ISSN 2277 – 6362
International Journal of Luminescence and Applications Vol.1 (I)

$Ce^{3+} \rightarrow Tb^{3+}$ energy transfer in $Na_6Pb_4(SO_4)_6Cl_2$ halosulphate phosphor

P.S. Thakre[1], S.C. Gedam[2#], S.J. Dhoble[3], R.G. Atram[3]

[1] Hutatma Rashtriya College of Science, Ashti, Wardha - 442202, India
[2] K. Z. S. Science College, Kalmeshwar, Nagpur - 441501, India
[3]Department of Physics, R.T.M. Nagpur University, Nagpur-440033, India
Corresponding Author: *gedam_sc@rediffmail.com*

Abstract

$Na_6Pb_4(SO_4)_6Cl_2$: $Ce^{3+}$and $Na_6Pb_4(SO_4)_6Cl_2$: Ce^{3+}, Tb^{3+} new halosulphate phosphors were synthesized by solid state diffusion method. The effects of Tb^{3+}co-doping on the photoluminescence (PL) characteristics of the phosphors have been studied. The photoluminescence (PL) emission spectra peaks 340 nm for Ce^{3+} and 490, 550, 580 nm for $Ce^{3+}\rightarrow Tb^{3+}$ which could be attributed to 5d→ 4f and $^5D_4 \rightarrow {}^7F_J$ (J = 4,5,6) transitions respectively. Energy transfer from $Ce^{3+} \rightarrow Tb^{3+}$ and has been discussed. Photoluminescence (PL) characterization of phosphor and energy transfer phenomenon has been reported in this paper.

Keywords:*Photoluminescence, energy transfer, terbium,halosulfate*

1 INTRODUCTION

The luminescence properties of co-activator compounds have received considerable interest with the utilization of efficient energy migration on sensitizer to activator. An energy transfer phenomenon has lead to the development of new and efficient photoluminescence materials. There has been considerable interest in the development of advanced luminescent materials for applications such as large flat panel displays, for example, PDPs (plasma display panels) and FEDs (field emission displays). The properties of these materials arise from complex interactions among the host structure, activators, and defects and interfaces, all of which are strongly dependent on composition [1, 2].

In searching of new luminescent materials for emissive displays, selection of host materials is an essential issue. For example, the ligand field of hosts may modify the colors of the emissions of the activators [3, 4]. The emission spectra of rare earth ions almost remain the same in different hosts, but the luminescent efficiency, chemical stability and durability largely depend on the physical properties of the hosts selected. Comparing with the alkali earth sulfides [5, 6] widely used for phosphor hosts in the past, alkaline earth sulphates are chemically stable in ambient environment, and are used as host materials in recent years. $Na_6Pb_4(SO_4)_6Cl_2$ is selected as a host material for the work.

Rare earth doped sulphate-based materials are the important phosphors over the last few decades for various applications. Ce, Tb is mainly used as a green emitting phosphor for fluorescent lamps because of its high quantum efficiency and stability at high temperature. Calcium sulfate activated with Dy^{3+} is known as a phosphor used in thermoluminescence dosimetry (TLD). The TL glow curves and the TL emission spectra of $SrSO_4$:Tb^{3+} and $BaSO_4$:Tb^{3+} were reported by Dixon and Ekstrand [7].

The compounds $Na_6Pb_4(SO_4)_6Cl_2$ (Caracolite) [8, 9], $Na_6Cd_4(SO_4)_6Cl_2$ [10], $Na_6Ca_4(SO_4)_6(OH)_2$ (Cesanite) [11, 12] are known as members of the sulfate apatite group, all-crystallizing in space group $P6_3/m$. The apatite-like compound $K_6Ca_4(SO_4)_6F_2$ was described by Vazquez [13] and Fayos et al. [14]. In contrast to the other sulfate apatite structures this compound crystallizes in the space group $Pna2_1$ with disordered SO_4^{2-} groups. Recently, we have reported new halosulphate phosphors [15, 16]. As it is well known that

Ce^{3+} is an efficient sensitizer, especially for Tb. Our approach is to develop phosphors via sensitization or energy transfer.

By this paper we report the synthesis of $Na_6Pb_4(SO_4)_6Cl_2$ material by solid state diffusion technique and explained the energy transfer mechanism in $Ce^{3+} \rightarrow Tb^{3+}$ ions. The work shows very efficient phosphors can be obtained by sensitizer Ce^{3+} ions on the basis of the $Na_6Pb_4(SO_4)_6Cl_2$: Tb^{3+} ions.

2 EXPERIMENTAL

$Na_6Pb_4(SO_4)_6Cl_2$: Ce, Tb phosphor was prepared by solid state diffusion method. Na_2SO_4 , $PbSO_4$ and NaCl and sulphate salt of Cerium, and Terbium of AR grade were taken in a stoichiometric ratio to obtain $Na_6Pb_4(SO_4)_6Cl_2$:Ce ; $Na_6Pb_4(SO_4)_6Cl_2$:Ce,Tb

$$2Na_2SO_4 + 4PbSO_4 + 2NaCl \rightarrow Na_6Pb_4(SO_4)_6Cl_2$$

The compounds were obtained by heating it at 800^0C for 24 hours. The samples were then annealed to cool slowly at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible. The powder was used in further study. The photoluminescence (PL) emission spectra of the samples were recorded using Fluorescence spectrometer (Hitachi F-4000). The same amount of sample was used in every case. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

3.RESULTS AND DISCUSSION

3.1 Ce^{3+} emission

Figure 1A shows X-Ray diffraction pattern of $Na_6Pb_4(SO_4)_6Cl_2$ material that matched with the standard JCPDF data No. 27-1416. The XRD pattern did not indicate the presence of the constituents such as Na_2SO_4, $PbSO_4$ or NaCl and other likely phases, which is the direct evidence for the formation of the desired compound. These results indicate that the final product was formed in homogeneous form.**Figure 2A** shows photoluminescence excitation spectra of $Na_6Pb_4(SO_4)_6Cl_2:Ce^{3+}$, a broadband is observed at around 260 nm (λ_{em} = 340 nm). **Figure 2B** shows the PL emission spectra of Ce^{3+} ions in $Na_6Pb_4(SO_4)_6Cl_2$ phosphor with different concentration under excitation 260 nm wavelength of light. The peaks are observed at 340 nm for all concentrations, and assigned to the 5d → 4f transition of Ce^{3+} ions.

With increasing concentration of Ce^{3+} ions the peak intensity of 340 nm increases and maximum intensity observed for 5 mole % of Ce^{3+} ion (**Figure 2C**). This indicates that the $Na_6Pb_4(SO_4)_6Cl_2$ lattice is more suitable for higher concentrations of Ce^{3+} ions .The PL emission spectra of $Na_6Pb_4(SO_4)_6Cl_2$:Ce phosphor shows the Ce^{3+} emission at 340 nm due to 5d → 4f transition of Ce^{3+} ion. The variation of PL emission intensity observed may be due to cross-relaxation between Ce^{3+} ions in case of heavy concentration of Ce^{3+}. **Figure 2D** shows energy level diagram of Ce^{3+} in $Na_6Pb_4(SO_4)_6Cl_2$.

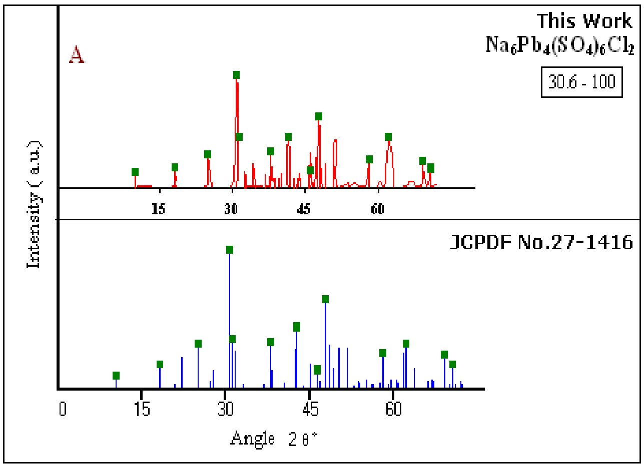

Figure 1 (A) XRD Pattern of $Na_6Pb_4(SO_4)_6Cl_2$

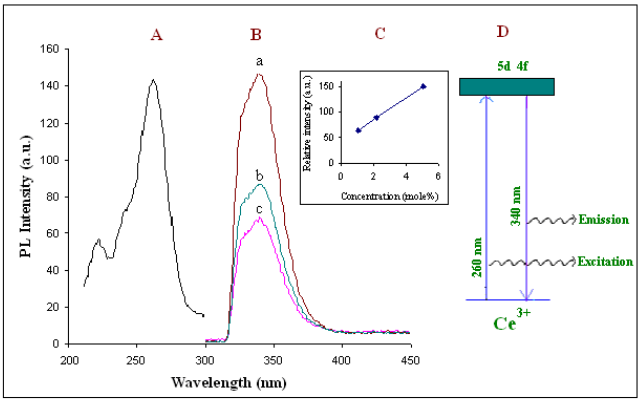

Fig 2 (A) Excitation spectra of $Na_6Pb_4(SO_4)_6Cl_2:Ce_{5mole\%}$ (λ_{exc} = 260 nm);Fig (B) PL emission spectra of $Na_6Pb_4(SO_4)_6Cl_2$: Ce (a) 5mole% b) 2 mole% c) 1 mole% (λ_{em} = 340 nm); Fig (C) Increase in intensity as the concentration increases; Fig (D) Energy level diagram of Ce^{3+} in $Na_6Pb_4(SO_4)_6Cl_2$

3.2 $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer

The energy transfer process was first considered theoretically by Forster in 1948 and by Dexter in 1953 [17, 20]. The overlap of the normalized Ce^{3+} emission and Tb^{3+} excitation is found much better. The energy transfer from the Ce^{3+} to Tb^{3+} could be very efficient. This could improve the excitation efficiency and brightness.

Figure 3A shows the PL excitation spectra of $Na_6Pb_4(SO_4)_6Cl_2$:$Ce_{5\%}$, $Tb_{0.1\%}$ is observed at 340 nm and PL emission spectra of $Na_6Pb_4(SO_4)_6Cl_2$: $Ce_{5\%}$, $Tb_{0.1\%}$ is observed at 490, 550 nm and small peak at 580 nm **(Figure 3B)**. From the result, three emission transitions have been observed: 1) $^5D_4 \rightarrow {}^7F_6$ (490 nm); 2) $^5D_4 \rightarrow {}^7F_5$ (550 nm); 3) $^5D_4 \rightarrow {}^7F_4$ (580 nm). The transition $^5D_4 \rightarrow {}^7F_5$ can be responsible for green color observation as a single peak. The Ce emission moves further to the lower energy side due to the new host ligands. Thus the energy transfer rate should be much higher. Thus $Na_6Pb_4(SO_4)_6Cl_2$: Ce, Tb must be interesting blue and green phosphors and may hold promise in applications to display devices. **Figure 4** shows schematic energy level diagram indicating $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer in $Na_6Pb_4(SO_4)_6Cl_2$.

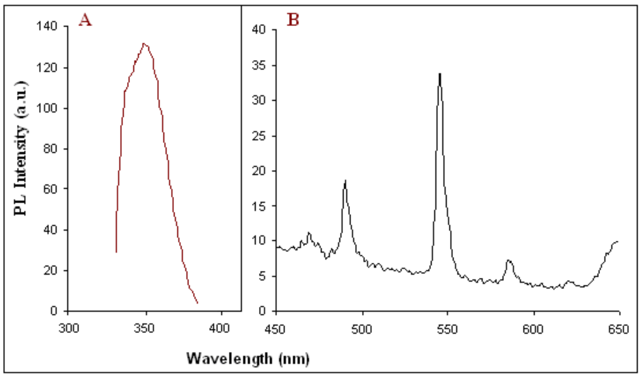

Fig 3(A): PL excitation (B) PL emission spectra of $Na_6Pb_4(SO_4)_6Cl_2Ce_{.5\%}$, $Tb_{0.1\%}$ for the emission of 550 nm

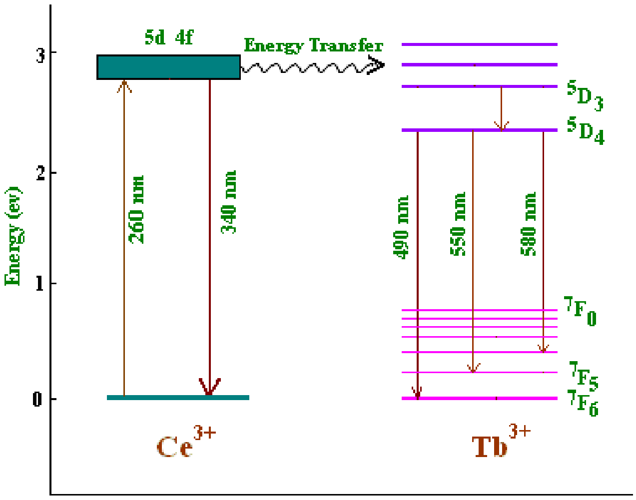

Fig.4: $Ce^{3+} \rightarrow Tb^{3+}$ Energy transfer in $Na_6Pb_4(SO_4)_6Cl_2$.

4. CONCLUSION

In this paper, luminescence in $Na_6Pb_4(SO_4)_6Cl_2$ inorganic host is reporting for the first time. $Na_6Pb_4(SO_4)_6Cl_2$: Ce^{3+}; $Na_6Pb_4(SO_4)_6Cl_2$: Ce^{3+}, Tb^{3+} phosphors have been prepared by the solid state diffusion method. Luminescence characteristics of the phosphors do not show individual Tb^{3+} emission, while in the presence of co-activator it shows Tb^{3+} emission in present matrix. The emission of Ce^{3+}, Tb^{3+} in $Na_6Pb_4(SO_4)_6Cl_2$ phosphor may be useful for scintillation, TL dosimetry display device and lamp industry respectively. Therefore this new inorganic host is suitable for the various sensitizers, activators and thus the luminescence phenomena.

ACKNOWLEDGEMENT

One of us SCG is thankful to UGC, New Delhi, India for providing financial assistance.

References:

1 Blasse, G.; Grabmaier, B.C. Luminescent Materials; Springer-Verlag: Berlin, 1994.
2 Wang, J., Yoo, Y., Gao, C., Takeuchi, I., Sun, X., Chang, H., Xiang, X.-D., Schults, G. Science 1998, 279, 1712.
3 Jia D., Zhu J., Wu B., J. Electrochem. Soc. 2000, 147 (1) 386.
4 O'Brien T.A., Rack P.D., Holloway P.H., Zerner M.C., J. Lumin. 1998, 78, 245.
5 Jia D., Wu B., Zhu J., J. Lumin. 2000, 90, 33-39.
6 Jia D., Zhu J., Wu B., J. Lumin. 2000, 91, 59-65.
7 Dixon R. L. and Ekstrand K. E., J. Lumin. 1974, 8, 383.
8 Schneider W., Jahrb N.f. Miner. Monatshefte 1967, 284.
9 Schneider W., Jahrb N.f. Miner. Monatshefte 1969, 58.
10 Perret R. and Bouillet A. M., Bull. Soc. Fr. Miner. Crystallogr. 1975, 98, 254.
11 Cavaretta G., Mottana A., and Tecce F., Miner. Mag. 1981, 44, 269.
12 Tazzoli V., Miner. Mag. 1987, 47, 59.
13 Vazquez F.T., Cem. Concr. Res. 1985, 15, 581.
14 Fayos J., Watkin D. J., and Perez-Mendez M., Am. Miner. 1987, 72, 209.
15 Gedam S.C., Dhoble S.J. and Moharil S.V., J. lumin. 2006, 121 (2) 450
16 Gedam S.C., Dhoble S.J. and Moharil S.V., J. lumin. 2007, 124 (1) 120
17 Forster Th., Ann. Phys. 1948, 2, 55.
18 Dexter D.L., J. Chem. Phys. 1953, 21 (5) 836.
19 Nakazawa, E. Phosphor Handbook, in: S. Shionoya, W.M. Yen (Eds.), CRC Press, Boca Raton, Boston, London, New York, Washington, DC, 1999, p. 102.
20 Sommerdijk J.L., Van Der Dose J.A.W., De Bye P.H., Verberne J.M, J. Lumin. 1976, 14, 91.