

Effect of Host Structure and Concentration on the Luminescence of Eu^{3+} and Tb^{3+} in Borate Phosphors

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Eu^{3+} and Tb^{3+} doped in nanocrystalline InBO_3 , GdBO_3 , and LaBO_3 having three different morphs of calcite (CaCO_3) such as Calcite, Vaterite, and Aragonite, respectively, were synthesized by glycine–nitrate combustion method. Luminescence due to Eu^{3+} and Tb^{3+} doped individually as well as simultaneously in these three different morphs of calcite were investigated and compared. Also the effect of concentration of dopant ions on the luminescence was studied. The highest photoluminescence emission intensity was observed for $\text{RE}_{0.05}\text{M}_{0.95}\text{BO}_3$ ($\text{RE} = \text{Eu}^{3+}$, Tb^{3+} , $\text{M} = \text{In}$, Gd , La) samples. Further increase in doping led to concentration quenching of the luminescence. In case of the co-doped borates, the energy transfer between the co-doped rare earth ions was influenced by the host crystal structure. This study reveals that there is remarkable effect of the crystal structure of host and concentration of dopant ions on the luminescence.

I. Introduction

OVER the past several years, phosphors have been considered as technologically important components for the functionality and success of many lighting and display systems.^{1–3} Extensive research has been done on the phosphors that convert vacuum ultraviolet (VUV) light into visible light, which are generally used in mercury-free fluorescent lamps and plasma display panels. It is well established that phosphor luminescence depends on the type of host material and the dopant species (activator). A suitable host should exhibit a sufficiently large band gap so that emission from the activator will not be absorbed, but not so large as to waste the major fraction of the energy by excitations, that require much greater energy than needed for relaxation.

Under this perspective, borates such as InBO_3 , GdBO_3 , and LaBO_3 with high band gaps of 5.6, 7.0, and 7.0 eV, respectively, have been proposed as promising host materials for optically active materials such as the rare earth ions.^{4,5} This large band gap strengthens their potential application in UV optics and also provides a wider range of wavelengths over which phase matching for most efficient NLO wavelength conversions may be realized. Of the three borates, InBO_3 is structurally the simplest compound as $\text{In}_2\text{O}_3\text{--B}_2\text{O}_3$ shows the calcite type (CaCO_3) structure, GdBO_3 ($\text{Gd}_2\text{O}_3\text{--B}_2\text{O}_3$) shows the vaterite (CaCO_3) structure while LaBO_3 adopts the aragonite structure.⁶ As host matrix in the phosphor, these borates exhibit high transparency in the ultraviolet (UV) and VUV region, good chemical stability, high

refractory properties (with a melting point of 1610°C, 1590°C, and 1660°C for InBO_3 , GdBO_3 , and LaBO_3 , respectively) and high optical quality.^{4,5} The emission of rare earth ions is due to optical transitions within the f -manifold e.g. Tb^{3+} ($4f^8$) and Eu^{3+} ($4f^7$). Europium and terbium are the most popular ions due to their strong red and green luminescence, respectively.

It is well known that performances of the materials are closely related to the processing technique. The method of synthesis of the phosphors has played a significant role in determining their luminescence properties. Phosphors were conventionally synthesized via a solid-state reaction process, using powdered raw materials as the starting reactants.^{7–10} Due to their relatively large grain size, these phosphors require a relatively high sintering temperature to obtain phosphors with designed compositions and desired performances. To reduce the sintering temperature, it is necessary to use powders of phosphor compounds in very small grain sizes and narrow size distribution. For this purpose, submicron and nano-sized materials have been synthesized by various wet-chemistry methods, over the past several years, including hydrothermal synthesis,¹¹ chemical co-precipitation,¹² sol–gel process,^{13–14} etc.

Recently gel-combustion synthesis is being widely employed for the synthesis of nano phosphors.^{15–17} It is an excellent technique due to its short processing time, low processing temperature, low cost, and high yield as well as good ability to achieve high purity in making single or multiphase complex oxide powders. This investigation reports the study of the luminescence of rare earth-doped orthoborates prepared by gel-combustion method, the correlation between crystal structure of host lattice and the luminescence of rare earth ions and interaction between the rare earth ions in co-doped phosphors.

II. Experimental Procedure

The Eu^{3+} and Tb^{3+} -doped InBO_3 , GdBO_3 , and LaBO_3 were prepared by a gel-combustion method. The reagents used are indium oxide (In_2O_3), gadolinium oxide (Gd_2O_3), lanthanum oxide (La_2O_3), europium oxide (Eu_2O_3), and terbium oxide (Tb_4O_7). They are dissolved in 50% HNO_3 to prepare their corresponding nitrates. Boric acid (H_3BO_3) is used as a source of boron. Glycine is used as fuel. All chemicals used are AR grade.

For the combustion synthesis, the stoichiometric amount of oxidants (metal nitrates) and fuel (glycine) are calculated which is based on the concept of propellant chemistry.¹⁸ Boric acid is used as a source of boron as it is a neutral compound and hence, neither extra oxidizer nor fuel is required. The stoichiometric amount (O/F Ratio 1:1.66) of the respective oxidizers and fuel are then mixed together in de-ionized water to obtain the homogeneous aqueous mixture. The aqueous solution is then heated $\sim 300^\circ\text{C}$. The solution boils, then evaporates and is converted into the viscous gel

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