Synthesis and Photoluminescence Characteristics of Rare Earth Activated some Silicate Phosphors for LED and Display Devices

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Abstract— Silicates are important class of materials due to their applications in many diverse areas. They proved to be an effective materials for various processes and materials related to applied mineralogy including technical and medieval glasses, blast furnace linings and combustion ashes. This study reports the synthesis and luminescence of Eu, Ce, Dy and Sm activated $K_4CaSi_3O_9$ and $BaCa_2Si_3O_9$ phosphors. The luminescent characteristics of RE (RE^{3+} = Eu, Ce, Dy and Sm) -doped $K_4CaSi_3O_9$ and $BaCa_2Si_3O_9$ compounds have been investigated for the first time in detail and may be application in the field of LED and display device.. X-ray powder diffraction measurements confirmed the cubic phase structure of titled compounds. Good characteristics luminescence is observed in all as-prepared samples. The obtained results may have the potential application in the NUV white light emitting diode.

Keywords— Photoluminescence, Phosphors, light emitting diode

1. INTRODUCTION

Recently, more efforts have been made for the development of rare-earth (RE) ions activated luminescent materials for their wide range of potential applications in optoelectronic devices, temperature sensors, solid-state lighting (SSL), optical communication systems and luminescent probes or labels in biological systems and so on [1–5]. Among them, solid state lighting is one of the focused area because, the solid state white light emitting diodes (WLEDs) have more advantageous properties than the traditional incandescent or fluorescent lamps [1].Therefore, the development of new phosphors is one of the most important tasks in designing luminescent devices for SSL.

The materials composed of oxides, silicates, aluminates, aluminoborates, aluminosilicates, nitrides, borates, etc., plays crucial roles for potential applications in solid state lighting. Among these hosts, silicates are the brilliant luminescent hosts for solid state lighting especially for white light emitting diodes due to their high chemical–physical stability. Also, they have variety of crystal structures involving interesting luminescent properties, excellent luminescence efficiency and broad absorption band.

It is well known that the alkaline earth silicates have collection of properties such as good and high temperature strength, creep resistance, chemical inertness, thermal stability, low thermal expansion and conductivity [6-7] which makes them strong candidates for many practical applications. Owing to these remarkable qualities, we were motivated to select $K_4CaSi_3O_9$ and $BaCa_2Si_3O_9$ host for the present work.

The primary interest of this study is to focus the emission properties of rare earth such as Eu, Ce, Dy, and Sm in $K_4CaSi_3O_9$ and $BaCa_2Si_3O_9$ host and also to study optical properties of these phosphors. This may be the first report of this kind.

2. EXPERIMENTAL

2.1 Synthesis of $BaCa_2Si_3O_9$ and $K_4CaSi_3O_9$

The $BaCa_2Si_3O_9$ Cyclosilicate phosphors were prepared by the precipitation based method. All reactants used in the synthesis were of Analytical Reagent grade. The phosphors were precipitated from aqueous solutions of barium and calcium nitrates by slowly adding Na_2SiO_3 solution. The precipitate formed was filtered, dried and then annealed in air at 750°C for 1 h. For preparing various activated phosphors, appropriate metal nitrate was added in the desired quantity to the starting solution and similar procedure was followed. In some cases, for reducing the Ce and Tb activators to the desired trivalent state, the phosphors were heated at 750°C in the reducing atmosphere provided by burning charcoal in a covered crucible.

$K_4CaSi_3O_9$ samples were prepared by the solid state diffusion method. Samples were obtained from the raw materials of metal carbonates such as K_2CO_3 and $CaCO_3$ with silicic acid ($SiO_2.9H_2O$), were stoichiometrically weighed out. For preparing phosphors, appropriate metal Carbonates was added in the desired quantity to the starting material and similar procedure was followed. Firstly the mixture was heated up to 800 °C for 6 h. After that the samples were crushed in a mortar and were heated

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up to 850 °C and kept at this temperature for 10 h. Again After second homogenization, the sample was mixed thoroughly and heated at 900°C for 12 h in a covered crucibles. In some cases for reducing activator to desired trivalent state, the phosphors were heated at 900°C in the reducing atmosphere provided by burning charcoal.

2.2 Characterization

The prepared material was crushed to fine powder and used for further characterization. To confirm the crystal phase of the synthesized material, X-ray diffraction pattern was recorded at room temperature. The measurement were made in a range of Bragg angle (10-80°) using an X-ray diffractometer Rigaku Miniflex II with Cu-Kβ target, a curved graphite monochromator, a flat plate sample holder in a Bragg–Bentano para-focussing optics configuration. The X-ray generator is operated at tube output voltage 15 KV and current at 30 mA with the fixed scan speed at 2°/ min in a continuous scanning mode with a fixed divergence slit of 1.25°. The photoluminescence excitation and emission spectra were measured on Shimadzu, RF 5301 PC-4000 Spectroflurophotometer with spectral slit width of 1.5 nm in the range 220–700 nm. 150W xenon lamp was used as a source of excitation.

3. RESULTS AND DISCUSSION

3.1 XRD Pattern of $BaCa_2Si_3O_9$ Host

X-ray diffraction pattern of pure $BaCa_2Si_3O_9$ powder sample prepared via precipitation method annealed at 750°C is shown in Fig.1 along with the International Center for Diffraction Data (ICDD) database of Card No. 15-0063.
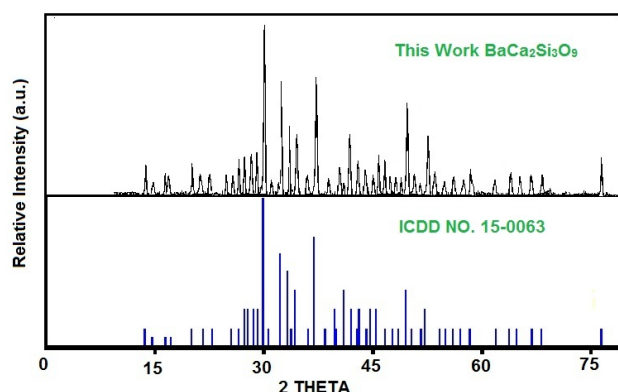

Fig. 1: XRD pattern of $BaCa_2Si_3O_9$ host

The obtained result suggest that nearly all the diffraction peaks of prepared $BaCa_2Si_3O_9$ host agree well with the International Center for Diffraction Data (ICDD) of Card No. 15-0063 and no other diffraction peaks from raw materials were detected. Thus, confirmed the formation of $BaCa_2Si_3O_9$ host.
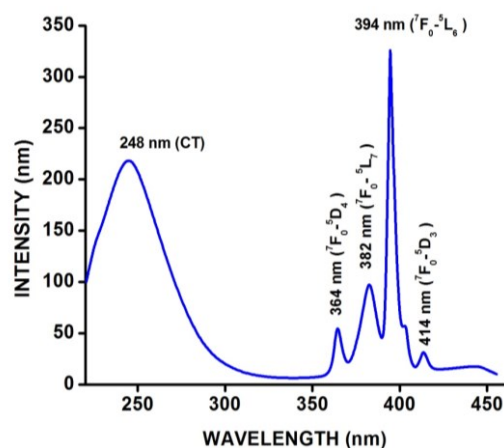
3.2 Photoluminescence of $BaCa_2Si_3O_9$:Eu^{3+}

Fig. 2: Excitation spectra of $BaCa_2Si_3O_9$:Eu^{3+}

Fig.2 and 3 shows the photoluminescence spectrum of Eu^{3+} activated $BaCa_2Si_3O_9$ phosphors monitored at 615 nm at room temperature. The excitation spectrum consists of two regions in which the broad band at 220–320 nm originated from the charge–transfer (CT) band between Eu^{3+} ion and the neighboring oxygen ions which is clearly shown in Fig.2. Also, the region in the wavelength range of 350–450 nm consists of several sharp lines which correspond to the f–f transitions of Eu^{3+} ions from the ground state $^7F_0$ to the excitation levels.
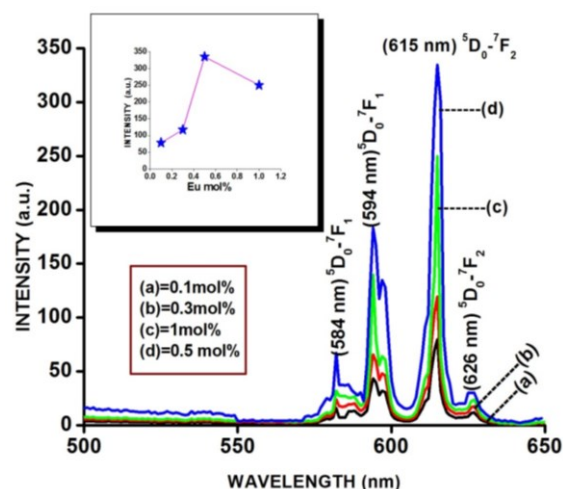

Fig. 3: Emission spectra of $BaCa_2Si_3O_9$:Eu^{3+}

The sharp intense peak around 364 nm ($^7F_0$-$^5D_4$), 382 nm ($^7F_0$-$^5L_7$), 394 nm ($^7F_0$-$^5L_6$) and 414 nm ($^7F_0$-$^5D_3$) are the characteristic transitions of Eu^{3+} ions in the host lattice [8-9]. Among all the excitation maxima, the peak around 394 nm is the most prominent excitation assigned due to the $^7F_0$-$^5L_6$ transition and charge-transfer band (248 nm) is also strong whose intensity is inferior to that of 394 nm. This excitation matches well with the emission of NUV chips, which is exactly required for NUV LED converting phosphor. The photoluminescence emission spectra of

$BaCa_2Si_3O_9$:Eu^{3+} (0.1–1mol %) phosphors excited under the excitation at 394 nm is shown in Fig. 3. The strong and sharp peaks observed in the emission spectra are initiated from the $^5D_0$-^7F_J transitions, indicating the existence of Eu^{3+} ions in $BaCa_2Si_3O_9$:Eu^{3+} matrix. In the range of 500-650 nm, the emission spectrum of Eu^{3+} is mainly consist of hypersensitive $^5D_0$-$^7F_2$ transition at 615 nm and some weaker transitions such as $^5D_0$-$^7F_1$ (584 nm, 594 nm) and $^5D_0$-$^7F_2$ (626 nm). Normally, $^5D_0$-$^7F_{2,\ 4}$ are electric dipole transitions, whereas $^5D_0$-$^7F_{1,\ 3}$ are magnetic-dipole transitions. The emission maxima located at 615 nm due to the $^5D_0$-$^7F_2$ transition of Eu^{3+} reveals that the electric-dipole transition is dominant. This electric-dipole transition is parity forbidden f–f configuration transition, which would only occur when Eu^{3+} ions occupy lattice sites without inversion symmetry. This implies that in present host, Eu^{3+} ion is locate in lattice sites without inversion symmetry [10-11]. The maximum intensity was observed at 5mol% concentration of europium ion.
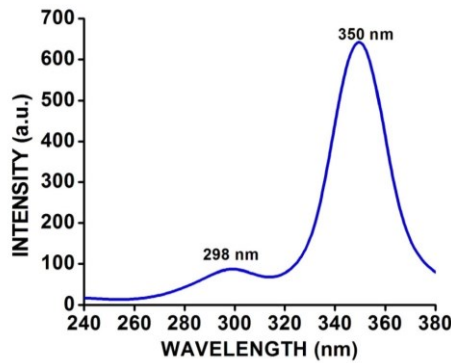
3.3 Photoluminescence of $BaCa_2Si_3O_9$:Ce^{3+}
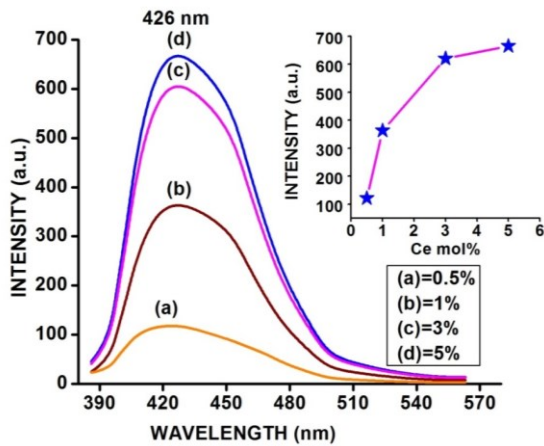

Fig. 4: Excitation spectra of $BaCa_2Si_3O_9$:Ce^{3+}

Fig. 5: Emission spectra of $BaCa_2Si_3O_9$:Ce^{3+}

Fig. 4 and 5 shows the excitation and emission profile of Ce^{3+} in $BaCa_2Si_3O_9$. The excitation spectrum of $BaCa_2Si_3O_9$:Ce^{3+} comprises of two bands centered at 298 and 350 nm which corresponds to the electronic transitions from the ground state to the different crystal field splitting bands of the excited 5d states of Ce^{3+} ion [12].Under 350 nm excitation, $BaCa_2Si_3O_9$:Ce^{3+} (Fig.5) showed a blue emission band due to the $5d^1$-$4f^1$ transition of Ce^{3+}, consisting of a broad band in the range of (380–570 nm) centered at 426 nm. Usually, Ce^{3+} emission has doublet character due to the splitting of its 4f ground state, and the energy difference of this splitting between $^2F_{7/2}$ and $^2F_{5/2}$ of Ce^{3+} is about 2000 cm^{-1} due to the L-S splitting of ^2F_J level [13]. Dependence of photoluminescence intensity as a function of Ce^{3+} doping concentration is shown in the inset of Fig.5. Maximum intensity increased and reached at maximum for 5 mol % of Ce content.

3.4 Photoluminescence of $BaCa_2Si_3O_9$:Dy^{3+}

Fig.7 shows the excitation spectra of Dy^{3+} doped $BaCa_2Si_3O_9$. Here, we observed four excitation bands in the spectra centered at 299 nm, 326 nm, 351 nm and 386 nm. In which first two excitation bands appeared due to the splitting of $^6H_{15/2}$-$^4M_{17/2}$ transition and latter two are ascribed due to the $^6H_{15/2}$-$^6P_{7/2}$ and $^6H_{15/2}$-$^4I_{13/2}$ respectively. The emission spectra of $BaCa_2Si_3O_9$:Dy^{3+} phosphors with (0.1-1mol %) concentration of Dy^{3+} ion is
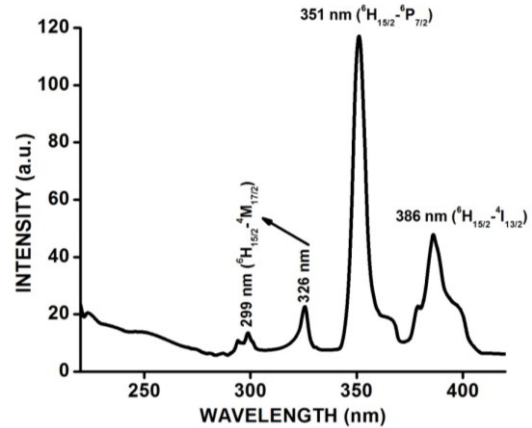
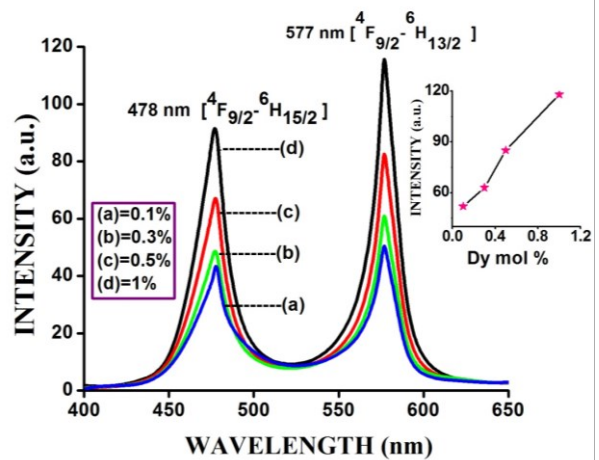**Fig. 7: Excitation spectra of $BaCa_2Si_3O_9$:Dy^{3+}**

Fig. 8: Emission spectra of $BaCa_2Si_3O_9$:Dy^3

shown in fig.8. There exist two strong bands in emission spectra of Dy^{3+} doped $BaCa_2Si_3O_9$ phosphor initiated from the origin of same excitation wavelength, centered at 478 nm (blue) and 577 nm (yellow), which corresponds to $^4F_{9/2}$-$^6H_{15/2}$ and $^4F_{9/2}$-$^6H_{13/2}$ transitions, respectively [14].

The blue ($^4F_{9/2}$-$^6H_{15/2}$) emission assigned due to the magnetic dipole transition and the yellow ($^4F_{9/2}$-$^6H_{13/2}$) emission attributed to the hypersensitive (forced electric dipole) transition with the selection rule, $\Delta J = 2$. The emission intensity increased with the increase in the content of Dy^{3+} ion, and reached a maximum value at 1mol%.

3.5 Photoluminescence of $BaCa_2Si_3O_9$:Sm^{3+}

Fig.9 presents the excitation spectrum of $BaCa_2Si_3O_9$:Sm^{3+} phosphor consists of mainly four components starting from 300-500 nm appeared due to the excitation from the ground-level $^6H_{5/2}$ to higher energy levels of Sm^{3+} ion. The peaks observed at 337 nm, 358 nm, 373 nm and 401nm are corresponding to the transitions $^6H_{5/2}$–$^4H_{7/2}$, $^6H_{5/2}$ – $^6F_{9/2}$, $^6H_{5/2}$ – $^4D_{5/2}$ and $^6H_{5/2}$–$^4K_{11/2}$ respectively [15]. The emission spectra of $BaCa_2Si_3O_9$:Sm^{3+} with varying concentrations (0.2-2mol %) monitored under the excitation of 401 nm is shown in Fig.10. The emission spectrum has exhibited three emission transitions, which are assigned to $^4G_{5/2}$-$^6H_{5/2}$ (560 nm), $^4G_{5/2}$-$^6H_{7/2}$ (595 nm) and $^4G_{5/2}$-$^6H_{9/2}$ (648 nm) transitions. Among these three emission bands, the transition $^4G_{5/2}$-$^6H_{7/2}$ (595 nm) has shown a strong orange luminescence. The transition $^4G_{5/2}$-$^6H_{7/2}$ with $\Delta J = \pm 1$ is a magnetic dipole (MD) allowed one but it is also electric dipole (ED) dominated, the other transition $^4G_{5/2}$-$^6H_{9/2}$ is purely ED one [16].
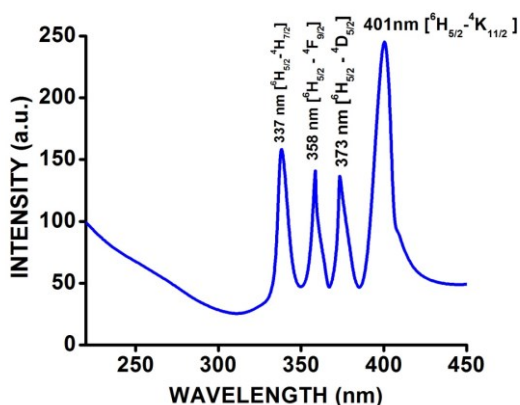
Fig. 9: Excitation spectra of $BaCa_2Si_3O_9$:Sm^{3+}

The maximum intensity is observed at 2mol% and no quenching of luminescence was observed up to 2mol% concentration of samarium ion. Similar results have been observed for Eu, Ce, Dy and Sm -doped $K_4CaSi_3O_9$ phosphors. Results presented here are reported in [17]. Thus, all the studied samples exhibited interesting

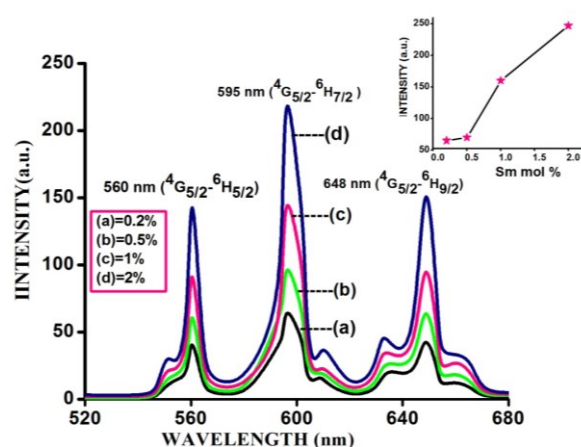characteristic emission properties in their respective regions.

Fig. 10: Emission spectra of $BaCa_2Si_3O_9$:Sm^{3+}

4. CONCLUSIONS

A series of new phosphors of RE^{3+}, (Ln = Eu, Ce, Dy, Sm) doped $BaCa_2Si_3O_9$ and $K_4CaSi_3O_9$ were successfully synthesized. The detailed investigation on the photoluminescence properties of RE^{3+}, (Ln = Eu, Ce, Dy, Sm) activated $BaCa_2Si_3O_9$ and $K_4CaSi_3O_9$ is carried out. All the studied samples exhibited interesting characteristic emission properties of LED and display devices. We hope that this study can be helpful in understanding the optical properties of trivalent Eu, Ce, Dy, and Sm in further research of optical materials.

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