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Preparation and emission study of divalent samarium formed in air fired samples of $Sm:Ba_2B_{10}O_{17}$

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ABSTRACT

Trivalent samarium has been found to be reduced to the divalent state during the air firing process of the preparation of 5% $Sm:Ba_2B_{10}O_{15}$. This is the first time that the formation of divalent samarium has been reported as a function of the preparation of this material. The product was prepared from a co-precipitated borate which was fired at 750 °C with an additional 30% boric acid. The resulting product was confirmed by x-ray analysis and exhibited only divalent samarium emission. Based upon the observed emission, the primary samarium site can be assigned a site symmetry of C_{2v}. The emitting samarium ion appears to occupy a tetrahedral boron site in this material.

1. Introduction

The use of co-precipitation methods to prepare samples of samarium doped alkaline earth metal borates in which the samarium ion has been reduced to the divalent species in air fired samples has been reported for $Sm:SrB_4O_7$ [1], $Sm:BaB_8O_{13}$ [2,3], and $Sm:Sr_2B_{16}O_{26}$ [4]. In each of these instances, the analogous material has also been prepared by solid state/ceramic methods in air or with the addition of a reducing atmosphere [5–7]. Recently, a new barium borate composition has been identified as $Ba_2B_{10}O_{17}$ [8]. It has been studied crystallographically [8] and has been investigated as a supporting matrix for the incorporation of trivalent samarium as a yellow phosphor [9]. However, it has never been reported that air firing of $Ba_2B_{10}O_{17}$ could reduce incorporated lanthanide ions or that it could act as a host to divalent samarium. In previous preparations of this system, the samples were prepared by mixing barium carbonate, boric acid, and samarium oxide and firing the mixture at 880 °C [9]. These synthetic parameters resulted in the retention of trivalent samarium in the prepared product.

When samarium and barium are co-precipitated with sodium tetraborate, the resulting precipitate often includes incorporated sodium ions and varying alkaline earth:boron ratios in the precipitate [2]. Refluxing and washing of the dried precipitate with saturated boric acid solution has proven to remove the sodium impurity and coalesced the material into a consistent high boron composition that upon firing produced the octoborates of barium [2] and strontium [4]. In the current report, a similar method using deionized water to reflux and wash the precipitate has yielded a similarly consistent low borate composite. When fired with additional boric acid, the material not only produces the $Ba_2B_{10}O_{17}$ matrix, but also results in emission consistent with the formation of divalent samarium.

2. Material, methods, and instrumentation

$Sm:Ba_2B_{10}O_{17}$ was prepared by air firing the borate co-precipitate of a mixed samarium:barium solution. A 5% Sm^{3+}: 95% Ba^{2+} chloride solution was added to a large excess of aqueous saturated $Na_2B_4O_7$. The resulting precipitate was collected and then dried at 165 °C. The solid was ground and added to 150 ml of deionized water which was heated to boiling with stirring and allowed to reflux for about one hour. After which, the hot solution was allowed to settle and the solid collected. The solid was washed three times with 100 ml cold water and again dried at 165 °C. Boric acid was added in concentrations of 28–33% by mass, all of which resulted in the desired product as confirmed by x-ray analysis and emission spectroscopy. The ground mixture was wetted with a 5% acetic acid solution and the resulting paste placed on a porcelain tile suitable for firing. The tile was placed into a muffle furnace at 750 °C for five short fires (5 min each, 25 min total) with grinding between each step. After the short duration fires, the sample was returned to the 750 °C furnace for an extended firing of 18–60 h. The product was removed from the tile and ground to form a fine dark grey powder. This coloration may result from residual carbon from the acetic acid, although similar coloration can also result in samples wetted with just water. An orange/salmon coloration has often been observed to be associated with samarium incorporated into similar materials [1,4]. However this coloration has not been reported with the formation of divalent samarium in barium borates [2,3,6].

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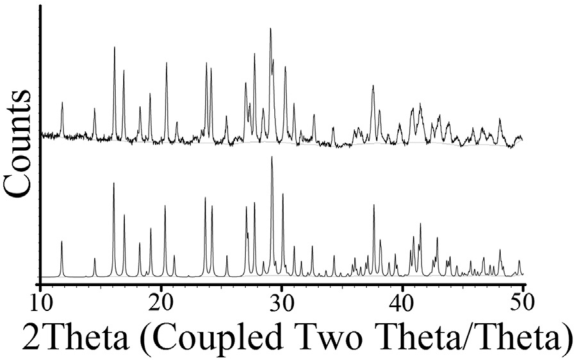

Fig. 1. X-ray diffraction pattern of 5%Sm:$Ba_2B_{10}O_{17}$ prepared by air firing of the co-precipitated sample (top) and x-ray calculated based on the results of Liu et al. [7] (bottom).

The five short firing steps followed by the extended firing produced the formation of the matrix and the desired reduction. In the study of these materials the authors have observed that the short firing steps often do not provide a significant reduction of the samarium in the species, while extended initial firing often results in mixed borates in the product. It is assumed that the short fires result in setting the crystal structure and composition based upon the stoichiometric amounts of the materials included (without the loss of evaporated boric acid). The additional extended fire then results in the reduction of the samarium ion.

Confirmation of the generation of the $Ba_2B_{10}O_{17}$ matrix in the sample was provided by powder x-ray diffraction. The x-ray diffraction data was collected on a Bruker D2 Phaser utilizing sealed tube CuK$\bar{\alpha}$ radiation ($\lambda = 1.5418$ Å) and operated at 30 kV and 10 mA. The sample was mounted on a horizontal stage for a 282 mm diameter goniometer equipped with a Lynxeye detector. Data were collected using a step width of 0.01° and step time of 0.3 s with a 2θ range of 8.0–50.0°. The Bruker diffraction measurement and EVA software packages were used for data collection and processing. The x-ray pattern generated from the product is shown in Fig. 1. The diffraction pattern is in general agreement with that reported in the literature for samples prepared by the ceramic method [8].

The high-resolution, emission spectrum was collected on a micro-Raman/photoluminescence spectrometer (Horiba Scientific). The sample was excited with an argon-ion laser (Coherent, Inova 305) at 351 nm. The laser power incident upon the sample was ~30 mW. The emitted light was dispersed by a 600 grooves/mm grating (~0.051 nm resolution).

3. Results and discussion

The high resolution emission spectrum covering the spectral range from 500 nm to 850 nm which was collected from the prepared sample is shown in Fig. 2. The use of 351 nm light should excite both Sm^{2+} and Sm^{3+} in the sample through broad ultraviolet absorption bands. Trivalent samarium has been studied in this material [9] and three broad emission manifolds of overlapping peaks centered near 560, 600, and 645 nm have been reported [9]. The emission associated with Sm^{2+} usually includes several sharp emission features near 680, 700, 725, 760, and 810 nm corresponding to $^5D_0 \rightarrow {}^7F$ electronic transitions (as seen in Fig. 2). Additional minor features corresponding to the $^5D_1 \rightarrow {}^7F$ transitions are often identified near 625, 640, and 660 nm (as seen in Fig. 2). A very broad 5d – 4 f Sm^{2+} emission transition is often observed overlapping the sharper 4–4f transitions (as seen in Fig. 2).

As is apparent from Fig. 2, the characteristic triple set of emission manifolds indicative of trivalent samarium as described by Li et al. [9] are conspicuously absent. In previous studies of samarium reduction there has usually been a small percentage of residual Sm^{3+} emission [1–7]. This emission was found to be decreased by the addition of glacial acetic acid in the formation of the octoborate samples [2,4], but the trivalent samarium emission was never eliminated. That does not appear to be the case when samarium is doped into $Ba_2B_{10}O_{17}$. Each of the emission features that are apparent can be specifically assigned to divalent samarium. This complete loss of Sm^{3+} emission occurs even without the addition of glacial acetic acid. While the absence of trivalent samarium emission cannot show complete reduction of the samarium ion, the formation and stabilization of the divalent samarium species in this material appears to be quite good under the experimental conditions presented.

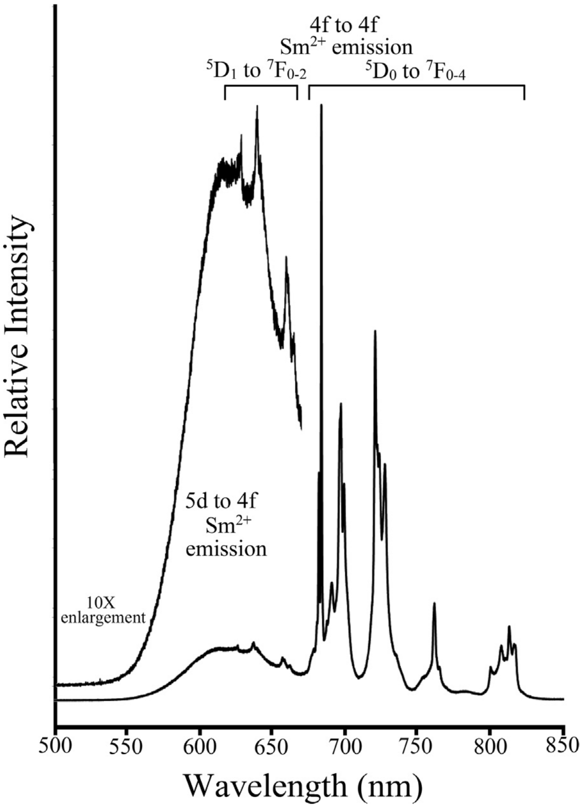

Fig. 2. Emission spectrum of 5%Sm:$Ba_2B_{10}O_{17}$.

The emission spectrum that was collected from this material was found to be consistent with regard to samarium reduction, emission intensities, and peak positions with additional boric acid concentrations ranging from 28% to 33% by mass. When the concentration of boric acid was decreased to 20–24%, a BaB_4O_7 component was identified in the x-ray analysis of the material although the emission was consistent with that shown above. Similarly, when the boric acid concentration was increased to 45–50% by mass, the x-ray analysis revealed a BaB_8O_{13} component in the matrix.

The emission spectrum collected from this material was also found to be consistent with regard to samarium concentration. Variations in concentration of samarium in the material from 1% to 10% of the metal ion content did not result in any apparent variation in the observed emission of the material at room temperature. This appears to indicate minimal interactions between the incorporated samarium ions, although further study of the material may reveal an interaction.

The emission spectrum corresponding to the $^5D_0 \rightarrow {}^7F$ features which covers the spectral range from 675 to 820 nm is expanded in Fig. 3. A major feature (at 684.0 nm) can be specifically assigned to the $^5D_0 \rightarrow {}^7F_0$ transition. A second smaller feature (at 682.4 nm) and some much smaller features (678.8, 681.0, and 687.7 nm) are also apparent, indicating that the divalent samarium ion may be occupying multiple sites in the compound. The three features that can be associated with