

SEM, XRD and Photoluminescence Behavior of Erbium Doped Calcium Silicate Phosphor

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Abstract -Er doped Calcium silicate phosphor was synthesized by combustion method at initiating temperature of 1000^o C, using urea as a reducer. 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^o C, 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), energy dispersive x-ray spectroscopy (EDX), photoluminescence (PL). Under Scanning Electron Microscopy analyses, nanoparticles are observed only when calcium is incorporated. The chemical composition of the sintered CaSiO₃:Eu³⁺ phosphor was confirmed by EDX spectra, The PL spectra indicate that CaSiO₃: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 phospho. Therefore, it is considered to be a new promising orange-red emitting phosphor for white light emitting diode (LED) application.

1 Introduction

Rare-earth doped oxyapatites are well known in applied science field as luminescent materials. Recently, nano-sized 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, Er(NO₃)₃·5H₂O can be a promising complement to the CaSiO₃ composite due to the f-f transitions within the ⁴f₁₁ electronic shell of Er³⁺ 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

Er³⁺ 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 Er³⁺ ions in the host CaSiO₃ enables the understanding of the luminescence properties that change in response to the variation in both Er³⁺ concentration and CaSiO₃ from fundamental and technological viewpoints. This paper reports on the emission of Er³⁺ ions in the host CaSiO₃ composite under 482 nm laser excitation, from downconversion processes. Samples were prepared with different Er³⁺ concentrations in CaSiO₃ ratio and both intensities and lifetime of the down-conversion were evaluated for the distinction and improvement of the intensity of Er³⁺ ions emissions. Structural and functional group analyses by X-ray diffraction, SEM and EDX were also discussed. The Luminescence properties were discussed by PL behavior. Such emissions by down conversion are a result of the phase transformation from monoclinic to tetragonal phases due to the Er³⁺ concentration and surface defects.

2. Experimental procedures

2.1. Synthesis

Er³⁺ doped CaSiO₃ phosphor were prepared by combustion synthesis. The starting material include calcium nitrate (Ca(NO₃)₂·4H₂O; Merck), silica fumes (SiO₂, 99.9% surface area 200 m²/g), europium nitrate Er(NO₃)₃·5H₂O and urea (NH₂CONH₂). 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 CaSiO₃ 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 (λ = 0.154056 nm). The thermoluminescence (TL) data were collected using a Thermoluminescence Reader (Integral- Pc Based) Nucleonix TL 1009I. Er³⁺ doped CaSiO₃ 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 (JEOL-JSI microscope) fitted with EDX. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

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 CaSiO₃:Er³⁺ for different mole % of CaSiO₃ are shown in Fig. 1. The position and intensity of diffraction peaks of the prepared CaSiO₃Er³⁺ 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 CaSiO₃ phosphor. The phase structure of the CaSiO₃Er³⁺ phosphor is a kermanite type structure which belongs to the tetragonal crystallography with space group P421m (113 space number and D32d space group), this structure is a member of the melilite group and forms layered compound. CaSiO₃ monoclinic phase is present in large abundance along with small trace of Ca₂SiO₄ 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 [CuKα (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 2θ = 24.15 (1 1 1), 29.04 (2 1 0), 31.26 (2 1 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, 76 nm, 70 nm,

69 nm, 66 nm, 65 nm was calculated, respectively and the average crystallite size is ~70.00 nm.

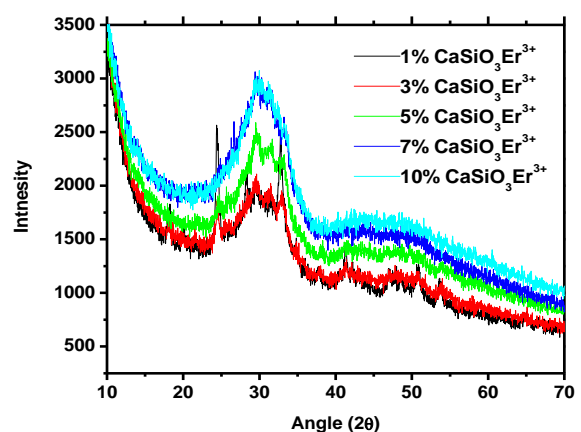


Fig. 1: XRD patterns of CaSiO₃:Er³⁺ phosphor.

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 CaSiO₃:Er³⁺ phosphor is shown in Fig. 2(a, b, c, d) with different magnification. The surfacemorphology 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.

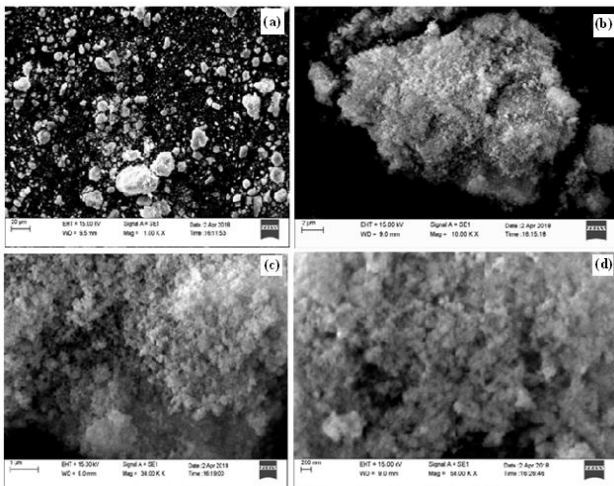


Fig. 2: Fig. 3 e (a, b,c,d) SEM image of CaSiO₃:Er³⁺ phosphor.

3.3. Energy dispersive X-ray spectroscopy (EDX)

The chemical composition of the powder sample has been measured using EDX spectra. It 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 CaSiO₃:Er³⁺EDXspectra of the phosphor. In EDX spectra, the presence of Ca,Si, O and Er, intense peak are present which preliminaryindicates the formation of CaSiO₃:Er³⁺phosphor in Fig. 3. The elements presents in the Weight% and Atomic% also determined which is represented in table 1.

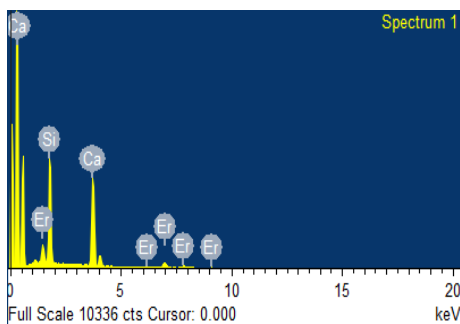


Fig. 3: EDX spectra of CaSiO₃:Er³⁺ phosphor.

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 CaSiO₃:Er³⁺ 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.

Thestrongest sharp peak correspond to excited state ⁴F_{5/2}from ground state ²I_{15/2} of the Er³⁺, when excited at 482 nm.

Fig. 4(b) shows the emission spectra of CaSiO₃:Er³⁺ phosphor in the range of 640 to 720 nm. The emission spectrum of our obtained samples was composed of sharp emission lines, corresponding to transitions from the excited states ²H_{7/2} to theround state. Such emissions in the luminescence spectra suggest the local environment of Er³⁺ is affected by the phase mixture, evidenced by the XRD patterns. The Er³⁺ions in the ⁴F_{7/2}level decay non-radiatively to the ⁴S_{3/2}, ²H_{11/2} level and benefit thetransition to the ⁴F_{9/2} level, rather than to the ⁴S_{3/2} level, whichresults in a decrease in the green emissions and increase in the redemissions. On the other hand, the variation in the luminescenceefficiency might also be attributed to the divergence of the localenvironment surrounding Er³⁺ ions and surface defects in theparticles of the host material. The surface is responsible for nonradiativeenergy transfers from the ²H_{11/2}, ⁴S_{3/2} level of the Er³⁺ions to the O-H vibrations. The various transition of Er³⁺ in the CaSiO₃ system indicated in figure 5.

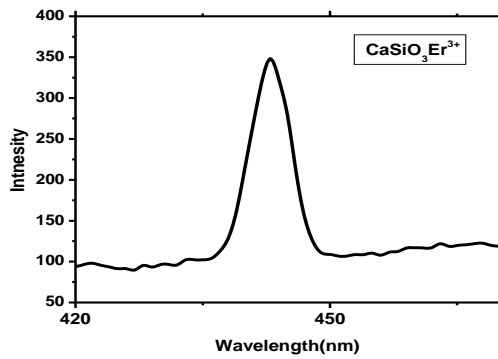


Fig. 4(a): Excitation spectra of CaSiO₃:Er³⁺ phosphor

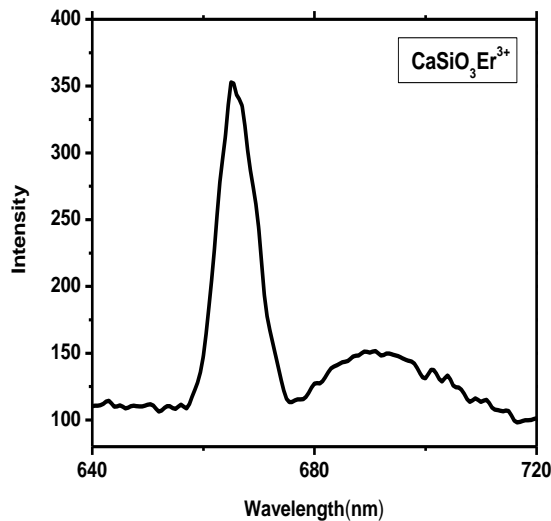


Fig.4(b): Emission spectra of CaSiO₃:Er³⁺ phosphor.

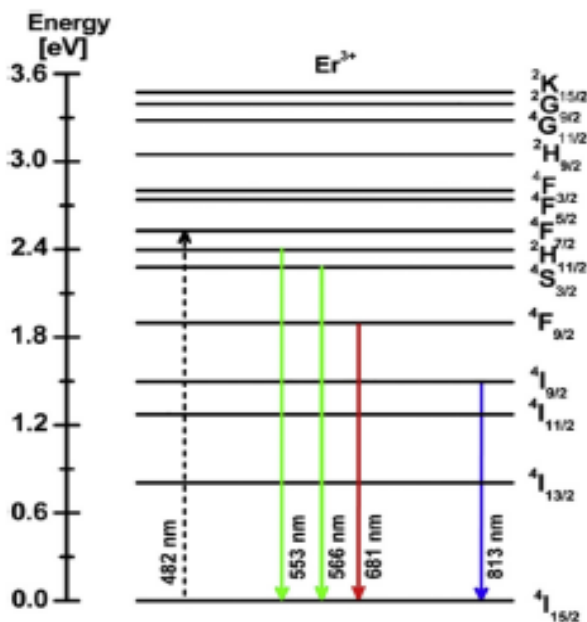


Fig 5: Energy level of Er³⁺ in the CaSiO₃ system indicating down-conversion under 482 nm excitation.

4. Conclusions

We reported on synthesis and fluorescence properties of Er³⁺ activated amorphous calcium silicate phosphor.

Er³⁺ on CaSiO₃ 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 Er³⁺ (1, 3, 5, 7 and 10 mol%). The analysis of the luminescence spectra of the excited ²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2} levels for ground state ⁴I_{15/2} revealed changes in the non-radiative relaxation mechanism are responsible for the luminescence quenching. The luminescence in systems with low Er³⁺ concentrations shows the dominance of a green band over a red band. Chromaticity color coordinates indicate Er³⁺ ions in CaSiO₃ systems enable the tuning of the emission color from orange to red through the control of the Er³⁺ 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 ⁴S_{3/2} can be attributed to the Er³⁺ concentration and surface defect.

The XRD analysis revealed that the compound is single phase CaSiO₃:Er³⁺ with triclinic structure. The absorption spectra show the absorption edge at λ = 435nm. The EDX spectra confirm the present elements in CaSiO₃:Er³⁺ 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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