Photoluminescence properties of Tb\(^{3+}\) doped lithium alumino-borate phosphor, LiAlB\(_2\)O\(_5\):Tb\(^{3+}\)
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Abstract
A novel green phosphor, Tb\(^{3+}\) doped LiAlB\(_2\)O\(_5\) (LABO) has been synthesized by the solution combustion method of corresponding metal nitrates (oxidizer) and urea (fuel) at furnace temperature as low as 550 °C. The phase purity and morphology of LABO samples have been characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Photoluminescence spectra of the phosphor at room temperature exhibited emissions at 489, 549 and 586 nm, which were assigned to the \(^{3}D_4\rightarrow^{7}F_6\), \(^{3}D_4\rightarrow^{7}F_5\) and \(^{3}D_4\rightarrow^{7}F_4\) transitions of Tb\(^{3+}\) respectively. Among them, the green emission at 549 nm (\(^{3}D_4\rightarrow^{7}F_5\)) was dominant. For the 549 nm emission, the excitation spectrum has strong excitation peak locates at 229 nm. The dependence of the emission intensity on the Tb\(^{3+}\) concentration for the Li\(_{(1-x)}\)AlB\(_2\)O\(_5\): xTb\(^{3+}\) (0.01 ≤ x ≤ 0.03) was studied. It was observed that 0.025 mol % of doping concentration of Tb\(^{3+}\) ions in prepared phosphor was optimum. Concentration quenching of Tb\(^{3+}\) emission in LABO has been studied.

Keywords: Green phosphors; LiAlB\(_2\)O\(_5\):Tb\(^{3+}\); combustion method; Photoluminescence.

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1.0 Introduction
In recent years, the new lighting and display technology such as light-emitting diodes (LEDs), plasma display panels (PDPs), and field emission displays (FEDs) have been proposed or developed in industry, which result in great interest in searching novel phosphors for these new applications [1-6]. Tb\(^{3+}\) doped materials have been widely used as green emitting phosphor due to its intense \(^{3}D_4\rightarrow^{7}F_5\) emission in the green spectral region. Previous studies have shown that Tb\(^{3+}\) doped phosphates, aluminates or borates exhibit relatively strong absorption in the NUV region and intense green emission with good color purity [7-10]. The Tb\(^{3+}\) is a kind of important activator with sharp \(4f\rightarrow4f\) emission peak in the green region of visible spectrum, specially generating green emission with good color purity centered at around 543 nm, corresponding to the \(^{3}D_4\rightarrow^{7}F_5\) transitions [11-12]. However, the absorption transition of Tb\(^{3+}\) is difficult to pump owing to the absolutely forbidden \(4f\rightarrow4f\) electric dipole transitions. In case of Tb\(^{3+}\) ion, the absorption is usually due to allowed \(f\rightarrow d\) transition from excited state of \(4f^{5}\ 5d^1\) configuration, the electron loses energy to lattice and blue region while \(^{3}D_4\rightarrow^{7}F_5\) emission is predomnantly green. At lower concentrations, blue emission is observed; but at higher concentration, there is an energy transfer between Tb\(^{3+}\) ions, e.g. the cross relaxation \(^{3}D_3\) + Tb\(^{3+}\) (\(^{7}F_0\)) → Tb\(^{3+}\) (\(^{3}D_3\)) + Tb\(^{3+}\) (\(^{7}F_0\)), due to which the blue emission gets quenched increasing the green emission at the same time. Tb\(^{3+}\) emission may be efficiently sensitized by transfer from sensitizer to \(4f^0\) levels. The energy transfer is introduced between the broad band excitation of \(4f\rightarrow5d\) transition ions and the sharp line emission of \(4f\rightarrow4f\) transition ions [13]. In this study, LiAlB\(_2\)O\(_5\):Tb\(^{3+}\) phosphors were prepared by conventional solid state reaction method. The phase and surface morphology of synthesized materials were investigated using the XRD and SEM. After synthesis and characterization of the phosphors, the photoluminescence properties of the synthesized phosphors were studied using a spectrophotometer at room temperature. Further the dependence of the emission intensity on the Tb\(^{3+}\) concentration for the Li\(_{(1-x)}\)AlB\(_2\)O\(_5\): xTb\(^{3+}\) (0.01 ≤ x ≤ 0.03) was studied in detail.

2.0 Materials and method
The powder samples of Tb\(^{3+}\) activated LABO phosphor were prepared by a solution combustion technique. In our previous work, many borate materials were successfully synthesized using this technique [14-18]. High purity starting materials, Li(NO\(_3\))\(_2\) (A.R.), Al(NO\(_3\))\(_3\).9H\(_2\)O (A.R.), Tb (NO\(_3\))\(_3\) (high purity 99.9%), H\(_3\)BO\(_3\) (A.R.), CO(NH\(_2\))\(_2\) (A.R.) were used for the phosphor preparation. The stoichiometric amounts of the ingredients were thoroughly mixed in an Agate Mortar with adding little amount of double distilled water. The material then transferred into china basin and heated on heating menthol at about 70°C so as to obtained clear solution. The solution was then introduced into a pre-heated muffle furnace maintained at temperature 550°C for combustion. The solution boils; foams and
ignites to burn with flame which gave a voluminous, foamy powder. Following the combustion, the resulting foamy samples were crushed to obtain fine particles and then annealed in a slightly reducing atmosphere provided by burning charcoal at temperature 750 °C for 2 hr and suddenly cooled to room temperature.

The prepared materials were characterized by powder XRD. Powder X-ray diffraction measurements were taken on Rigaku Miniflex II X-ray Diffractometer and compared with the ICDD file. PL & PLE measurements at room temperature were performed on Hitachi F-7000 spectrofluorometer with spectral resolution of 2.5 nm.

3.0 Results and discussion
3.1. X-ray diffraction pattern
The X-ray diffraction (XRD) technique was used to identify the phase composition, structure and their crystallinity. Fig. 1 shows the XRD pattern of LiAlB2O5:Tb3+ phosphor. The XRD pattern of the as prepared phosphor powder shows good agreement with standard ICDD File. The ionic radius of Tb3+ (0.923 Å) is larger than Li+ (0.76 Å) and Al3+ (0.535 Å); Tb3+ ions may enter into the host lattice to substitute Al3+ or Li+ or locate on the surface of the crystal. It would have greater tendency to occupy lithium as compared to aluminum sites.

3.2. SEM images of phosphor powders
The SEM photographs of LiAlB2O5:Tb3+ powder synthesized by using solution combustion method is shown in Fig. 2. The morphology of particles are crystalline and mostly with some random shaped crystals. The mean diameter of the particle is approximately 1 to 2 μm; the particles grow together and form larger aggregates, due to high temperature synthesis processes. It is clear that the particles are tightly bonded together to form large agglomerates.

3.3. Photoluminescence study
Fig. 3 gives the excitation and emission spectra of Tb3+ doped LABO phosphor. The excitation spectrum shows broad band ranging from 200 to 350 nm with intense peak around 229 nm. The as prepared phosphor compositions exhibits emission in the blue–green region is as shown in Fig. 4(A). The emission bands show a splitting pattern, such as 5D4→7FJ transition of Tb3+ (543 and 549 nm). LiAl2B2O5:Tb3+ powders exhibited several emission lines peaking at 489, 543, 549, 586 and 594 nm, which were assigned to the 5D4→7FJ (J=6, 5, 4, 3, 2) transitions of Tb3+. Among them, the green emission at 543 nm (5D4→7F5) was dominant.
Fig. 4: (A) Dependence of the PL intensities of Li_{1-x}Al_{2}O_{5}:xTb^{3+} (0.01 ≤ x ≤ 0.03) at λ_{ex}=229 nm at different Tb^{3+} concentrations. (B) The top inset shows the influence of the concentration on the emission intensity of Li_{1-x}Al_{2}O_{5}:xTb^{3+} (0.01 ≤ x ≤ 0.03) phosphor.

The cross-relaxation of adjacent Tb^{3+} ions led to the main emission peaks locate at 489 and 543 nm under excitation of 229 nm. Local crystal field symmetry around the Tb^{3+} cations can have a significant effect on electric dipole transitions. However, when the crystal size is decreased, surface defects decrease the local symmetry around the Tb^{3+} cations, increasing the intensity of the green emission.

3.3.1. Concentration quenching mechanism of Tb^{3+} in Li_{1-x}Al_{2}O_{5}:0.025Tb^{3+}

In order to optimize the green emission of Tb^{3+}, the concentration dependent emission intensity of Li_{1-x}Al_{2}O_{5}:xTb^{3+} (x=0.01,0.015, 0.02, 0.025, 0.03) was studied. Fig. 4(B) shows that the dependence of the emission intensities of Li_{1-x}Al_{2}O_{5}:xTb^{3+} (x=0.01,0.015, 0.02, 0.025, 0.03) phosphors under 229 nm excitation. However, the emission intensity of Tb^{3+} initially increases, then reaches a maximum at x=0.025, and finally decreases. The critical transfer distance (R_{c}) is the critical separation between donor and acceptor, at which the non radiative rate equals that of the internal single ion relaxation. It is approximately equal to twice the radius of a sphere with this volume [19]:

\[ R_{c} = 2\left(\frac{3V}{4\pi N}\right)^{1/3} \]  

Where \( \chi \) is the critical concentration, \( N \) the number of cation in the unit cell and \( V \) the volume of the unit cell (\( N=6, V=306.12 \text{ Å}^{3} \) for LABO). \( R_{c} \) is calculated to be about 12.49 Å. The resonant energy transfer mechanism consists of two types: exchange or multipolar interaction. For the exchange interaction, \( R_{c} \) is generally shorter than 0.3–0.4 nm. Therefore, the energy transfer mechanism in LABO: Tb^{3+} is considered as a multipolar interaction. The quenching mechanism is associated with the interaction between the one excited ion and another, and the emission intensity per activator ion follows the equation [20]:

\[ I_{I/x} = K[1 + \beta(x)^{Q/3}]^{-1} \]  

where \( x \) is the activator concentration; \( Q=6, 8, 10 \) for dipole–dipole (d–d), dipole–quadrupole (d–p), quadrupole–quadrupole (q–q) interactions, respectively; and \( K \) and \( \beta \) are the constants for the same excitation conditions in a given host crystal. The critical concentration of Tb^{3+} has been determined to be 0.025 mole. The plot of log(I/x) as function of log(x) in LABO: Tb^{3+} phosphor is obtained by using Dexter’s theory [21] , and shown in Fig. 5.

It represents that the dependence of log(I/x) on log(x) is linear and the slope is -1.733. The value of Q was calculated as 5.2 (close to 6). This suggests that the electric d–d interaction is responsible for the concentration quenching mechanism of Tb^{3+} emission in LABO: Tb^{3+} phosphor.

Fig. 5: Plot of log(I/x) as function of log(x) in Li_{1-x}Al_{2}O_{5}:0.025Tb^{3+} (x=0.01,0.015, 0.02, 0.025, 0.03) (λ_{ex}=229 nm).

The CIE chromaticity coordinates for Li_{0.975}Al_{2}B_{2}O_{7}:Tb^{3+} were calculated from the PL spectra under 229 nm excitation and marked with a white star in the CIE 1931 chromaticity diagram in Fig. 6. The chromaticity coordinates (x,y) of this phosphor are (0.2944,0.6988), respectively, which indicates that the emission color of the as prepared phosphors is located in the green region.
Fig. 6: Chromaticity coordinates of Li_{0.975}AlB_2O_5:0.025Tb^{3+} phosphor in the CIE 1931 chromaticity diagram.

4. Conclusions
The phosphor LiAlB_2O_5:Tb^{3+} has been successfully synthesized by using a simple, time saving and cost effective solution combustion technique. The as synthesized phosphor shows mainly two emission bands located at blue (489 nm) and green band (544 nm) corresponding to the ^5D_4→^7F_5 transition spectra region originated from the transition of Tb^{3+} ions. It is found that 0.025 mol% doping concentration of Tb^{3+} ions in LABO phosphor is optimum in the host lattice. LABO:Tb^{3+} phosphor can be used for generating green light under UV radiation.

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References: