



## LUMINESCENT BEHAVIOR OF Tb<sup>3+</sup> AND Pr<sup>3+</sup> IONS IN RARE EARTH OXIDE

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**Abstract-** Trivalent rare earth ions are used as an efficient emitting center in a variety of commercial phosphors. Photoluminescence spectra of Lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) doped with (1%) Tb<sup>3+</sup> and (1%) Pr<sup>3+</sup> ions were investigated. The phosphor were synthesized by co-precipitation method and annealed at 1000°C. X-ray powder diffraction (XRD) analysis confirmed the formation of La<sub>2</sub>O<sub>3</sub>. Photoluminescence measurements indicate that the La<sub>2</sub>O<sub>3</sub>: Tb<sup>3+</sup> phosphor exhibit efficient green emission around 543 and 550 nm and La<sub>2</sub>O<sub>3</sub>: Pr<sup>3+</sup> phosphor shows emission around 495 and 508 nm under UV excitation. Photoluminescence measurements indicate that the phosphor exhibit efficient characteristic emission under UV excitation.

**Keywords** - photoluminescence; rare earth ion; Lanthanum oxide; co-precipitation.

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### Introduction

Several oxides based materials are well known commercial phosphors e.g. Y<sub>1.94</sub>Eu<sub>0.06</sub>O<sub>3</sub> is red tri-colour lamp phosphor, Y<sub>1.9</sub>Eu<sub>0.1</sub>O<sub>3</sub> is red emitting CTV phosphor. Mg<sub>2</sub>SnO<sub>4</sub>:Mn is green emitting phosphor, Lu<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> is X-ray scintillator. ZnO is FED phosphor host and is also used in solid state lighting. In fact ZnO:Zn is one of the earliest known green emitting phosphors with near UV excitation. Unfortunately, no energy transfer from ZnO to RE<sup>3+</sup> result [1]. Strong Mn<sup>2+</sup> emission with near UV excitation is reported in SrZnO<sub>2</sub> and K<sub>2</sub>Cd<sub>3</sub>S<sub>4</sub> [2] host. Eu<sup>3+</sup> doped oxides were studied earlier in context of lasers[3] and CTV[4]. Eu<sup>3+</sup> doped oxides were extensively studied by Blasse and coworker [5-8] and Ropp [9]. Gd<sub>2</sub>O<sub>3</sub>: Eu<sup>3+</sup> is red emitting PDP (plasma display panel) phosphor, Al<sub>2</sub>O<sub>3</sub>:C<sup>2+</sup> is optical stimulated luminescence (OPL) and thermoluminescence dosimetry (TLD), Al<sub>2</sub>O<sub>3</sub>:Ti is used in laser. La<sub>2</sub>O<sub>3</sub> has largest band gap of the rare earth oxide, while also having the lowest lattice energy, with very high dielectric constant, ε=27. Lanthanum oxide has p-type semiconducting properties because its resistivity decreases with an increase in temperature, average room temperature resistivity

is 10 KΩ-cm. The melting point of La<sub>2</sub>O<sub>3</sub> is 2315°C. La<sub>2</sub>O<sub>3</sub> is widely used in industry as well as in the research laboratory. It is used to develop optical materials and ferroelectric materials. La<sub>2</sub>O<sub>3</sub> is an ingredient for the manufacture of piezoelectric and thermoelectric materials. It is also used in X-ray imaging intensifying screens.

In this paper we report synthesis and photoluminescence of La<sub>2</sub>O<sub>3</sub>: Tb<sup>3+</sup> (1mol%) and La<sub>2</sub>O<sub>3</sub>: Pr<sup>3+</sup> (1mol%).

### Experimental

La<sub>2</sub>O<sub>3</sub> phosphor doped with different impurities was prepared by co-precipitation method using oxalic acid. The La<sub>2</sub>O<sub>3</sub> (99.99%, IRE) and dopants (Tb<sub>4</sub>O<sub>7</sub>) (99.99%, IRE) and (Presidium nitrate) (99.99%, IRE) were weighed as per the stoichiometric calculations. The weighed quantities of La<sub>2</sub>O<sub>3</sub> and dopant were dissolved in dil. HNO<sub>3</sub> (s.d.fine chem. AR) separately. The solutions were mixed. Stoichiometric amount of Oxalic acid (GR) solution was then slowly added to the mixture. The precipitate so obtained in the form of oxalate was separated by filtering, dried and thoroughly crushed to yield

fine powder. It was decomposed by heating in air at 1000°C for 90 min. X-ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer. Photoluminescence (PL) spectra in the spectral range 220-700 nm were recorded at room temperature on Hitachi F-4000 spectro-fluorimeter with spectral slit widths of 1.5 nm.

### Crystal Structure

At low temperatures, La<sub>2</sub>O<sub>3</sub> has an A-M<sub>2</sub>O<sub>3</sub> hexagonal crystal structure space group p-3m1 shown in fig.1. The La<sup>3+</sup> metal atoms are surrounded by a 7 coordinate group of O<sup>2-</sup> atoms, the oxygen ions are in an octahedral shape around the metal atom and there is one oxygen ion above one of the octahedral faces [10]. On the other hand, at high temperatures the Lanthanum oxide converts to a C-M<sub>2</sub>O<sub>3</sub> cubic crystal structure. The La<sup>3+</sup> ion is surrounded by a 6 coordinate group of O<sup>2-</sup> ions [11].

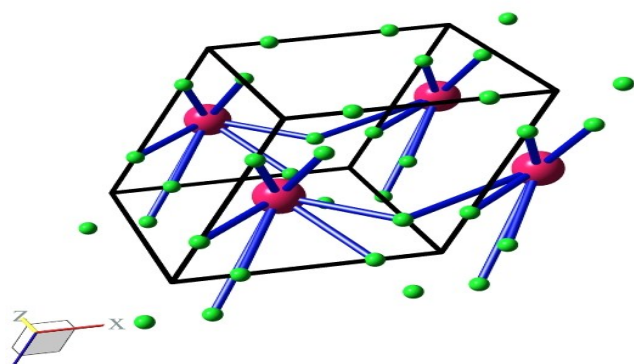


Fig. 1- 7- coordinated La in La<sub>2</sub>O<sub>3</sub> structure

### Result and Discussion

Fig 2- shows the comparison of XRD patterns of the as-prepared La<sub>2</sub>O<sub>3</sub> powder with the ICDD data file 83-1345. An excellent match is seen.

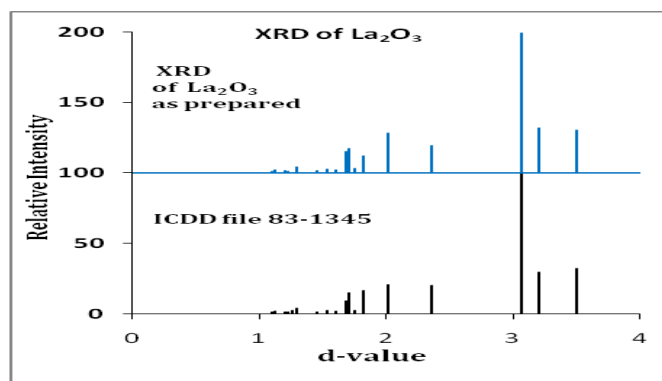


Fig. 2 XRD of La<sub>2</sub>O<sub>3</sub>

### La<sub>2</sub>O<sub>3</sub>:Tb<sup>3+</sup>

Terbium shows strong excitation corresponding to allowed transition between <sup>7</sup>F<sub>6</sub> ground state of 4f<sup>8</sup> configuration to the levels of 4f<sup>7</sup>5d<sup>1</sup> configuration. Quite often, this falls in deep UV or VUV region of the spectrum. Intense UV-excited luminescence of Tb<sup>3+</sup> can be observed only if f-d excitation band is located in this region, or if there is energy transfer from the sensitizer or host, which absorbs in UV region, to one of the

levels of 4f<sup>8</sup> configuration of Tb<sup>3+</sup>. From the excited state the ion relaxes in several steps to <sup>5</sup>D<sub>j</sub> levels of 4f<sup>8</sup> configuration. Line emission corresponding to f-f transitions is observed. Commonly observed, most intense lines are around 485 nm and 543 nm corresponding to <sup>5</sup>D<sub>4</sub> à <sup>7</sup>F<sub>6</sub> and <sup>5</sup>D<sub>4</sub> à <sup>7</sup>F<sub>5</sub> transitions, respectively. At low concentrations blue emission is dominant. Near UV emission around 385 nm corresponding to <sup>5</sup>D<sub>3</sub> à <sup>7</sup>F<sub>6</sub> transition is also observable. For high concentrations, these emissions are quenched by cross relaxation <sup>5</sup>D<sub>3</sub> (Tb<sup>3+</sup>) + <sup>7</sup>F<sub>6</sub> (Tb<sup>3+</sup>) à <sup>5</sup>D<sub>4</sub> (Tb<sup>3+</sup>) + <sup>7</sup>F<sub>0</sub> (Tb<sup>3+</sup>) and the green emission becomes dominant.

Fig. 3- shows results of PL measurements on La<sub>2</sub>O<sub>3</sub> activated with (1mol%)Tb. Emission spectrum (fig.3, curve a) shows some broad lines due to transitions <sup>5</sup>D<sub>4</sub> à <sup>7</sup>F<sub>j</sub>. The 489 nm emission line is attributed to <sup>5</sup>D<sub>4</sub> à <sup>7</sup>F<sub>6</sub> transition, 543 and 550 nm peaks attributed to <sup>5</sup>D<sub>4</sub> à <sup>7</sup>F<sub>5</sub>, small peak at 586 nm attributed to <sup>5</sup>D<sub>4</sub> à <sup>7</sup>F<sub>4</sub> transition and 620 nm attributed to <sup>5</sup>D<sub>4</sub> à <sup>7</sup>F<sub>3</sub> transitions [12-14]. The excitation spectrum (fig.3, curve b) shows two peaks. The excitation maxima occur at 275 nm which corresponds to the intra- configurational transition from the ground state <sup>7</sup>F<sub>6</sub> of 4f<sup>8</sup> configuration to the lowest state of 4f<sup>7</sup>5d<sup>1</sup> configuration and 229 nm peak is probably a matrix excitation band.

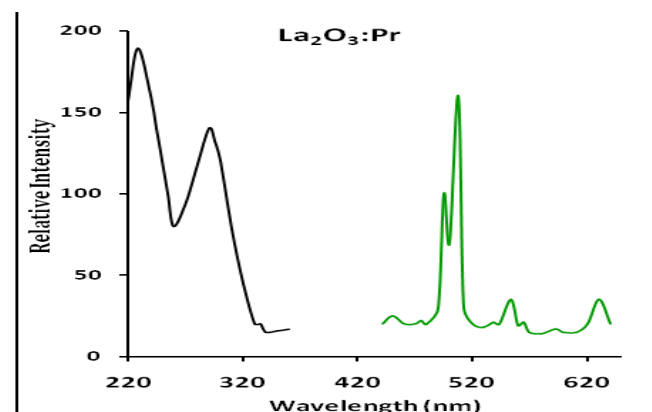
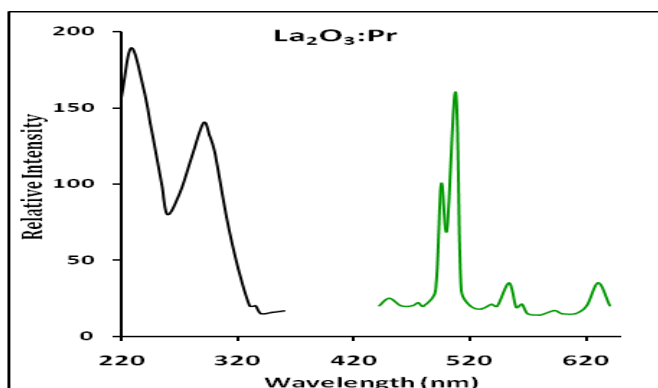


Fig. 3- PL spectra of La<sub>2</sub>O<sub>3</sub>:Tb<sup>3+</sup> (1 mol%) a) Emission curve maxima at 543nm b) Excitation curve maxima at 275 nm

### La<sub>2</sub>O<sub>3</sub>:Pr<sup>3+</sup>

Like Tb<sup>3+</sup>, intense UV excited luminescence of Pr<sup>3+</sup> can be observed only if f-d excitation band is located in this region or if there is energy transfer from host which absorbs in UV region to one of the levels of 4f<sup>2</sup> configuration of Pr<sup>3+</sup>. Pr<sup>3+</sup> emission can be observed in UV, blue, green or red region depending on the position of the f-d excitation band [15]. In most cases this band is situated in VUV region.

For La<sub>2</sub>O<sub>3</sub>:Pr<sup>3+</sup> (1 mol%), emission peak (fig.4, curve a) around 495 and 508 nm was observed which can be attributed to <sup>3</sup>P<sub>0</sub> à <sup>3</sup>H<sub>4</sub> transition of Pr<sup>3+</sup>. Some other peaks of much smaller intensities around 538, 554, 625 nm are also observed. The excitation spectrum (fig.4, curve b) contains two bands around 228 and 290nm. The excitation maxima occurring around 228 nm is the matrix excitation band while the longer wavelength 290 nm band may be attributed to f-d excitation.



**Fig. 4-** PL spectra of  $\text{La}_2\text{O}_3:\text{Pr}^{3+}$  (1 mol%) a) Emission curve maxima at 508nm, b) Excitation curve maxima at 228 & 290 nm

### Conclusion

$\text{La}_2\text{O}_3:\text{Tb}^{3+}$  and  $\text{La}_2\text{O}_3:\text{Pr}^{3+}$  phosphors are successfully prepared by co-precipitation method using oxalic acid. The 230 nm peak which is always present in excitation spectra irrespective of the activator used is probably a matrix excitation band. The excitation spectra of both these phosphor shows good overlap over a region around 254 nm which make it good candidate for tricolor lamp. The  $\text{La}_2\text{O}_3:\text{Tb}^{3+}$  phosphor exhibit efficient green emission around 543 and 550 nm and  $\text{La}_2\text{O}_3:\text{Pr}^{3+}$  phosphor shows emission around 495 and 508 nm under UV excitation. Both these phosphors mentioned in this paper were found to be stable; no change in the PL properties was observed for the phosphors stored for several months. Samples were also found to be stable against UV irradiation that was used for the PL measurements. No changes in spectral positions or intensities were observed during several, successive PL runs.

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