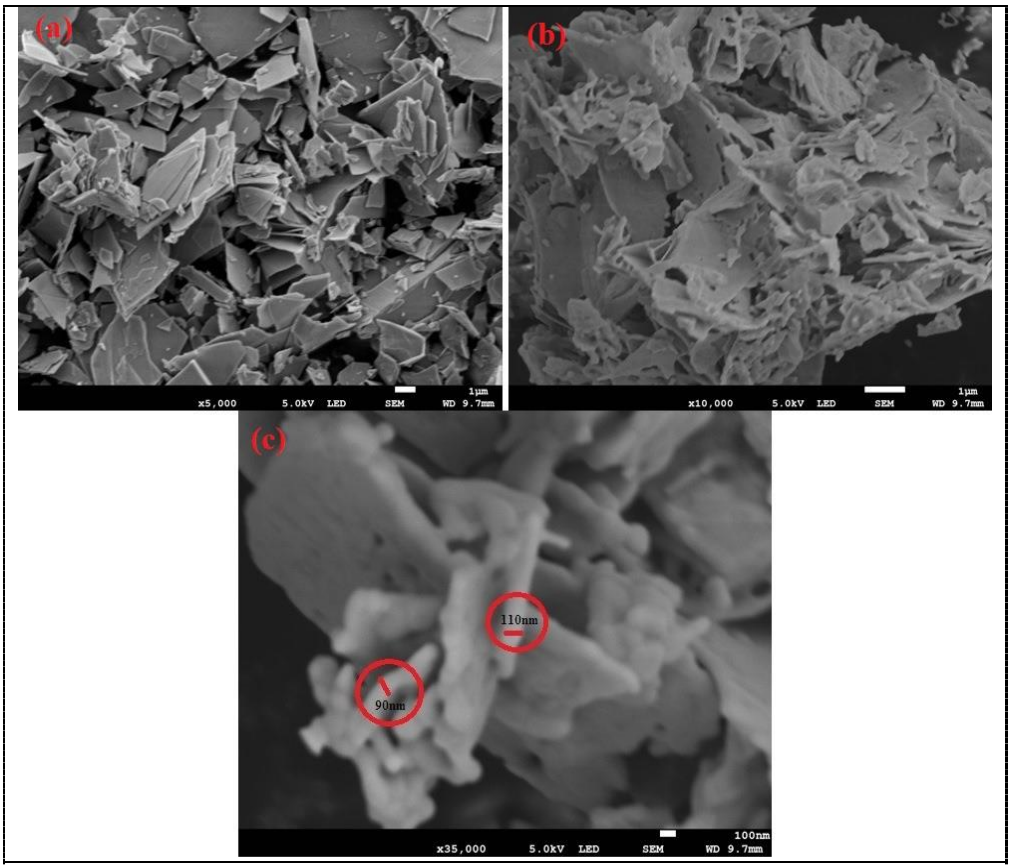

Figure 2. SEM images of the Gd_2O_3:Eunanosheets (a) without and, (b) and (c) with CuO incorporation.

Fig. 3 shows the EDS spectra of the prepared materials corresponding to that in Fig. 2(a) and (b). The EDS patterns shown in Fig. 3(a) and (b) confirmed the elemental presence of all the components of the prepared phosphors. The peak of carbon is found in both cases due to the use of carbon tape to stick the sample during characterization. Also a weak peak of aluminum detected at about 1.5 keV might be due to contamination from the use of the alumina crucible during the preparation of the samples.

The optical photographs of the phosphor samples are given as insets in Fig. 3(b). From the photographs we can see that the colour of the material has changed from white to brown/black on adding the amount of CuO from 1.0 to 5.0 mol%.

3.2 Luminescence study

The room temperature PL emission spectra of the Eudoped and CuO codoped Gd_2O_3 phosphor excited by a 325 nm He-Cd laser and recorded in the 375-750 nm range are shown in Fig. 4. The whole emission spectra comprised of two parts, one is a broad band ranging from 375-550 nm and the other consisting of several sharp peaks ranging from 550-750 nm. The broad band centered at about 440 nm is assigned to the Eu^{2+} emission through the $^4f_6{}^5d_1$ (5d) excited state to the $^8S_{7/2}$ ($^4f_7$, i.e. 4f) ground state transition [14]. A few sharp emission peaks are detected in the orange-red region which is attributed to Eu^{3+} emission via the excited $^5D_0$ state to different ground states $^7F_{0,\ 1,\ 2,\ 3,\ 4}$ transitions [14, 15]. On comparing the emission spectra it was found that the emission band that corresponded to Eu^{3+} has decreased whereas that which corresponded to the Eu^{2+} has increased drastically on the incorporation of 1 mol% CuO. As the Eu^{3+} ions can occupy the Gd^{3+} sites without inversion symmetry therefore the electric dipole transition $^5D_0 \rightarrow {}^7F_2$ is dominant [14] and the formation of more Eu^{2+} active centres in presence of CuO ions is the result of capturing unoccupied Cu^{2+} s-d states[16]. The total emission intensity throughout the recorded region was suppressed on addition of more CuO (in the case of 3 and 5 mol% CuO) because of Cu-Cu clustering inside host lattice [17].

The emission peak at about 612 nm was dominant over the others in the case of the singly Eu doped materials which resulted in a strong red emission from the material. On the other hand the broad blue band peaking at 440 nm has been dominant over the red in the case of the CuO doping and hence an intense blue emission was observed from the sample. This change in colour of the emitted light from the samples was confirmed by the corresponding calculated colour coordinates. The CIE chromaticity diagram with the indicated coordinate positions is given as an inset of Fig. 4.

4. Conclusion

Strong red and blue light emitting sheet-like Eu/CuO doped/codoped Gd_2O_3phosphors have been successfully synthesized via a low temperature combustion process. The XRD analysis confirmed the cubic phase Gd_2O_3 with some monoclinic CuO impurities. SEM images have shown sheet-like structures of the prepared phosphors with thickness in the nanometer range. Optical spectroscopy of the synthesized phosphors resulted in intense red and blue emissions upon a 325 nm laser excitation in the case of without and with CuO incorporation, respectively. The PL emission spectra have shown the emissions corresponding to Eu^{2+} and Eu^{3+} both which was affected by the CuO incorporation. The calculated colour coordinates of emitted radiation were found to be (0.60, 0.32), (0.21, 0.15), (0.18, 0.13) and (0.19, 0.14) in the case of without, 1 mol%, 3 mol% and 5 mol% CuO doping.

Acknowledgements

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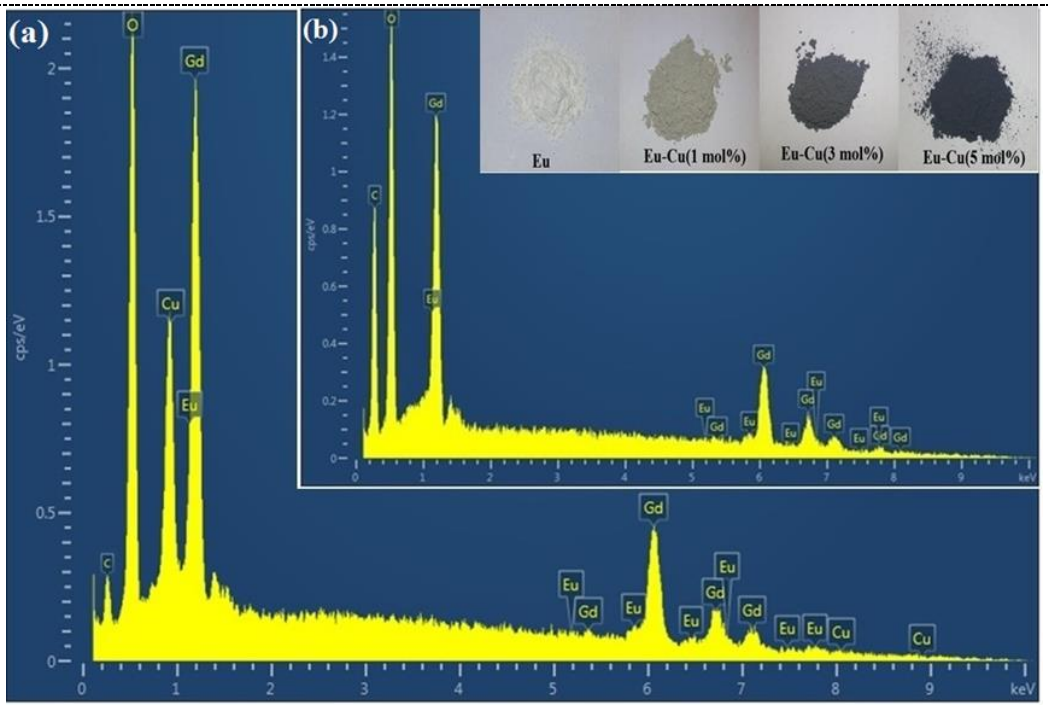

Figure 3. EDS images of the Gd_2O_3:Eu with (a) CuOand (b) without CuO nanosheets with their optical photographs as indicated.

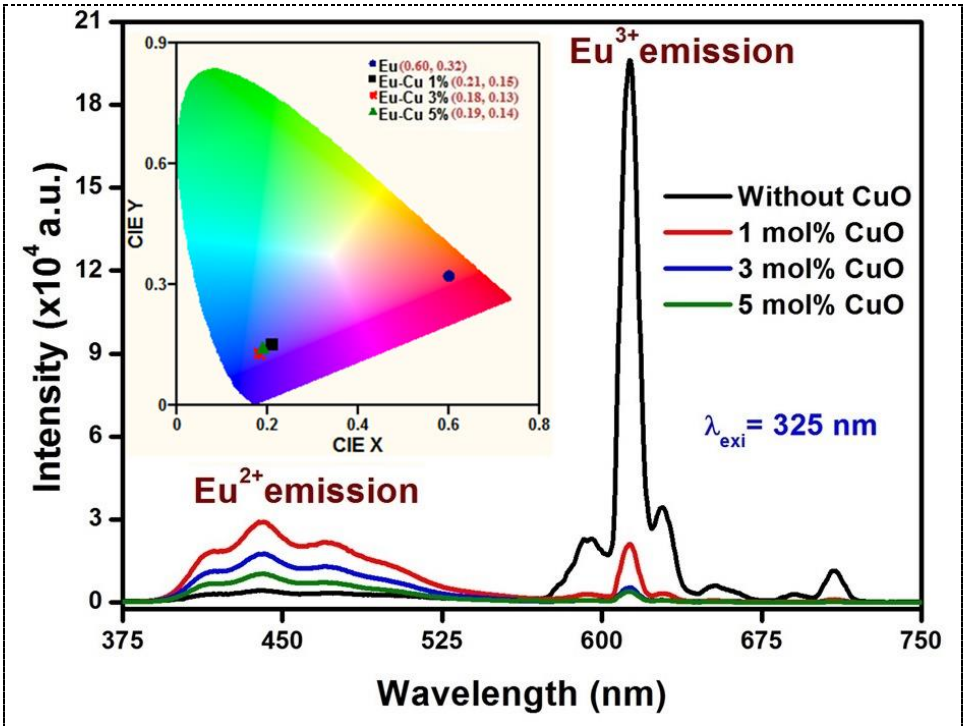

Figure 4. PL emission spectra of the Gd_2O_3:Eunanosheets with different CuO concentration and corresponding colour coordinates (inset).

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