Luminescence of Tm\(^{3+}\), Yb\(^{3+}\) Co-doped CaLaAlO\(_4\)/LaAlO\(_3\) Mixed Phase Phosphor for Solid-state Lighting Application

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1. INTRODUCTION

In the last century, many researchers have utilized rare earths (REs) in different host lattices as luminescent centers [1 – 3]. The inorganic luminescence material (phosphors) produced by doping with REs features a variety of electronic transitions within the 4f configuration [4]. These upconversion luminescence (UCL) materials find their applications in solid-state lighting (SSL) devices (light emitting diodes, luminescence lamps), plasma display panels, biological imaging, lasers, anticontrol, and solar cells [5, 6]. In comparison with traditional luminescence materials, UCL has low energy consumption, a long lifetime, and low excitation energy [7]. The RE-doped UCL materials can convert two or more low energy photons into an excited state that has a narrow-line emission covering blue, red and NIR regions [12]. However, the luminescence efficiency of Tm\(^{3+}\) single doped host material is low [13]. This is because Tm\(^{3+}\) ions have many relaxation paths at the excited state. To enhance the UCL efficiency, Tm\(^{3+}\) ions can be co-doped with a sensitizer such as Yb\(^{3+}\) due to their closely matched intermediate-excited state [4]. Additionally, the absorption energy of Yb\(^{3+}\) matched well with the commonly used 980 nm laser diode for UCL [14]. Yb\(^{3+}\) is a good sensitizer that transfers the energy it absorbed to the activator [6, 7].

The host matrix has much influence on the luminescence properties of the dopants [5]. This is because it provides a platform for the energy transfer mechanism [7]. In this regard, efforts have been made to formulate a suitable host matrix that can effectively accommodate this configuration for efficient luminescence properties. Tm\(^{3+}/\text{Yb}^{3+}\) has been incorporated in different host matrices such as BaLaAlO\(_4\) [15], LaAlO\(_3\) [16] Y\(_2\)O\(_3\) [8] Na\(_2\)Y\(_2\)B\(_2\)O\(_7\) [17], La\(_2\)O\(_3\)-TiO\(_2\)-ZrO\(_2\) [18], SrLaAlO\(_3\) [19], ZrTi\(_2\)O\(_7\) [20], Ga\(_3\)O\(_3\)-Bi\(_2\)O\(_3\)-PbO [21] and K\(_2\)Gd(PO\(_4\))(WO\(_4\)) [12] phosphors for blue illumination. Also, these co-dopants are good and efficient luminescent centers with enhanced colour purity for SSL. CaLaAlO\(_4\) phosphor has been scarcely researched. It belongs to a perovskite structure family ABCO\(_4\), where A is a divalent cation, B and C are REs and transition metals, respectively [22]. This host matrix doped with REs provides excellent chemical and structural stability with efficient luminescent properties.
In this work, we reported the mixture of phases material CaLaAlO4/LaAlO3: 0.5 %Tm3+, xYb3+ phosphors powders for the first time, at varying concentrations of Yb co-dopant concentration. The optical absorbance and energy bandgap of the pure and CaLaAlO4/LaAlO3: 0.5%Tm3+, Yb3+ phosphor experimentally has also been determined for the first time. The UCL properties have been investigated in detail. It is found that the bluish-white emitting phosphor will have a potential application in SSL technology.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of CaLaAlO4-LaAlO3: 0.5%Tm3+, xYb3+ phosphors

CaLaAlO4/LaAlO3: 0.5 %Tm3+, xYb3+ phosphors were prepared through a simple solution combustion method. The materials used were calcium nitrate tetrahydrate [Ca(NO3)2 4H2O (99.0 %)], lanthanum nitrate hexahydrate [La(NO3)3 6H2O (99.9 %)], aluminium nitrate nonahydrate [Al(NO3)3 9H2O (99.999 %)], urea [CO(NH2)2 (99.5 %)], thulium nitrate pentahydrate [Tm(NO 3)3 5H2O (99.9 %)] and ytterbium nitrate pentahydrate [Yb(NO 3)3 5H2O (99.999 %)]. The reagents used were of analytical grade. To prepare the phosphors, the stoichiometric amounts of all the oxidants together with urea were dissolved in double deionized (DI) water and a magnetic stirrer was used to stir the solution for about 30 minutes. After which the entire mixture was transferred into the heating furnace at 620 °C. During the heating process, the oxidants react explosively with an organic fuel (urea), and inflammable gases such as CO2, NH3 and NO2 are produced [23], leaving behind the fluffy product.

The fluffy product (As-synthesized) formed was ground in an agar mortar into a fine powder and pressed into pellets. The pellets were then annealed at 1080 °C for 6 hours in air to obtain a crystalline phosphor. Throughout the synthesis, the amount of Tm was fixed (Tm = 0.5 mol%), while the Yb amount was varied (x = 0, 1, 3, 5, 7, and 10 mol%). The obtained samples were ground, packaged, and labelled as CLAO, CLAO 0, CLAO 3, CLAO 5, CLAO 7 and CLAO 10 respectively. The co-doped samples such as CLAO: Tm, Yb phosphors were named as CaLaAlO4/LaAlO3: 0.5 %Tm3+, xYb3+.

2.2. Characterization of CaLaAlO4/LaAlO3: 0.5%Tm3+, xYb3+ phosphors

The crystalline phase of the synthesized CLAO: Tm, Yb phosphors was identified by using X-ray diffraction. We used Cu Kα radiation (λ = 1.5406Å) on an X-ray diffractometer (Bruker, Advance D8), and the data were collected over the 20 angle in the range of 20°—80° with the scanning speed of 2°/min. Scanning electron microscopy (SEM) was employed to analyse the morphological composition of the phosphors (JEOL ARM200F, Peabody, MA, USA). Fourier Transform Infrared (FTIR) data was obtained by IRTracer-100, which was used to identify the IR absorptions in the phosphors. The optical absorbance spectra of the pure and CLAO: Tm, Yb phosphors were obtained using a UV-Vis-NIR Spectrophotometer (Cary-5000 Agilent) in the wavelength range of 200—800 nm. The Up-conversion Luminescence (UCL) properties were measured at room temperature using an ocean optic Spectrometer USB 2000 under 980 nm laser diode excitation. All measurements were acquired at room temperature.

3. RESULTS AND DISCUSSION

3.1. Structural analysis and morphological characterization of CLAO: Tm, Yb

The crystallinity and structural effect of the co-dopants on the CLAO host matrix were investigated by applying XRD. Fig. 1a presents the X-ray diffraction patterns of undoped and CLAO: Tm, Yb phosphors.

![Fig. 1a– The XRD pattern of CLAO: Tm, Yb; b–percentage of phase content in the samples as a function of Yb mol % co-dopant concentration](image)
The crystallite sizes of the phosphor (tetragonal and hexagonal phases) were determined by taking the averages of the prominent and most symmetric peaks of each phase. The Debye Scherer’s equation was employed (2).

\[ D_{hkl} = \frac{k\lambda}{\beta_{hkl} \cos \theta_{hkl}} \]  

where \( D_{hkl} \) is the average crystallite size; \( \lambda \) symbolizes the Cu_K\text{a} radiation wavelength (1.5406 Å); \( \theta_{hkl} \) is the Bragg’s angle (in radians); \( K \) refers to the shape factor (\( k = 0.9 \)); \( \beta_{hkl} \) is the FWHM in radians. The calculated average crystallite sizes for the tetragonal phase are in the range of 20 to 27 nm, while those of the hexagonal phase are in the range of 20 to 25 nm. The percentage phase content (tetragonal CaLaAlO\(_4\) and hexagonal LaAlO\(_3\)) was determined and presented in Fig. 1 b. As the Yb content increases, the CaLaAlO\(_4\) phase becomes prominent, while that of LaAlO\(_3\) gradually decreases. This result agrees well with the XRD pattern of the synthesized samples. It can be seen from the XRD pattern that, the increase in Yb content stabilizes the CaLaAlO\(_4\) phase, whereas a decrease in the intensity of the LaAlO\(_3\) perovskite phase was observed. This result suggests that more of the Tm\(^{3+}\)/Yb\(^{3+}\) ions preferentially occupy the CaLaAlO\(_4\) phase than the LaAlO\(_3\) perovskite structure, resulting to the decrease in the intensity of the hexagonal phase.

The site occupancy of Tm\(^{3+}\) and Yb\(^{3+}\) ions in the host crystal is determined by the ionic radii and the valence state [22]. Considering the charge similarity, Tm\(^{3+}\) and Yb\(^{3+}\) ions would prefer to occupy the La\(^{3+}\) site instead of the Ca\(^{2+}\) site. Therefore, the site occupancy can be determined using the radius percentage (\( R_e \)):

\[ R_e = \frac{R_h(CN) - R_d(CN)}{R_h(CN)} \times 100\% \]  

where \( R_h(CN) \) is the ionic radius of the host, while \( R_d(CN) \) is the radius of the dopant, CN refers to the coordination number. For the tetragonal phase, \( R_h(CN) \) in 8-coordination Tm\(^{3+}\) (1.052 Å) and Yb\(^{3+}\) (1.042 Å) substituted in the host cation La\(^{3+}\) (1.216 Å) [25]. Therefore, the value of \( R_e \) between the Tm\(^{3+}\) in the La\(^{3+}\) ions was determined as 13.49 %. On the other hand, the estimated value of \( R_e \) between the Yb\(^{3+}\) in La\(^{3+}\) cation site is 14.31 %. It is reported that the value of \( R_e \) should not be more than 15 % [19], therefore, Yb\(^{3+}\) and Tm\(^{3+}\) will conveniently be substituted in the La\(^{3+}\) cation site in the CaLaAlO\(_4\) phase.

3.2. FTIR analysis of the CaLaAlO\(_4\)/LaAlO\(_3\): 0.5 %Tm\(^{3+}\), Yb\(^{3+}\) phosphors

In Fig. 3 a, we showcase the FTIR spectrum of the as-synthesized material, representing the powder before annealing treatment for the CLAO sample. Notable absorption peaks at 3610 cm\(^{-1}\), 2170 cm\(^{-1}\), 2029 cm\(^{-1}\), 1415 cm\(^{-1}\), 869 cm\(^{-1}\) and 724 cm\(^{-1}\) are observed, which are attributed respectively, to the vibrations OH-, C-C bond, N-O bond, and M-O bonds (with M = Al, La) [27–30].
Fig. 3b shows the FTIR spectra of undoped and CLAO: Tm, Yb phosphors recorded in the range of 400 cm\(^{-1}\) – 4000 cm\(^{-1}\). The FTIR is useful in determining the quenching centers of photoluminescence in phosphor materials.

It is worthy to note that the hydroxyl group enhances the non-radiative phenomenon in the upconversion luminescent materials. The sharp IR band at 3645 cm\(^{-1}\) is ascribed to the hydroxyl group (OH\(^{-}\)). This mode of vibration indicates the presence of water molecules in the samples. The hydroxyl group could quench the photoluminescence and reduce the emission efficiency of the phosphor [27]. The IR bands observed at 2029 cm\(^{-1}\) and 2170 cm\(^{-1}\) belong to the C-C bond. The broad peak observed at 1447 cm\(^{-1}\) belongs to the N-O vibration mode [28]. With the increment in Yb\(^{3+}\) contents, this band is shifted by 27 cm\(^{-1}\). The IR absorption band observed at 443 cm\(^{-1}\) is due to the stretching and bending vibration of the Al-O bond in AlO\(_6\) octahedron coordination. While the bands at 671, 717 and 878 cm\(^{-1}\) are assigned to the stretching vibrations of the La-O bond in the LaO\(_{12}\) dodecahedron [29]. The infrared absorption bands between 1000 cm\(^{-1}\) and 400 cm\(^{-1}\) belong to the metal-oxygen bond deformation mode [30]. These absorption bands are present in all the CaLaAlO\(_4\)/LaAlO\(_3\) annealed samples.

3.2. Absorbance and optical bandgap of the pure and CaLaAlO\(_4\)/LaAlO\(_3\): 0.5\%Tm\(^{3+}\), Yb\(^{3+}\) phosphors

Fig. 4a presents the absorption spectra of pure and CLAO: Tm, Yb phosphors. We observed two absorption bands, one located at 253 nm and another at 440 nm.

![Absorption spectra of CLAO and CLAO: Tm, Yb phosphors](image)

The band at 440 nm is the broadband ascribed to defect states in the lattice [31]. The absorption peak at 253 nm is observed only in Yb-doped samples and can be ascribed to the charge transfer (CT) band between Yb\(^{3+}\) ions and the ligand O\(^{-2}\) atom (Yb – O) [32, 33]. Since the band is not broad, it means the change in the distance of Yb\(^{3+}\) ion and the ligand between the conduction band and the excited state is small, thus, the intermediate-coupling scheme was observed [34]. The optical bandgap for the phosphor was determined using Tauc’s equation:

\[
\alpha h\nu = A(h\nu - E_g)^n,
\]

where \(A\) is called the proportionality constant; \(h\nu\) and \(E_g\) refers to energies of the photon and bandgap, respectively, \(\alpha\) refers to the absorption coefficient. The exponential value \(n\) is the index which stands for direct allowed (\(n = \frac{1}{2}\)), indirect allowed (\(n = 2\)) , direct forbidden (\(n = \frac{3}{2}\)) and indirect forbidden (\(n = 3\)) transitions, respectively. To determine the energy bandgap, a plot of \((\alpha h\nu)^\frac{1}{n}\) versus \((h\nu)\)
was done, and the linear fit was extrapolated to the \((ahv)^2 = 0\) on the energy axis see Fig. 4 b. The value of \(n'\) was determined by testing for direct and indirect allowed transitions. It was observed that, the increase in Yb concentration, decreases the energy bandgap of the material. The estimated energy bandgap for a pure sample and the CLAO: Tm, Yb phosphors decreases between 5.23 eV and 4.73 eV. This is evident that Yb\(^{3+}\) ions are substituted well in the host. The bandgap values indicate that the phosphor is an insulating material. To determine the refractive index of the phosphor, we used the relation [19]:

\[
\frac{n^2 - 1}{n^2 + 1} = 1 - \sqrt{\frac{\varepsilon_g}{20}},
\]

where \(n\) is called the refractive index and \(\varepsilon_g\) is the optical bandgap of the phosphor. The refractive index was determined to be 1.706, 1.717, 1.719, 1.724, 1.732, 1.734, and 1.764 corresponding to CLAO, CLAO 0, CLAO 1, CLAO 3, CLAO 5, CLAO 7, and CLAO 10, respectively. We also noticed that \(n\) and Yb\(^{3+}\) concentration increases correspondingly. This increment enhances the photoluminescence properties [19].

### 3.3. Photoluminescence properties of 
CaLaAlO\(_4\)/LaAlO\(_3\): 0.5%Tm\(^{3+}\), xYb\(^{3+}\) phosphor

To investigate the luminescence properties of CLAO: Tm, Yb phosphor, the upconversion luminescence was performed. Fig. 5 a presents the upconversion emission spectra of CLAO: Tm, Yb phosphors, in the wavelength range of 400 nm to 900 nm. The spectra showed three emission bands centred at 478 nm (blue), 654 nm (red), and 801 nm (NIR). These emission peaks can be attributed to the \(^1\)G\(_4\) → \(^3\)H\(_6\), \(^1\)G\(_4\) → \(^3\)F\(_4\), and \(^3\)H\(_4\) → \(^3\)H\(_6\) electronic transitions of Tm\(^{3+}\) ions, respectively [15, 19, 35]. It was observed that, the intensity of CLAO: Tm, Yb phosphor was very low both in the visible and the infrared region. To optimize the UC emission intensity, the Yb\(^{3+}\) concentration was varied (CLAO 0 to CLAO 10). From the spectra, we observed that as the concentrations of Yb increase (CLAO 0 to CLAO 7), the emission at the near-infrared region appears most intense followed by blue and then red emission in that order. At CLAO 10, the intensity of blue emission (478 nm) becomes prominent, whereas the red emission (654 nm) maintains its weak intensity value with an increasing trend. Grigorjevaite and Katelnikovas [12] observed a similar behaviour at varying Tm\(^{3+}\) ion contents. In general, increasing Yb\(^{3+}\) contents favor the UCL both in the visible and near infrared regions. It is worthy to note that quenching does not occur in the host crystals. This proves that quenching is solely dependent on the host matrix, the amount of dopants, and elevated temperature. Yang et al observed quenching at 20 mol% of Yb in Yb:YAG [36]. Similarly, BaLaAlO\(_4\): Tm\(^{3+}\), Yb\(^{3+}\) observed quenching at 6 mol% concentration of Yb\(^{3+}\) ions [13]. The prominent peak observed at 478 nm (blue) is due to energy transfer from the Yb\(^{3+}\) to Tm\(^{3+}\) ions [17]. The inset in Fig. 5 a shows the photograph of UC blue emission at CLAO 10. The percentage contributions of blue and red emissions were also calculated. The percentage contribution of blue emissions in the visible region ranges between 2.73 % and 39.75 % to the overall emissions. While the red emission has 2.43 % to 15.68 % contribution in the visible region. The effect of the sensitizer on the luminescence process was also studied, and a plot of the intensity against the Yb\(^{3+}\) ion concentration is presented in Fig. 5 b. As the concentration of Yb\(^{3+}\) increases, the emission intensity increases progressively. The continuous increase in the emission intensity can be attributed to the enhancement in the photoluminescence process.

![UCL emission spectra of CLAO: Tm, Yb phosphor](image)

### 3.4. Commission internationale de l’éclairage (CIE) and colour map

Fig. 6 presents the CIE diagram obtained from UCL emission for the CLAO: Tm, Yb phosphor samples. The colour coordinates (CIE 1931) excited under a 980 nm laser diode are dependent on Yb\(^{3+}\) ion concentrations. The CIE values fall within the bluish white region, but gradually shift towards the blue region as the concentration of Yb increases. Thus, the prepared phosphor emits an efficient tunable emission from bluish white to blue light. The color emission is tuned toward the blue region due to the low contribution of red emission (16 % contribution to the overall visible emission). The CCT values are used to determine the light quality. It is established that the CCT values below 3200 K are considered warm light, while the values above 4200 K fall within the cool light region [37]. Then, we calculated the CCT values using the Mc Cammy equation [10]:

\[
CCT = -437n^3 + 3601n^2 - 6861n + 5514.31.
\]

![CIE diagram](image)
where \( n = (x - x_c)/(y - y_c) \), whereas \( x_c = 0.332 \) and \( y_c = 0.186 \) is the epicentre of iso-temperature. The calculated values of the CIE\((x,y)\) chromaticity coordinates obtained from the CIE calculator at varying amounts of Yb\(^{3+}\) ions are presented in Table I. It was observed that the values obtained from CCT are within the cool light source [10]. The color purity of the synthesized samples was also determined using the dominant wavelength (478 nm). The increase in Yb concentration increases the color purity of the samples. The best color purity for the sample was obtained as 79.76 % (see Table 1) as compared to the other Yb\(^{3+}\) doping concentrations. The high value of the color purity means that the phosphor could be considered as an important component for white light emission diodes (WLED).

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**REFERENCES**


9. Laguta, V., Buryi, M., Pejchal, J., Utičná, K., Římal, V., Chian, V., Stepankova, H., Zagorodniy, Y., Nikl, M. Incorporation of the Ce\(^{3+}\) Activator Ions in LaAlO\(_4\) Crystals:
Novel BaLaAlO$_4$:Yb$_3^+$,(X mol%),Tm$_3^+$ (0.5 mol%) Phosphors


https://doi.org/10.3390/ma16031305


https://doi.org/10.1016/j.jlumin.2021.118104


15. Etafo, N.O., Oliva, C.J., Garcia, C.R., Mtz-Enríquez, A.I., Ruiz, J.J., Avalos-Belmontes, F., Lopez-Badillo, C.M., Gomez-Solis, C., Enhanceding of the Blue/NIR Emission of Novel BaLaAlO$_4$:Yb$_3^+$,(X mol%),Tm$_3^+$ (0.5 mol%) Upconversion Phosphors with the Yb$_3^+$ Concentration (X = 0.5 to 6) Inorganic Chemistry Communications 137 2022: pp. 109192.

https://doi.org/10.1016/j.inoche.2021.109192


https://doi.org/10.1016/j.optamat.2019.109365


https://doi.org/10.1039/C4RA15891A


https://doi.org/10.1364/OME.5.000676


https://doi.org/10.13039/3061003


https://doi.org/10.1016/j.ijleo.2019.05.020

21. Strezp, A., Glowacki, M., Szatko, M., Potrzasaj, K., Lisiecki, R., Rybu-Romanowski, W., Spectroscopic Properties of Thulium Doped (Li$_{0.5}$Zr$_{0.5}$)$_2$Si$_2$O$_7$ (LGSO) Single Crystals Journal of Luminescence 220 2020: pp. 116962.

https://doi.org/10.1016/j.jlumin.2019.116962


https://doi.org/10.1016/j.optamat.2018.05.037


https://doi.org/10.1007/s10854-019-02544-x


https://doi.org/10.22241/jiraset.2018.3034


https://doi.org/10.1107/S0567739476001551


https://doi.org/10.1364/OE.402111


https://doi.org/10.1038/srep31207


https://doi.org/10.1109/JDT.2015.2457953


https://doi.org/10.1016/j.jcrysgro.2014.09.015


https://doi.org/10.1016/j.jssc.2020.121576


https://doi.org/10.1016/S0022-2313(00)00214-3

34. **Goud, K.M., Ramesh, C., Rao, A.** Spectroscopic Properties and Energy Transfer in Lead Bismuth Gallium Borate Glasses Codoped with Tm$^{3+}$ and Yb$^{3+}$ *International Journal of Research Engineering and Technology* 6 (1) 2017: pp. 215 – 220. https://doi.org/10.17577/IJERTV6IS010163


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