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Synthesis and optical characterization of CeF_3: Al^{3+} nanoparticles

A. Mochasebeh musa [a,*], M. Zahedifar [a,b], E. Sadeghi [a,b]

[a] Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan, I.R. Iran
[b] Physics Department,University of Kashan, Kashan, I.R. Iran
* a.moghadam71@yahoo.com

Abstract: Aluminum doped cerium fluoride (CeF_3:Al^{3+}) nanoparticles were successfully synthesized by co-precipitation method. Optical properties were analyzed using X-ray diffraction pattern (XRD)، field emission scanning electron microscopy (FE-SEM), photoluminescence spectroscopy (PL) and absorption spectroscopy (UV-vis). The crystalline size of approximately 20 nm with hexagonal structure were identified from XRD pattern which is in accordance with (FE-SEM) image. Photoluminescence spectrum under excitation with wavelength of 300 nm has two peaks at 462 and 549 nm. Band gap was also obtained using absorption spectrum and was compared with that of pure cerium fluoride crystalline which revealed lower band gap for (CeF_3: Al^{3+}). Luminescent properties are given by 5d → 4f transitions enabled by $4f^15d^0$ electron configuration of the valence shell of Ce^{3+} ions.

Keywords: Cerium fluoride, Photoluminescence, Nanoparticles, Band gap, Absorption spectrum, Co-precipitation.

Introduction

The members of the family of lanthanides are called rare earth elements that have the same chemical and physical characteristics. The trivalent ion of lanthanides has unique characteristics that is result of F-F transitions within 4f electron layer of those hosts. Due to its photophysical and biological characteristics, it is widely used in biochemical fields. Compared with the conventional oxide-based luminescent materials, fluorides are advantageous as fluorescent host materials owing to their low vibrational energies, and the subsequent minimization of the quenching of the excited state of the rare-earth ions [1]. The main advantage of two groups of materials including quantum dots and added lanthanides as semiconductor solid nanomaterials is that they are organic fluorescent compounds. For this reason, lanthanides seem to be adding minerals to all the needs of modern industrial and medical applications, New light sources, light detectors document security and bio-indicators [2]. Cerium fluoride single crystal was studied intensively in 1990. It is known as phosphorus which has been widely studied in various fields. Its luminescence feature is due to electron transfer from 5d-4f. Due to high chemical stability; its luminescence can be characterized by high quantum yield, low phonon energy and relatively large Stokes shift. Changes in CeF_3 luminescence spectrum can be made by selecting an ion as an impurity in crystals [3]. The energy transfer process that is from Ce^{3+} can be transmitted by creating a defect in the crystalline lattice. Therefore, reducing the number of defects or removing created defects and stopping energy transmission is one of the important factors for changing the optical efficiency [4]. Cerium fluoride forms in a triangular crystalline with the group of space P3C1 (D3d). Cerium ions in crystalline CeF_3 are surrounded by 9 anions of fluorine and have a symmetric C_2 site [5]. Ce^{3+} ions can be used as a sensitizer as they possess high absorbance coefficient due to allowed 4f–5d transitions [6-9]. There are various types of nano structural growth (CeF_3) made by changing the morphology of the nanoparticles or the nucleoside method. In this study, the production of cerium fluoride nanoparticles (CeF_3) made by co-precipitation method and the effect of impurities on its photoluminescence have been investigated.

Materials and method

Cerium fluoride was synthesized by co-precipitation method. For this purpose, three products of cerium nitrate, ammonium fluoride, aluminium nitrate and methanol, all from a merck company with a high degree of purity were used. Initially, 2 mmol of $Ce(NO_3)_3$ was solved in 20 cc methanol on a magnetic stirrer. Solution of ammonium fluoride was made with 6 mmol NH_4F and 10 cc methanol at 60°C. Aluminium nitrate solution was prepared by solving 0.5% molar ratio aluminium nitrate in 10 cc methanol. After preparing a homogeneous solution, aluminium nitrate was added drop wise to the cerium nitrate solution. Afterwards, the third solution was added. The final solution was placed on a magnetic stirrer for 1 hour until a cerium fluoride deposit was formed. After this step, in order to separate impurities from the sediment, the solution washed in a centrifuge machine for several times and was placed in the oven at 180°C for 2 hours. The final product is a white powder of aluminium doped cerium fluoride.

Results and Discussion

The $CeF_3:Al^{3+}$ nanoparticles were examined by XRD with an analytical device, under a wavelength of 0.154 nm. From Figure 1 it is seen that crystalline cerium fluoride with a hexagonal structure and a spatial group of p3c1 (D3d) is formed which is in agreement with the reference 0045-18 card number. The size of the nanoparticles is obtained from the Debye- Scherer relation in which λ is the wavelength of the incident beam, k is a constant and β is full width at half maximum (FWHM).

$$D = \frac{k\lambda}{\beta \cos(\theta)} \quad (1)$$

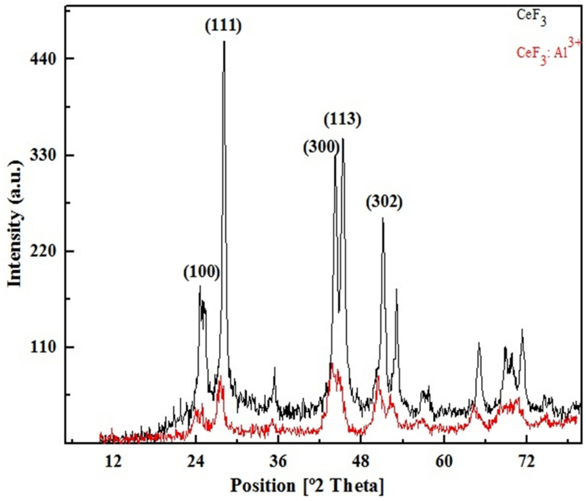

Fig. 1. XRD patterns of the CeF_3 and CeF_3: Al^{3+} nanoparticles.

The calculated size for nanoparticles is approximately 22 nm. A slight change in XRD pattern is due to presence of impurities in the crystalline structure. The second analysis of FE-SEM shows that the shape and size of the particles located on the surface. This analysis for cerium fluoride nanoparticles with aluminium impurities is shown in Fig. 2. Homogeneity and uniformity of crystalline cerium fluoride are evident in this figure. The nanoparticle`s size was identified to be approximately 18 nm which matches the size obtained from the XRD spectrum.

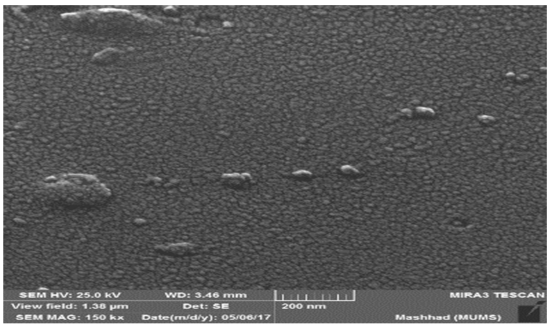

Fig. 2. FE-SEM image of the $CeF_3:Al^{3+}$ nanoparticles.

Photoluminescence spectrum of CeF_3 from 5d- 4f in Ce^{3+} ion has been observed at 380 nm [10].The absorption and emission transitions of Ce^{3+} are allowed electric-dipole transitions between the electronic states, for which the wave functions have opposite parities. This result occurs in a very high absorption coefficient and a fluorescence life span of about 8 to 10 seconds [11].

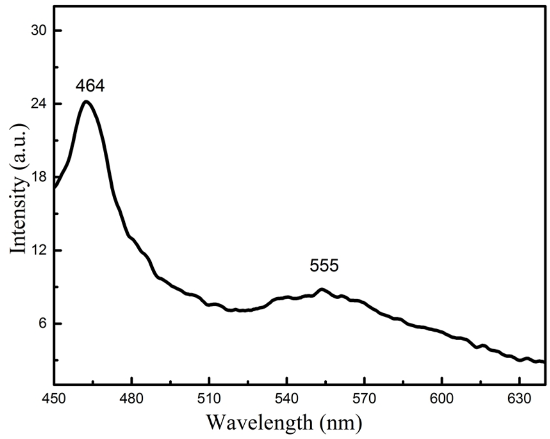

Fig 3. PL emission spectrum of CeF_3: Al^{3+} nanoparticles.

In Figure 3 the emission at 464 nm is due to the presence of aluminium in the crystal which shifts the emission peaks of CeF_3 [12]. The size of nanoparticles plays an important role in changing the features of UV absorption spectrum. In addition, it is a powerful method for investigating the optical properties of semiconductor nanoparticles [12]. In general, UV absorption is related to electron transport from the occupied to higher empty levels [13]. As seen in figure 4, the aluminium impurity transmits the peaks to shorter wavelengths. The initiation of CeF_3 absorption from 4f-5d level is below 280 nm wavelength [14]. The presence of impurities in nanoparticles causes a change in the band gap. The band gap of the nanoparticles was calculated using the absorption spectrum by Tauc relation:

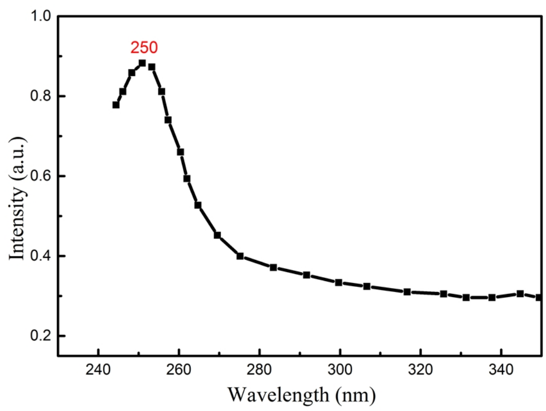

Fig. 4. UV spectrum of CeF_3: Al^{3+} nanoparticles.

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (2)$$

α is the absorption coefficient and n= 1, 4 which refers to the direct or indirect transitions which in cerium fluoride it is direct, so n =1 [15]. In Figure 5 band gap is shown for

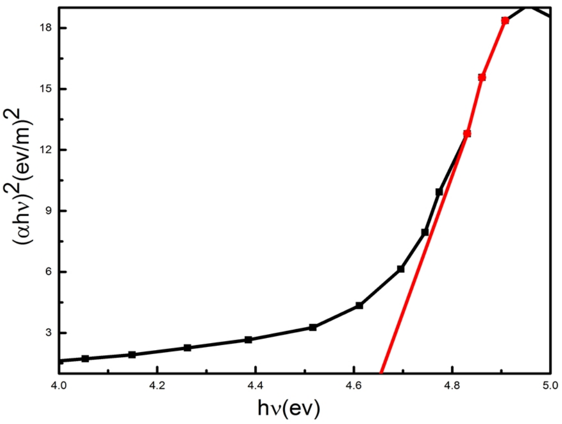

Fig. 5. Energy band gap of the CeF_3: Al^{3+} nanoparticles.

cerium fluoride with aluminium impurity. It is observed that the presence of impurity decreases the band gap. This reduction can be compared with the band gap of bulk cerium fluoride which lies between 4.9 and 4.65 eV **[**15**]**.

Conclusions

In this study cerium fluoride nanoparticles doped with aluminum were synthesised by co-percipition method and the effect of impurity on optical properties was investigated. By comparing the XRD spectrum of CeF_3 and CeF_3: Al^{3+}, it was observed that aluminum reduces the peak intensity. The aluminum-induced emission spectrum was also observed at 464 nm. The absorption spectrum was affected by presence of defects created in the crystal due to impurity. The band gap of these nanoparticles was reduced by adding Al impurity to the host cystal.

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