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Synthesis and Luminescence Characteristics of Gd^{3+} Activated $LiCa_4(BO_3)_3$ Phosphor

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Abstract

$LiCa_4(BO_3)_3$ doped Gd^{3+} phosphor was successfully and intentionally synthesized by the modified conventional solid state diffusion (SSD) method. The phase purity of sample was characterized by powder X-ray diffraction (XRD). The photoluminescence (PL) property was studied using a Hitachi F-7000 spectrophotometer at room temperature. The sample $LiCa_4(BO_3)_3$: Gd^{3+} show intense narrow UVB emission of Gd^{3+} at 314 nm (corresponds to $^6P_J \rightarrow {}^8S_{7/2}$) under the excitation of 275 nm. The emission spectrum of the phosphor is observed in the UV region and hence the phosphor can be potential candidate for medical applications.

Keywords: Narrow UVB, XRD, Photoluminescence.

Introduction

The use of artificial source of ultraviolet radiation is well recognized for the UV therapy[1,2]. It has been reported that UV therapy is useful for treating more than 40 types of skin diseases and disorders such as such as psoriasis[3], or vitiligo[4], morphea[5], hyperbilirubinemia[6] usually known as infant jaundice was treated by using UV radiation.

The skin disorders such as Psoriasis, Vitiligo, Atopic dermatitis etc have been alternatively treated using narrow UVB phototherapy. The UVB spectrum further divided as narrowband ultraviolet B (N-UVB) and broadband ultraviolet B (B-UVB). B-UVB radiation was one of the choices for the treatment of Psoriasis for decades[7].

A variety of reports tells that the most effective range of UVB for the treatment of skin disorders is in the long-wavelength part of the UVB spectrum i.e., between 305 and 315 nm[8-10].

Around 1988 a source of narrow band UVB i.e 311nm was ready to use. This has modernized the phototherapy using UVB source. The phosphor LaB_3O_6:Gd^{3+}, Bi^{3+} is commercially used in narrow UVB phototherapy lamps. The borate host material such as $LaBO_3$, LaB_3O_6, LaB_5O_9 and YBO_3 doped with Gd^{3+} ions reported by Sonekar *et al.*[11].

In the present work, Gd^{3+} doped $LiCa_4(BO_3)_3$ material was successfully and intentionally synthesized by the modified conventional solid state diffusion (SSD) method. The phase purity of synthesize material was characterized using the powder X-ray Diffractometer (XRD). Afterword the photoluminescence property of the synthesized material was studied using a spectrofluorometer at room temperature.

Materials and Methods

Synthesis of phosphor: The phosphor $LiCa_4(BO_3)_3$ doped with Gd^{3+} was prepared by modified solid state diffusion method which was well discussed by Palan *et. al*[12-16]. The stoichiometric amounts of high purity (Analytical Reagent) starting materials Lithium nitrate (LiNO3), Calcium nitrate ($(CaNO_3)_3$), Gadolinium nitrate ($Gd(NO_3)_3$) (99.99% purity), Boric acid (H_3BO_3) have been used for preparation of phosphors.

The appropriate amount of starting materials with minute amount of double distilled water were mixed thoroughly in a china basin to obtain homogeneous solution. The solution was slowly heated at lower temperature at 90ºC in order to remove the excess of water contents.

The thick paste obtained after heating is then transferred into a microwave furnace maintained at 200º C for 1 hr. After that the temperature of microwave furnace was increased up to the 400º C and kept material for 1 hr. Then sample was grinded by using mortar pestle and faced to the microwave furnace maintaining at temperature 900º C for 2hr then quenched to room temperature. The resultant powder sample was then characterized using powder XRD, and Spectrofluorometer.

Characterizations of sample: The study of phase purity of $LiCa_4(BO_3)_3$:Gd^{3+} sample was done using Rigaku miniflex II X-ray diffractometer (XRD) by selecting the scan speed of 6.000 /min and Cu Ka (k = 1.5406 Å) radiation within the range 10 - 80º. The PL and PLE spectrum was measured on fluorescence spectrophotometer (Hitachi F-7000) at room temperature. All the parameters of fluorescence spectrometer were kept constant throughout the analysis of samples.

Results and Discussion

X-ray diffraction analysis (XRD): The studies on novel Lithium calcium tetra borate phosphor was one of the interesting issue which have been proved to be efficient in the application of light-conversion. $LiSr_4(BO_3)_3$ doped with Pb^{3+} phosphor was reported by Ilhan Pekgozlu[17] as a novel UV emitting phosphor prepared by solid state synthesis method. At this point we are replacing strontium by calcium (hold the same valence) to get $LiCa_4(BO_3)_3$ prepared using conventional solid state synthesis method.

The X-ray diffraction patterns of $LiCa_4$ $(BO_3)_3$ doped with activator Gd^{3+} are shown in Figure-1. The observed diffraction peaks of material were not identical with any data present in the ICDD data base. By establishing the relation with the reported material, taking into consideration that the starting raw materials are weight as per the given chemical composition of $LiCa_4(BO_3)_3$:Gd matrix, therefore it was named as $LiCa_4(BO_3)_3$ phosphor in this paper. As a result, we consider that the acquired unknown phase is probable to be a novel phase.
The supplementary studies of this phosphor are still being carried on. According to results we conclude that the synthesized sample are not the physical mixtures of precursor but a new host $LiCa_4$ $(BO_3)_3$. The complete structures of this phosphor are at rest under study. Hence, X-ray diffraction data of $LiCa_4$ $(BO_3)_3$ new material reported in this paper.

Photoluminescence Analysis: Figure-2 represents photoluminescence excitation (PLE) and photoluminescence emission (PL) spectra for $LiCa_4$ $(BO_3)_3$:Gd^{3+} phosphor. The phosphor gives the strong excitation having maximum intensity at 276 nm. In excitation we observed some weak peaks between 245 - 255 nm correspond to $^8S_{7/2}$ to ^6D_J transition of Gd^{3+} ion. The photoluminescence spectrum shows sharp and strong emission in the narrow band UVB region around 314 nm corresponding to $^6P_J \rightarrow {}^8S_{7/2}$ transition under excitation of 276 nm. The emission spectra consists of a weak line at 304 nm correspond to the $^6P_{5/2} \rightarrow {}^8S_{7/2}$ transition of the Gd^{3+} ion. The value of Stokes shift was found to be 4384 cm^{-1}.

Conclusion

In this work $LiCa_4(BO_3)_3$ phosphor has been effectively and intentionally synthesized by using modified solid state diffusion method. The room temperature photoluminescence spectra of synthesized $LiCa_{3.995}Gd_{0.005}(BO_3)_3$ phosphor show emissions at wavelengths 314 nm under 276 nm excitation radiation. This emission wavelength is in narrow band UVB region of electromagnetic spectrum. As a result, $LiCa_{3.995}Gd_{0.005}(BO_3)_3$ phosphor is better candidate as the narrow band UVB emitting phosphor for phototherapy applications.

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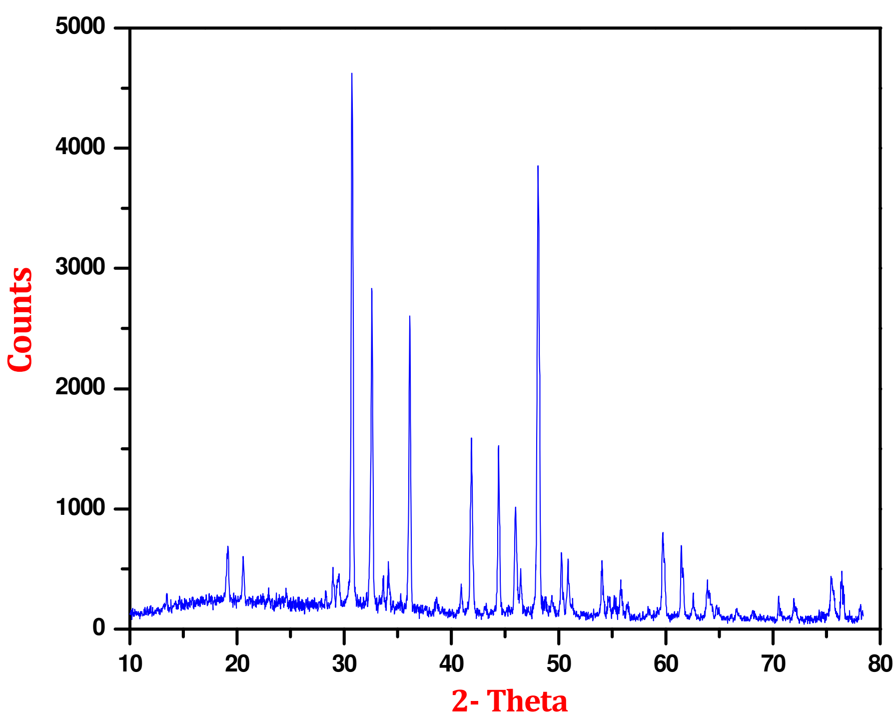

Figure-1
XRD patterns of the $LiCa_4(BO_3)_3$: Gd^{3+} phosphor synthesized by Solid state diffusion method

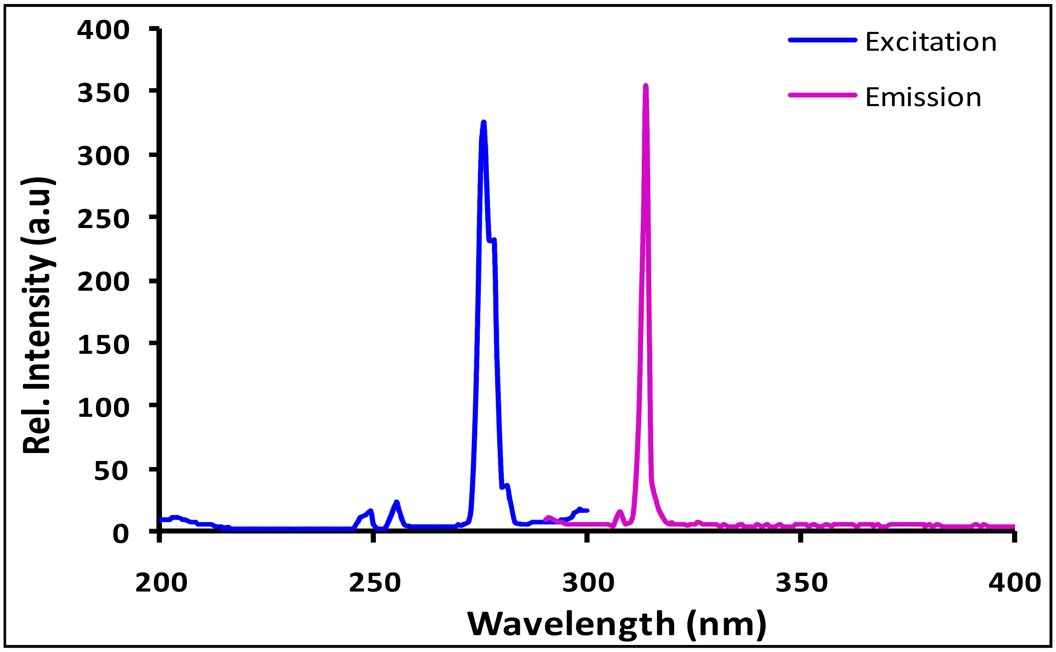

Figure-2
Photoluminescence spectra of $LiCa_4(BO_3)_3:Gd^{3+}$ at room temperature

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