White light emitting dysprosium doped lanthanum oxalate single crystals

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Abstract: Single crystals of Lanthanum oxalate [La2 (C2O4)3]10H2O and Dy3+ doped Lanthanum oxalate [La2−xDyx (C2O4)3]10H2O with x=0.1, 0.15, 0.2 were grown by gel method and characterised by X-ray powder diffraction analysis. Thermal stability of sample was investigated by thermo gravimetric analysis. UV-Visible absorption and photo-luminescent studies were also conducted. The emission spectrum on exciting at 271nm and 364 nm were recorded in which Dy3+ ions showed four emission bands at positions 458nm (blue), 478 nm (blue), 572 nm (yellow) and 655 nm (red) corresponding to transitions 7F9/2 → 7H9/2, 7F9/2 → 7H15/2, 7F9/2 → 7H11/2 and 7F9/2 → 7H11/2 respectively. The CIE coordinates, colour purity and CCT values were calculated, and all these parameters show that Dy3+ doped lanthanum oxalate single crystals are suitable candidates for white light emitting applications.

Keywords: Crystal, Dy3+ doped Lanthanum oxalate, Photoluminescence, white light

1. INTRODUCTION

The characteristic optical and magnetic behaviour of rare earth elements are the main target of intensive research towards various applications in modern technology, especially for more sophisticated device development in lasers and in solid state lighting applications [1, 9]. Among the modern lighting devices, solid state phosphor converted white light phosphors are now replacing the conventional light sources such as incandescent and fluorescent lamps [2]. The hall marks of solid-state phosphor converted white light phosphors are their high efficiency, reliability and easy maintenance. The lighting technology is still in search of UV or blue LED excitable red, green, blue, yellow, or even single-phase white light emitting phosphors with superior photoluminescence qualities [3]. Rare earth based luminescent materials offer excellent colour purity, resulting from sharp emission of trivalent rare earth ions. It has superior photostability and high quantum efficiency, suitable for application in various lighting and display devices, such as LED’s, electro luminescent displays, bio imaging, etc. [4].

The crystal structure of La2 (C2O4)3 is identical to Dy2 (C2O4)3 [5]. Besides, La3+ is optically inactive in the visible region assuring the intrinsic absorption, emission and photoluminescence characteristics of Dy3+ ion. Thus the ideal neutral matrix, Lanthanum oxalate is used to study the photoluminescence emission of Dy3+. Dysprosium usually exists in the trivalent state, Dy3+ when it is present in compounds. Based on the nature of host lattice, dysprosium is a potential activator ion which provides multiple emission colours, i.e., depending on the symmetric or asymmetric site occupancy of Dy3+ ions in the host matrix, it emits yellow, blue or even white light [6]. In this work, the single crystals of Dy3+ doped Lanthanum oxalate at various doping concentrations of 10, 15 and 20% were grown and the variation of luminescence intensity at different doping concentration of Dy3+ were studied. The
emission characteristics were investigated to explore the possibility of their use in white light emitting applications.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis and Growth of Dy$^{3+}$ doped lanthanum oxalate single crystals

Synthesis of Dy$^{3+}$ doped La$_2$(C$_2$O$_4$)$_3$ single crystals is achieved by controlled diffusion of Dy$^{3+}$ and La$^{3+}$ ions through the silica gel. Aqueous solutions of lanthanum nitrate and dysprosium nitrate are separately prepared, each at 0.5M concentration. The two solutions were mixed in the appropriate stochiometric ratios (9:1, 8.5:1.5 and 8:2) to get the 10%, 15% and 20% stock solution. To this, concentrated nitric acid was mixed in 1:2 ratio and is used as the supernatant solution. This solution was poured gently over the properly set hydro silica gel (pH 7.0) prepared by dissolving sodium metasilicate in water (specific gravity 1.03 gm./cc) mixed with C$_2$H$_2$O$_4$ (aq.) 0.5M, taken in test tubes for proper setting. The crystals appeared in all the test tubes in one or two days and is grown to its full size (4x2x1 mm) in two weeks. A representative photograph of the growth system is shown in fig.1, along with an enlarged image of a single crystal separated out showing the morphology.

![Fig. 1. (a) Growth system of dysprosium doped lanthanum oxalate crystals (b) Photograph of a single crystal of dysprosium doped lanthanum oxalate](image)

2.2 Characterization

X-ray powder diffraction patterns of the grown samples were collected on a Rigaku table top X-ray diffractometer over a 2θ range 5 - 65°[1]. Shimadzu thermal analyser DT-40 was used for Thermo gravimetric analysis. UV-Vis-NIR absorption spectrum of the sample was obtained on a Varian Cary UV-Vis-NIR spectrophotometer. HORIBA Jobin–Yvon Fluoromax-4 spectrofluorometer was used to record the photoluminescence emission spectra. [14].

3. RESULTS AND DISCUSSION

3.1 X-ray powder diffraction analysis

X-ray powder diffraction data of undoped lanthanum oxalate single crystals and Dy$^{3+}$ doped lanthanum oxalate crystals at doping concentrations of 10% and 20% were recorded and are depicted in fig.2. Well defined and sharp diffraction peaks show the single crystal nature of the grown samples. The observed diffractograms of the Dy$^{3+}$ doped samples are similar to diffraction pattern of undoped sample, confirming the formation of single crystals of Dy$^{3+}$ doped lanthanum oxalate decahydrate in isostructural phase [7].
3.2 Thermo Gravimetric Analysis

Single crystal structure of lanthanum oxalate decahydrate has coordinated and non-coordinated H$_2$O molecules [5]. The ten H$_2$O molecules within the crystal guarantee the evaluation of thermal behaviour of this substance to understand its decomposition and dehydration process. All the non-coordinated lattice H$_2$O molecules are loosely bound within the lattice while coordinated H$_2$O molecules are strongly bound with the La$^{3+}$ ions accommodated closer to the oxalate rings [9]. The thermograms of the synthesized lanthanum oxalate and 10% Dy$^{3+}$ doped lanthanum oxalate samples in nitrogen atmosphere are shown in fig.3.

The thermograms reveal that weight loss is almost continuous until 650°C for pure sample and 670°C for the doped, while the corresponding residual mass percentages are 54.61% and 54.21%, respectively indicates the formation of lanthanum oxide in the former and lanthanum dysprosium oxides in the later. Since the curves are very similar except minimal differences, the discussion is
limited to the lanthanum oxalate sample only. Neglecting the adsorbed water, the curve up to ~350°C corresponds to the removal of seven water molecules which are non-coordinated to the metal ion and having a weight loss of 20.94%. On increasing the temperature beyond 350°C, a dip observed at around 400°C probably relative to the liberation of three coordinated H₂O molecules. Further increase in temperature, weight loss continues up to 575°C with a total weight loss of 45.97%. This weight loss relative to the removal of three coordinated H₂O molecules and three molecules of CO₂ with the formation of lanthanum oxy-carbonate. On increasing the temperature up to 700°C one more CO₂ molecule is liberated leaving behind lanthanum oxide with a total weight loss of 54.61%. The thermograms reveal that the lanthanum oxalate and Dy³⁺ doped lanthanum oxalate crystals are identical in internal structural composition, probably Dy³⁺ replaces the La³⁺ ions.

3.3 UV-Visible Absorption Spectroscopy

The room temperature absorption spectra of dysprosium doped lanthanum oxalate single crystals at various concentrations of Dy³⁺ (5%, 10%, 15% and 20%) are depicted in fig.4. The strong intense peak positioned at 255 nm is ascribed to the charge transfer band arising from 2p orbital of O²⁻ ion to the f orbital of Dy³⁺ ion. The remaining peaks are due to the intra configurational 4f-4f transitions of Dy³⁺. They are located at 295, 299, 326, 339, 351, 365, 382, 389, 427, 453, 474 and 760 nm. The electronic transitions are originating from the ground state 6H₁₅/₂ of Dy³⁺ to the states 4F₉/₂, 4H₁₃/₂, 6P₃/₂, 4D₅/₂, 6P₇/₂, 6P₅/₂, 4F₇/₂, 4I₃/₂, 4G₁₁/₂, 4I₁₅/₂, 4F₁₅/₂ and 6F₃/₂ respectively [8].

![Absorption spectra of dysprosium doped lanthanum oxalate single crystals with Dy³⁺ concentrations 5%, 10%, 15% and 20%.](image)

3.4 Photoluminescence excitation

The photoluminescence excitation spectra of Dy³⁺ doped lanthanum oxalate single crystals (10%, 15% and 20% doping concentrations) are recorded in the range 250 - 550 nm on monitoring the 4F₉/₂ → 6H₁₃/₂ emission transition of Dy³⁺ ion at 572 nm and are shown in fig. 5.
The emission at 572 nm is monitored for excitations in the range 250 – 550 nm. These spectra have a broad band ranging (235- 280 nm). This arises owing to the charge transfer transition from 2p orbital of O\(^2\)- to the f orbital of Dy\(^{3+}\) and the 4f-5d transition of Dy\(^{3+}\) in Lanthanum lattice. This broad band is followed by sharp peaks due to the f-f transitions of dysprosium ions in the range 280 - 525 nm [6, 9]. The electronic transitions arising from the 4f\(^5\) configuration of dysprosium ions observed in the spectrum at the positions 295 nm, 300 nm, 325 nm, 338 nm, 351 nm, 364 nm, 388 nm, 399 nm, 425 nm, 449 nm, 473 nm and 522 nm” [9] are attributed to the transitions from the ground state \(^6\)H\(_{15/2}\) of Dy\(^{3+}\) to the states \(^4\)F\(_{3/2}, \ ^4\)H\(_{13/2}, \ ^6\)P\(_{3/2}, \ ^4\)D\(_{5/2}, \ ^6\)P\(_{5/2}, \ ^4\)F\(_{7/2}, \ ^4\)I\(_{15/2}, \ ^4\)I\(_{13/2}, \ ^4\)F\(_{9/2}\) and \(^6\)F\(_{3/2}\) respectively. The crystal field effect accounts to the more intense peaks in the spectrum. Peaks at 351, 364 and 388 nm are relatively intense peaks of which 364 nm is the highest peak.

3.5 Photoluminescence Emission Studies

Emission spectra of Lanthanum dysprosium oxalate single crystals at 10%, 15% and 20% Dy\(^{3+}\) concentrations with excitation wavelengths 271 nm and 364 nm in the spectral range 400 nm to 700 nm were recorded and are given in fig.6.
The emission spectra in both the case shows four bands at positions 458, 478, 572 and 655 nm correlating to transitions \(^1I_{15/2} \rightarrow ^8H_{15/2}\), \(^4F_{9/2} \rightarrow ^8H_{11/2}\), \(^4F_{9/2} \rightarrow ^8H_{13/2}\) and \(^4F_{9/2} \rightarrow ^6H_{11/2}\) respectively. The intensity of emission shows similar pattern, where the intensity increases with increase in doping concentration of Dy\(^{3+}\) ion. Among the various emissions the maximum emission intensity is observed at 572 nm which lies in yellow region. The next maximum occurs at 478 nm which lies in blue region. The remaining two emissions are less intense, however, among them the higher intensity is observed for the band at 458 nm which also lies in blue region while the peak at 655 nm has the lowest intensity and falls in red region.

The dysprosium ion has blue emission at 478 nm. This is due to magnetic dipole transitions which is unaffected by crystal field surrounding the Dy\(^{3+}\) ion in the lanthanum lattice. But the peak at 572 nm is due to the forced electric dipole transition having the selection rule \(\Delta L = 2, \Delta J = 2\), which depends on the surrounding crystal field of the dysprosium ion in the lanthanum lattice [9]. The blue emission \((^1F_{9/2} \rightarrow ^6H_{15/2})\) becomes prominent when the Dy\(^{3+}\) ion is in a Centro symmetric site in the lanthanum lattice. The dominance of yellow emission \((^4F_{9/2} \rightarrow ^6H_{13/2})\) in the present case shows Dy\(^{3+}\) ions within non- Centro symmetric site of the lanthanum lattice [6].

### 3.6 Chromaticity Coordinates and colour purity

CIE coordinate of the 20% Dy\(^{3+}\) doped lanthanum oxalate single crystal are calculated from emission spectra based on the standards given in CIE 1931. The calculated coordinates are represented as shown in fig.7. The CIE co-ordinate of 20% Dy\(^{3+}\) doped La\(_2\) (C\(_2\)O\(_4\))\(_3\) single crystal for excitations 271nm, 351nm, 364 nm and 388 nm are (0.3212, 0.3706), (0.3126, 0.3705), (0.3117, 0.3694) and (0.3083, 0.3676) respectively and they fit to the white region. The respective colour purities are 8.2, 7.5, 7.5 and 7.9%. The essential requirement of a white light emitting material is its low colour purity. Since pure white light emitting materials are having colour purity close to zero. The calculated CIE coordinate for Dy\(^{3+}\) doped lanthanum oxalate single crystal compares well with other dysprosium doped near white light emitting phosphors: Sr\(_2\)SiO\(_4\): Dy\(^{3+}\) (0.32,0.389) : Dy\(^{3+}\) (0.35,0.389), BaY\(_2\)ZnO\(_5\) and Ba\(_3\)Y(PO\(_4\))\(_3\), Dy\(^{3+}\) (0.347,0.381) [9-12]. In the present case the CCT values ( 5930 K, 6271 K, 6313 K and 6462 K) lies in the acceptable range 3500K -6500K[13].

![Fig.7. CIE diagram of Dy20% doped Lanthanum oxalate crystals](image-url)
4. CONCLUSIONS

Single crystals of dysprosium doped lanthanum oxalate at different doping concentrations were synthesised by hydro silica gel growth technique. The structural characterization was carried out by X-ray powder diffraction analysis. The thermal response of the samples was analysed by TGA. Photoluminescence studies indicated the possibility of exciting dysprosium doped lanthanum oxalate crystals in UV and visible regions. The luminescence emission analysis revealed the strong emission in blue, yellow regions lead to white light emission as evidenced by the calculated CIE coordinates. This study indicates the possible use of this material as a potential white light emitter.

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