Synthesis and spectroscopic studies of Eu, Dy & Gd doped strontium zirconate phosphors

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Rare-earth-activated inorganic phosphors have been widely used in the fluorescent lamps LED based white light generation, radiation dosimetry and biomedical applications (1,2). The photoluminescence (PL) observed in these materials are attributed to the f–f or f–d transitions of rare-earth ions. The intensity of emission depends on the site symmetry of the dopant ions and the nature of the host matrix. Activator-doped oxide ceramics with perovskite structure (ABO_3) have received great attention due to their potential applications in the field of solid oxide fuel cells, hydrogen sensors, electronic ceramics, superconductors, steam electrolysis, catalysis, and solid-state lighting. These perovskites are very stable both chemically and physically and hence can be used in various environments. Especially, these phosphors are potential candidates in field emission display (FED) and plasma display panel (PDP) devices, since they are sufficiently conductive to release electric charges stored on the phosphor particle surfaces. The luminescence properties of ABO_3 (perovskite) -type oxide phosphors (A = Ca, Sr, and Ba; B = Ti, Zr, Si, Hf, etc.), activated with rare-earth ions, including Sm^{3+}, Tm^{3+}, Eu^{3+} , and Tb^{3+} have been investigated. Among these, $SrZrO_3$ is a compound with a high melting point (over 2,600 ^{o}C), which can be used as a high-temperature material. Its proton conductivity at elevated temperatures makes it a promising candidate for use in electrochemical devices. $SrZrO_3$ perovskite structure (ABO_3) is built up from ZrO_6 octahedra that form a network by sharing corners, in combination with Sr^{2+} ion, which fills the hole in between the octahedra. The coordination number of Sr-ion and Zr-ion are 8 and 6 respectively.

$SrZrO_3$ has been prepared by several synthetic routes including solid-state reaction, sol–gel, co-precipitation, and hydrothermal methods. Goncalves et al. (3) have synthesized Tm^{3+}:$SrZrO_3$ by polymeric precursor method, wherein heat treatment has been done under oxygen flow between 400–700 ^{o}C. The conventional solid-state reaction route requiring temperatures in excess of 1400 C suffers from inhomogeneous and coarse sample formation with non-uniform size distribution. For good luminescence characteristics, phosphors must have fine size, narrow size distribution, non-aggregation, and spherical morphology. Similarly other synthesis methods have several disadvantages, such as the evaporation of solvents resulting in phase segregation, alteration of the stoichiometry due to incomplete precipitation, expensive chemicals, and time-consuming processes. Combustion synthesis route was reported to yield a single phase compound, without intermediate grinding or annealing steps (4).

In the present talk, the spectroscopic investigations carried out in our laboratory on rare earth doped $SrZrO_3$ phosphors will be presented.Brief details of the studies are given below:

(i) **$SrZrO_3$:Eu^{3+}** nanoparticles with a size of about 100 nm were synthesized by a simple gel combustion route and characterized by X-ray diffraction, scanning electron microscopy, dynamic light scattering and photoluminescence (PL) techniques. Time resolved emission data (TRES) of the phosphor showed that, two different types of Eu^{3+} ions were present in the lattice.. The first type was a long lived species (τ= 6.1 ms) present at relatively higher symmetric site of Sr^{2+}, while the second was a short lived species (τ= 1.0 ms) present at relatively lower symmetric Zr^{4+} site, which gets selectively excited at 296 nm. The trend observed for the two species in the Judd-Ofelt parameters, Ω_2 and Ω_4, confirmed the existence of the RE ion in two different environments (5).

(ii)**$SrZrO_3$:Dy^{3+}** phosphor was prepared by gel-combustion synthesis using citric acid as fuel and ammonium nitrate as oxidizer. X-ray diffraction patterns confirmed the formation of orthorhombic phase of $SrZrO_3$ with minor impurity, which disappears at high temperature. The morphological investigation was carried out using scanning electron microscopy. The luminescence study revealed that these phosphors predominantly exhibit near white light emission, when excited by 229 nm UV light due to strong $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition at 577 nm (yellow),strong $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition at 482 nm (blue) and weak $^4F_{9/2} \rightarrow {}^6H_{9/2}$ transition at 677 nm (red). Enhancement in emission intensity was observed with increase in the annealing temperature of the phosphor. The CIE chromaticity coordinates of the phosphors were observed to fall in the white light domain of the chromaticity diagram (6).

(iii) **$SrZrO_3$: Gd^{3+}** was prepared by gel-combustion route using citric acid as fuel. The prepared samples was characterized by X-ray diffraction , scanning electron microscopy and dynamic light scattering. Upon UV light excitation (274 nm), the phosphor exhibited a strong and sharp UV emission at 313 nm, which is ascribed to $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} ions. Life time spectroscopy showed the presence of two types of Gd^{3+} ions. The EPR spectrum of $SrZrO_3$: Gd^{3+} exhibited typical U-shape with resonance signals having effective g values at g = 2.0, 2.8, 4.8 and 6.00. The signals with g values at 2.8, 4.8 and 6.0 were assigned as due to presence of Gd^{3+} ion at Sr^{2+} site having high coordination number (C.N=8), while relatively sharp signal at g =2.0 was attributed to isolated Gd^{3+} ion in polycrystalline region (7).

In conclusion, rare earth doped $SrZrO_3$ perovskite phosphors were synthesised, characterised and their spectroscopic properties were investigated. While $SrZrO_3$:Eu^{3+} was found to be an intense red emitting phosphor, $SrZrO_3$:Dy^{3+} showed near white light emission with 229 nm excitation, suggesting that its potential as a white light emitting phosphor.

References:

1. X-Y Sun, J-C Zhang, X-G Liu, L-W Lin, Ceram. Int. 38 (2012) 1065.
2. S.Das, A.A.Reddy, S.S.Babu, G.V.Prakash (2011) J Mater. Sci .46 (2011)7770.

3. M.D.Goncalves, L.S.Cavalcante, J.C.Sczancoski, J.W.M.Espinosa, P.S. Pizani, E. Longo,L.V.Rosa *Opt.Mater.*31 (2009)1134.
4. A.Zhang, M. Lu, G. Zhou, Y. Zhou, Z.Qiu, Q.Ma. J. Alloy Compd. 468 (2007) L17–L20.
5. S.K.Gupta , M.Mohapatra, V.Natarajan and S.V.Godbole, J. Mater. Sci. 47 (2012) 3504. (2012).
6. S.K.Gupta, M.Mohapatra, V.Natarajan and S.V.Godbole, Intern. J. Appl. Ceram. Techn. 10 (2013) 593.
7. S. K. Gupta, R.M. Kadam, V. Natarajan, S.V. Godbole, (submitted to Mat. Sci. &Engg.).