

Structural, Photoluminescence And Thermoluminescence Properties Of Erbium Doped Calcium Silicate Phosphor By Solid State Reaction Method

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Abstract - The silicates of calcium are known for their thermal stability, high temperature strength, low thermal expansion, cheap residence and chemical inertness. Silicate phosphor are used for a fluorescent, a cathode-ray tube, a luminous body, a vacuum ultraviolet excitation light emitting element etc. Calcium Silicate acquires a higher luminous efficiency when it is doped with rare earth activated ions. In present work the silicate is prepared by combustion method at initiating temperature of 1000^oC, using urea as a reducer and activated by Er³⁺. The prepared CaSiO₃:Eu³⁺ phosphor was characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDX), photoluminescence (PL), Thermoluminescence and decay characteristics. The chemical composition of the sintered CaSiO₇:Eu³⁺ phosphor was confirmed by EDX spectra, The PL spectra indicate that CaSiO₇:Eu³⁺ can be excited effectively by near ultraviolet (NUV) light and exhibit bright orange-red emission with excellent color stability. The PL broadness and fluorescence lifetime of ⁴I_{13/2} → ⁴I_{15/2} transition were typically in the range of 50-70 nm and 2.2 – 2.5 ms respectively. CIE color coordinates of phosphor is suitable as green red light emitting phosphor with. Therefore, it is considered to be a new promising pink-light emitting phosphor for white light emitting diode (LED) application.

Key Words: *Silicate materials, Combustion Synthesis, Thermoluminescence, Photoluminescence*

1.INTRODUCTION

Recently, nanosized luminescent materials doped with rare earth (RE) ions have attracted intensive attention not only for their unique physical properties but also for their potential

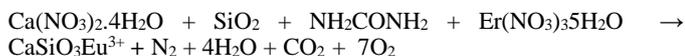
applications in developing novel phosphors and building miniature optoelectronic devices. Because the reduction of particle size can result in remarkable modifications of some of their bulk properties, nanosized phosphors or optoelectronic devices usually exhibit novel capabilities, such as higher luminescent efficiency and better resolution of images in lighting and display[1,2] The lanthanide ions doped alkaline earth silicates are an important class of phosphorescence materials because of their high quantum efficiency in visible region, long persistence of phosphorescence, good stability, color purity and good chemical, thermal and radiation resistance [3]. The potential benefit of lanthanide ions as activators has now well established in the field of luminescence [4]. Different activators contribute significantly in tailoring the afterglow properties of phosphors from few seconds to many hours [5]. The emission spectra of lanthanide ions almost remain the same in different host, but the luminescent efficiency, chemical stability and durability largely depends on the physical properties of host selected [6]. Erbium ion (Er³⁺) has been considered as one of the most popular and efficient ions for obtaining infrared to visible up-conversion and broadband emission at 1.5 μm under the 980 nm excitation. The transition, ⁴I_{15/2} → ⁴I_{11/2} (980nm) of Er³⁺ ion gives poor ground state absorption. Materials with lower phonon energy can effectively restrain the multi-phonon relaxation of the energy level and CaSiO₃ powder has emerged as a candidate due to its good mechanical properties, microstructure stability and lower phonon energy [7,8]. In contrast, little attention has been paid to its optical properties in CaSiO₃ systems at different Er³⁺ concentrations. [9] Er³⁺ ions in the host CaSiO₃ composite have attracted interest due to their possible application in visible and near-infrared regions. Their local environment can provide a surrounding for the coexistence of Er, and optically activate Er³⁺ ions [10].

Therefore, $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ can be a promising complement to the CaSiO_3 composite due to the f-f transitions within the $4f_{11}$ electronic shell of Er^{3+} ions, i.e., $4F_{9/2}$, $2H_{11/2}$ and $4S_{3/2}$ for ground state $2I_{15/2}$ [11,12]. Such transitions occur when Er^{3+} ions occupy a lattice site of no inversion symmetry and are associated with electric dipole. Conversely, the electric dipole emission is forbidden when occupies a site of inversion symmetry. In this sense, the analysis of the luminescence emission of Er^{3+} ions in the host CaSiO_3 enables the understanding of the luminescence properties that change in response to the variation in both Er^{3+} concentration and CaSiO_3 from fundamental and technological viewpoints. This paper reports on the emission of Er^{3+} ions in the host CaSiO_3 composite under 482 nm laser excitation, from downconversion processes. Samples were prepared with different Er^{3+} concentrations in CaSiO_3 ratio and both intensities and lifetime of the down-conversion were evaluated for the distinction and improvement of the intensity of Er^{3+} ions emissions. Structural and functional group analyses by X-ray diffraction, SEM and EDX were also discussed. The Luminescence properties were discussed by TL and PL behavior. Such emissions by down conversion are a result of the phase transformation from monoclinic to tetragonal phases due to the Er^{3+} concentration and surface defects.

2. EXPERIMENTAL PROCEDURES

2.1. Synthesis

Er^{3+} -doped CaSiO_3 phosphor were prepared by combustion synthesis. The starting material include calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; Merck), silica fumes (SiO_2 , 99.9% surface area $200 \text{ m}^2/\text{g}$), europium nitrate $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and urea (NH_2CONH_2). Stoichiometric composition of the 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. Mixture was placed over a muffle furnace heated to a temperature of 1000°C - 1500°C . Gaseous products such as oxides of carbon and nitrogen are released as the mixture undergoes dehydration and ignition. Once ignited, the combustion propagates on its own without the need of any external heat. The silicate in a foamy form was obtained finally. Assuming total combustion of the redox mixture for the synthesis of CaSiO_3 could be written as:



2.2. CHARACTERIZATION

X-ray diffraction of the prepared phosphor was recorded in a wide range of Bragg angle 2θ using a Bruker D8 advanced X-ray diffraction measuring instrument with Cu target radiation ($\lambda = 0.154056 \text{ nm}$). The thermoluminescence (TL) data were collected using a Thermoluminescence Reader (Integral- Pc Based) Nucleonix TL 1009I. Er^{3+} doped CaSiO_3 were prepared at temperature of 1000 - 1500°C .

Photoluminescence (PL) data were collected using by RF-5301PC SHIMADZU spectrofluorophotometer (RF-5301PC). Surface morphology and EDX analysis performed with the help of SEM (ZEISS EVO Series Scanning Electron Microscope Model EVO 18) fitted with EDX. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm.

3. RESULTS AND DISCUSSION

3.1 XRD

In order to determine the phase structure, powder XRD analysis has been carried out. The XRD patterns of $\text{CaSiO}_3\text{:Er}^{3+}$ for different mole % of CaSiO_3 are shown in Fig.1. The position and intensity of diffraction peaks of the prepared $\text{CaSiO}_3\text{Er}^{3+}$ phosphor were matched and found to be consistent with the standard XRD pattern (COD card No. 96-900-6941) by MATCH 2 software. In Fig. 1, it can be concluded that prepared samples are chemically and structurally CaSiO_3 phosphor. The phase structure of the $\text{CaSiO}_3\text{Er}^{3+}$ phosphor is akermanite type structure which belongs to the tetragonal crystallography with space group P421m (113 space number and D3 2d space group), this structure is a member of the melilite group and forms a layered compound. CaSiO_3 monoclinic phase is present in large abundance along with small trace of Ca_2SiO_4 as orthorhombic phase. The crystal field symmetry and hence the effect of field on the shifting of emission lines is strongly dependent on the relative contents of these two phases. The average crystallite size was calculated from the XRD pattern using Debye Scherrer relation $D = \frac{k\lambda}{\beta \cos\theta}$ where D is the crystallite size for the (hkl) plane, λ is the wavelength of the incident X-ray radiation [CuK α (0.154 nm)], β is the full width at half maximum (FWHM) in radiations, and θ is the corresponding angle of Bragg diffraction. Sharper and isolated diffraction peaks such as $2\theta = 24.15$ (1 1 1), 29.04 (2 1 0), 31.26 (21 1), 36.44 (3 1 0), 38.93 (3 0 1), 44.55 (2 1 2) were chosen for calculation of the crystallite size. Based on the Debye-Scherrer's formula, the crystallite size is ~ 79 nm, 76nm, 70 nm, 69 nm, 66 nm, 65 nm was calculated, respectively and the average crystallite size is ~70.00 nm.

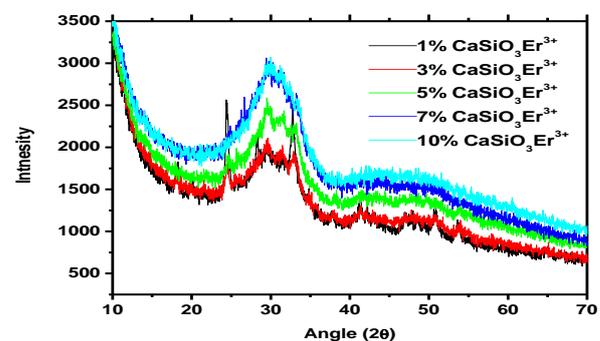


Fig. 1: XRD patterns of $\text{CaSiO}_3\text{:Er}^{3+}$ phosphor.

3.2 Scanning Electron Microscopy (SEM)

It is known that the luminescence characteristics of phosphor particles depend on the morphology of the particles, such as size, shape, size distribution, defects, and so on. The surface morphology of the $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor is shown in Fig. 2(a, b, c, d) with different magnification. The surface morphology of the particles was not uniform and they aggregated tightly with each other. From the SEM image, it can be observed that the prepared sample consists of particles with different size distribution. In addition, there are some big aggregates is also present due to high temperature heat treatment.

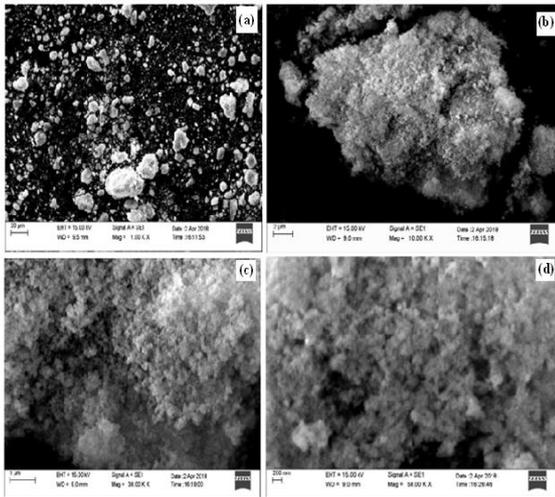


Fig. 2: Fig. 3 e (a, b, c, d) SEM image of $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor.

3.3. Energy dispersive X-ray spectroscopy (EDX)

The chemical composition of the powder sample has been measured using EDX spectra. EDX is a standard procedure for identifying and quantifying elemental composition of sample area as small as a few nanometers. The existence of Er is clear in their corresponding EDX spectra. Their appeared no other emission apart from calcium (Ca), silicon (Si) and oxygen (O) in $\text{CaSiO}_3:\text{Er}^{3+}$ EDX spectra of the phosphor. In EDX spectra, the presence of Ca, Si, O and Er, intense peak are present which preliminary indicates the formation of $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor in Fig. 3. The elements presents in the Weight% and Atomic% also determined which is represented in table 1.

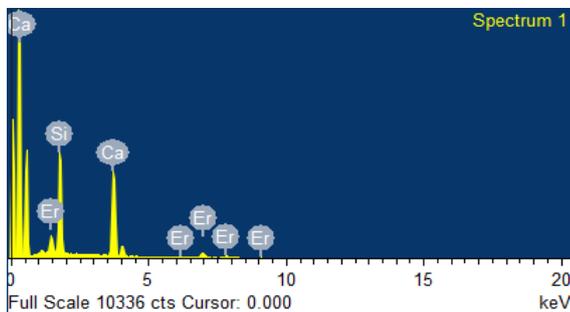


Fig. 3: EDX spectra of $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor.

Table 1. Element present in sample

Element	Weight%	Atomic%
Si K	34.00	49.17
Ca K	45.17	45.77
Er L	20.83	5.06
Total	100.00	100.00

3.4. Photoluminescence (PL)

The excitation spectrum of $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor monitored at 500 nm emission is given in Fig. 4(a). It exhibit a broad band in the UV region centered at about 440 nm, and several sharp lines between 450 to 480 nm. The broad band between 420 and 450 nm, the broad absorption band is called charge transfer state (CTS) band due to the euridiumoxygen interactions, which is caused by an electron transfer from an oxygen 2p orbital to an empty 4f shell of iridium and the strongest excitation peak is at about 440 nm. The strongest sharp peak correspond to excited state $^4\text{F}_{5/2}$ from ground state $^2\text{I}_{15/2}$ of the Er^{3+} , when excited at 482 nm.

Fig. 4(b) shows the emission spectra of $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor in the range of 500 to 900 nm. The emission spectrum of our obtained samples was composed of a series of sharp emission lines, corresponding to transitions from the excited states $^2\text{H}_{7/2}$ to the round state. Such emissions in the luminescence spectra suggest the local environment of Er^{3+} is affected by the phase mixture, evidenced by the XRD patterns. The Er^{3+} ions in the $^4\text{F}_{7/2}$ level decay non-radiatively to the $^4\text{S}_{3/2}$, $^2\text{H}_{11/2}$ level and benefit the transition to the $^4\text{F}_{9/2}$ level, rather than to the $^4\text{S}_{3/2}$ level, which results in a decrease in the green emissions and increase in the red emissions. On the other hand, the variation in the luminescence efficiency might also be attributed to the divergence of the local environment surrounding Er^{3+} ions and surface defects in the particles of the host material. The surface is responsible for nonradiative energy transfers from the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ level of the Er^{3+} ions to the O-H vibrations. The various transition of Er^{3+} in the CaSiO_3 system indicated in figure 5.

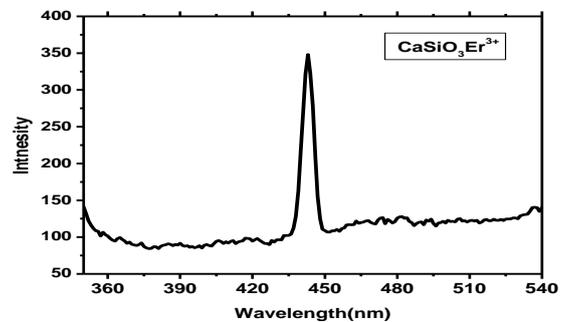


Fig. 4(a): Excitation spectra of $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor

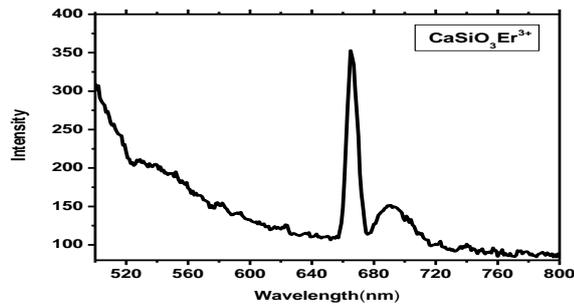


Fig.4(b): Emission spectra of CaSiO₃:Er³⁺ phosphor.

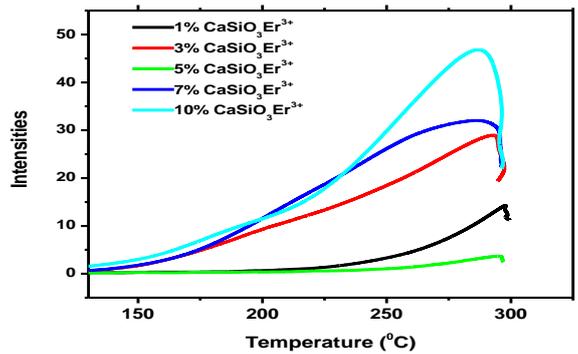


Fig. 6: TL glow curve of CaSiO₃:Er³⁺ phosphor.

Fig. 6(a): TL glow curve of γ - irradiated for different concentration at irradiation dose 1180Gy (120min).

Fig. 6(b) shows that the TL spectra of CaSiO₃:Er³⁺ exhibits a broad emission band centered around 280nm. It is reported that electron traps in these crystals may be the O²⁻ vacancy and hole traps may be the Ca²⁺ vacancies or the bridging oxygen Ca – O – Si [13]. The UV light excites the ⁴I_{15/2} electron of Er³⁺ to the ⁴F_{3/2} energy levels. The excited electron is expected to be transferred to the nearby O²⁻ vacancy created at the O(2) sites, for example through downward hopping. The electron immediately relaxes to the stable states and is trapped. On the other hand, the hole produced at Er³⁺ by the UV excitation moves toward a Si⁴⁺ vacancy and is self trapped at an Ca(2) site, forming Ca²⁺ through the electron phonon interaction. Such trapped electron and self – trapped hole are strongly associated with the O²⁻ and Si⁴⁺ vacancies produced under the crystal growth process. The holes move back to Er³⁺ in the crystal by thermal excitation and are retrapped. Heating of the phosphor leads to detrapping of the traps and radiative recombination at Er³⁺ give rise to thermoluminescence.

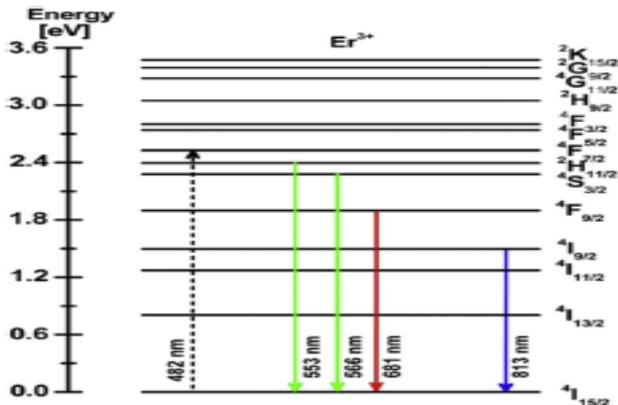


Fig 5: Energy level of Er³⁺ in the CaSiO₃ system indicating down-conversion under 482 nm excitation

3.5. Thermoluminescence (TL) studies

Thermoluminescence is one of the most useful methods to study the trap level in long lasting phosphors and the measurement of the TL curves could reveal some new facts about the persistent luminescence mechanisms too. Fig.6(a) shows the TL glow curve of γ - irradiated for different concentration at irradiation dose 1180Gy (120min.). It is clear that the TL intensity increases with increasing concentration of Er³⁺ and attains a maximum value for 10 mole % and it decreases with further increase in concentration of Er³⁺. Because of an increase in the activator concentration, the distance between the activators gets shorter. The interaction of the ions increases and the energy transfer comes into being. On the other hand, a decrease in the activator concentration decreases the energy stored by the ions. Consequently, there is an optimum in the activator concentration, resulting from the trade-off of the above two factors. As is seen from fig. the favorable concentration of Er³⁺ in CaSiO₃ phosphor is about 10 mole% (relative to Ca²⁺). It is also observed that the TL intensity increases with increase in γ exposure time up to 1180Gy.

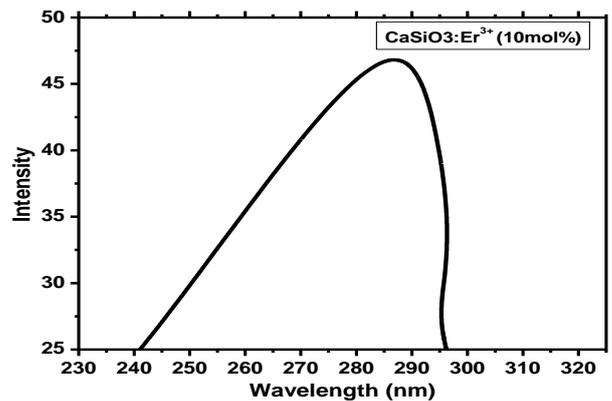


Fig.6(b): TL spectra of CaSiO₃:Er³⁺ (10 mole %)

4. Conclusions

Er^{3+} on CaSiO_3 powders was prepared by the solid-state reaction method at room temperature and studied by several characterization techniques for the understanding of their spectroscopic properties and adoption of a phase mixture at various concentration of Er^{3+} (1, 3, 5, 7 and 10 mol%). The analysis of the luminescence spectra of the excited ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ levels for ground state ${}^4\text{I}_{15/2}$ revealed changes in the non-radiative relaxation mechanism are responsible for the luminescence quenching. The luminescence in systems with low Er^{3+} concentrations shows the dominance of a green band over a red band. Chromaticity color coordinates indicate Er^{3+} ions in CaSiO_3 systems enable the tuning of the emission color from orange to red through the control of the Er^{3+} concentration increase. The green and red bands at 567 and 683 nm exhibit lifetimes of up to 153.3 and 172.7 ms, respectively. Such a slightly shorter lifetime of ${}^4\text{S}_{3/2}$ can be attributed to the Er^{3+} concentration and surface defect.

The XRD analysis revealed that the compound is single phase $\text{CaSiO}_3:\text{Er}^{3+}$ with triclinic structure. The absorption spectra show the absorption edge at $\lambda = 435\text{nm}$. The EDX spectra confirm the present elements in $\text{CaSiO}_3:\text{Er}^{3+}$ phosphor. From the with different magnification it is seen that the surface morphology of the particles was not uniform and they aggregated tightly with each other. It can be observed that the prepared sample consists of particles with different size distribution.

Thus it is concluded that this phosphor exhibits efficient orange-red emission and excellent color stability, indicating that it has favorable properties for application as near ultraviolet LED conversion phosphor.

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