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Site spectroscopy of Eu^{3+} doped- ZnS nanocrystals embedded in sodium carboxymethyl cellulose matrix

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ABSTRACT

The work investigates the incorporation of Eu^{3+} ion in ZnS crystal through spectroscopic studies. ZnS: Eu^{3+} nanocrystals was synthesized via the precipitation technique. Elemental composition analysis indicates a non-stoichiometric distribution between Zn and S. X-ray diffraction studies show lattice expansion demonstrating that Eu^{3+} ions were incorporated in the host lattice. Annealing temperature gave rise to lattice contraction relative to the as-synthesized indicating a partial expulsion of the ion from the crystal due to heat treatment. Eu^{3+} ions site symmetry probing from optical features show that trivalent europium were situated both at the nanocrystals surface and at the Zn^{2+} ion site. Weak energy transfer from host to activator ion occurred probably mainly through exchange interaction and the transfer process was defect mediated.

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1. Introduction

In recent years, nanostructured semiconductors have attracted considerable attention [1–3]. The most attractive features of nanostructured systems are their size and shape dependent optical properties [4–6]. Zinc sulphide is a wide band gap (3.60 *eV*) semiconductor that has been extensively used for many applications including cathode ray tubes, electroluminescence, solar cells and UV semiconductor lasers [7]. Beside the wide band gap, the relative ease with which the optoelectronic properties of this semiconductor can be tailored by controlling its shape and size has made it more attractive. Similarly, europium III ion (Eu^{3+}) has been widely studied because of its intense red line emission which makes it a strong candidate for applications as phosphors [8,9]. Therefore, it was expected that doping Eu^{3+} ion in ZnS nanocrystal would produce excellent red light emitting phosphor.

Based on this expectation, a number of research have been carried out to introduce Eu^{3+} ion into ZnS host, but the physical mechanisms responsible for the $^5D_0 \rightarrow {}^7F_2$ emission of the activator ion in this host has remain controversial [2]. There are still many open questions; the first one is the site occupancy of the activator ion in the host matrix given the large differences in the size and charge of Eu^{3+} (r = 95 p.m. for six coordination number) and Zn^{2+} (r = 60 p.m. in four-fold coordination for blende-type structures) ions [10,11]. The second question is whether indeed there can be energy transfer through the host to the activator ion given the energy mismatch between them, and the low phonon energy (350 cm^{-1}) of the host which is unlikely to assist in the energy transfer process [11]. The third open important question is the mechanism at the origin of the observed $^5D_0 \rightarrow {}^7F_2$ emission under the host excitation?

In this article, we have through detailed optical spectroscopic studies given explanation on the luminescence properties of Eu^{3+} -doped ZnS nanophosphors (capped sodium carboxy methyl cellulose) including the possible location of the activator ion in the host. The energy transfer process between the host ZnS and the Eu^{3+} ion was also investigated. Sodium carboxy methyl cellulose (CMC) is a polymer with two functional groups (R-OH and R-COO) which enables it to perform two important functions; first to stabilize and isolate the nanoparticles against aggregation during the growth process in the polymer matrix and second, to serve as a confined medium that protects the nanoparticles surface after

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drying. The advantage of the carboxy methyl cellulose matrix (CMC) is that it is a renewable matrix with large quantity of carboxyl groups in the polymer chain, which is capable of coordinating both the rare earth ion and the host cation.

2. Experiment

ZnS: Eu^{3+} nanophosphors capped with sodium carboxy methyl cellulose (CMC) were synthesized by the precipitation technique. All reagents used were of analytical grade and were used without further purification. In a typical synthesis, $ZnSO_4 \cdot 7H_2O$ (0.2 M) was mixed with 0.1464 g $EuCl_3.6H_2O$ (to obtain molar ratio of $[Eu^{3+}]/[Zn^{2+}]$ = 1mol%) in 100 ml of deionized water. The mixture was refluxed at the boiling point of water (100 °C) for 1 h and cooled to room temperature. This was followed by the addition of CMC and pH adjustment to the required value of 4.0. Then 100 ml of $Na_2S \cdot 9H_2O$ (0.2 M) was added drop wise with continuous stirring at room temperature. Stirring was continued after the last drop of S^{2-} precursor solution was added for another 15 min. A powdered sample was obtained by treating the precipitate through centrifugation and drying at 90 °C for 6 h. The same procedure was followed for the 5 mol% Eu^{3+} doping. For the purpose of optical characterization, small quantities of the freshly precipitated samples were dissolved in ethanol solution and spin-coated on a glass slide to obtain thin films. Both the powdered samples and their corresponding thin films were subjected to post-synthesis annealing in a sulfur-rich (sulfurizing) atmosphere. The annealing temperature was set to 300 °C with annealing time being 35 min. The precipitation reaction mechanism for the formation of ZnS: Eu^{3+} nanophosphors is given by equation (1);

$$Zn^{2+}_{(aq)} + Eu^{3+}_{(aq)} + S^{2-}_{(aq)} \xrightarrow{H_2O} ZnS : Eu^{3+} \downarrow \quad (1)$$

From the synthesis process described above, the formation of ZnS:Eu^{3+} in CMC matrix can be described as follows; the addition of zinc nitrate and europium trichloride to the CMC solution form Eu-CMC and Zn-CMC complexes through electrostatic interaction between Zn^{2+} and Eu^{3+} with the carboxylic and hydroxyl groups in the CMC matrix. The Zn^{2+} ions displaces two Na^+ ions at the $-COO^-$ head group. On the other hand, the Eu^{3+} ion can form a coordination to the CMC molecule in two ways; through ionic bonding with -COO^-, $Eu(OOC)_3$, and with O atom of -OH and ether bond $Eu(OC_2)_3$ [12], respectively. When Na_2S solution is added to the mixture, Zn^{2+} ions will react with S^{2-} ion to precipitate ZnS nanoparticles (NPs) within the CMC matrix while also forming some Eu-CMC complex. However, the formation of Eu − S bond is preferred to the Eu-CMC complex [13]. Therefore, Eu-CMC complex will dissociate as it gets nearer to the surface of ZnS NPs allowing the separated Eu^{3+} ion to be adsorbed on the surface of the NPs [13]. Sulfurization could lead to the formation of more ZnS nanoparticles, Eu_2S_3 or Na_2S with no possible coordination between S^{2-} and CMC. Probably, most of the CMC coordinated Eu^{3+} ions are further adsorbed on the surface of the nanoparticles due to the removal of carbon and oxygen at 300 °C.

All samples were studied by X-ray powder diffraction (XRD) measurements using PANalytic X'Pert PRO diffraction machine (Cu Kα). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) was carried out using Carl-Zeiss Scanning Electron Microscope. Absorption and photoluminescence spectroscopy were performed using JENWAY 6405 UV/VIS spectrophotometer and Jobin Yvon monochromatic coupled (ICCD) Camera with pulse laser (ESKPLA) as the exciting source, respectively. Other characterization techniques include Fourier Transform Infrared Spectroscopy (FTIR) using Perkin-Elmer ATE-FT-IR 100 spectrometer, and Perkin-Elmer STA 6000 Thermogravimetric analyzer.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows SEM images of as-synthesized and annealed samples of ZnS: Eu^{3+}, typical CMC and CMC with dispersed Eu^{3+} ions. The image of as-synthesized sample shows agglomerates with irregular shapes. After heat treatment, the particles became segregated with increased sizes. Un-doped CMC sample in Fig. 1(c) shows rod-like structures that are distinctively separated from one another, but this morphology changed into a compacted arrangement after doping with Eu^{3+} cations (Fig. 1(d)). It means that Eu^{3+} acted as a cross-linker between CMC molecules in a way that it filled up the spaces between the molecules. Table 1 shows the elemental quantification for as-synthesized and annealed ZnS: 5 mol% Eu^{3+} samples. The results show the presence of Zn, Eu, and S elements in a non-stoichiometry ratio and with no impurities (except oxygen) recorded. Since the XRD patterns (see following discussion) show pure phase zinc blende structure of ZnS for all the samples except the annealed 5 mol% Eu^{3+} doped sample, the oxygen may come from; adsorbed water on the samples surfaces, from the coordinated oxygen in the CMC matrix or from the measurement environment.

Fig. 2 shows X-ray diffraction patterns of as-synthesized and annealed ZnS: Eu^{3+} nanoparticles capped with sodium carboxymethyl cellulose (CMC). All samples display three broad diffraction peaks which are indexed to the (111), (220) and (311) reflexions of cubic zinc sulphide structure with a space group of $F\bar{4}3m$ in accordance with JCPDS card no. 800020. In addition to these peaks, the heat treated sample with 5 mol% Eu^{3+} ion has others 2θ peaks situated at 19.08, 28.91, 32.16, 33.89, 38.17 and 48.78°. Previously, we reported these peaks to originate from ZnO, $Zn(OH)_2$, $ZnSO_4$, adsorbed water or Eu_2O_3 [14,15]. However, since some of these peaks appear to be shifted, and fitted well the JCPDS card no. 390859, we believe they may be due to the emergence of $ZnEu_2O_4$ phase after heat treatment. Peaks at 33.89° and 38.17° are indexed to the (200) and (331) planes of the cubic ZnS based on the above. The other peaks are chronologically indexed to the (200), (300) (311), (400) and (422) reflexions of $ZnEu_2O_4$. Stress induced by size/charge mismatch from Eu^{3+} ion doped crystal may create crystal instability which could lead to phase segregation as observed in this work. High doping concentration and heat treatment may also increase the instability in the system thereby enhancing this phase segregation in the case of the annealed 5 mol% Eu doped samples. Another observation from Fig. 2 is the broadened diffraction peaks which suggests small crystallites [16]. Crystallite sizes, D_{hkl} were calculated from the (111) peak of each sample by using the Scherrer equation:

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad (2)$$

where β_{hkl} is the full width at half the maximum height of the *hkl* plane, θ_{hkl} is diffraction angle of (111) plane and λ is the wavelength of incident Cu Kα X-ray. The results of crystallite sizes, lattice constant, d-spacing and unit cell volume are presented in Table 2. Comparing the calculated lattice parameters with those of bulk ZnS from standard JCPDS file no. 80020, and with values obtained by Pal et al. for ZnS: Eu^{3+} nanoparticles [17], it is clear that the unit cell volume shows significant expansion along crystal planes. Following the opinions of [18,19], since Eu^{3+} ion (r = 95 p.m. for 6-coordination number) has a larger ionic size than the substituent

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