Luminescence Properties of Cu Doped CaF_2 Nanostructure

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Abstract : Nanostructures of calcium fluoride (CaF_2) doped with Cu was synthesized by the co-precipitation method and studied for their photoluminescence (PL) properties. The PL emission spectrum of pure CaF_2 nanostructure has a broad band in the 370–500nm range. Similar spectra was observed in case of Cu doped sample. The SEM and XRD pattern shows that a mixture of spherical and cubic shape structures. These structures have size in the range of 20-80nm.

Keywords: CaF_2, Nanostructure, Photoluminescence, PL.

I. Introduction

Nanoscale materials or nanostructures have attracted huge attention due to their unique properties. They have a potential to be used in a variety of applications. A large number of individuals and research groups from different fields have produced different nanomaterials and studied their properties. These include structural, optical, electrical, magnetic, mechanical, and dosimetric properties [1–5]. Many methods of preparations have also been developed in the last two decades, where different nanostructures like nanoparticles, nanocubes, nanowires, nanorods, and so forth, of several materials have been produced [6]. Recent investigations have showed that the optical, luminescent, and other properties can be modified by the shape and size of the nanostructures. The role of impurities in the host of these nanostructure is another parameter that can be used to modify their properties [7-9].
For huge applications, it is irrelevant whether the luminescence is fluorescence or phosphorescence. Either way the current range of applications is extensive. The thermoluminescence of CaF2 :Mn, a material that was very broadly used in subsequent as a TL dosimeter. The many powdered crystal phosphors that are normally nonelectroluminescent, become electroluminescent if they are mixed with suitable powdered metals or with some nonmetals of good electrical conductivity. Lehmann described the effect of contact electroluminescence in which nonelectroluminescent phosphors become electroluminescent by mechanically mixing them with suitable powdered metals. Calciumfluoride (CaF2) is a wide band gap material with a large-scale transparency. Therefore, color center formation is possible just by irradiating CaF2 by ionizing radiation [10-12]. The material has a relatively lowZeffective, making it suitable for ionizing radiations used in radiotherapy. It was reported that this material is suitable as a laser material particularly, when doped with rare earth elements [13-15].The nanostructure form of CaF2 was synthesized by different methods [16-19]. However, the TL and PL properties of this nanomaterial have not been well studied. Few studies were focused on the effect of different dopants on its optical properties [12-15]. In this work, Cu doped CaF_2 nanopowder was synthesized by the chemical co precipitation method. Synthesized nanomaterials was characterized by XRD, SEM, and PL.

II.Experimental

Cu doped CaF_2 nanocrystalline samples was synthesized by the chemical co precipitation method. The samples of CaF_2 was synthesized by using water and ethanol as solvents at a ratio of 1 :1.The desired concentration of calcium chloride (CaCl2) was dissolved in triply distilled water. The normality of the solution was kept at 0.2N. This solution was mixed with ammonium fluoride (NH4F) solution (has a normality of 0.2N). The solution of ammonium fluoride was added to that of calcium chloride dropwise with continuous stirring magnetically. The formed precipitate was filtered out and washed with distilled water and ethanol several times. The resulting powder samples, thus obtained, were dried at 70^0C in an oven for 3 hours. The used chemicals in this experiment are highly pure and were of AR grade. The dopants used in this study were incorporated in their chloride forms. A typical concentration of these impurities, that is, 0.2mole%, is used The morphology of these samples was studied by a field emission scanning electron microscopy (FESEM), JSM-7500 F Photoluminescence (PL) emission spectra were recorded at an excitation wavelength of 275 nm using a fluorescence spectro-photometer, Hitachi F-4000.

III. Results and Discussion

Figure 1 shows SEM images at different magnifications ((a) and (b)) of pure CaF_2 sample. These images show a mixture of spherical and cubic shape structures. These structures have sizes in the range of 20–80nm.The produced nanostructures have a good particle size distribution. As mentioned in Section 2 that the used compounds of $CaCl_2$ and NH_4F were dissolved in water: ethanol mixture at a ratio of 1 : 1. This ratio was found to provide small nanostructures, while other ratios showed bigger particles.

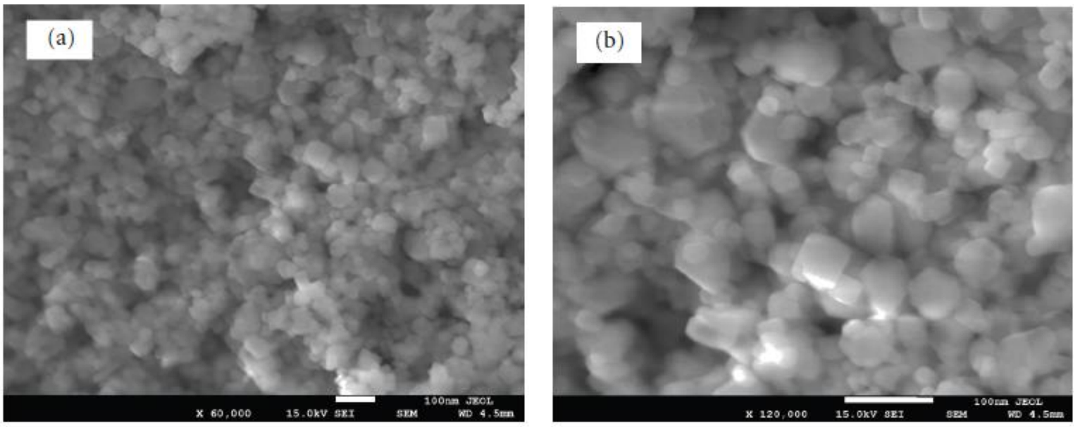

Figure 1: SEM images of the as-synthesized CaF2 nanostructures taken at different magnifications

Figure 2. The PL emission spectra of the as produced nanostructures of pure (curve (a)) and doped CaF2 samples . As mentioned above, the samples of CaF2 nanostructures were doped with Cu+ at a concentration of 0.2mole% and their PL result is shown in curves (b). Pure sample (curve (a)) shows a broad band in the 370–500 nm range. This band might be induced due to the formation of color centers. These centers perhaps could be created by oxygen defects within the host of CaF2.

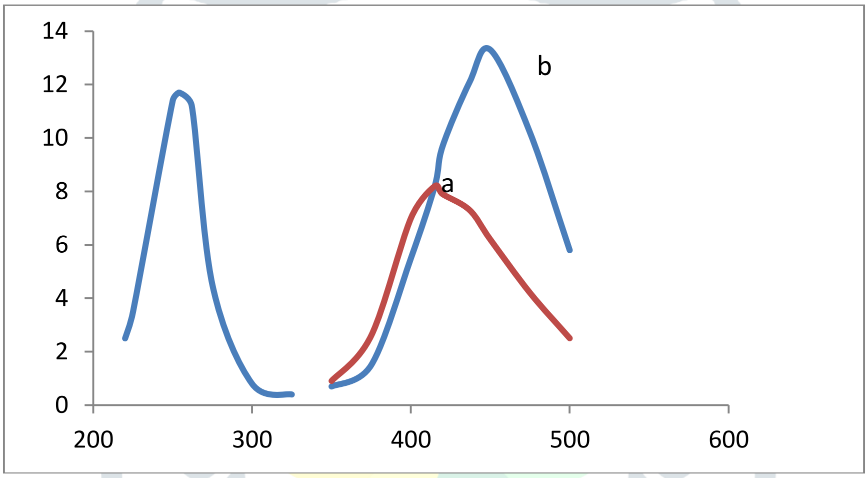

Figure 2: PL emission spectra of the as-synthesized nanostructures of pure and doped CaF_2 samples, doped with 0.2 mole%.

It has been reported that oxygen defects (contaminations) can induce such emission bands, but at the higher wavelength side of the visible region. In the present CaF_2 nanostructures, reducing the particle size could shift the emission bands to the lower wavelength, which might be due to a widening induced in the band gap of the material. The PL emission spectra of Cu doped sample shown in Figure are almost similar to that of pure CaF_2 (curve (a)), but with a slight PL enhancement.

Figure 3 shows XRD pattern of the as-synthesized pure CaF2 sample.

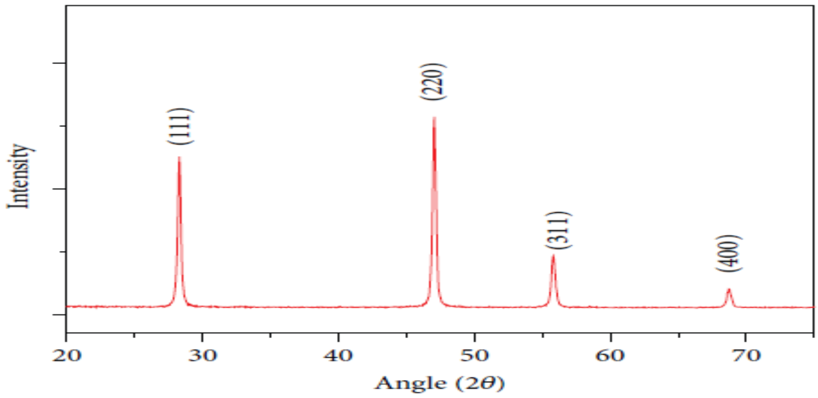

Figure 3: XRD pattern of the as-synthesized CaF2 nanostructures.

Several diffracted peaks can be seen with hkl values indicating a complete crystalline structure in a cubic phase (JCPDS Card number 87-0971). The displayed peaks correspond to values (1 1 1), (2 2 0), (3 1 1), and (4 0 0). The XRD pattern presents broad peaks revealing the small crystallite size of the synthesized samples. This result is similar to that reported in the literature [20]. The nanocrystalline size was calculated using Scherer's formula and found to be around 35 nm. This value is close to that observed by SEM (Figure 2). XRD of the doped samples was also studied, but the result is similar to that of pure CaF_2 nanostructure.

IV.Conclusions

CaF_2 nanocrystalline samples were synthesized by the chemical coprecipitation method. SEM images of CaF_2 sample show a mixture of spherical and cubic shape structures. These structures have sizes in the range of 20–80nm.The produced nanostructures have a good particle size distribution .PL emission spectra result shows a broad band in the 370–500 nm range. The nanostructures have attracted huge attention in the last two decades due to their unique properties. They have a potential to be used in a variety of applications.

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