**UV:VISIBLE EXCITABLE PHOTOLUMINESCENCE SPECTRA FOR VARIABLE CONCENTRATION OF Tb3+ IN Al2Sr2La2O8 :EU PHOSPHOR**

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**Abstract*:* -** This paper reports the Photoluminescence properties of Al2Sr2La2O8 :Eu with different concentrations of trivalent Terbium as dopant. This phosphor is synthesized using the solid state diffusion reaction. The emission spectra recorded for ASL:Eu,Tb varying, when excited with 268 and 278nm. The PL emission peaks are founded at 468,514,541,544,556,582,588,597,616 & 627nm with different intensities. However the peaks at 541,588, and 627 nm intensities are found to be well resolved with less emission strength. Increasing concentration of Tb acted as killer in ASL:Eu. This may be due to the reason that when Tb3+ activator is excited with light of sufficient energy, such as UV light, its 4f8electrons would be raised to the higher 4f7, 5d1 level and then fed to the 5 D3,4 excited states, from which fluorescence is produced by transitions to the 7FJ (J = 1–6) ground states. Though the excited 5d electron is exposed, Tb3+ transitions involve only a redistribution of electrons within the inner 4f sub-shell, and thus similar emissions are usually observed from different types of host lattices, with the 5D4 → 7F5 green emissions at ∼541 nm being dominant. The crystallite size is calculated through XRD. The shape of the crystal is determined by SEM. However the PL studies of the final products were found to be interesting from display device point of view. The present work suggests a convenient, cost-effective method for white phosphor, which may lead to potential applications in solid state lighting.

**Key words:** - Photoluminescence, Phosphor rare-earth ions, X-ray diffraction [XRD], Scanning Electron Microscopy [SEM], Energy Dispersion Spectrum [EDS], Solid State Reaction technique

**1. Introduction:**

Aluminate compounds haven been utilized as host materials of lamp phosphors for many years, Due to their relatively low material cost, and reasonable stability these are used in lamp application. The development of the first synthesized aluminates phosphor can be traced back to 1970. In the 1980’s rare-earth-activated aluminate phosphors were practically used in (BAM: Eu) fluorescent lamps. This was the first application of rare-earth-activated aluminates in tri band fluorescent lamps and represented a landmark in this history of fluorescent lamp development.

Recently various phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices. There is very much interesting in light emitting diodes (LEDs) with emission wavelengths in the ultraviolet**-**to**-**infrared range. LED technology has flourished for the past few decades. High efficiency, reliability, rugged construction, low power consumption and durability are among the key factors for the rapid development of the solid-state lighting based on high-brightness visible LEDs. In this context, the search for stable, inorganic rare-earth-based phosphors with high absorption in the yellow and orange spectral region is an attractive research task. The white LEDs have several advantages over the conventional incandescent and fluorescent lamps due to its high power efficiency, long lifetime, non-pollution and flexibility in design process. This composition could be considered as an alternative approach due to advantages such as lower production cost, simpler manufacture procedure, non- hygroscopic and environmental-friendly characteristics.

**2. MATERIALS AND EXPERIMENTAL METHODS:**

All the chemical reagents were analytically pure and used without further purification. **Al2Sr2La2O8 :Eu,** Tb phosphor samples were prepared by the conventional solid state reaction method. Aluminum oxide(Al2O3), Strontium carbonate(SrCO3), Lanthanum oxide(La2O3) were taken as raw materials for the host and the molar ratio of rare earths Europium oxide(Eu2O3) and Terbium oxide(Tb4O7) are taken as activator ion which is doped in host at different concentrations. The base materials and activator were mixed and ground thoroughly using agate mortar and pestle prior to this all the materials are weighed as per the required quantities. Acetone is added to get uniform mixing of the oxides while grinding using agate mortar and pestle for 30 minutes. Al2Sr2La2O8 : Eu Phosphor is synthesized using standard solid state reaction with varying Tb (0.1, 0.2, 0.3, 0.4, 0.7, 1.0, 1.5, 2.0 and 2.5%) molar concentration. To prepare Aluminum Strontium Lanthanate (ASL:Eu) doped with various concentrations of Tb, consists of heating stoichiometric amounts of reactants at 1200°C for 2 hours in a muffle furnace. The phosphor materials were cooled to room temperature naturally. The received powder being ground thoroughly using an agate mortar, to ensure the best homogeneity and reactivity. All the phosphor samples were characterized by X-ray diffraction using (Synchrotron Beam Indus -II). The Photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using Xenon lamp as excitation source at display research Lab, Department of Applied Physics, Faculty of Technology and Engg., M.S.University, Baroda. The emission and excitation slit were kept at 1.5 nm, recorded at room temperature.

Basic Reaction of the Al2Sr2La2O8: Eu Tbx phosphors:

 1200 oC, 2 Hrs

#  Al2O3 + La2O3 + 2SrCO3 + Eu2O3 + Tb2O3 Al2Sr2La2O8: Eu, Tb

 Air

**3. Results and Discussions:**

**3.1 Photoluminescence studies of Tb3+ doped Al2Sr2La2O8 :Eu3+ phosphor:**

 This section describes the PL studies of ASL:Eu (0.5%) and Tb concentration is varied from 0.1 to 2.5 mol %. Figure 1 shows the PL emission and excitation spectra of the ASL: Eu (0.5%) varying Tb (0.1%,0.2 %, 0.3%, 0.4% , 0.5%, 0.7%, 1.0%, 1.5% , 2% and 2.5%) concentration. It is found the excitation spectra spreads from 235 to 300 nm with peaking around 254, 268 and 278nm with relatively good intensity when compared to ASL:Tb,Eu excitation spectra. The excitation spectra are recorded, while monitoring at 627nm. It is interesting to note that as Tb concentration increases in ASL:Eu, the Tb3+ excitation intensity decreases, when the absorption band is considered and compared. The Tb excitation intensity decreases from 160 to 16 units as the Tb concentration increases to 0.1 - 2.5 mole percentage. Since the ASL:Eu varying Tb did not give any good intensity emission, only 278nm excitations are presented in this section.



Fig.2 represents various PL emissions of 0.1 to 2.5 % Tb doped Al2Sr2La2O8: Eu excited with 278nm. Fig. 3 is the variation of Tb concentration in ASL:Eu and behaviour of subsequent PL emissions when excited with 278nm. Table.1 contains various emission peak intensities of Tb doped Al2Sr2La2O8: Eu under different excitations presented for better comparison and understanding.

Only Tb3+ → Eu3+ transfer can be observed for the Tb3+/Eu3+ pair, since the 5 D3,4 excited states of Tb3+ lie higher than the 5 D 0,1 emission states of Eu3+ and both the ions have relatively fixed energy levels for the 4f electrons. The Tb3+ → Eu3+ energy transfer is of high efficiency ( can be ∼90%, for example), because of significant overlapping of the emission spectrum of Tb3+ with the excitation spectrum of Eu3+. With such an energy transfer, occurring via electric multi pole interactions, the emission color of Tb3+/Eu3+ co-doped in ASL can be finely tuned between red and green by varying the atomic ratio of the two.



**Table 1: Intensities of various emission peaks of Tb (0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1.0, 1.5, 2.0, 2.5 mol%) of ASL: Eu(0.5%) phosphor under 278 nm excitation**

|  |  |  |
| --- | --- | --- |
| **S.No.** | **Sample** | **Emission Intensities under 278nm** |
| **468** | **514** | **541** | **556** | **582** | **588** | **597** | **615** | **627** |
| **1** | **Al2Sr2La2O8: Eu(0.5%), Tb(0.1%)** | 41 | 30 | 107 | 45 | 36 | 113 | 49 | 62 | 147 |
| **2** | **Al2Sr2La2O8: Eu(0.5%), Tb(0.2%)** | 27 | 18 | 62 | 27 | 22 | 73 | 29 | 35 | 88 |
| **3** | **Al2Sr2La2O8: Eu(0.5%), Tb(0.3%)** | 19 | 11 | 30 | 14 | 10 | 34 | 14 | 17 | 37 |
| **4** | **Al2Sr2La2O8: Eu(0.5%), Tb(0.4%)** | 12 | 7 | 14 | 7 | 5 | 14 | 7 | 7 | 14 |
| **5** | **Al2Sr2La2O8: Eu(0.5%), Tb(0.5%)** | 21 | 14 | 27 | 13 | 11 | 26 | 14 | 13 | 27 |
| **6** | **Al2Sr2La2O8: Eu(0.5%), Tb(0.7%)** | 15 | 8 | 15 | 7 | 7 | 15 | 7 | 7 | 13 |
| **7** | **Al2Sr2La2O8: Eu(0.5%), Tb(1.0%)** | 8 | 4 | 7 | 6 | 3 | 7 | 3 | 3 | 6 |
| **8** | **Al2Sr2La2O8: Eu(0.5%), Tb(1.5%)** | 10 | 5 | 7 | 5 | 4 | 6 | 4 | 3 | 4 |
| **9** | **Al2Sr2La2O8: Eu(0.5%), Tb(2.0%)** | 11 | 6 | 9 | 7 | 4 | 5 | 4 | 3 | 3 |
| **10** | **Al2Sr2La2O8: Eu(0.5%), Tb(2.5%)** | 12 | 7 | 8 | 6 | 4 | 5 | 4 | 3 | 3 |

**3.2 XRD Pattern of Tb3+ doped Al2Sr2La2O8 :Eu3+ phosphor:**

 Fig.4 is the X-Ray diffraction (XRD) patterns of the phosphors, it is found that most of the phosphors are in single phase. The crystallite size is calculated using Scherer’s formula for all the samples using the formula, D= Kλ/βcosθ.

 **Fig.4 XRD pattern of 0.5% Eu doped Al2Sr2La2O8: Tb(0.1%) phosphor**

 For Eu (0.5%), Tb(0.2%) ASL phosphor, the crystallite size is 55.10nm. Addition of Tb 0.2% did not affect the crystallite size of ASL:Eu. However with the addition of 0.5% Tb to Al2Sr2La2O8 Eu(0.1%), the crystallite size reduced to 51.6 nm.

 As it is observed, the same host containing the same concentration (1.5%) of RE3+ dopant forms different crystallite sizes. The variation may be due to the RE3+ ions diameter. Higher the diameter of the ions, lesser is the crystallite size. In the present case ‘Tb’ doped phosphor has 5% less crystallite size, when compared to Eu doped phosphor.

**3.3 SEM diagram of Al2Sr2La2O8: Eu(0.5%), Tb(0.1%) Phosphor:**

 Figure 5 is the SEM micrographs of ASL: Eu (0.5%) (Tb 0.1%), phosphor of 550, 1000 and 2700 magnification. The 2700 magnification is of 20 microns scale, wherein the particles are nearly spherical in shape having size 4 – 6 microns. This phosphor exhibited relatively good PL intensity among the ASL:Eu, Tb phosphors presented in figure 1.



**Fig.5 SEM images of 0.1% Tb doped Al2Sr2La2O8:Eu(0.5%) phosphor**

. **3.3 EDS Spectrum of Al2Sr2La2O8: Eu(0.5%), Tb(0.1%) Phosphor:**

 Fig 6 is the EDS spectra of the phosphors under characterization. From the EDS spectrum, it is found most of the phosphors consist of host and dopants only. However Figure show the presence of few impurity elements like Nickel, Cobalt. Other elements are in ppm level, which can be found from intensities on the Y – axis of EDS (Energy Dispersion Spectrum) spectra of different phosphors. The impurities Nickel and Cobalt come from the rare earth oxides used in the preparation and are present in trace level.

**Fig. 6 EDS spectrum of 0.1% Tb doped Al2Sr2La2O8 :Eu(0.5%) phosphor**



 **Fig.7 Energy Level Diagram of Eu3+ Fig.8** **Energy Level diagram of Tb3+**

 **Conclusions:**

* When the Tb3+ co-doped ASL:Eu is excited with 278 nm, the emission at 588 and 627 nm are dominant.
* With increasing concentration of Tb3+, only Eu3+ emissions are seen, which may be due to the energy transfer from Tb3+  to Eu3+ and/ or quenching of Tb 3+ emission by killer sites such as defects, vacancies etc.
* All the peaks observed at 468, 541, 588 and 627 are the allowed transitions of Eu3+, the intensities of all the observed peaks are relatively good for Tb doped ASL:Eu prepared using standard solid state reaction.
* When the ASL:Eu is prepared with Tb as varying dopant, all the primary colours from near blue, green, yellow and red is observed; as the Tb concentration increases from 0.1 to 2.5% , only 541nm peak with less intensity is present.
* XRD analysis shows that the synthesized composition retains the mostly single phase, the crystallite size is 55.10nm.
* SEM investigation confirms the particles nearly spherical in shape having size 4 - 6 microns.
* EDS technique the impurities Nickel and Cobalt come from the rare earth oxides used in the preparation and are present in trace level.

**References:**

* 1. Wu X L, Li J-G, Ping D-H, Li J K, Zhu Q, Li X D, Sun X D and Sakka Y 2013 J. Alloys Compd. 559 188.
	2. S. Shinoya, W.M. Yen, Phosphor Handbook, Laser and Optical Science and Technology Series, CRC Press, Boca Raton, 1999.
	3. K.V.R. Murthy et al, Journal of Lumin., Vol.124, Issue 2, (2007), Pages 217-220.
	4. K V R Murthy, et al, MRB, Vol.41, 10, (2006), 1854-1860.
	5. K V R Murthy, et al Philosophical Magazine Letters, Vol.90, No.9, Sept2010, 653–662.
	6. Ch.Kishore Babu, K.V.R.Murthy, B.Subba Rao,P.Sujitha, Synthesis and characterization of SrS: Eu,Ga Phosphor, International Journal on Science Innovations and Discoveries (IJSID)2012,2(3),ISSN: 2249-5347.
	7. Yen, W.M et.al,., Inorganic Phosphors, CRC Press.Boca Raton, FL (USA),(2004).
	8. Maniquiz M C, Jung K Y and Jeong S M 2010, J. Electrochem. Soc. 157 H1135
	9. Hipolito M G, Ocampo A C, Fregoso O A, Martinez E, Mendoza J G and Falcony C 2004 Phys. Status Solidi a 201 72
	10. Song H W and Wang J W 2006 J. Lumin. 118 220
	11. Ratinen H 1972 Phys. Solid State A 12 447
	12. Klimczak M, Malinowski M, Sarnecki J and Piramidowicz R 2009 J. Lumin. 129 1869
	13. Heyes A L, Seefeldt S and Feist J P 2006 Opt. Laser Technol.38 257
	14. Wang H, Yang J, Zhang C M and Lin J 2009 J. Solid State Chem. 182 2716
	15. Yang J, Li C, Quan Z, Zhang C, Yang P, Li Y, Yu C and Lin J 2008 J. Phys. Chem. C 112 12777
	16. Zhu Q, Li J-G, Li X D and Sun X D 2009 Acta Mater. 57 5975
	17. Di W, Wang X, Zhu P and Chen B 2007 J. Solid State Chem.180 467
	18. Wu X L, Li J-G, Li J K, Zhu Q, Li X D, Sun X D and Sakka Y 2013 Sci. Technol. Adv. Mater. 14 015006
	19. Azuel F 2004 Chem. Rev. 104 139
	20. Raukas M, Basun S A, van Schaik W, Yen W M and Happek U 1996 Appl. Phys. Lett. 69 3300 Sci. Technol. Adv. Mater. 16 (2015) 014902
	21. D.Srinivasa Rao, P Sai Raju, B.Subba Rao and K. V. R. Murthy International Journal of Luminescence and its applications (IJLA), Volume 4(II), 04/04/2014, ISSN 2277 – 6362
	22. D. Srinivasa Rao, P. Sai Raju, Sk. Erfan, B. Subba Rao and K.V.R.Murthy, International Journal of Advanced Research in Physical Science (IJARPS) , Volume 2, Issue 1A, PP 130-132, January, 2015 ISSN: 2349-7874 (Print)
	23. P. Sai Raju, D. Srinivasa Rao, B.Subba Rao and K. V. R. Murthy International Journal of Luminescence and its applications (IJLA) Volume 4(II), 04/04/2014, ISSN 2277 – 6362
	24. P Sai Raju, K Suresh, K. V. R. Murthy, D. Srinivasa Rao and B.Subba Rao International Referred Journal of Engineering and Sciences (IRJES) ISSN (Online) 2319-183X, (Print) 2319-1821, Volume 4, Issue 5 (May 2015), PP.24-29.
	25. K.V.R.Murthy, P. Sai Raju, D. Srinivasa rao, Sk. Erfan and B. Subba Rao International Journal of Advanced Research in Physical Science (IJARPS) Volume 2, Issue 1A, PP 119-121, January, 2015 ISSN: 2349-7874
	26. D. Srinivasa Rao, P. Sai Raju, B. Subba Rao and K.V.R.Murthy, International Journal of Recent Scientific Research Research, Vol. 6, Issue, 9, pp.6430-6434, September, 2015