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YBO_3 versus Y_3BO_6 host on Tb^{3+} luminescence

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ABSTRACT

Undoped and Tb^{3+} doped YBO_3 and Y_3BO_6 were prepared by co-precipitation method in ethylene glycol medium at 100 °C followed by annealing at 800 °C. The spin allowed $4f^8 \rightarrow 4f^7 5d^1$ (low spin) and spin forbidden $4f^8 \rightarrow 4f^7 5d^1$ (high spin) transitions of Tb^{3+} are well resolved in YBO_3 host as compared to Y_3BO_6. This has been attributed to difference in the distribution of local environment around Y^{3+}/Tb^{3+} in these hosts. $^5D_4$ and $^5D_3$ levels of Tb^{3+} decays much faster in Y_3BO_6 host as compared to YBO_3. Increased phonon energy of Y_3BO_6 host compared to YBO_3 facilitates faster cross relaxation process between $^5D_3$-$^5D_4$ and $^7F_6$-$^7F_0$ energy level pairs of Tb^{3+} in the former leading to decrease in the corresponding excited state lifetime values. Green emission, from Tb^{3+} in Y_3BO_6 host, is found to have better colour purity compared that from YBO_3 host, as revealed by corresponding CIE coordinates. From these studies it is established that factors like excited state lifetime and colour purity must be considered together while choosing suitable yttrium borate based hosts for luminescent applications.

1. Introduction

Luminescent materials based on lanthanide borates are potential candidates for light sources and display panels as they possess high thermal and chemical stability with exceptional optical damage threshold [1,2]. Due to wide versatility in the structural arrangement of borate structural units, it would be of interest to investigate such systems for fundamental understanding regarding the influence of structure on luminescence properties. From binary Ln_2O_3-B_2O_3 phase diagram, existence of three different crystalline compounds of composition $LnBO_3$, $Ln(BO_2)_3$ and Ln_3BO_6 have been identified [3]. Preparation and characterization of $LnBO_3$ (with Ln = Y^{3+}, Gd^{3+}, La^{3+}, etc.) phase in a variety of shapes and sizes, with and without lanthanide ions doping, have been extensively explored [4–17]. It is generally accepted that $LnBO_3$ phase formed by smaller lanthanide ions (Sm to Lu and Y) exists in monoclinic crystal system having vaterite type structure whereas those with higher ionic radii values like La^{3+}, Nd^{3+} etc., exist in aragonite type structure with hexagonal close packed orthorhombic unit cell [18,19]. Interesting luminescence properties have been reported from these samples on exposure to UV radiation. Unlike $LnBO_3$, the other phases like $Ln(BO_2)_3$ and Ln_3BO_6 are scantly investigated. Peters et al. [20] have reported that, $Gd(BO_2)_3$ co-doped with Ce^{3+} and Mn^{2+}, upon excitation at 254 nm gives strong green emission. This has been attributed to energy transfer from Ce^{3+} to Gd^{3+} and subsequently to Mn^{2+}, which gives characteristic green emission. Co-doping Gd^{3+} in $La(BO_3)_2$:Tb or $La(BO_3)_2$:Eu improves Tb^{3+} and Eu^{3+} luminescence upon VUV excitation [21]. It is also known that lanthanide borates like $La(BO_3)_2$ and $Gd(BO_3)_2$ crystallizes in monoclinic crystal structure in which La^{3+}/Gd^{3+} ions occupy sites with C_2 symmetry in the respective lattices [21].

Among the three different lanthanide borates, Ln_3BO_6 phase is the most lanthanide rich and exists in three crystalline modifications depending upon the size of lanthanide ion [22,23]. For lanthanide ions from La to Nd, Ln_3BO_6 phase crystallizes in $P2_1/c$ space group. Space group changes to C2/m, C2 (or Cm) for borates of Pm to Yb [23]. Lutetium borate also crystallizes in a space group corresponding to that of Pm-Yb borates, however its unit cell is different from that of the latter. The compound Y_3BO_6 with and without doping Eu^{3+} has been investigated for their structural and luminescence properties [23–27]. It can be considered as a compound with molecular formula $Y_{17.33}(BO_3)_4(B_2O_5)_2O_{16}$, wherein Y^{3+} ions exist in both YO_7 and YO_8 configurations [23]. ^{11}B MAS NMR studies have confirmed that Boron atoms in Y_3BO_6 exist in BO_4 and two different types of BO_3 structural units with varying quadrupolar coupling constants [25]. Based on luminescence studies of Eu^{3+} doped Y_3BO_6, Boyer et al. [26] have identified six crystallo-graphically different types of Eu^{3+}/Y^{3+}sites in Y_3BO_6 lattice. Li et al. [28] have demonstrated that under same experimental conditions, Eu^{3+} doped La_3BO_6 is a better luminescent material compared to Eu^{3+} doped Y_3BO_6. Chadeyron et al. [29] have observed that, Y_3BO_6:Eu can be combined with blue and green phosphors for generation of white light displays based on deep ultra violet (DUV) excitation. A similar observation is also made by Pradal et al.

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[30], for Y_3BO_6:Eu-PVP composites, which are potential candidates for next generation white light emitting diodes.

It is evident from the above that, Y_3BO_6 is an important host for luminescence applications. Further the host is lanthanide rich compared to other two phases in binary Y_2O_3-B_2O_3 system and also unlike other two phases, boron exists in multiple configurations in Y_3BO_6. It is therefore interesting to compare the nature of host sensitive excitations of lanthanide ions such as Ln-O charge transfer (for example Eu-O charge transfer) and 4f→5d transitions (for example 4f→5d transition of Ce^{3+} and Tb^{3+}), in both Y_3BO_6 and YBO_3 hosts. Due to difference in nature of YO_n polyhedra in Y_3BO_6 compared to YBO_3, the average ionic character in Y-O bonds must be quite different in both the phases and this can have tremendous influence on Ln-O charge transfer transitions as well as 4f→5d transition of other lanthanide ions. For example, upon UV excitation (Eu-O charge transfer excitation), red emission intensity from Eu^{3+} is much more intense when doped in Y_3BO_6 lattice compared to YBO_3 [27].

The lanthanide ion, Tb^{3+}, is a special case as there exists maximum extent of exchange interaction between spins corresponding to excited $4f^7$ and $5d^1$ states. This can result in large energy difference between spin allowed and spin forbidden f-d transitions of Tb^{3+} depending on the host. In addition to this, phonon energy of host is expected to be different in Y_3BO_6 host compared to YBO_3 host due to difference in nature of boron structural units in these two samples. A comparative evaluation of the luminescence properties Tb^{3+} in both hosts will be helpful for the basic understanding of luminescence properties of different lanthanide borates, which are potential candidates for display applications. Keeping this in mind we have carried out detailed luminescence studies on Tb^{3+} doped Y_3BO_6 samples and the results have been compared with that of YBO_3:Tb sample. To the best of our knowledge this is the first time that a comparative study is being reported on the luminescence properties of Tb^{3+} ion in the above-mentioned hosts.

2. Experimental

2.1. Sample preparation and characterization

Terbium doped (1 at%) and undoped samples of Y_3BO_6 and YBO_3were synthesized by polyol method using analytical grade yttrium oxide (Y_2O_3), boric acid (H_3BO_3) and terbium oxide (Tb_4O_7) as precursor materials. Firstly, stoichiometric amounts of Y_2O_3 and Tb_4O_7 were mixed with 1 ml conc. HCl solution with excess water in a 100 ml beaker and heated up to ~ 90–100 °C. Once the solution volume decrease to 2–3 ml, solution is cooled, 5–10 ml conc. HCl was added and again heated to 90–100 °C. This was repeated number of times so that complete dissolution of the powder sample occurs. This solution (5 ml) was then transferred into a round bottom flask, containing 20 ml ethylene glycol and was slowly heated up to 80 °C followed by the addition of required quantity of boric acid and urea (3 g). The temperature was maintained at 100 °C for 2 h. After the reaction, the precipitate was collected by centrifugation and subsequently washed with ethyl alcohol and acetone, and dried under ambient conditions. Same procedure was repeated for undoped samples of Y_3BO_6 and YBO_3 except that terbium oxide was not added initially. As prepared samples were annealed at 800 °C for 5 h.

X-ray diffraction (XRD) studies were carried out using a Philips powder X-ray diffractometer (model PW 1071) with Ni filtered Cu-Kα radiation. Rietveld refinement of the XRD patterns was performed using GSAS software. Cosine Fourier series function has been chosen for background and Type-2 function in GSAS software has been chosen for peak profile during refinement. Fourier Transform Infrared (FTIR) measurements were carried out on Bomem (MB 102) spectrometer. Samples were powdered with dry KBr and made in the form of a thin pellet and mounted inside the sample chamber, prior to IR measurements. Photoluminescence and excited state lifetime measurements were carried out using an Edinburgh Instruments FLSP 920 system equipped with a 450 W Xe lamp and a 60 W microsecond flash lamp as the excitation sources. All emission spectra were corrected for the detector response and excitation spectra for the lamp profile. For lifetime measurements, 60 W micro second flash lamp, operating at a frequency of 100 Hz, was used. Pulse duration was around 1–2 μs and decays were recorded over 4000 channels. Multichannel scaling technique available with Edinburgh instrument was used for decay measurements. Scanning Electron Microscopic (SEM) studies were carried out using a CamScan MV 2300CT/100 machine attached with an energy dispersive X-ray analyser.

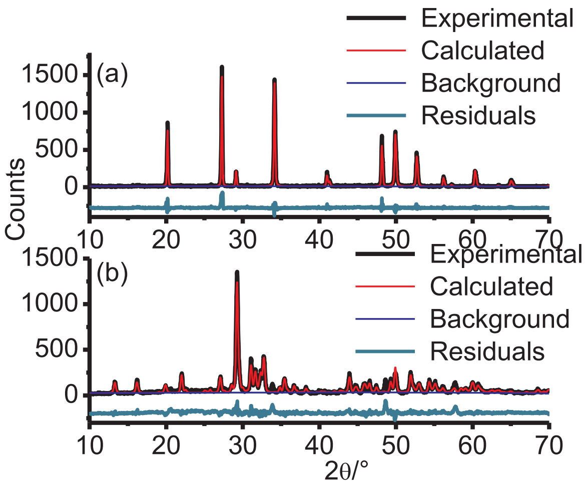

Fig. 1. Rietveld refined XRD patterns of (a) YBO_3 and (b) Y_3BO_6 samples annealed at 800 °C. The χ^2 values for YBO_3 and Y_3BO_6 are a 2.1 and 1.85 respectively. Corresponding values for R(F^2) are 0.30 and 0.35 respectively.

3. Results and discussion

Fig. 1(a) and (b) shows Rietveld refined XRD patterns of YBO_3 and Y_3BO_6 respectively annealed at 800 °C. Both the patterns are characteristic of the single phase nature of YBO_3 and Y_3BO_6. Lattice constants obtained from refinement of the diffraction patterns are given in Table 1. The compound YBO_3 contains only one type of Y and Boron in the lattice with an average Y-O and B-O bond length values around 2.34 Å and 1.65 Å respectively. The compound Y_3BO_6 corresponds to a phase with molecular formula $Y_{17.33}(BO_3)_4(B_2O_5)O_{16}$ containing little excess of B_2O_3 as reported by Lin et al. [24] and consists of crystallographically 9 different Y and 4 different B atoms in the lattice. Y exists in both YO_7 and YO_8 polyhedra whereas boron exists in both BO_4 and BO_3 structural units. It belongs to monoclinic crystal system with space group Cm having average Y-O and B-O bond length values around 2.60 Å and 1.53 Å respectively, as revealed by the Rietveld refinement (Table 1). Average crystallite size calculated based on Debye-Scherrer formula is found to be ~ 36 nm for YBO_3 and ~ 40 nm for Y_3BO_6.

Figs. 2 and 3 show the SEM images of YBO_3 and Y_3BO_6 samples obtained by monitoring both secondary electrons and back scattered electrons. It is clear from the images that the micro-structure of the two

Table 1
Values of lattice parameters, average Y–O and B–O bond lengths in both YBO_3 and Y_3BO_6 samples.

Sample	Lattice parameters				Bond length values	
	a (Å)	b (Å)	c(Å)	β	Average Y–O bond length (Å)	Average B–O bond length (Å)
YBO_3	11.328(2)	6.527(4)	9.546(1)	113.05°	2.34(2)	1.65(3)
Y_3BO_6	18.162(2)	3.651(1)	14.001(3)	119.69°	2.60(1)	1.53(3)