Enhanced Photoluminescence Properties of $\text{BaAl}_2\text{O}_4: \text{Ce}^{3+}/\text{Li}^+$ Yellow Phosphors

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Abstract

$\text{Ce}^{3+}/\text{Li}^{+}$ activated barium aluminate phosphor (BAO) was synthesized by conventional solid-state reaction method. The crystal structure of the synthesized phosphor was analyzed by X-ray diffraction (XRD) and Raman spectroscopy analysis. FT-IR spectrum results revealed the characteristic vibration bands present in the synthesized phosphor. Surface composition analysis of the prepared samples was examined using X-ray photoelectron spectroscopy (XPS). PL emission band observed at 589 nm was assigned to 5D excited level corresponding to $^2\text{F}_{5/2}$ transition in yellow region under the excitation wavelength of 320 nm. Yellow light emission was confirmed by the Commission Internationale de L'Eclairage (CIE) chromatic coordinate graph. The color purity of $\text{BAO}: 0.5\text{Ce}^{3+}$, $\text{BAO}: 0.5\text{Ce}^{3+}, 0.1\text{Li}^{+}$ was found to be 78.4 %, 81.3 % whereas the measured lifetime was 4.333, 4.738 ns respectively.

Introduction

Alkaline earth aluminates doped with rare earth ions have attracted considerable attention as a research topic owing to the properties like long-afterglow phosphorescence, fast scintillation due to their thermal & chemical stability, high quantum efficiency [1] and their potential applications in the areas of safety improvement, radiation detection and light emitting diodes (LEDs) [2]. Right now, due to low cost and simple fabrication, the combination of yellow phosphors (YAG: Ce) and a blue LED has been the popular route for white light generation [3]. Vasilica Tucureanu et al., reported enhancement of optical properties of Ce^{3+} doped YAG prepared by co-precipitate method [4]. D. Jia et al., reported long persistent $\text{BaAl}_2\text{O}_4:\text{Ce}^{3+}$ phosphor with persistence luminescence longer than 10 h [5]. M. Ayvacikli reported copper-doped barium aluminate synthesized by the conventional ceramic method, emitting green light [6]. A rare-earth trivalent metal ion cerium (Ce^{3+}) doped aluminate based phosphors synthesized by Foka et.al., exhibited photoluminescence with emission peaks in the long UV region [7]. Cerium and Manganese doped BaAl_2O_4 were synthesized by Simone et. al., Mn doped BaAl_2O_4 's emission color was investigated and it was found that by changing the concentration of the Mn as co-dopant ion, the emission color can be tuned [8]. Researchers observed an enhancement in the luminescence properties of phosphors by doping with Li^{+} ions in order to stabilize the oxidation state of dopant, thereby increasing the luminescence properties [9]. To enhance the luminescence intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$, B^{3+} phosphors, Li^{+} dopant was used as a charge compensator. Li^{+} co-doped $\text{SrAl}_2\text{O}_4:\text{Eu}^{3+}$ was used in the production white UV light-emitting diodes (LEDs) [10]. Y.N. Zhu et al., observed an enhancement of PL intensity in the case of $\text{Y}_2\text{O}_3:5\% \text{Eu}^{3+}$ phosphors co doped with Li^{+} [11].

In the present work, we report the synthesis of barium aluminate (BaAl_2O_4) phosphors doped with different concentration of cerium (Ce^{3+}) and co-doped with Lithium (Li^{+}) by using conventional solid state reaction method. The crystal structure and photoluminescence properties of $\text{Ba Al}_2\text{O}_4: x \text{Ce}^{3+}, y \text{Li}^{+}$ Phosphors were investigated in detail.

Experimental and characterization technique

$\text{Ba}_{(1-x-y)}\text{Al}_2\text{O}_4$: $x\text{Ce}^{3+}$, $y\text{Li}^+$ phosphors were prepared using solid-state reaction (SSR) method, taking stoichiometric composition of high purity oxide chemicals. Starting material such as Barium carbonate (BaCO_3 ; Sigma Aldrich), Aluminum oxide (Al_2O_3 ; Alfa Aesar), Cerium (IV) oxide (CeO_2 ; sigma) and Lithium carbonate (Li_2CO_3 ; sigma) were mixed homogeneously using agate mortar for 30 min. Small amount of ethanol was added in order to ensure homogeneity mixing of the starting composition. Then the mixed powder was transferred into alumina crucibles and placed inside a box type furnace and the temperature was increased at a heating rate of $5^\circ\text{C}/\text{min}$. During the process, the synthesized temperature was maintained at 1100°C for 12 hrs. The obtained powders were reground and heated at 1100°C for 12hr in a reducing atmosphere where carbon powder was used as a reduction agent. Later the obtained phosphors were subjected to different characterizations.

Crystalline phase of the synthesized material was identified by X-ray diffraction (XRD; PANalytical) analysis with $\text{Cu-K}\alpha_1$ radiation of wavelength ($\lambda = 1.5406 \text{ \AA}$), working voltage 40 kV and current 40 mA with step size 0.026. The X-ray data were analyzed by Rietveld Refinement using full proof package. Raman spectroscopy was performed on the synthesized BaAl_2O_4 compound using a laser with wavelength of 532 nm in the range of 100 cm^{-1} to 900 cm^{-1} . The obtained Raman data was smoothed using a Savitzky-Golay filter and the base line was corrected using an adaptive iteratively reweighted penalized least square (airPLS) algorithm [12]. Fourier transformed infrared (FTIR) spectroscopy (Bruker, Alpha T) was used to perform vibrational spectroscopic analysis of the synthesized phosphors. The composition profile of the sample was recorded using X-ray Photoelectron Spectroscopy (XPS) (ULVAC-PHI, PHI 5000 version probe III). The photoluminescence (PL) spectra of the synthesized phosphor were recorded by spectrofluorometer (Shimadzu, RF-5301PC, Japan) using a xenon lamp as the excitation source. Fluorescence lifetime decay measurements was observed DeltaProTM fluorescence lifetime system (HORBIA Scientific) using diode laser as a excitation source.

Results And Discussion

Powder XRD pattern of pure, $x\text{Ce}^{3+}$ doped BaAl_2O_4 ($x = 0.1, 0.5$ and $1 \text{ M.W \%}$) and Li^+ co-activated BaAl_2O_4 : 0.5Ce^{3+} , $y\text{Li}^+$ ($y = 0.1, 0.5$ and $1 \text{ M.W \%}$) is shown in the Fig. 1. The XRD pattern is in well agreement with standard JCPDS pattern data No.17-0306 with space group P6_322 , which exhibit hexagonal structure along with minor impurities peak around 24° , due to the presence of BaCO_3 [8, 13]. In spite of Ce and Li doping, no change in the XRD pattern is observed. Figure.2 represents the Rietveld refinement of pure BAO using full proof suite and BaAl_2O_4 stuffed tridymite structure in the AlO_4 tetrahedral site. In the refinement at low angle 24° there was no Bragg position (green line), which indicates the presence of minor impurity phase existing in the sample. The lattice parameters obtained by Rietveld refinement are listed in table 1, which are in good agreement with previous reports. [14].

Figure 3. shows the Raman spectra of the synthesized BaAl_2O_4 . The Raman spectra shows 4 distinct peaks at 244 cm^{-1} , 415 cm^{-1} , 591 cm^{-1} and 691 cm^{-1} corresponding to F_{2g} (1), E_g , F_{2g} (2) and F_{2g} (3) modes. The wavenumbers and the sequence of these modes (F_{2g} (1) < E_g < F_{2g} (2) < F_{2g} (3)) conform to the characteristic modes exhibited by aluminate spinels [15].

The F_{2g} (1) Raman mode observed at $\sim 244\text{ cm}^{-1}$ along with a shoulder observed at 199 cm^{-1} are assigned to the translation of the tetrahedron in the crystal structure, which is typically occupied by Ba^{2+} ions [16]. The E_g mode observed at $\sim 415\text{ cm}^{-1}$ has been attributed to the movement of oxygen atoms along the T-O bonds, (i.e.) bonds between the tetrahedral sites, occupied by Ba^{2+} ions, and oxygen [15]. A shoulder can be observed on the E_g mode at $\sim 395\text{ cm}^{-1}$. This can be attributed to the cation disordering caused by the bending mode of Al ions on the tetrahedral sites [15]. There isn't much work discussing the origins of the F_{2g} (2) peak observed at $\sim 591\text{ cm}^{-1}$. It has been assigned to the symmetric bending of oxygen with respect to the cations at the tetrahedral sites [16]. Shoulders to the left and right of the F_{2g} (2) mode can be observed in Fig. 3. Further examination would yield information about the origin of the disorders causing the breakdown of Raman selection rules. The nature of the octahedral cation dictates the position of the F_{2g} (3) mode, observed at 691 cm^{-1} [15]. However, few authors have assigned this mode to the asymmetric bending or stretching of oxygen with respect to the tetrahedral cation [16]. Group theory analysis predicts the occurrence of an acoustic mode A_{1g} and its wavenumber is likely to be $> F_{2g}$ (3) [15]. Chromates and ferrites are known to exhibit intense A_{1g} modes while in contrast, aluminates (BaAl_2O_4) are known to exhibit weak A_{1g} peaks. A weak peak can be observed at $\sim 760\text{ cm}^{-1}$ from Fig. 3 corresponding to A_{1g} mode.

Figure 4. shows the FTIR spectra of pure, 0.5% Ce^{3+} doped BAO and Li^+ co-activated BaAl_2O_4 : 0.5 Ce^{3+} , 0.1% Li^+ . It can be observed that all the synthesized samples exhibit absorptions peaks at 662, 732, 803, 856, 1021 and 1450 cm^{-1} . The four absorption peaks centered around frequency range of 600–1000 cm^{-1} can be designated to the stretching vibrations of Al–O, Ba–O and Ba–O–Al in the synthesis BaAl_2O_4 phosphors, respectively. The absorption peak at 1450 cm^{-1} can be designated to the stretching vibration of AlO_4 in a unit of the tetrahedral BaAl_2O_4 phosphors, which confirms the formation of the BaAl_2O_4 phase [17].

Compositional analysis of BAO: 0.5 Ce^{3+} phosphors, performed using X-ray photoelectron spectroscopy (XPS) is shown in Fig. 5. Ba 3d, Al 2p, O 1s and Ce 3d core levels of the BAO: 0.5 Ce^{3+} are from the photoelectron signals. Two peaks present at approximately 790 eV ($3d_{5/2}$) and 795.4 eV ($3d_{3/2}$) confirm the presence of Ba 3d, which matches well with the reported data. Al 2p spectrum consists of two peaks at 72.3 eV ($2P_{3/2}$), 73.5 eV ($2P_{1/2}$), which affirms the presence of Al metal and Al-O, respectively. Photoelectron signal from O 1s, observed at 530.4 eV and 531.3 eV can be attributed to the formation of metal oxides and metal carbonates [18]. Ce 3d composed of two multiplets to spin-orbit split $3d_{5/2}$ and $3d_{3/2}$, respectively. The binding energy peaks at 906 eV, 901.54 eV ($\text{Ce}^{4+} 3d_{5/2}$) and peaks at 896.49 eV,

890.14 eV ($\text{Ce}^{4+} 3d_{3/2}$) is assigned to Ce 3d. Four photoelectron signal peaks at 898.4 eV, 904.2 eV and 884.4 eV, 887.5 eV is assigned to $\text{Ce}^{3+} 3d_{5/2}$ and $\text{Ce}^{3+} 3d_{3/2}$ [13, 19, 20].

Figure 6. shows the photoluminescence excitation spectra of BAO: xCe^{3+} ($\text{x} = 0.1, 0.5$ and $1 \text{ M. W } \%$) phosphor. The spectrum was recorded in the range of 260 to 350 nm for the emission wavelength 589 nm. Excitation spectrum at 320 nm ($^2\text{F}_{5/2}$ - excited 5D states) corresponds to the transition to 4f-5d from the ground state of Ce^{3+} ion. Generally, Ce^{3+} has two ground states of $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ due to the spin-orbit interaction [21].

Figure 7. shows the emission spectra of phosphors recorded in the range between 400 to 700 nm. It shows the photoluminescence emission spectra of BAO: xCe^{3+} ($\text{x} = 0.1, 0.5$ and $1 \text{ M. W } \%$) and BAO: 0.5% Ce^{3+} co-doped with Li^+ phosphor under excitation wavelength of 320 nm. The comparison of PL emission spectra of only Ce^{3+} doped and Ce^{3+} doped with Li^+ co-doped is shown in the inset of Fig. 7. The phosphor exhibits broad peak centered at 589 nm which signifies a transition from excited level 5D to $^2\text{F}_{5/2}$ [22]. The transitions of the yellow light emission of the Ce^{3+} rare-earth element belongs to the electric dipole transition which is tuned by Ce^{3+} ion site [23].

The critical energy distance (R_c) can be calculated using Blasse Eq. (1) [24].

$$R_c = 2 \times \sqrt[3]{\left[\frac{3V}{4\pi N X_c} \right]} \quad (1)$$

Here N represents the number of Z cations in the unit cell (i.e. 8)

V is the Volume of unit cell ($\text{\AA}^3$) = 830.4 $\text{\AA}^3$

X_c is the critical concentration = 0.5

The interaction between Ce^{3+} ions is stimulated by increasing doping concentration but non radiative energy transfer between the doping ions can lead to either electric multipolar or exchange interactions. Generally, exchange interactions take place a smaller value of R_c ($< 5 \text{\AA}$), otherwise electric multipolar interactions dominate. For BAO: Ce^{3+} phosphors the value of R_c was found to be 15.83 $\text{\AA}$, herein the electric multipolar interactions take place [13, 25]. To enhance the luminescence intensity of barium aluminates, different concentration of Li^+ ions are doped into highest luminescence of BAO: 0.5 Ce^{3+} host matrix. Researchers reported the successful enhancement of luminous intensity by co doping Li^+ with CaO: Ce^{3+} , CaTiO: Dy , and $\text{Ca}_2\text{SrAl}_2\text{O}_6: \text{Ce}^{3+}, \text{Mn}^{3+}$, $\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Ce}^{3+}$ matrix [26, 27, 28, 29]. It is noted that the luminescence intensity can be further increased at suitable Li^+ ion concentration. Initially the luminescence intensity increases and then decreases with the increase of Li^+ concentration. Li^+ ion doped into BAO: xCe^{3+} host lattice, the Li^+ ion radii (76 pm) in turn lead to occupy the defect site due the smaller ionic radius, which changes the symmetry of local environment of Ce^{3+} in crystal lattice and prevents the

relaxation between Ce^{3+} ion. As a result, the luminescence intensity is enhanced by co-activator Li^+ ion [10, 30].

Exact emission color of phosphors for both BAO: $x \text{ Ce}^{3+}$ ($x = 0.1, 0.5$ and $1 \text{ M.W } \%$) and BAO: $0.5 \text{ Ce}^{3+}, y \text{ Li}^+$ ($y = 0.1, 0.5$ and $1 \text{ M.W } \%$) was identified using the Commission International del'Eclairage (CIE) chromaticity coordinates (X, Y) graph as shown in Figure. 8, 9, respectively. It can be seen that the emission is located in yellow region [31]. From the above results, BAO: $0.5\text{Ce}^{3+}, 0.1\text{Li}^+$ phosphor can be considered as a proper source for emitting yellow light under 320 nm excitation wavelength. Calculated CIE chromaticity coordinates of the phosphors is shown in inset of Figs. 8 & 9. The color purity of the synthesized phosphors is found by given expression. (2). [32]

$$\text{Color purity} = \frac{\sqrt{(x-x_i)^2 + (y-y_i)^2}}{\sqrt{(x_d-x_i)^2 + (y_d-y_i)^2}} \times 100 \quad \text{————— (2)}$$

Here,

x, y is the chromaticity coordinate $0.5\% \text{ Ce}^{3+}$ doped BAO ($x = 0.4864, y = 0.4412$) and BAO: $0.5\% \text{ Ce}^{3+}, 0.1\% \text{ Li}^+$ of the sample ($x = 0.49868, y = 0.44171$)

x_i, y_i are the coordinates of the illuminate point ($x_i = 0.3101, y_i = 0.3162$)

x_d, y_d are the coordinate of dominant emission wavelength of $0.5\% \text{ Ce}^{3+}$ doped BAO ($x_d = 0.5550, y_d = 0.4423$) and BAO: $0.5\% \text{ Ce}^{3+}, 0.1\% \text{ Li}^+$ of the sample ($x_d = 0.5568, y_d = 0.4455$)

In this Present work, the synthesized phosphors displayed a color purity 78.4% and 81.3% for $0.5\% \text{ Ce}^{3+}$ doped BAO and BAO: $0.5\% \text{ Ce}^{3+}, 0.1\% \text{ Li}^+$, respectively. Correlated color temperature (CCT) value of the phosphors is calculated using McCamy empirical formulae (3) and (4). In the current work CCT value of $0.5\% \text{ Ce}^{3+}$ doped BAO phosphor and BAO: $0.5\% \text{ Ce}^{3+}, 0.1\% \text{ Li}^+$ are 2583 K and 2450 K , respectively. Results indicate that both doped phosphors are close to value of warm yellow light ($< 4000 \text{ K}$) [33].

$$\text{CCT} = -449n^3 + 3525n^2 - 6823.3n + 5520.33 \quad \text{————— (3)}$$

$$\text{Where, } n = \frac{x-x_e}{y-y_e} \quad \text{————— (4)}$$

Here, $x_e = 0.332, y_e = 0.186$, is the epicenter

Figure 10 and 11 shows the lifetime decay spectra of BAO: $x\text{Ce}^{3+}$ ($x = 0.1, 0.5, 1 \text{ MW } \%$) and BAO: $0.5\% \text{ Ce}^{3+}, x\text{Li}^+$ ($x = 0.1, 0.5, 0.1 \text{ MW } \%$) phosphors excited under 320 nm . $0.5 \text{ MW } \%$ Ce^{3+} ion doped BAO phosphor exhibited high decay lifetime values when compared to other percentage of Ce^{3+} dopant. Figure 11 results show a decrease lifetime with increase in Li^+ ion concentration. The curves are fitted with biexponential function indicated with red line in the spectra.

Fitted by a biexponential function is given Eq. (5) [34].

$$y = y_0 + A_1 \exp \left\{ -\frac{t}{\tau_1} \right\} + A_2 \exp \left\{ -\frac{t}{\tau_2} \right\} \text{--- (5)}$$

Here,

A_1, A_2 - weighting parameters,

τ_1, τ_2 - components of lifetime decay.

The average lifetime is calculated using the Eq. (6) given below:

$$t_{\text{avg}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \text{--- (6)}$$

The calculated average lifetimes of BAO: 0.5Ce³⁺ and BAO: 0.5Ce³⁺, 0.1Li⁺ phosphors are 4.333 and 5.63 ns respectively. The result indicate that the Li⁺ doping results in the enhancement of lifetime in Ce³⁺ doped BAO phosphor. When the Li⁺ ion concentration increases in BAO: 0.5 Ce³⁺ phosphor, the life time decreases due to non-radiative transition 5d→4f between the Ce³⁺ ion.

From Luminescence decay spectra, the lifetimes of 0.5% Ce³⁺ ions increase with increase of Li⁺ ion, which is due to the energy transfer from the Ce³⁺ to Li⁺ ions. The energy transfers efficiency (η_{ET}) was found using Eq. (7) [35].

$$\eta_{\text{ET}} = 1 - \left\{ \frac{\tau_{0.5\text{ce}}}{\tau_{x\text{Li}}} \right\} \text{--- (7)}$$

Here,

$\tau_{0.5\text{ce}}$ - lifetimes of BAO: 0.5Ce³⁺

$\tau_{x\text{Li}}$ - lifetimes of BAO: 0.5% Ce³⁺, xLi⁺ (x = 0.1, 0.5, 1 MW%)

The calculated values of energy transfer efficiency are 23.09%, 13.40% and 09.41% for BAO: 0.5% Ce³⁺, xLi⁺ (x = 0.1, 0.5, 1 MW%), respectively.

Conclusion

Light emission display in Yellow to orange region was confirmed by CCT value and CIE chromaticity graph of phosphors BAO: xCe³⁺ (y = 0.1, 0.5 and 1 M.W %) and BAO: 0.5%Ce³⁺, y% Li⁺ (y = 0.1, 0.5 and 1 M.W %) synthesized by solid state reaction method. The synthesized phosphor emitted yellow (589 nm)

light when excited with a radiation of wavelength 320 nm due to excited 5D states to $^2F_{5/2}$ transition. The observed lifetime decay of synthesized phosphors BAO: $x\text{Ce}^{3+}$ and BAO: $0.5\%\text{Ce}^{3+}$, $y\%\text{Li}^{+}$ are 4.33, 4.78 ns respectively. In conclusion, the yellow light source BAO: $0.5\%\text{Ce}^{3+}$, $0.1\%\text{Li}^{+}$ phosphor may be a crucial phosphor as a solid state lighting devices application.

Declarations

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Figures

Figure 1

Powder XRD pattern of BAO: x Ce³⁺ ($x=0, 0.1, 0.5, 1$ M. W %) and BAO: 0.5Ce^{3+} , y Li⁺ ($y=0.1, 0.5$ and 1 M.W %)

Compound	MgAl ₂ O ₄
Structural Parameters	
a=b(Å)	5.2202
c (Å)	8.7905
α, β, γ (°)	90, 90, 120
Space group	P6 ₃ 22
Structure	hexagonal
Goodness of fit (χ^2)	1.98

Figure 2

Rietveld refinement pattern and illustration of AlO₄ tetrahedral site in the BaAl₂O₄ stuffed tridymite structure.

Figure 3

Micro Raman spectra of as synthesized BAO

Figure 4

FTIR spectra of pure BAO, 0.5%Ce³⁺ doped BAO and BAO: 0.5%Ce³⁺, 0.1%Li⁺

Figure 5

XPS Spectra for Ce³⁺ doped BAO phosphors

Figure 6

Photoluminescence excitation spectrum for BAO: 0.5% Ce³⁺ phosphor.

Figure 7

Photoluminescence emission spectrum for BAO: $x\text{Ce}^{3+}$ ($x=0.1, 0.5$ and 1 M.W %) and BAO: $0.5\% \text{Ce}^{3+}, y \text{Li}^{+}$ ($y=0.1, 0.5$ and 1 M.W %) phosphors. (Insert: comparison spectrum)

Figure 8

CIE coordinates of BAO: $x\text{Ce}^{3+}$ ($x=0.1, 0.5$ and 1 M.W %) phosphors.

Figure 9

CIE coordinates of BAO: 0.5% Ce³⁺, y Li⁺ (y=0.1, 0.5 and 1 M. W %) phosphors.

Figure 10

Luminescence decay spectra of the (a) BAO: 0.1% Ce³⁺ (b) BAO: 0.5% Ce³⁺ (c) BAO: 1% Ce³⁺

Figure 11

Luminescence decay spectra of the (a) BAO: 0.5% Ce³⁺, 0.1% Li⁺, (b) BAO: 0.5% Ce³⁺, 0.5% Li⁺ and (c) BAO: 0.5% Ce³⁺, 1% Li⁺ phosphors.