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Role of NH_4Cl as Flux on Photoluminescence Properties of $Ca_{1-x}ZrO_3:Eu_x$ ($x = 0.05$) Synthesized by Solution Combustion Route

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$CaZrO_3$ ceramics exhibits high chemical, thermal and structural stability. However, its application as a host for various luminophores/activators has not been clearly explored. In present study, $CaZrO_3$ doped with Eu^{3+}, as a potential orange-red phosphor and the effect of NH_4Cl as flux during combustion synthesis is investigated. $Ca_{1-x}ZrO_3:Eu_x$ ($x = 0.05$) nanophosphor was prepared through a low temperature, one pot solution combustion synthesis approach using glycine as fuel. Various wt.% of NH_4Cl (wt.% = 0, 1, 3, 5, 7) as flux added to the reaction mixture and combustion reaction was performed. X-ray diffraction results showed that the addition of flux has significant effect on the crystallite size and the crystallinity of $Ca_{1-x}ZrO_3:Eu_x$ ($x = 0.05$) phosphor. From SEM morphology, the particles were found to be significantly agglomerated. The extent of agglomeration varies with varying the wt.% of flux. The photoluminescence excitation and emission spectra were recorded under similar condition to evaluate the effect of flux on the optical properties. Interestingly, the amount of flux was found to have significant effect on the photoluminescence emission characteristics. The photoluminescence intensity was found to be the maximum when the flux used was 5 wt.% and further increase in flux amount the photoluminescence intensity decreases. The mechanistic aspects of effect of flux on the photoluminescence were also discussed.

Keywords: Calcium zirconate, Solution combustion, Photoluminescence, Flux.

INTRODUCTION

Current phosphors in use for various applications are mostly made of inorganic materials, owing to easier production, better stability and cost effectiveness. Proven that the low temperature synthesis is the most desired due to economic considerations, the material requires calcination or annealing at high temperatures post synthesis for phase formation [1,2]. Hence, work on ceramic based host materials are of the most importance as the material offers better resistance to degrade in terms of thermal and mechanical aspects. $CaZrO_3$ as a choice of host in this work is not only a ceramic but also a perovskite. Inherently disordered perovskites tend to exhibit some distinct excitation and emission due to the defects in the perovskite phases [3]. Oxide phosphors are more thermally stable and most likely used in applications such as field emission and plasma panel displays [4]. These are the reasons which makes $CaZrO_3$ an interesting host material.

The absorption of incident energy in phosphors is done by either the host material or the intentionally doped impurity. The doped impurity is also known as the localized emission center. The impurity is chosen as a dopant, usually a transition metal ion or a rare earth ion. Rare earth ions are more preferable over the transition metal ions as in case of former the *f*-electron energy level responsible for the luminescence, which are shielded from the external fields by outer shell *s*- and *p*- electrons, in contrast in transition metal ions the outer *d*- electrons are affected by crystal electric fields [5]. Rare earth doped phosphor materials also enhance the performance of the devices in many cases [6]. Hence, the rare earth doping is considered as important for luminescent materials.

In most of the cases, irrespective of the host material the doped rare earth ion determines the emission wavelength and hence the colour of light emitted. It is reported that the Eu^{3+} is known for red emission [7,8], Sm^{3+} for orange-red emission [9-11], Ce^{3+} for blue emission [12,13], Dy^{3+} for blue as well as yellow emission [14,15], *etc*. The emission wavelength and hence the emission colour is directly related to the heat radiation. This is the reason of red colour emission, which has relatively broader wavelength, is preferred over the shorter blue end. Co-doping of ions are also of significance, which can be adopted by altering the existing bandgap of the material [16,17], in order to provide the charge compensation [18] and to obtain a broader excitation range [19]. Thus, a change in the emission intensity [20] and the wavelength [21] can be made possible, meanwhle a white light emission can be obtainable by this means, achieving white is an important parameter for lighting applications.

In order to improve the emission further after the design of host and dopant material, flux aided synthesis is adopted. In this technique, in addition to the required precursors, an additional fluxing agent such as KCl, $CaCl_2$, Na_2CO_3, Li_2CO_3 and K_2CO_3 were also used [22]. This addition often results in the morphological variation in the product [23]. Optical properties are sensitive to the morphology and hence affect the luminescence properties of the material. Several studies report enhancement in the emission observed due to the added fluxing agent [24]. In this work, investigation of $CaZrO_3$ as the host material adopting Eu^{3+} as the activator is synthesized using NH_4Cl as fluxing agent. The concentration of Eu^{3+} doping is maintained constant and a variation in the NH_4Cl concentration is carried out.

EXPERIMENTAL

The chemicals utilized as precursors were of analytical grade (Merck Ltd., India) and used as supplied. The precursors were calcium nitrate ($Ca(NO_3)_2{\cdot}6H_2O$, 99.99%), zirconium nitrate ($ZrO(NO_3)_2{\cdot}xH_2O$, 99.99%), europium oxide (Eu_2O_3, 99.99%), ammonium chloride (NH_4Cl, 99.99%), nitric acid and glycine ($C_2H_5NO_2$, 99%).

Characterization: PXRD (Powder X-ray Diffraction) spectra were recorded using Shimadzu 7000 X-ray diffractometer at radiation CuKα ($\lambda = 1.54$ Å). Perkin-Elmer Rx1 instrument was used to record FTIR spectra. Scanning electron microscopy (SEM) was carried out using a JEOL (JSM-840A) instrument. Being the $CaZrO_3$ material as insulator, a gold conductive sputtering was done for coating. The recording for photoluminescence (PL) studies were performed using Jobin-Yvon Spectro fluorimeter (Fluorolog-3), which utilized a 450W Xenon lamp as the source for excitation. All the measurements for analysis were performed at room temperature.

Synthesis of europium doped $CaZrO_3$: The synthesis of $CaZrO_3$ for the present work was carried out by combustion solution route. The material being doped with Eu^{3+} is expressed as $Ca_{1-x}Eu_xZrO_3$. The concentration of Eu^{3+} was maintained as a constant at 0.05, while the fluxing agent (NH_4Cl) varied as wt.% (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6). A 1:1 solution of HNO_3 was prepared and used for the oxide to nitrate conversion of Eu_2O_3 [25]. The dissolved solution of HNO_3 and the oxides were heated on a sand bath until only the nitrate solids remain in the crystallization dish. The obtained solids were dissolved into distilled water, followed by the addition of the nitrates of calcium and zirconium stoichiometrically to the same solution along with the fluxing agent and glycine as fuel. The solution was stirred well until all solids were dissolved. The dish was then placed into a muffle furnace which was preheated to 500 ± 20 ºC. The temperature was maintained in the same range through the synthesis procedure. The water in the solution evaporates and escapes initially and then the fuel ignites the uniform mixture resulting in combustion for a few seconds in the form of a flame. Fluffy and white powders were seen to be a continuous outcome of the combustion. Thus, $CaZrO_3$:Eu^{3+} was obtained as the product within a short duration by this simple procedure. The obtained product was heated at 700 ºC for 3 h for calcination. The same procedure was used for all the variations of the dopants synthesized.

RESULTS AND DISCUSSION

PXRD analysis: In order to determine the phases of the synthesized $Ca_{0.95}Eu_{0.05}ZrO_3$, XRD analysis was performed post calcination at 700°C for all the flux concentrations (wt.% = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6). The diffraction peaks exhibit a clear orthorhombic phase in all cases and also matches with the JCPDS card 35-0790 [26]. All the peaks show that there are no changes due to the varying concentrations of NH_4Cl fluxing (Fig. 1). No impurity peaks were observed and hence the prepared material is pure. Thus, a flux during the process of preparation of phosphor contributes not only the reaction of nanopowders but also in the luminescent center in phosphors [24]. $CaZrO_3$ as a host has two possible accommodative cationic sites for the Eu^{3+} ions to replace. Taking the ionic radius of Ca^{2+} (1.12 Å), Zr^{4+} 0.72 Å) Eu^{3+} (0.95 Å) [27] ions into the consideration, it is more likely that the Eu^{3+} ions tend to occupy the Ca^{2+} sites as the Zr^{4+} ionic radius is much smaller than that of the dopant. This optimized concentration has been considered from our previous study [26]. No additional peaks were

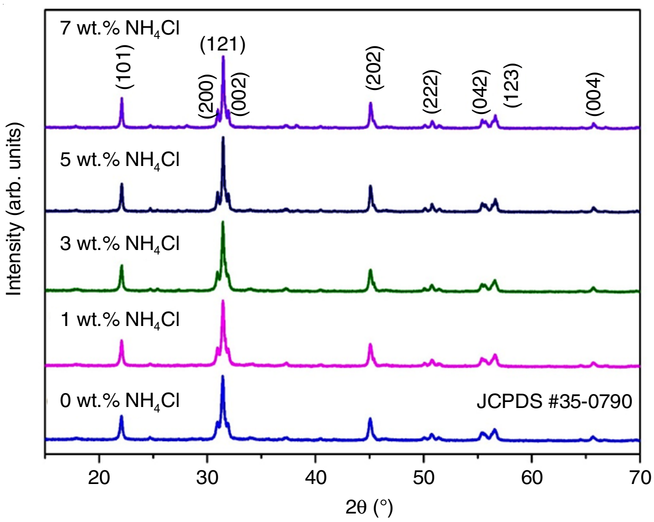

Fig. 1. PXRD patterns of $Ca_{1-x}ZrO_3$: Eu_x ($x = 0.05$) with different wt.% of NH_4Cl flux

observed in any of the diffraction plots, suggesting no residue of NH_4Cl. As the flux concentration increases, the peak intensity of the samples increases resulting in the more structural orientation of the particle. The particle size and Williamson-Hall (WH) plot (Table-1) shows that as the flux concentration increases particle size also increases as a result strain decreases which reveals that flux can make crystallinity better. Further increasing the flux amount there is no significant variation in the particle size, which signifies that 5 wt.% of NH_4Cl is sufficient for better crystallization of the sample.

TABLE-1
ESTIMATED PARTICLE SIZE, STRAIN AND DISLOCATION DENSITY VALUES OF $Ca_{1-x}ZrO_3$: Eu_x (x = 0.05) WITH DIFFERENT wt.% OF NH_4Cl FLUX

NH_4Cl conc. (wt%)	Particle size (nm)		Strain	
	WH plot (nm)	Debye Scherer (nm)	WH plot (10^{-3})	Micro strain (10^{-3})
0.0	39.4	29.5	4.550	1.301
1	39.9	26.9	2.697	1.441
2	38.5	27.9	2.145	1.336
3	37.4	32.6	1.880	1.106
4	30.7	32.4	5.040	1.114
5	39.3	31.9	3.810	1.145

SEM analysis: Scanning electron micrographs of the prepared $CaZrO_3$:xEu^{3+} (x = 0.05) having different weight percentage of NH_4Cl flux are shown in Fig. 2a-e. For the comparison purpose micrographs of similar magnification of different samples were analyzed. The morphology of the sample with 0 wt.% NH_4Cl shows a smooth surface structure with few irregular particles. The surface also consists of small voids due to the gaseous by products released during the product formation [26]. However, the micrograph images of 1 and 3 wt.% flux shows more porous and bigger voids. The surface seems to be made of agglomerated interconnected particle unlike smooth surface seen in sample without flux. It is interesting to note that the SEM images of samples with 5 and 7 wt.% shows clear particle agglomerates and a particle growth in these samples were also observed. The voids seen in other samples were also found in the prepared samples containing 5 and 7 wt.% flux. A variation in the particle agglomeration and surface structure variation might be due to the more homogeneous combustion reaction. This is due to the fact that the flux is stable in molten state at the point of combustion reaction propagation and helps in the better mixing of the reactants leading to the more fruitful exothermic combustion. Thus, the presence of bigger particles and voids are justified.

Photoluminescence studies: Fig. 3b shows the photoluminescence emission spectra of $Ca_{0.95}Eu_{0.05}ZrO_3$ with varying flux concentration excited at 396 nm where position of the emission peak not changed evidently. The spectra consist of peaks at 594, 612 and 623 nm, which are correspond to Eu^{3+} transitions $^5D_0 \rightarrow ^7F_J$ (J = 0, 1, 2, 3 and 4) respectively which is similar to our earlier report [26]. It is observed that a bright orange red peak, which is a hypersensitive electric dipole transition is high intense than the other transitions. It is clearly observed that the emission intensity increases with increasing the concentration of NH_4Cl flux from 0 wt.% to 5 wt.%. The highest emission intensity was obtained for the prepared sample with 5 wt.% NH_4Cl flux with an almost four time emission

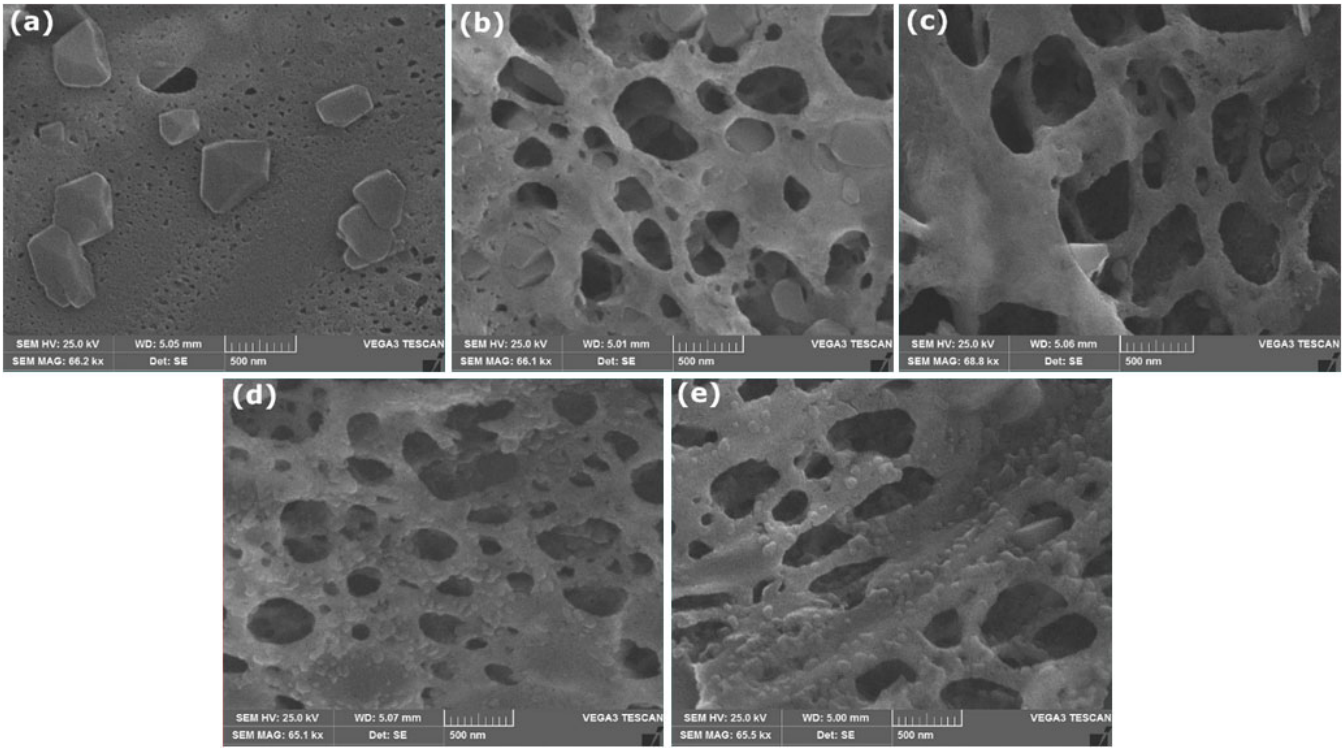

Fig. 2. Scanning electron micrographs of of $Ca_{1-x}ZrO_3$:Eu_x (x = 0.05) with different wt.% of NH_4Cl flux (a) 0 wt.% NH_4Cl (b) 1 wt.% NH_4Cl (c) 3 wt.% NH_4Cl (d) 5 wt.% NH_4Cl (e) 7 wt.% NH_4Cl

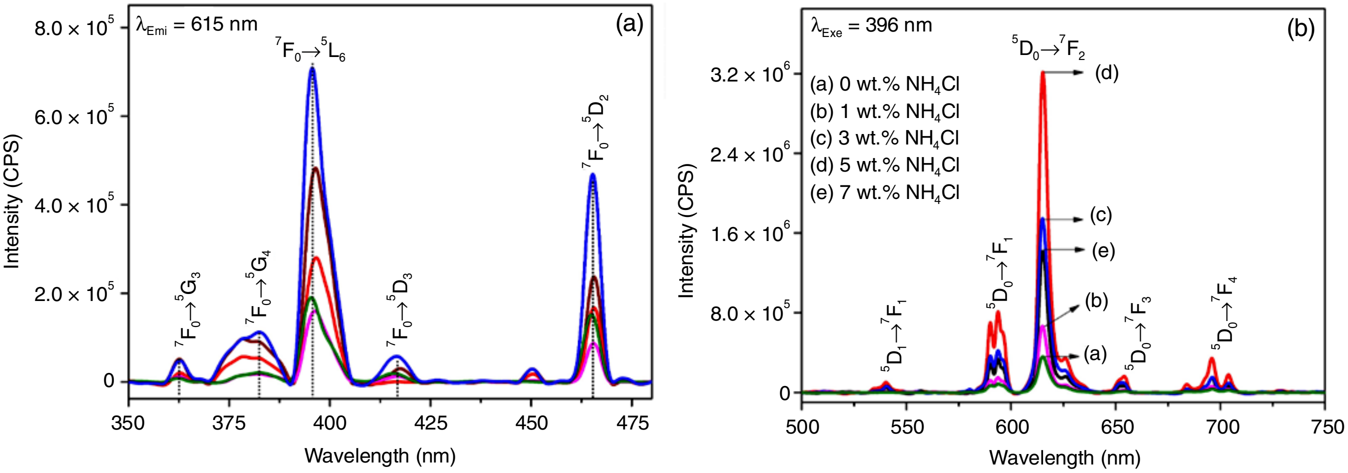

Fig. 3. (a) Photoluminescence excitation spectra and (b) Photoluminescence emission spectra of $Ca_{1-x}ZrO_3$: Eu_x ($x = 0.05$) with different wt.% of NH_4Cl flux (a) 0 wt.% NH_4Cl (b) 1 wt.% NH_4Cl (c) 3 wt.% NH_4Cl (d) 5 wt.% NH_4Cl (e) 7 wt.% NH_4Cl

intensity over that of the sample synthesized without flux. The photoluminescence enhancement may originate in the narrower particle size distribution and the uniformness of the particle shape of the phosphor prepared with NH_4Cl flux. Which in turn results an enhancement of the solubility of Eu^{3+} ions in the host material to facilitate the formation of the host materials luminescence center. It is known that the phosphor with regular morphology and fine size can improve the packing density and produce uniform luminescence intensity.

The chromaticity diagram (Fig. 4) and its coordinates are the way to visualize the sample performance in lightning applications. For general lightening system, the parameters like CRI, luminous efficacy of radiation, CIE coordinates and its deviation plays an important role. The value of optimized $CaZrO_3$ with 5 wt. % of NH_4Cl is (x, y) = (0.645, 0.345). The CIE coordinates are in bright red region which is very close to NTSC system standard for red (0.67,0.33) [28].

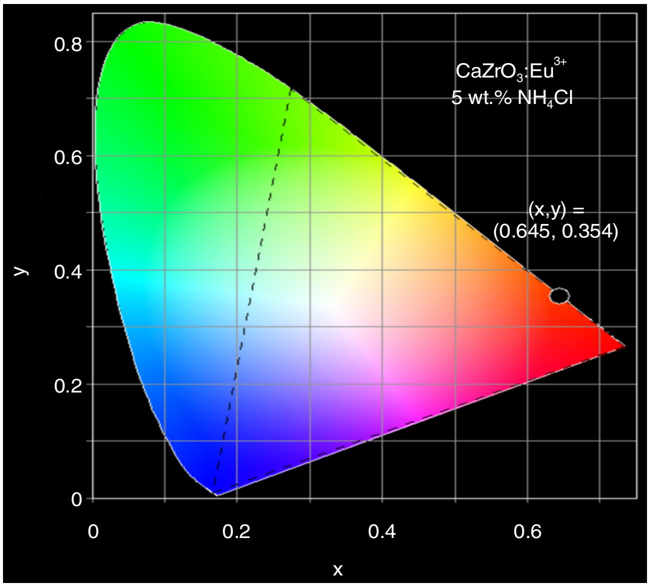

Fig. 4. Colour coordinates of $Ca_{1-x}ZrO_3$:Eu_x ($x = 0.05$) with 5 wt.% NH_4Cl as flux. The CIE 1931 coordinates are obtained using the photoluminescence emission spectrum

Conclusion

In summary, $CaZrO_3$:xEu^{3+} ($x = 0.05$) was synthesized by flux mediated solution combustion synthesis. Different wt.% (1, 3, 5, 7 and 9) of NH_4Cl was used as flux during the synthesis. The quantity of flux added has a significant influence on the structural and microstructural properties of the $CaZrO_3$:xEu^{3+} phosphor. With the addition of flux, the crystallite size increases while the micro strain in the lattice as evaluated from WH plot decreases. With varying flux quantity, the surface morphological features of the samples are greatly varied. Smooth and surface with smaller voids were found in prepared samples without flux but with increasing flux bigger voids and increased agglomeration of particles were also observed in SEM images. These surface structural variations were attributed to the homogeneous combustion reaction which was aided by the presence of flux in the molten state. Photoluminescence emission spectra recorded at excitation wavelength 396 nm showed a series of emission peaks corresponding to *f-f* transitions. With increase in flux quantity, the photoluminescence emission intensity increases and beyond 0 wt.% of NH_4Cl flux photoluminescence quenching was observed. The quenching in photoluminescence beyond optimum concentration is attributed to the growth of particles that results in easier cross relaxation among the dopant ions.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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