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Near white light emission from K^+ ion compensated $CaSO_4:Dy^{3+},Eu^{3+}$ phosphors

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Abstract

$Dy^{3+}:Eu^{3+}$ doped calcium sulfate ($CaSO_4:Dy^{3+},Eu^{3+}$) phosphors co-doped with various K^+ compensator concentrations were synthesized by recrystallization method. These orthorhombic phased phosphors showed intense multi-color near white light. The multi-color aspect ratios and the emission life times were strongly dependent on K^+-concentration. These results suggest that the rare-earth (Re^{3+}) ions are situated at the sites of Ca^{2+} and the site occupancy was being compensated by K^+ ions. The near white light emission and large lifetimes suggest that present phosphor could be potentially applied as a blue excited white light-emitting phosphor for light emitting diodes.

Keywords: Orthorhombic $CaSO_4$; Rare-earth doped; Photoluminescence; Charge compensation; White light phosphors

1. Introduction

There has been an increasing interest for white light-emitting diodes (W-LEDs) to replace the conventional incandescent and fluorescent lamps due to advantages in the energy consumption and environmental benefits [1–4]. However, the most common way to generate white light is the combination of blue LEDs with yellow and red-emitting phosphors. Rare-earth (RE) doped crystalline phosphors, especially with the oxide based inorganic hosts, are most desirable because of their unique spectroscopic properties such as long lifetime, saving energy, reproducibility, safety and its environment-friendly characteristics [1–6]. Single phased calcium sulfate ($CaSO_4$) is uniquely placed between fluorides and other oxide hosts and considered to be good wide optical bandgap host for white light phosphors due to its excellent chemical and environmental stability [5]. Lakshmanan et al. reported the development of a highly sensitive green phosphor, $CaSO_4$:Tb,Na, to achieve an efficient quantum-splitting phosphor [6]. Salah et al. reported thermo and photoluminescence of Dy^{3+} and Ce^{3+}–Eu^{3+} doped $CaSO_4$ based mixed phosphors [7,8]. Yamashita et al. observed strong green emission in Tb^{3+} doped $CaSO_4$ phosphors [9]. Also there were reports on $CaSO_4:Eu^{3+}$, $CaSO_4:Ce^{3+}$ to establishing $CaSO_4$ as a potential material for liquid crystal display (PLLCD), optical storage and cathodoluminescent devices [5,10].

Introduction of monovalent alkali ions into alkaline earth sulfates and borates generally considered as a sensitizer to enhance the emission efficiency of rare earth dopants remarkably [6,11]. Recently we have reported the enhanced luminescence properties and improved crystallinity in the rare earth doped $KCaBO_3$ host and the predominant effects due to occupation of rare-earth ions into the charge compensated sites of Ca^{2+} ions [11].

In general, a deeper understanding of rare-earth doping and corresponding phosphor applications in $CaSO_4$ is relatively less explored. Further, the development of white light emitting rare-earth doped alkaline earth sulfates was not been studied so far. Therefore it is of considerable interest to study the multi-color emitting rare-earth doped sulfates for W-LED applications, as they relatively low cost with interesting structural features. In this paper we present a detailed investigation on structural and optical properties of $CaSO_4:Dy^{3+},Eu^{3+}$ phosphor with varied charge compensation by K^+ ions. These studies are reported for the first time and can help the development of white light phosphors for potential applications.

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2. Experimental details

The Dy^{3+}:Eu^{3+} doped calcium sulfate ($CaSO_4$) phosphors with varied charge compensator (K^+) concentrations were synthesized via recrystallization method [5,6] by mixing $CaCO_3$ and conc. H_2SO_4 in stoichiometric ratio, adding of 1 mol% Dy_2O_3, 1 mol% Eu_2O_3 and x ($x = 0$–4) mol% of KCl in the mixture. Then the mixture was eventually heated at around 700 °C for 120 min and was cooled to room temperature by rapid cooling. Finally, the obtained solid phosphor was grounded to obtain fine powder. The X-ray diffraction (XRD) data for all these polycrystalline samples was collected on XPERT-PRO Diffractometer with CuKα radiation ($\lambda = 1.54$ Å). The morphology was recorded from JSM-6390LV Scanning Electron Microscope (SEM). The sample was gold coated using a sputter coater Polaron SC7610 system. The steady-state and time-resolved photoluminescence measurements were carried using home built setups using 410 nm (~30 mW) diode laser as excitation source. The emission from the sample was dispersed into a monochromator (Acton SP2300) coupled to a photo multiplier tube (PMT) through appropriate lens system. For time resolved emission, mechanical chopper, lock-in amplifier, and digital storage oscilloscope were additionally employed to record the transient response. Conventional emission and excitation spectral measurements were measured by using Fluorolog-3 (model FL 3-11) modular spectrofluorimeter with single Czerny-Turner grating excitation and emission monochromators having a 450 W Xe arc lamp as the excitation source and a PMT as the detector purchased from Horiba-Jobin Yvon.

3. Results and discussions

3.1. X-ray diffraction and SEM studies

The room temperature XRD patterns of x mol% K^+ ($x = 0$, 3 and 4) doped $CaSO_4$:Dy^{3+},Eu^{3+} phosphors are depicted in Fig. 1. The sharp and single peaks of the XRD pattern were indexed according to the standard $CaSO_4$ diffraction patterns (JCPDS 01-074-2421). These results suggest the resultant phosphor is a single phase polycrystalline nature having orthorhombic crystal structure with space group of *Bbmm63* [12,13]. The estimated unit cell parameters of co-doped $CaSO_4$:Dy^{3+},Eu^{3+} phosphors are slightly deviated (Table 1) from that of reported $CaSO_4$ values (JCPDS 01-074-2421). In general, the XRD studies indicating that upon doping (with Dy^{3+}, Eu^{3+} and K^+ ions) no significant changes in the crystal structure is observed, suggesting that these dopants might have occupied the cationic sites in the host lattice structure, following the charge balancing: $2Ca^{2+} = Dy^{3+}$ (or Eu^{3+}) + K^+. A similar result was also previously reported in the case of Cu^{2+} and Mn^{2+} doped $CaSO_4$ systems [13]. The enhancement in some of the XRD peak intensities (e.g. (0 2 0), (2 1 0), (2 2 0)) is due to the incorporation of K^+, which probably improved crystallinity. However, for more than 4 mol% of K^+-doping, the observed diffraction peak intensities (compared to (0 2 0) and (2 1 0)) are relatively less intense. At such higher concentrations it is probably difficult for K^+ ions to be fully introduced into Ca^{2+} sites for charge compensation; hence the excess K^+ ions induce defects which eventually decrease the crystalline nature. This discussion will be further extended in the emission studies. The microscopic studies of the as prepared phosphor powders (Fig. 2) showed micro granularity of particle sizes in the range of 0.5–2.0 μm.

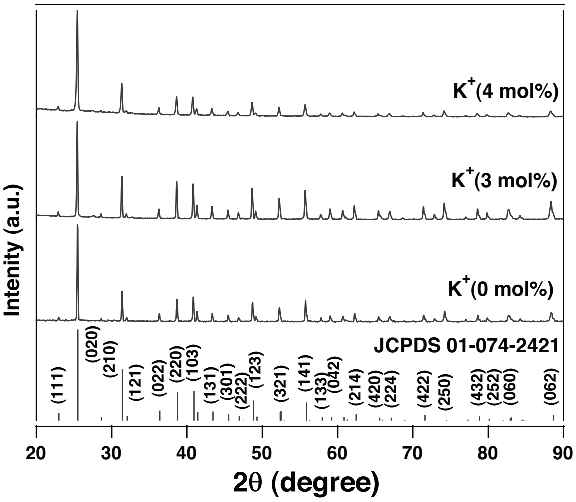

Fig. 1. Room temperature X-ray diffraction pattern of x ($x = 0$, 3 and 4) mol% K^+ doped $CaSO_4$:Dy^{3+}, Eu^{3+} phosphors. Standard $CaSO_4$ data (JCPDS 01-074-2421) is also given for comparison.

3.2. Photoluminescence studies

The room-temperature photoluminescence (PL) spectra of $CaSO_4$:Dy^{3+},Eu^{3+} phosphor were recorded and results are

Table 1
Estimated lattice parameters, yellow-to-blue (Y/B) and red-to-orange (R/O) integrated emission ratios, chromaticity coordinates and emission life times of x mol% K^+ co-doped $CaSO_4$:Dy^{3+},Eu^{3+} phosphors.

K^+ concentration (x mol%)	Lattice parameters (in nm)			Y/B ratio	R/O ratio	CIE coordinates		Life time, τ (in ms)	
	a	b	c			X	Y	574 nm	616 nm
0	0.624	0.698	0.699	1.41	1.85	0.4279	0.3513	1.38	2.22
1	–	–	–	1.46	2.29	0.4451	0.3983	1.31	2.71
2	–	–	–	1.68	1.94	0.4378	0.3932	1.35	2.25
3	0.624	0.699	0.698	1.64	2.03	0.4257	0.3937	1.34	1.98
4	0.715	0.700	0.700	1.65	2.00	0.4567	0.3937	1.23	1.90
JCPDS 01-074-2421	0.623	0.698	0.697	–	–	–	–	–	–

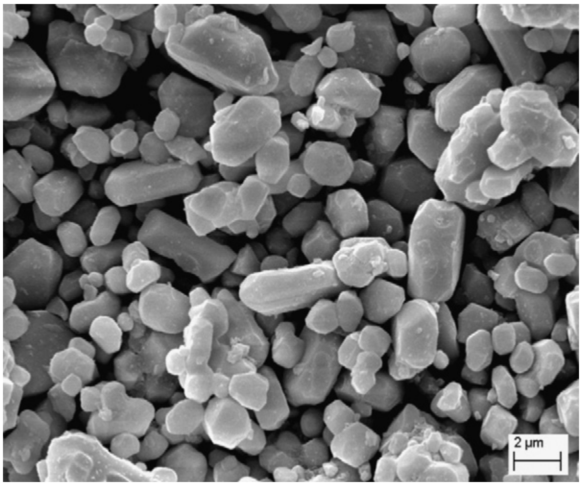

Fig. 2. SEM image of $CaSO_4:Dy^{3+}$, Eu^{3+} phosphor.

given in Fig. 3. The strong emission containing rich spectral lines of characteristic Dy^{3+} and Eu^{3+} rare earth ions, which covers full desired white light spectral range i.e. from 400 nm to 750 nm. The emission lines at 483, 574, 658, 695 and 750 nm, are attributed to the transitions of $^4F_{9/2} \rightarrow {}^6H_{J/2}$ (J = 15, 13, 11, 9 and 7) of Dy^{3+} ions respectively, while the emission lines at 594, 616, 653 and 701 nm are from $^5D_0 \rightarrow {}^7F_J$ (J = 1–4) transitions of Eu^{3+} ions. Without K^+ doping, the dominant emission is from the hypersensitive electric dipole transition at 616 nm ($^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}), whereas for all other doped phosphors, the dominant emission is from 574 nm of Dy^{3+} ion, corresponding hypersensitive $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition.

Due to restricted solubility of rare-earth in $CaSO_4$, several efforts have been made recently to increase the emission efficiency of rare earth doped $CaSO_4$ [6]. At higher concentration of rare-earths, the emission intensities are decreased due to concentration quenching effects. Therefore, the use of monovalent charge compensator impurities (such as Na^+ and K^+) showed promising effects on the enhancement of rare-earth emission in alkali/alkaline earth based materials [6,11]. However, the charge neutrality demands removal of three Ca^{2+} ions to introduce two rare earth (Re^{3+}) ions for effective lattice substitution, which could eventually restricts the Re^{3+} concentration. Hence, additional doping of K^+ is expected to remove such Ca^{2+} vacancies and facilitates Re^{3+} ion solubility on account of charge balancing: $2Ca^{2+} = Dy^{3+}$ (or Eu^{3+}) + K^+. In this present $CaSO_4:Dy^{3+},Eu^{3+}$ phosphor, the K^+ ion is used as a charge-compensator to substitute some of the Ca^{2+} ions. As seen from the earlier XRD studies, the doping ($Dy^{3+}$and Eu^{3+} and K^+ ions) showed no significant change in the crystal structure, suggesting these doped ions might have occupied the cationic sites in the host lattice structure. As seen from Fig. 3, a monotonic increase of PL intensities up to 6.5 times with K^+ concentrations (up to 3 mol.%) is observed. However, above 3 mol% concentration the charge balance could be represented as $3Ca^{2+} = 2Dy^{3+}$ (or Eu^{3+}) + vacancies, and due to such excessive negative charge the interstitial defects therefore decreases the emission spectral intensities. Overall, the emission intensities from both Dy^{3+} and Eu^{3+} rare earth ions were found to increase with the increase of K^+ doping. However, the relative emission spectral intensities show moderate dependence with charge compensation (K^+) doping. The reason could be that the K^+ doping only facilitates the rare earth solubility by allowing the Dy^{3+}/Eu^{3+} ions (1 mol% each) to occupy the Ca^{2+} sites through charge balancing mechanism.

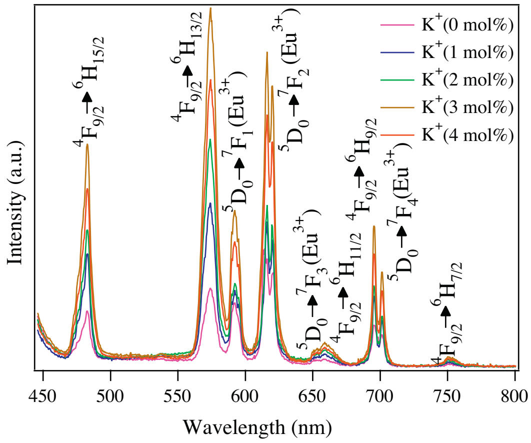

Fig. 3. Room-temperature emission spectra of x mol% K^+ (x = 0–4) co-doped $CaSO_4:Dy^{3+}$, Eu^{3+} phosphor (λ_{ex} = 410 nm).

Additionally, the spectral features are slightly dominated by the Dy^{3+} ion emission line 574 nm (of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition). Upon the comparison of ionic radii, the Ca^{2+} (0.112 nm) and K^+ (0.133 nm) radii are closer to Dy^{3+} ions (0.112 nm) and much larger than Eu^{3+} ions (0.108 nm). Therefore, K^+ ion doping favors the incorporation of Dy^{3+} into the host lattice, therefore the dominance of emission centers of Dy^{3+} ions.

The excitation spectra of all K^+ compensated $CaSO_4$:Dy^{3+},Eu^{3+} phosphors for 616 nm emission of Eu^{3+} (see Fig. 4a) exhibits several excitation bands between 310 nm and 550 nm spectral region. These excitation energies are from the ground state electronic transitions of $^7F_0$, $^7F_1$ and $^7F_3$ to different excited states of Eu^{3+}ions. The rich excitation spectra below 400 nm are useful for color rendering property for commercial white light LED with the common UV/NUV/blue excitation sources such as GaN based LED chips. While the K^+ ion doping improves the excitation spectral features, no traces of Dy^{3+} excitation energies found in the excitation spectra monitored at Eu^{3+} emission (616 nm). This indicates the less influence of inter-ion energy transfer between Dy^{3+} and Eu^{3+} ions. In order to confirm this result, the excitation spectra were also monitored at Dy^{3+} ion (574 nm) emission (Fig. 4b) and the spectra only shows the electron transitions from the ground state of Dy^{3+}, $^6H_{15/2}$ to different excited states without any traces of excitation lines belong to Eu^{3+} ions. This further confirms the limited role of inter-ion energy transfer from Eu^{3+} to Dy^{3+}, vice versa.

The hypersensitive to non-hypersensitive emission intensity ratios of Dy^{3+} and Eu^{3+}, the yellow-to-blue (Y/B) ($^4F_{9/2} \rightarrow {}^6H_{13/2}/{}^4F_{9/2} \rightarrow {}^6H_{15/2}$) of Dy^{3+} and red-to-orange (R/O) ($^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$) of Eu^{3+}, gives an insight into the covalent nature, site asymmetry effects and local structure [14–17]. These R/O and Y/B ratios for different concentrations of K^+

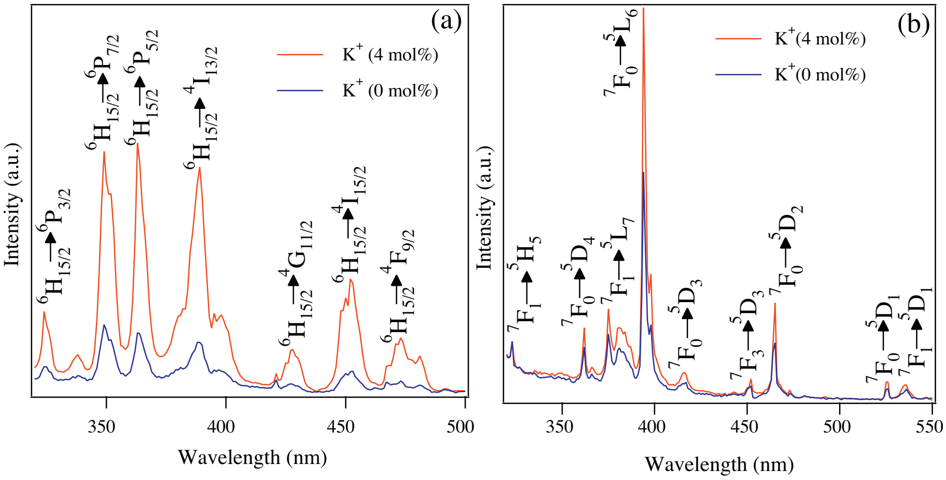

Fig. 4. Room-temperature excitation spectra of x mol% K^+ ($x = 0$ and 4) co-doped $CaSO_4$:Dy^{3+},Eu^{3+} phosphor, detection at (a) 616 nm (Eu^{3+}: $^5D_0 \rightarrow {}^7F_2$) and (b), 574 nm ($Dy^{3+}$: $^4F_{9/2} \rightarrow {}^6H_{13/2}$).

doped phosphors are estimated and listed in Table 1. It is observed that both the ratios are found to be more than 1.0 and showed substantial improvement with the additional K^+ doping. Comparatively larger Y/B and R/O ratios suggest the pronounced nature of covalency and indicate that the rare-earth ions are situated in the sites of different valencies (in this case Ca^{2+}), where the local site symmetry is deviated from inverse center [11,14–17].

The PL lifetimes (τ) for the most intense emission lines (574 nm of Dy^{3+} ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and 616 nm of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$)), in the K^+ doped $CaSO_4$:Dy^{3+},Eu^{3+} phosphors are also recorded. Example decay curves are given in Fig. 5a, and corresponding lifetimes were tabulated in Table 1. These PL decay curves are predominantly follows a single exponential i.e., $I = I_0 \exp(-t/\tau)$, where I_0 is the initial emission intensity and τ is the life time[18]. The obtained PL decay time values obtained from the single exponential fits are given in Table 1. Single exponential behavior indicates the homogeneous distribution of doping ions inside the host matrix and no influence of inter-ion energy transfer between the rare-earth ions. This result further supports our emission and excitation spectral analysis also. Broadly, the larger emission lifetimes are useful for the potential optoelectronic applications such as displays and solid state lighting [19,20].

Most importantly, it is observed from the emission characteristics that by appropriately adjusting K^+ ion doping, it is possible to obtain near-white emission. In order to visualize the white light emission, the chromaticity coordinates of the present phosphors excited at 410 nm are were calculated and listed in Table 1 and the CIE diagram is depicted in Fig. 5b. It can be seen that typical white light is achieved in the present phosphors, composed of multi-color emission from both Dy^{3+} and Eu^{3+} ions.

In general, the most common approach to produce white light is to combine a blue LED chip with a yellow phosphor, for example, the combination of InGaN LED (400–450 nm) and Ce^{3+}-doped yttrium aluminum garnet (YAG) phosphor are currently available [21–23]. However, such near-white output is limited to bluish white (cold white light) and to produce yellowish white light through red (warm white light) that can be efficiently excited by UV-blue LEDs (such as GaN or InGaN based) is of great demand to produce white light in BGR (blue-green-red) mode [21–23]. The present phosphors codoped by yellow emitting Dy^{3+} combined with red emitting Eu^{3+}, which

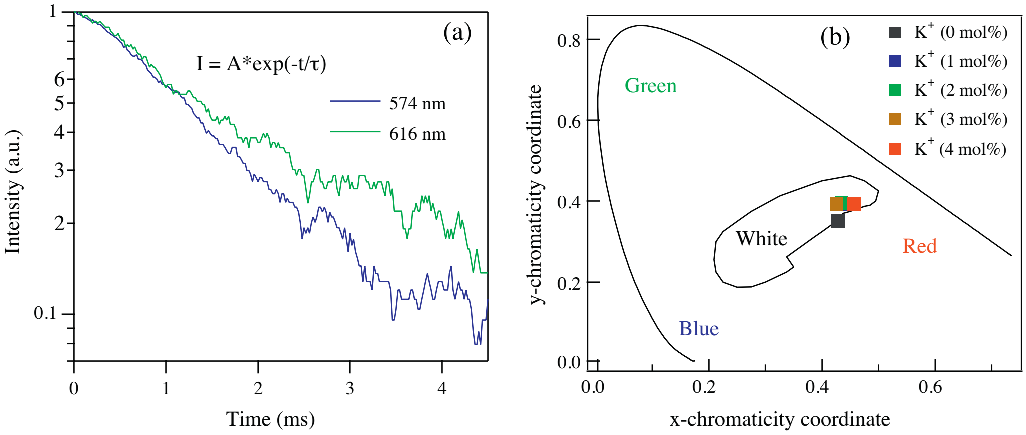

Fig. 5. (a) The emission decay curves of 574 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$ of Dy^{3+}) and 616 nm ($^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}) emissions in 4 mol% K^+ co-doped $CaSO_4$:Dy^{3+},Eu^{3+} phosphor and (b) chromaticity diagram of x mol% K^+ ($x = 0$–4) co-doped $CaSO_4$:Dy^{3+},Eu^{3+} phosphors at room-temperature ($\lambda_{ex} = 410$ nm).

can be easily excited by blue-violet LEDs are of much importance for such near white light applications. This could further easily be tuned and improved by changing the concentration K^+-ions.

4. Conclusions

Near white-light emitting $CaSO_4$:Dy^{3+},Eu^{3+} phosphors with various K^+ compensator concentrations were successfully synthesized. These phosphors showed multi-color emission of yellow-blue from Dy^{3+} and red-orange from Eu^{3+} ions. The structural and optical studies confirm that the rare earth ions are situated at the covalent sites of Ca^{2+} and the site occupancy was compensated by K^+ without any defects. Furthermore, relatively large emission lifetimes and near white light emission suggest the possible potential applications of these phosphors in optoelectronic devices.

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