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Synthesis and Photoluminescence study of $LaF_3:Gd^{3+}$ phosphors for Phototherapy Application

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Abstract

The narrowband UVB emitting phosphor LaF_3 doped with various concentration of Gd^{3+} ions were successfully synthesized by wet chemical synthesis method with RAP (Reactive Atmospheric process). The crystal structure and the phase purity of samples were characterized using powder X-ray diffractometer. Crystallographic data obtained for LaF_3 phosphor matches well with the reported data. Gd^{3+} ions were successfully incorporated in the LaF_3 host lattice separately and their photoluminescence properties were analyzed at room temperature. The Phosphor shows sharp and intense emission at 311 under the excitation of 275 nm due to $^6P_J \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} ions. Optimum concentration of Gd^{3+} ions in the prepared phosphor was found to be 0.04 mol. For this concentration the critical distance R_0 was calculated to be 13.78Å.

Keywords: Wet Chemical Synthesis, Photoluminescence, XRD, Narrowband UVB

1. Introduction

The UV radiation differentiated as per their Biological and Physical characteristic and divides into three parts such as UV-C: the rays that do not pass through the earth's atmosphere (200-290 nm) UV-B: the rays responsible for nearly all biological effects following sun light exposure including tanning, burning and skin cancer, (290-320 nm) and UV-A: those rays closest to the visible spectrum that pass through glass and are the least harmful to the skin (320-400nm).

Recently the treatment of skin diseases using artificial sources of ultraviolet (UV) radiation in controlled condition is well established. UV therapy is useful for treating more than 40 types of skin diseases and disorders such as psoriasis [1], or vitiligo [2], which could be treated by UV-B radiation, and lichen sclerosus [3], morphea [4] scleroderma [5], cutaneous T-cell lymphoma, lupus erythematosus [6], which could

be treated by UV-A radiation. In the treatment of hyperbilirubinemia [7], commonly known as infant jaundice. The basis of phototherapy is believed to be the direct interaction of light of certain frequencies with tissues to cause a change in the immune response. In the treatment of skin diseases, few methods are currently used: phototherapy with narrowband UVB (310 - 313 nm) and photochemotherapy PUVA, with UVA (365 nm) and psoralens as photosensitizers. In 1976, Fischer published a study wherein he evaluated the "healing" effects of 313, 334, 365, and 405 nm light on psoriasis. He concludes that, 313 nm light exerted a potent clearing effect on psoriasis than the longer wavelength [8].

Over the last decade, lanthanide doped fluorides (LnF_3) have been intensively studied as promising luminescent materials. LnF_3 are featured with low phonon energy of the crystal lattice (e.g. LaF_3 = 350 cm^{-1}), resulting in a relatively high QY of luminescence and diminished nonradiative relaxation of their excited states. Fluoride materials captured the attention due to their properties such as reasonably high thermal conductivity, good enough mechanical hardness, and high chemical stability, multicolor luminescence [9], long radiative lifetimes (several ms) [10], invariable luminescence in time [11], low cytotoxicity, well defined crystal structures and possibilities of easy surface modifications. Zhang et al., has reported that the UC emission of Ho^{3+} was changed from green to red in cubic phase $NaYF_4$: Yb^{3+}/Ho^{3+} NCs by introducing Ce^{3+} [12].

The Yttrium fluoride (YF_3) phosphor has been studied since the 1969's, that shows YF_3 is an ideal host for optically active rare earth's (RE's) mostly because of its low phonon energies (530 cm^{-1}) and a wide band gap (10.5 eV), which diminish the probability for non-radiative relaxation [13, 14]. M. Domineberges et al. reported the optical study of Ce^{3+} ion in YF_3 phosphor [15]. Pankratov *et al.*, has reported the intrinsic spectroscopic properties of YF_3 phosphor have been investigated for scintillation applications [16]. Yan et al. have successfully synthesized Eu^{3+} doped yttrium hydroxide fluoride mesocrystals by facile hydrothermal route to explore the possible application in optical thermometry [17].

The Lanthanum fluoride phosphor possesses a large band gap (10.1 eV), is an ideal host for studying Ce^{3+} fluorescence for scintillators because the 4f and 5d levels of cerium are located in the gap of the host lattice [18]. R.E. Kroon et al. has reported the decay study and energy transfer mechanism of Ce^{3+} and Tb^{3+} ions in LaF_3 phosphor [19]. Guss *et al*. [20] fabricated LaF_3: Ce^{3+} nanoparticles mixed with oleic acid and characterized their optical, physical, and radiation detector properties.

2. Materials and Methods

2.1. Synthesis Method

The phosphors LaF_3:Gd^{3+} were successfully prepared by wet chemical synthesis method with RAP (Reactive Atmospheric process). The precursors chemicals La_2O_3 (99.99 %, AR), Gd_2O_3 (99.90 %, AR) and Hydrofluoric acid used for synthesis of phosphor. The detail of molar ratio of each precursor used for phosphor synthesis is given in Table 1.

The starting materials were taken in a proper stoichiometric ratio mixed together in a Teflon beaker. A small quantity of double distilled water (D.W.) was added and paste was formed. After that, the solution of HNO_3 was added drop by drop and mixture was simultaneously heated slowly at 80ºC, till the completely

clear homogeneous solution was obtained. The solution was further heated to remove the excess of nitric acid. Little quantity of double distilled water was again added. The resulting solution was considered as $La(NO_3)_3$:Gd^{3+}. Later, the Hydrofluoric acid (HF) was added drop by drop in solution using syringe to get precipitate. Filtered the precipitate and washed by DDW few times and then dried under an infrared (IR) lamp. The dried powder was finally heated at 500°C for 1 hr.

Table 1. Molar Ratio of each precursor used for synthesis

Sr. No.	Products	Corresponding reaction with balanced molar ratios of precursors
1	$La_{(1-x)}F_3$: $_xGd^{3+}$	$_{(1-x)}La_2O_3 + HF + {}_xGd_2O_3$ {In stock solution form 1gm = 100ml} $\xrightarrow{\Delta}$ $La_{(1-x)}F_3$: $_xGd^{3+}$ + Gaseous products (H_2O, fluorine acid and NO_2) (x = 0.002, 0.005, 0.01, 0.03 and 0.04) Δ (Heating) at 500°C for 1 h.

2.2. Characterizations

The phase purities of LaF_3:Gd^3 samples were studied using Rigaku miniflex II X-ray Diffractometer with scan speed of 4.0°/min and Cu Ka (k = 1.5406 Å) radiation. Photoluminescence properties were measured on (Hitachi F-7000) fluorescence spectrophotometer at room temperature. The parameters such as spectral resolution, width of the monochromatic slits (1.0 nm), photomultiplier tube (PMT) detector voltage and scan speed were kept constant throughout the analysis of samples.

3. Results and Discussion

3.1. XRD Analysis

The diffraction pattern is usually used to identify the crystal structure and the phase purity of the sample. **Fig. 3.1** show the powder X-Ray Diffraction patterns of LaF_3:Gd^{3+} sample prepared by using wet chemical synthesis method. The XRD pattern for LaF_3:Gd^{3+} agrees well with the ICDD file no. **(00-032-0483)**. This agreement indicates that the material was successfully prepared using the wet chemical synthesis method. The crystal structure of the prepared materials can be refined to be Hexagonal, with lattice parameter a = 7.187 Å, b = 7.187 Å, c = 7.350 Å.

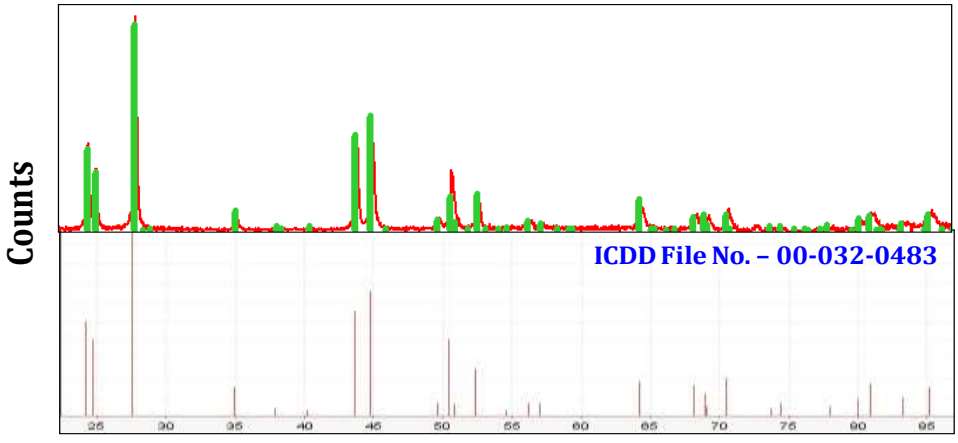

Fig. 1. X-ray diffraction pattern of LaF_3 phosphor.

3.2. Photoluminescence Spectra

3.2.1. PL measurement of $LaF_3:Gd^{3+}$ phosphors

Fig.2. represented the excitation and emission spectra of $LaF_3:_xGd^{3+}$ (x = 0.005, 0.01, 0.02, 0.03 and 0.04) phosphors. The double shoulder excitation peak observed at 272 nm - 282 nm maximum at 275 nm corresponding to $^8S_{7/2} \rightarrow {}^6I_J$ transition of Gd^{3+} ions. Under the excitation of 275 nm phosphor shows intense and sharp Narrow Band UVB (NB-UVB) emission at 311 nm corresponds to the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions of the Gd^{3+} ions. There was weak line was observed at 307 nm due to the $^6P_{5/2} \rightarrow {}^8S_{7/2}$ transition of the Gd^{3+} ions.

In addition, the emission intensity of phosphor increases with increasing concentration of an activator (Gd^{3+} ions) and achieve a maximum intensity for the concentration of 0.04 moles of Gd^{3+} ions. For LaF_3 system the quenching phenomena were not observed upto the 0.04 mol concentration of Gd^{3+} ion.

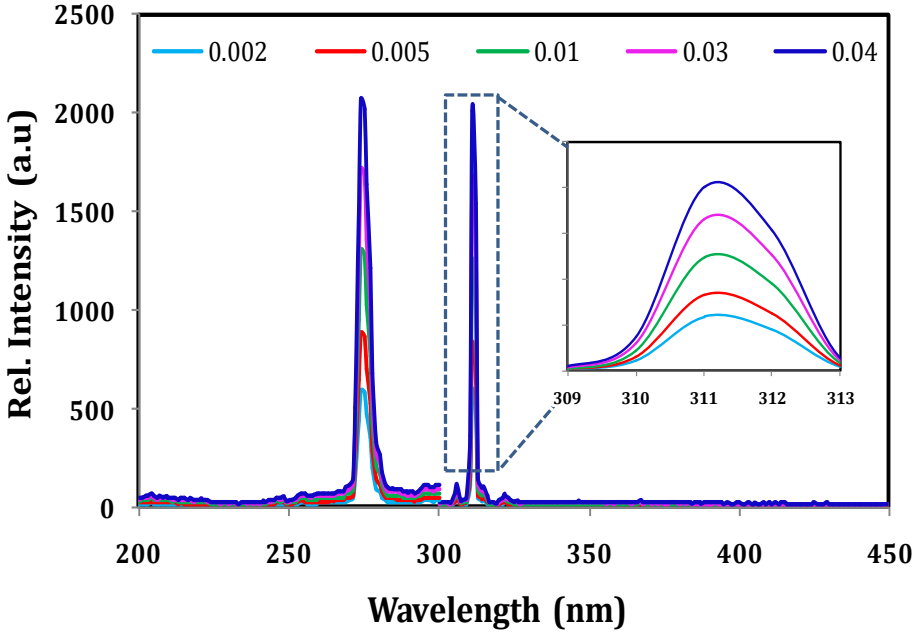

Fig. 2. Excitation and Emission spectra of $LaF_3:_xGd^{3+}$ (x = 0.002, 0.005, 0.01, 0.03, 0.04) phosphors.

According to Blasse, the average shortest distance between nearest activator ions is equal to the critical transfer distance (R_C). On other hand the critical distance (R_C) was nothing but the critical separation between donor (activator ion) and acceptor (quenching ion), at which the non-radiative rate equals that of the internal single ion relaxation. Hence the critical distance was calculated using the following equation,

$$R_C \approx 2 \times \left(\frac{3V}{4\pi x_c N} \right)^{\frac{1}{3}}$$

Where, V is the volume of the unit cell (in A^3), χ_C is critical concentration and N is the number of La^{3+} ions in the unit cell. By taking the value of above said parameters from the experimental results and the crystal structure of the compound LaF_3, the value of χ_C= 0.04, N= 6 and V= 328.80 $Å^3$, the critical distance R_C of LaF_3 doped with Gd^{3+} phosphor is calculated to be about 13.78 Å.

4. Conclusions

The inorganic narrow UVB emitting $LaF_3:Gd^{3+}$ phosphor was intentionally and successfully prepared by wet chemical synthesis method with RAP method which is low cost, low temperature and not required any other additive for initiation synthesis process. Photoluminescence properties in the UV region, which is used for phototherapy lamps, are studied. The XRD pattern of prepared sample found in agreements with the respective ICDD file no. **(00-032-0483)** and found to be in complete crystalline nature.

The photoluminescence spectra specify that the $LaF_3:Gd^{3+}$ gives sharp narrow UVB emission i.e. 311 nm under the 275 nm excitation attributed to $^6P_{7/2} \rightarrow {}^8S_{7/2}$ optical transition of Gd^{3+} ion. This narrow band UVB emission is of importance in medical phototherapy, biological agent detection, sterilization, and covert communication. The study of spectroscopic data has demonstrated that, with an increase in the concentration of gadolinium, the luminescence intensity of Gd^{3+} ions increase upto the 0.04 mol concentration of Gd^{3+} ion. Hence, we can conclude that $LaF_3:Gd^{3+}$ phosphor is useful for phototherapy lamp application because of its intense emission at NB-UVB region (311±2 nm).

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6. References

[1] Honigsmann H, Brenuer W, Rauschmeier W. Photochemotherapy for cutaneous T cell lymphoma. A follow-up study. *Am. Acad. Dermatol.*, 1984, **10:** 238.

[2] Scherschun L, Kim J J, Lim W H. Narrow band ultraviolet B is a useful and well tolerated treatment for vitiligo. *J. Am. Acad. Dermatol.*, 2001, **44:** 999.

[3] Kreuler A, Jansen T, Stucker M, Herde M, Hoffmann K, Altmeyer P, Vonkobyletzki G. Low-dose ultraviolet-A1 phototherapy for lichen sclerosus et atrophicus., *Clin. Exp. Dermatol.* 2001, **26:** 30.

[4] Hawk J L M, Sunbeds. *Radiat. Prot. Dosim.*, 2000, **91:** 143.

[5] Morita A, Kobayashi K, Isomura I, Tsuji T, Krutmann J. Ultraviolet A1 (340–400 nm) phototherapy for Scleroderma in systemic sclerosis . *J. Am. Acad. Dermatol.*, 2000, **43:** 670.

[6] Millard T P, Hawk J L M. Ultraviolet therapy in lupus. *Lupus*., 2001, **10:** 185.

[7] Dani C, Martelli E, Reali M F, Bertini G, Panin G, Rubaltelli F. Fiberoptic and conventional phototherapy effects on the skin of premature infants. *J. Pediatr.*, 2001, **138:** 438.

[8] Fischer T. UV-light treatment of psoriasis. *Acta. Dermatovener (Stockh).*, 1976, **56:** 473.

[9] N. Guo, Y. Song, H. You, G. Jia, M. Yang, K. Liu, Y. Zheng, Y. Huang, H. Zhang Eur. J. Inorg. Chem. 72 (2010) 4636.

[10] Pankratov, V., Kirm, M. and von Seggern, H., 2005. Intrinsic luminescence in yttrium trifluoride. J. Lumin. 113, 143-150.

[11] R. E. Kroon, H. C. Swart, O. M. Ntwaeaborwa, H. A. A. SeedAhmed. Physica B 439 (2014) 83–87.

[12] G. Y. Chen, H. C.Liu, G. Somesfalean, H. J. Liang, Z. G. Zhang, Nanotechnology. 20 (2009) 385704.

[13] Rast, H.E., Caspers, H.H. and Miller, S.A., 1969. Lattice vibrations and infrared properties of yttrium fluoride. Phys. Rev. 180, 890

[14] Krupa, J.C. and Queffelec, M., 1997. UV and VUV optical excitations in wide band gap materials doped with rare earth ions: 4f-5d transitions. J. Alloys Compd. 250, 287-292.

[15] Domineberges, M. and Loriers, J., 1985. Luminescence of trivalent cerium in yttrium fluoride YF_3.Comptes Rendus De L Academie Des Sciences Serie II 301, 915-918.

[16] Pankratov, V., Kirm, M. and von Seggern, H., 2005. Intrinsic luminescence in yttrium trifluoride. J. Lumin. 113, 143-150.

[17] G. Murali, B. Lee, R. Mishra, J. Lee, S. Nam, Y. Suh, D. Lim, J. Lee, S. Lee, Synthesis, luminescence properties and growth mechanisms of YF3: Yb3+/Er3+ nanoplates. J. Mater. Chem. C 3, 10107 (2015)

[18] A. Canning, A. Chaudhry, R. Boutchko, and N. Grønbech- Jensen, Phys. Rev. B 83, 125115 (2011).

[19] R. E. Kroon, H. C. Swart, O. M. Ntwaeaborwa, H. A. A. Seed Ahmed. Physica B 439 (2014) 83–87.

[20] P. Guss, R. Guise, D. Yuan, S. Mukhopadhyay, and R. O'Brien, J. Appl. Phys. 113, 0643031 (2013).