

International Journal of Luminescence and applications Vol5 (4) December, 2015, pages 465-467

Synthesis and PL study of UV emitting phosphor LiSr₄(BO₃)₃:Pb²⁺

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Abstract

Polycrystalline powder sample $\text{LiSr}_4(BO_3)_3$: Pb^{2+} material was prepared by a modified solid state diffusion method. The phase purity of synthesized material was confirmed using powder XRD. The photoluminescence property of synthesized material was investigated at room temperature. The emission and excitation band of the synthesized phosphor was observed at 325 nm and 290 nm respectively. The Stokes shift of $\text{LiSr}_4(BO_3)_3$: Pb^{2+} was measured to be 3832 cm^{-1} . The phosphor could find application in medical and lamp industry.

Keywords: Inorganic Borate, Photoluminescence, XRD, Stokes shift.

PACS Code: 78.55-m

1. Introduction

Ultraviolet radiation (UVR) makes up a fraction of the electro-magnetic spectrum, which can be further sub divided into: 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).

Ultraviolet (UV) irradiation for phototherapy is commonly used to treat refractory skin disease. UV therapy is useful for treating more than 40 types of skin diseases and disorders, such as psoriasis [1], Vitiligo [2], ofujisdisease [3], erythropoetic protoporphyria [4], pityriasisrosea [5], uremicpruitus [6] which could be treated by UV-B radiation and lichensclerosuset atrophicus [7], morphea [8], scleroderma [9], cutaneous T-cell lymphoma, lupuserythematosus [10] which could be treated by UV-A (340–400nm).

Phototherapeutic UV-A treatment, i.e., photo chemotherapy, was used to treat a number of diseases [11]. In 1974 reported the use of new high intensity UV-A tube in combination with oral 8methoxypsoralen in the treatment of psoriasis. This approach was more effective and was the real start of phototherapy, which revolutionized dermatological treatment. In PUVA therapy (Psoralen plus UV-A), suggested the use of broadband UV-B sources for skin treatments. During the subsequent years broadband phototherapy became an alternative for PUVA [12]. A wavelength range of 340-400 nm (UVA1) is also used to treat atopic dermatitis and Urticaria pigmentosa.

Divalent lead cations (Pb²⁺), as a well- known dopant for many different host lattices, is of great scientific, medical and industrial interest. Because of the diversity of the photo luminescent properties, it provides the possibilities of fabricating novel phosphor materials [13]. Inorganic luminescent materials containing metal ions with s² (Pb²⁺ etc.) configuration can be used in X-ray imaging devices, low pressure lamps, and high-energy physics. For example, BaSi₂O₅: Pb²⁺ emits a broad band around 350 nm under UV excitation, which is one of the earliest known phosphors for photocopying lamps [14]. Inorganic borate phosphors have attracted much attention due to their high stability, easy synthesis, and high UV transparency [15].

In this study, $LiSr_4(BO_3)_3$ material doped with Pb^{2+} ion was prepared by a modified solid state diffusion method. The synthesized material was characterized using the powder X-Ray Diffraction. After synthesis and characterization of synthesized $LiSr_4(BO_3)_3$ material, the photoluminescence properties of these phosphor was studied in detail using a fluorescence spectrometer.

2. Experimental

The phosphor $LiSr_4(BO_3)_3$ doped with Pb^{2+} (0.5 mol%) was prepared by modified solid state diffusion method. Stoichiometric amounts of high purity

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(Analytical Reagent) Lithium nitrate (LiNO₃), Strontium nitrate (Sr(NO₃)₂), Lead nitrate (Pb(NO₃)₃) (99.99% purity), Boric acid (H₃BO₃) were used for preparation of phosphors. The stoichiometric amount of starting materials with little 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 90° C in order to remove the excess of water contents. The thick paste obtained after heating is then transferred into a microwave furnace maintained at 200° C for 1 h. After that the temperature of microwave furnace was increased up to the 400° C and kept material for 1 hr. Then sample was grinded by using mortar pestle and faced to the microwave furnace maintaining at temperature 800° C for 2h., then quenched to room temperature. The resultant powder sample was then characterized powder XRD using and Spectrofluorometer.

The structural analysis of the synthesized material was carried out using X-ray Diffractometer (XRD: Rigaku Miniflex II, with Cu Ka irradiation (k = 1.5406 Å) with a scan speed of 6.00° /min in the range 10° to 90° . Photoluminescence measurement at room temperature was performed on a Hitachi F-7000 spectrophotometer equipped with a 450W Xenon lamp, in the range 200–400 nm, with spectral slit width of 1.0 nm and PMT voltage at 700V.

3. Result and Discussion

3.1 XRD analysis

Fig. 1 represents XRD pattern for Pb²⁺ doped LiSr₄(BO₃)₃ polycrystalline sample prepared by using modified solid state diffusion method. The XRD pattern for LiSr₄(BO₃)₃ agrees well with the standard data from ICDD file (01-073-3772). The XRD pattern also provides evidence to the completely crystalline nature of sample with single phase. The crystal structure of the prepared materials can be refined to be Cubic, with lattice parameter a = b = c = 14.9509 Å. The materials crystallize in the Centro symmetric space group Ia-3d (230). The ionic radii of Sr²⁺ ion (1.18Å) and Pb²⁺ ion (1.19Å) are nearly similar. Hence we can infer that Sr²⁺ ion will be substitutionally replaced by Pb²⁺ ion.



Fig.1. X-ray diffraction (XRD) pattern of LiSr₄(BO₃)₃:Pb²⁺ prepared by using modified solid state diffusion method

3.2 Photoluminescence

The luminescence property of Pb^{2+} in host material is diverse. It can be described by the ${}^{1}S_{0} - {}^{3}P_{0, 1}$ transition, which originates from the $6s^{2} - 6s^{1}6p^{2}$ inter-configurational transition. Typically at room temperature, emission is observed from the ${}^{3}P_{1} \rightarrow {}^{1}S_{0}$ transition [16], although at low temperatures the highly forbidden ${}^{3}P_{0} \rightarrow {}^{1}S_{0}$ emission is also observed [17].



Fig.1. Excitation and Emission spectra of LiSr₄(BO₃)₃:Pb²⁺ at room temperature.

As seen in Fig.2, the excitation band of the synthesized phosphor $LiSr_4(BO_3)_3$: Pb^{2+} was observed at 290 nm, which is assigned to the ${}^1S_0 - {}^3P_1$ transition. The emission band was observed at 325

nm from the ${}^{3}P_{1}$ excited state level to the ${}^{1}S_{0}$ ground state upon excitation with 290 nm. The emission band of LiSr₄(BO₃)₃: Pb²⁺ lies between 300 nm and 400 nm and is in the UV region. Due to non- splitting / absence of multiple peaks in the photoluminescence spectra, it is believed that the Pb²⁺ ions are incorporated into only one site in LiSr₄(BO₃)₃. So, activator ion (Pb²⁺) is expected to occupy the Sr²⁺ sites and not Li⁺ sites according to the ionic size considerations.

Stokes shift was calculated to be 3832 cm^{-1} . As a result of this small Stokes shift in $\text{LiSr}_4(\text{BO}_3)_3$: Pb^{2+} , it can be inferred that there is a small relaxation in the excited state.

4. CONCLUSIONS

The phosphor LiSr₄(BO₃)₃: Pb²⁺ doped with Pb²⁺ was prepared by modified solid state diffusion method. The XRD pattern of prepared sample found in agreements with the respective ICDD files and is in complete crystalline nature. The PL spectra specify that the LiSr₄(BO₃)₃: Pb²⁺ gives strong emission green emission under UV excitation. The main emission wavelength of LiSr₄(BO₃)₃: Pb²⁺ is at 325 nm for 284 nm excitation attributed from ³P₁ excited state level to the ¹S₀ ground state. Stokes shift was calculated to be 3832 cm⁻¹LiSr₄(BO₃)₃: Pb²⁺ is a good candidate for the broadband UV application.

ACKNOWLEDGEMENT

The author A. O. Chauhan is thankful to the Chairman of the FIST-DST Project at Sant Gadge Baba Amravati University, Amravati (MH), 444602 INDIA for providing XRD facility for this research work.

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