A SPECTROSCOPIC CHARACTERIZATION OF NOVEL $CaAl_{3-x}$ $(PO4)_3F_2$:Ce_x^{3+} ($0.1 \leq x \leq 5$) PHOSPHOR BY FACILE COMBUSTION METHOD

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ABSTRACT

A series of phosphors $CaAl_{3-x}(PO4)_3F_2$:Ce_x^{3+} ($0.1 \leq x \leq 5$) was synthesized using a facile combustion method using urea as a fuel and their structural ,morphological and photoluminescence properties were investigated. The phosphor could be excited by UV light of wavelength 264 nm and showed a broad blue emission with the wavelength ranging from 275-400 nm. The 5d levels corresponding to the $4f^1 \rightarrow 4f^0 5d^1$ transition of Ce^{3+} ions were identified . In this work, we report the synthesis and X-ray powder diffraction (XRD), photoluminescence (PL), scanning electron microscopy (SEM) of $CaAl_{3-x}(PO4)_3F_2$:Ce_x^{3+} ($0.1 \leq x \leq 5$)phosphors have been reported. Our work shows that $CaAl_{3-x}(PO4)_3F_2$:Ce_x^{3+} ($0.1 \leq x \leq 5$)has a strong absorption peak at 264 nm and gives emissions at 321 nm.

Keywords: Luminescence, X-ray diffraction, SEM & Phosphate

I. INTRODUCTION

Halo phosphate phosphors have attracted tremendous attention due to their intense luminescence intensities, high emission efficiencies, simple preparation techniques and wide application fields in illumination and display [1-3]. Phosphates usually show a rather short wavelength of optical absorption edge. This makes them suitable as hosts to accommodate active RE ions. The luminescence of RE-doped phosphates usually has a high thermal stability [4]. In certain cases they act as efficient emitters as well as sensitizing agents.

The spectroscopic properties of cerium (Ce^{3+}) ions are very well investigated in various phosphors, crystals and glasses [5–7]. However, up to now, there are no reports to investigate the luminescence of RE ions doped in this host. The luminescence and spectroscopic parameters of Ce^{3+} doped in $CaAl_3(PO4)_3F_2$ under excitation of ultraviolet (UV) were investigated for the following reasons. Firstly, the 5d level spectroscopy of Ce^{3+} ion is very simple, which has only one electron in the 4f shell and exhibits strong absorption and efficient fluorescence from the allowed interconfigurational $4f^1 \rightarrow 4f^0 5d^1$ transition. It has been reported that the spectroscopic parameters of Ce^{3+}, e.g., the positions of 5d level, can be used to predict the 5d energies of other lanthanides, since the influence of the crystal field and covalence of the host lattices on the 4f5d levels are approximately equal for all the RE ions [8].

In this study, Ce^{3+} doped $CaAl_3(PO4)_3F_2$ was prepared by combustion. Its structure was studied by XRD measurement. The luminescence properties of the Ce^{3+} ion were investigated under UV radiation. The spectroscopic parameters such as emission bands, 5d components of Ce^{3+} ion doped in $CaAl_3(PO4)_3F_2$ were discussed. So this research can be referential for the luminescence investigation of other RE ions doped in this phosphate.

2. Experimental:

2.1 Synthesis:

The Cerium doped $CaAl_3 (PO4)_3F_2$ phosphate phosphors were synthesized by the facile combustion method. The starting material were

taken as Calcium Nitrate [Ca(NO$_3$)$_2$] , aluminium nitrate [Al(NO$_3$)$_3$.9H$_2$O], di-ammonium hydrogen phosphate [(NH$_4$)$_2$HPO$_4$], Ammonium floride (NH$_4$F), Europium nitrate was prepared by dissolving europium oxide [Eu$_2$O$_3$] in nitric acid. All the reagents were of analytical grade from Merck with 99.99% purity were used without further purification. The correct amount of each excess urea [CO(NH$_2$)$_2$] were injected into the precursor solution or these compositions. The amount of metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valences of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. After stirring for about 20 min, precursor solution was transferred to a furnace preheated 750°C.

2.2 Measurements:-

Several complementary methods were used to characterize the prepared phosphors. The prepared host lattice was characterized for its phase purity and crystallinity by X-ray powder diffraction (XRD), using a PAN-analytical diffractometer (Cu–Ka radiation) at a scanning step of 0.01^0, continue time of 20 s and in the 2θ range 10-70^0; The photoluminescence measurements of excitation and emission were recorded on a Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample (2g) was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. All the measurements were conducted at room temperature.

3. Results and discussion:
3.1. XRD of CaAl$_3$ (PO$_4$)$_3$F$_2$:Ce^{3+} phosphor powder:

Fig. 1 gives the XRD patterns of CaAl$_3$(PO$_4$)$_3$F$_2$ material. However, the obtained diffraction peaks of all compounds do not match any data in the JCPDS base after careful comparison with the reported compounds for the obtained phase; it is carefully observed that there are no peaks of raw materials. It is found that the main phase does not agree to any JCPDS available. Different temperatures do not result in new other phase except the unknown main phase. Consequently, we speculate that the obtained unknown phase is likely to be a new phase.

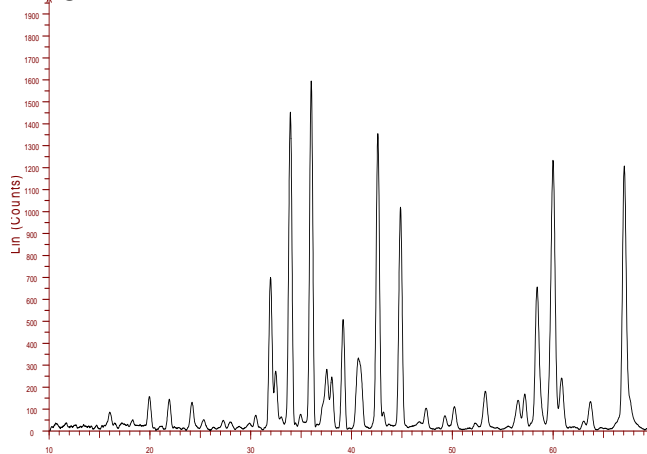With respect to this point, a further study is still being carried on.

Fig. 1 X-ray diffraction (XRD) patterns of CaAl$_3$ (PO$_4$)$_3$F$_2$:Ce

3.2. SEM of CaAl$_3$ (PO$_4$)$_3$F$_2$:Ce^{3+} phosphor powders:

Characterization of particles, surface morphology and size for nano crystals is done routinely using scanning electron microscope. The main advantage of SEM is that they can be used to study the morphology of prepared particles and composites. Fig.2 shows the SEM pattern of CaAl$_3$ (PO$_4$)$_3$F$_2$:Ce^{3+} phosphors prepared at 750^0 C. It is clearly seen that the grains prepared by combustion method are irregular in shape with particles size of about 2μm and 5μm. This shows that the combustion reactions of the mixtures took place well. The particles possess foamy like morphology formed from highly agglomerated crystallites. Hence it is suitable for solid state lighting (coating purpose). [9]
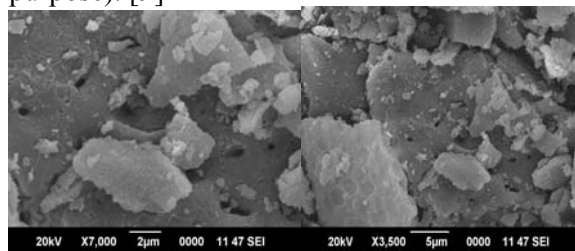

Fig. 2. SEM images of CaAl$_3$(PO$_4$)$_3$F$_2$: Ce^{3+} phosphor powders prepared by facile combustion method.

3.3 PL Properties of CaAl$_3$(PO$_4$)$_3$F$_2$:Ce^{3+} :

Ce^{3+} is a very good candidate as activator as well as sensitizer, for studying the behavior of 5d electrons. The 5d-level spectroscopy of Ce^{3+} is very simple. In the excited state, the 4f shell is empty and there is only one single 5d electron

interacting with the crystalline environment. In the ground state, Ce^{3+} ion has the (X_e) $4f^l$ configuration, which results in only two $4f^l$ energy levels, $^2F_{5/2}$ and $^2F_{7/2}$ [10] The spatially diffuse 5d electron orbital extends outward from the ion to overlap the neighbouring ligand ions, and is more strongly influenced by their motion. In consequence, the optical properties depend strongly on the structure of the host crystals. Both absorption and emission have a usually broadband character, showing splitting characteristic of ^2F_j states. As the position of the 5d band itself depends on the host, not only the Stoke's shift but also the spectral positions of both the excitation and emission bands are host-dependent. In phosphate, the emission is expected to be in the UV region. The luminescence of Ce^{3+} is quenched above the concentration of about 3mol%. Figures 3 & 4 show the PL excitation and emission spectra of Ce^{3+} ions in $CaAl_3(PO_4)_3F_2$ phosphors of different concentrations under light excitation at a wavelength of 264 nm. The unresolved peaks are observed at 321 nm with a broad band of 275 nm to 400nm , which are assigned to the 5d–4f transition of Ce^{3+} ions. Figure 5 shows the concentration of Ce^{3+} vs the PL intensity of $CaAl_3(PO_4)_3F_2$: Ce^{3+} The PL emission spectra of $CaAl_3$ $(PO_4)_3F_2$:Ce (3 mol%) phosphor show Ce^{3+} emission at 321nm due to 5d–4f transmission of the Ce^{3+} ions. The variation of PL emission intensity observed may be due to cross-relaxation between Ce^{3+} ions (in this process, an excited ion transfers only a part of its energy to another ion) in cases of heavy concentration of Ce^{3+} Figure 4. The emission intensities increase with an increase of Ce^{3+} content upto $x = 3$ mol % and then decreases by further increasing the Ce^{3+} content. The decrease is primarily because the energy absorbed by Ce^{3+} is released as a non-radiation transition instead of are light emission. Perhaps this is due to concentration quenching effect.(Fig. 5) Energy transfer between pairs of rare earth ions at dilution levels below the self-quenching limits is known to take place generally through multipolar interactions, such as dipole–dipole or dipole–quadrupole interactions [11–13]. The Ce^{3+} ion can be used as a sensitizer as well as an activator, depending on the splitting of 5d excited levels by the crystal field symmetry.
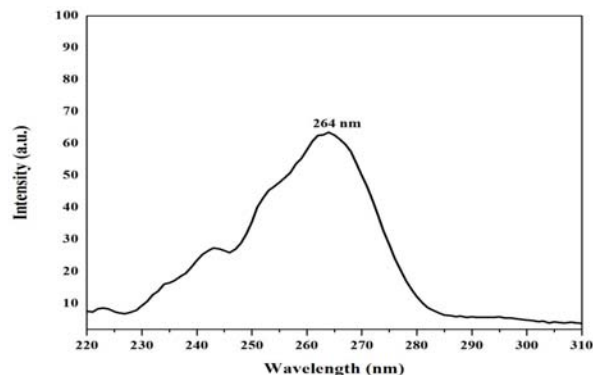

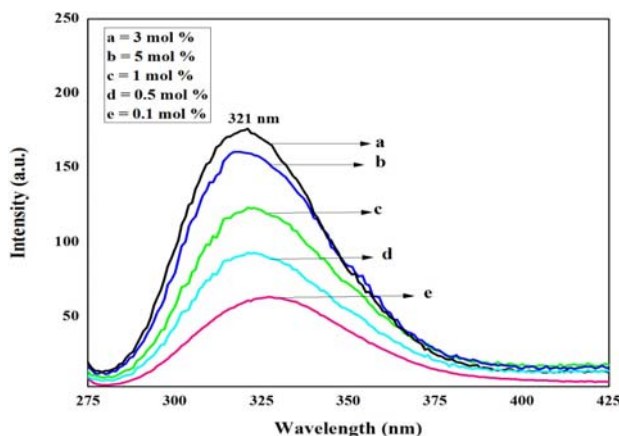Fig. 3. Excitation spectrum of $CaAl_3(PO_4)_3F_2$: Ce^{3+} phosphor powder monitored at 321 nm.

Fig. 4. Emission spectra of $CaAl_{3-x}(PO_4)_3F_2$: Ce_x^{3+} $(0.1 \leq x \leq 5)$ phosphor powder when excited at 264 nm.
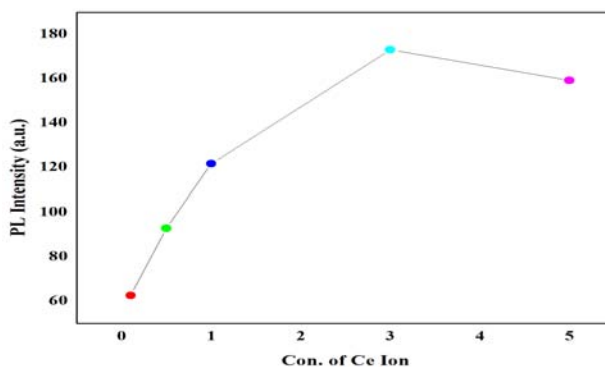

Fig.5. Concentration of Eu in emission spectra of $CaAl_{3-x}(PO_4)_3F_2$:Ce_x^{3+} $(0.1 \leq x \leq 5)$ phosphor powder with respect to intensity

The basic mechanism for scintillation in a Ce-doped material is that an incident ray will produce a large number of electron-hole (e − h) pairs in the host mate rial that transfer to the Ce site. The emission of light then corresponds to a 5d-4f transition on the Ce site from the Ce[Xe]$4f^05d^1$ excited state, usually referred to as (Ce^{3+}), to the Ce^{3+} ground state [Xe]$4f^l$ $5d^0$ (see Fig. 6). Trapping mechanisms on the host,

such as self-trapped excitons, hole traps, or electron traps, can quench or reduce the transfer of energy to the Ce site. A necessary condition for scintillation and luminescence is that the Ce 4f and 5d levels must be in the gap of the host material. If the Ce 4f level lies in the valence band of the host or the 5d level is in the conduction band, there will be no Ce-activated scintillation or luminescence. Our theoretical calculations for the prediction of candidate scintillator materials are based on studies of the Ce 4f and 5d levels relative to the valence-band maximum and conduction-band minimum of the host material, respectively [14].
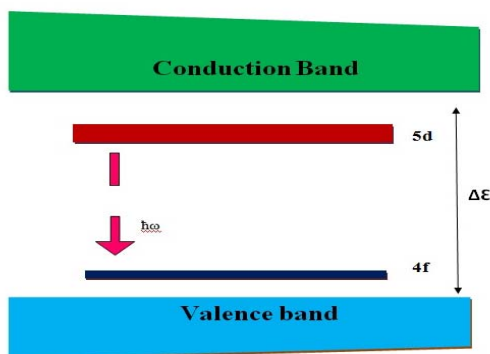

Fig. 6 Schematic diagram for a Ce-activated scintillator showing the positions of the Ce 5d and 4f levels relative to the conduction and valence band of the host material.

In the 5d→4f transition of Ce^{3+} ion, 4f is the lowest excited charge transfer state and t_1g is the molecular orbital of the surrounding ligand. Hence, Ce^{3+} ion was excited in this lattice at 264nm to check for its suitability for scintillating mechanism application. As shown in Fig. 7, the emission occurs from the lowest component of the 5 d configuration to the two-crystal field split levels ($^2F_{5/2}$ and $^2F_{7/2}$) of the 4f ground state. As the concentration of Ce^{3+} ion increases to 0.3mol%, the PL intensity also increases, due to more Ce^{3+} ions in the $CaAl_3(PO_4)_3F_2$: Ce^{3+} lattices. The 275–375nm PL emission was dominant at 3mol% Ce^{3+} ions. The observed Ce^{3+} emission in this phosphor can be used in scintillators according to an energy transfer process explained by Lempicki et al. [15] and Wojtowicz et al. [16,17]. According to this process, Ce^{3+} captures primary excitation energy (hυ) and becomes Ce^{4+}. After capturing a free electron (e_c) from the conduction band, Ce^{4+} will be converted to an excited Ce^{3+} ion or $(Ce^{3+})^*$. Relaxation to the, ground state will be accompanied by

emission of the scintillation photon hυ. This process can be summarized as follows:

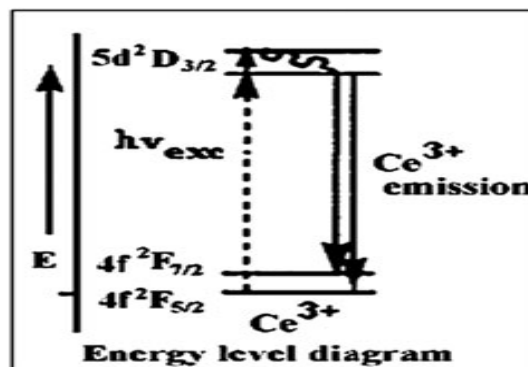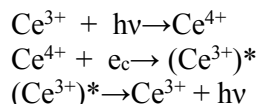$Ce^{3+} + hv \rightarrow Ce^{4+}$
$Ce^{4+} + e_c \rightarrow (Ce^{3+})^*$
$(Ce^{3+})^* \rightarrow Ce^{3+} + hv$

Figure 7. Energy level diagram of Ce^{3+}.

Conclusions:-

From the results presented here novel $CaAl_3(PO_4)_3F_2$:Ce^{3+} phosphor prepared by novel combustion method described here and formation of compound is confirmed by XRD. Strong luminescence of Ce^{3+} can be observed in the as prepared powders without any further heat treatment. Peak position (at 321nm) is not influenced by different concentrations of Ce^{3+} and only relative intensities vary when excited around 264 nm. Only intensity varies may be due to different synthesis method. Present phosphor shows the near UV emission for development of energy transfer based co-activated advanced phosphors for lamp industry and scintillation. Besides, full understanding of the nature of the competing processes and the dynamics of holes trapping by Ce^{3+} is still one of the challenging subjects in scintillation mechanism research.

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