



Synthesis and fluorescence properties of Sm^{3+} doped in $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$ phosphor

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Abstract

A series of Sm^{3+} doped $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$ (NSAB) orange-red emitting phosphor has been synthesized by slow evaporation technique. The phase purity and surface morphological features were characterized by X-ray diffraction (XRD) and scanning electron microscopic (SEM) investigations. The photoluminescence properties of NSAB: Sm^{3+} phosphor have been investigated. NSAB: Sm^{3+} phosphor can be effectively excited by 402 nm near-ultraviolet (NUV) light and features orange-red emission centered at 564, 601 and 649 nm corresponding to the $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$ ($J = 5/2, 7/2, 9/2$) transitions of Sm^{3+} ions, respectively. The optimum concentration of Sm^{3+} ions in NSAB is found to be 3.0 mol% . The luminescence quenching noticed at higher Sm^{3+} concentrations is ascribed to be electric dipole–dipole interaction according to Dexter's theory. Moreover, the chromaticity coordinate of NSAB: Sm^{3+} phosphor is calculated to be (0.382, 0.317). All results suggest that NSAB: Sm^{3+} phosphor is a kind of potential orange-red emitting phosphor.

Keywords: Photoluminescence (PL), rare earth ions, NSAB: Sm^{3+} , quenching mechanism.

1. INTRODUCTION

The evolution of luminescent materials has witnessed rapid advancement in research and development. Solid inorganic light-emitting materials or phosphors are the optoelectronic material of the 21st century because of their power-efficient potential over various illumination sources, eco-friendliness and resourceful display perspectives [1]. The borate materials have been extensively explored during the last several decades because of their promising applications in nonlinear optical (NLO) materials, birefringent materials, ferroelectric and piezoelectric materials, and host materials for luminescence [2].

Recently, researchers have taken interest in alkaline-earth metal aluminum borates because of their potential applications as luminescence hosts, for example, the luminescent properties of $\text{CaAl}_2\text{B}_2\text{O}_7:\text{Ce}^{3+}, \text{Tb}^{3+}$ and $\text{CaAl}_2\text{B}_2\text{O}_7:\text{Pb}^{2+}$ phosphors have been reported [3], and the photoluminescence properties of $\text{Eu}^{3+}, \text{Tb}^{3+}, \text{Eu}^{2+}$, and Pb^{2+} doped $\text{SrAl}_2\text{B}_2\text{O}_7$ have been studied in detail [4]. Generally, RE doped glasses are better than the crystalline materials because of their broad inhomogeneous bandwidths, cheap production cost, good thermal stability, simple manufacturing process and high doping capability [5-10].

Among the RE ions Sm^{3+} ions display reddish orange emission in the visible region and having applications in the undersea communication, high density optical storage, color displays and visible solid-state lasers [11]. Further, Sm^{3+} ions doped glasses exhibit peculiar optical properties due to its $^4\text{G}_{5/2} \rightarrow ^6\text{H}_J$ ($J = 5/2, 7/2, 9/2$ and $11/2$) transitions in all host matrices. The spectroscopic study of Sm^{3+} ions doped borate phosphors have been reported by many researchers [12] but still the PL properties of Sm^{3+} ions doped alumino-borate phosphors need to be improved for the design and development of new luminescent devices.

In this work, we report our investigation results on the luminescence properties in Sm^{3+} activated NSAB phosphor synthesized by using a slow evaporation technique for the first time. Moreover, the concentration quenching mechanism and SEM of as prepared phosphor were studied. Besides, NSABO: Sm^{3+} phosphor was confirmed both experimentally and theoretically by calculating the critical energy transfer distance between these ions. Sm^{3+} activated NSAB is a suitable phosphor for n-UV chip excited solid-state lighting.

2. Experimental

2.1. Sample preparation

Sm^{3+} doped NSAB phosphor was prepared by using the slow evaporation or solvent evaporation method. This method can be employed at relatively low temperatures and affords high controllability over particle size and homogeneity [13-19]. The stoichiometric amounts of high purity starting materials, $\text{Na}(\text{NO}_3)$ (A.R.), $\text{Sr}(\text{NO}_3)_2$ (A.R.), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (A.R.), $\text{Sm}(\text{NO}_3)_3$ have been used for phosphors preparation and they were mixed together in a china clay basin. A small quantity of deionized water was added to get a thick paste into which HNO_3 was added drop wise. The mixture was heated under observation at 50°C until the paste dissolved completely. The resulting solution was considered as NSAB: Sm^{3+} . The entire homogenous solution was then placed on a hot plate at 60°C to allow slow evaporation of water. Finally, after complete evaporation of water, the dried precursor obtained was crushed and annealed at 900°C to obtain white crystalline powder, NSAB: Sm^{3+} . A flow chart of the slow evaporation method is represented in Fig. 1.

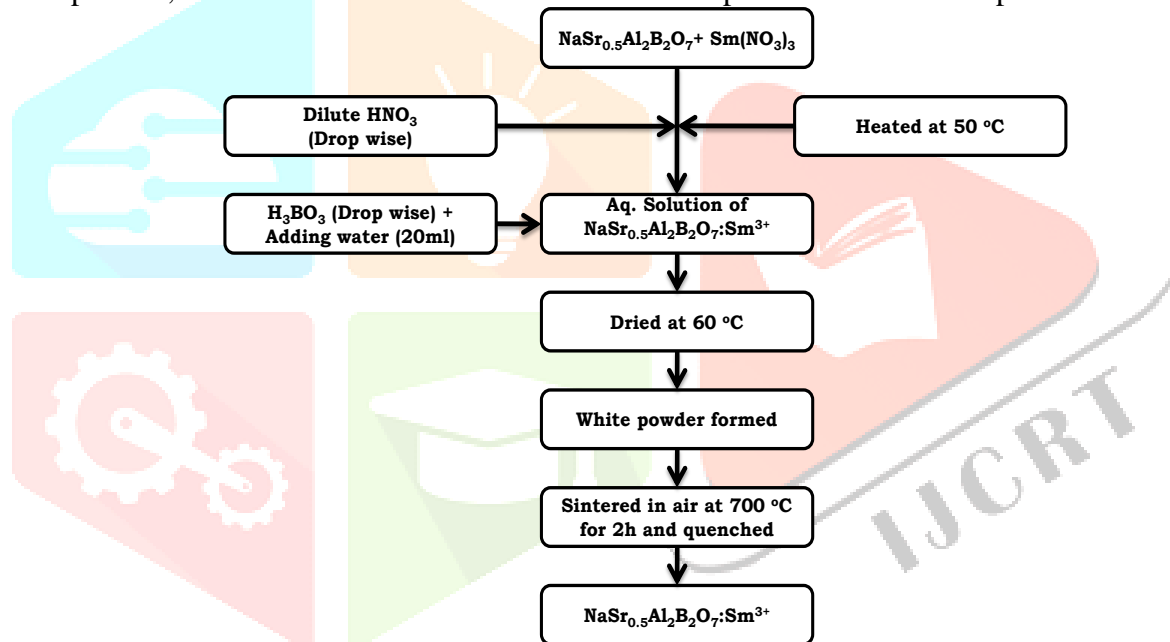


Fig. 1. Flow chart of the slow evaporation method used to synthesize NSAB: Sm^{3+} .

2.2. Material Characterizations

The phase and surface morphology of as prepared phosphors were characterized by X-ray diffraction measurements using Rigaku Miniflex II X-ray Diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda=1.54059 \text{ \AA}$) with scan speed $2^\circ/\text{min}$ and Field emission - scanning electron microscopy (FE-SEM) (Hitachi, Model-S4800 type II). The PL & PLE measurements at room temperature were performed on Hitachi F-7000 Spectrofluorometer with spectral resolution of 2.5 nm.

3. Results and Discussion

3.1. X-ray Diffraction Pattern

The XRD pattern of the host lattice of NSAB: Sm^{3+} is as shown in Fig. 2 and it was found to be in good agreement with the standard ICDD file No. 01-074-8644. There are no observable differences between these diffraction patterns, indicating that a little amount of doped RE ions has almost no effect on the NABO crystalline structure. The ionic size of Sm^{3+} (0.958 \AA) ion is smaller than that of Na^+ (1.02 \AA) and Al^{3+} (0.54 \AA) so the incorporation of the dopant may takes place in Na^+ lattice site in the crystal lattice.

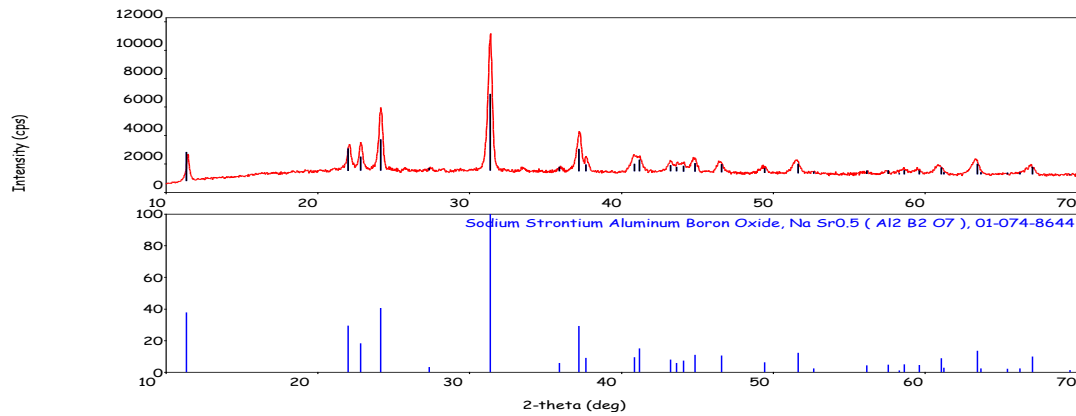


Fig 2. Powder XRD pattern of NSAB:Sm³⁺ phosphor.

3.2. SEM micrograph of phosphor powder

The SEM photographs of NSAB:Sm³⁺ powders prepared by solution combustion method is shown in Fig. 3. The shapes of the particles were observed to be random in nature with agglomeration for both the phosphors. The crystalline size of both the phosphors was observed to be varied in the range 0.3-2 μm .

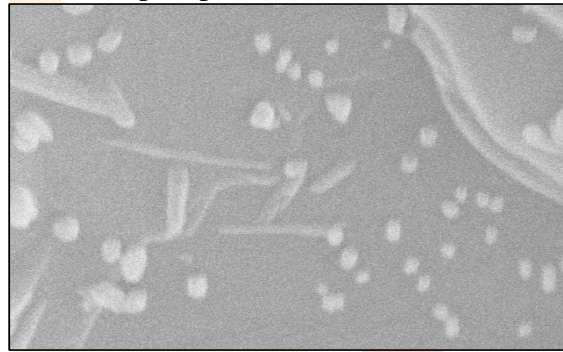


Fig 3. SEM images of NSAB:Sm³⁺.

3.3. Photoluminescence Analysis

3.3.1. Photoluminescence properties of NSAB:Sm³⁺ phosphor

Fig. 4 depict the spectral characteristics of NSAB:Sm³⁺ phosphor. To study the photoluminescence characteristics, the excitation spectrum was recorded for Sm³⁺ doped NSAB phosphor by monitoring the emission at 601 nm as depicted in Fig. 5. Among the observed excitation bands, the band centered at 402 nm due to 4f \rightarrow 4f inner shell transition of Sm³⁺ ion is very sharp and intense. Upon this excitation, the photoluminescence spectra for different concentrations of Sm³⁺ doped NSAB phosphors were recorded in the spectral range 450–750 nm. These spectra exhibit three emission bands centered at 564, 601 and 649 nm corresponding to the $^4G_{5/2} \rightarrow ^6H_J$ (J=5/2, 7/2, 9/2) transitions of Sm³⁺ ions, respectively. Among the observed emission transitions, the $^4G_{5/2} \rightarrow ^6H_{9/2}$ and $^4G_{5/2} \rightarrow ^6H_{11/2}$ transitions are purely electric dipole in nature ($\Delta J \leq 6$) whereas the other two transitions ($^4G_{5/2} \rightarrow ^6H_{5/2, 7/2}$) contain both electric and magnetic contributions ($\Delta J = 0, \pm 1$) [7]. The emission band corresponding to the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition possesses highest intensity. The luminescence intensity of Sm³⁺ in NSAB phosphors increases with the increase of its concentration, reaching a maximum at 3.0 mol% and then decrease for further rise of Sm³⁺ concentration.

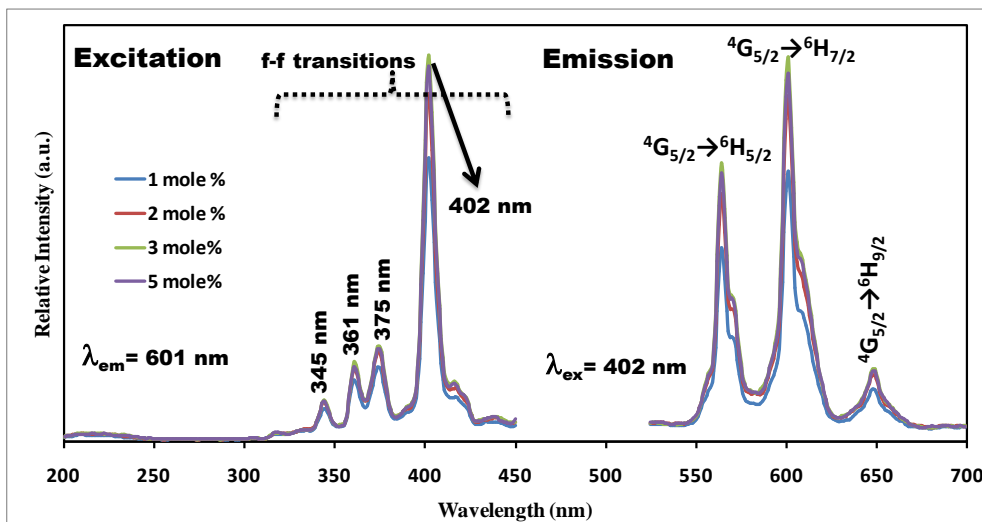


Fig 4. Excitation and emission spectra of NSAB:Sm³⁺ phosphor.

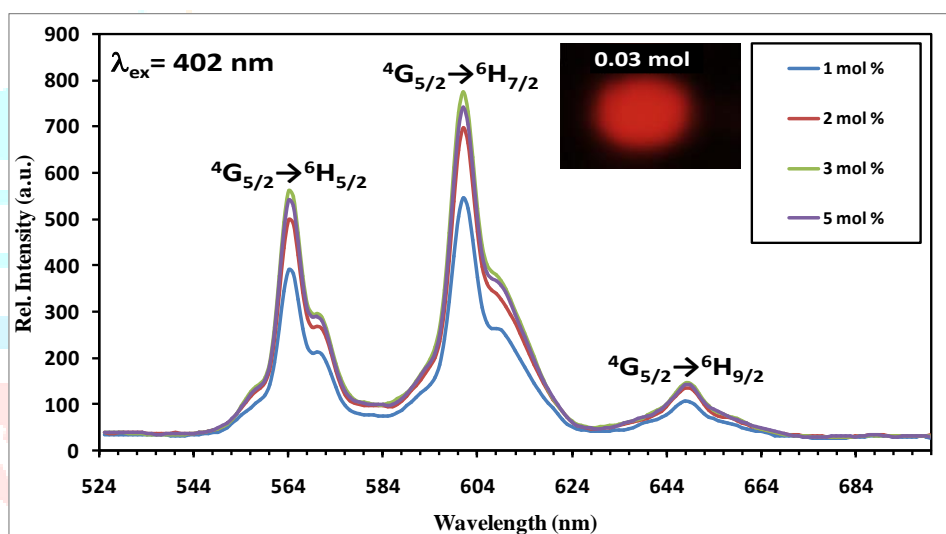


Fig 5. Dependence of the PL intensities of NSAB:Sm³⁺ at λ_{ex}=402 nm at different Sm³⁺ concentrations.

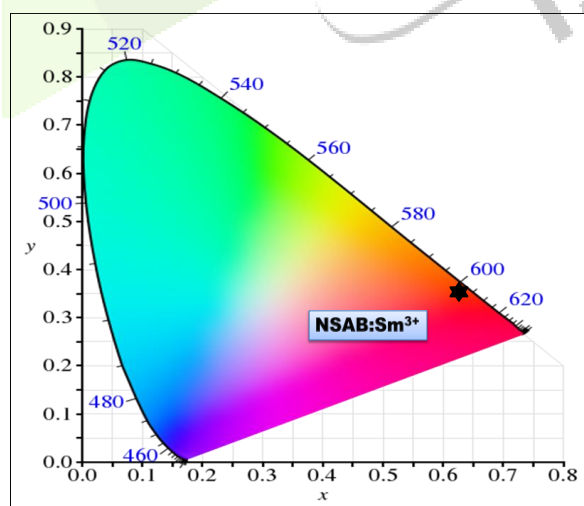


Fig 6. Chromaticity coordinates of NSAB:Sm³⁺ phosphor in the CIE 1931 chromaticity diagram.

3.3.2. Concentration quenching mechanism of NSAB:Sm³⁺ phosphor

According to Blasse [20], the critical transfer distance at optimum concentration can be calculated using Eq. (1):

$$R_c \approx 2 \left(\frac{3V}{4\pi\chi_c N} \right)^{1/3} \quad (1)$$

Where χ_c is the optimal concentration, V is the volume of the unit cell, N is the number of cations in the unit cell. The values of V and N of NSAB phosphor are 404.8 Å³ and 6. Using the optimal concentration χ_c , the critical transfer distance (R_c) for Sm³⁺ doped NSAB was approximately found to be 13.71 Å. The NSAB:Sm³⁺ phosphor exhibit intense green-red luminescence with Commission International de l'Eclairage in (CIE) chromaticity coordinates (x=0.63, y=0.36) which are duly located in the red-green region of CIE chromaticity diagram shown in Fig. 6 [21].

Conclusions

Rare earth Sm³⁺ activated NSAB phosphor was successfully synthesized by using solution combustion technique. The XRD patterns confirmed its phase structure and the FE-SEM image showed the closely packed particles with agglomerate phenomenon. The PL emission spectrum of Sm³⁺ ions at 402 nm excitation gives three bands centered at 564, 601 and 649 nm which corresponds to the ⁴G_{5/2}→⁶H_J (J=5/2, 7/2, 9/2) transition of Sm³⁺ ions as the surrounding offers high frequency vibrations. Based on the theoretical calculations, it is found that the exchange interaction is the major mechanism for concentration quenching of NSAB phosphor and the critical transfer distance was found 13.71 Å. Thus this phosphor may useful for solid state lighting and LED applications.

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