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Investigation of photoluminescence properties, thermal stability, energy transfer mechanisms and quantum efficiency of $Ca_2ZnSi_2O_7$: Dy^{3+}, Eu^{3+} phosphors

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ABSTRACT

Undoped, Dy^{3+} doped and Dy^{3+}, Eu^{3+} co-doped $Ca_2ZnSi_2O_7$ (CZS) phosphors were successively prepared using the solid state reaction method. The XRD and FE-SEM results revealed that the prepared phosphors have tetragonal crystal structure and agglomeration of particles. The energy band gaps of doped and co-doped phosphors were found to be increased as compared to undoped CZS. From the PL spectra, it was found that the energy transfer from sensitizer (Dy^{3+}) to activator (Eu^{3+}) ion in co-doped CZS: Dy^{3+}, Eu^{3+} phosphors were mainly due to quadrupole-quadrupole interaction. The prepared CZS: Dy^{3+}, Eu^{3+} phosphor the emission intensity retained almost 80% at 425 K of that measured at 300 K. The emission color had tuned with the incorporated of Eu^{3+} ion in CZS: Dy^{3+} phosphor. The quantum efficiency of CZS: Dy^{3+}, Eu^{3+} phosphor is 12.88%. All the results of CZS: Dy^{3+}, Eu^{3+} phosphors showed a great potential application as a white-emitting phosphor for solid state lighting application.

1. Introduction

In the recent year, the use of rare earth ion doped inorganic hosts has gained rapid growth in industry owing to the wide range of applications, such as light-emitting diodes (LEDs), cathode ray tubes (CRTs), vacuum fluorescent displays (VFDs), plasma display panels (PDPs), field-emission displays (FEDs), and X-ray imaging scintillators [1]. The serious global energy crisis and challenges of climate change have managed the development of white light-emitting diodes (WLEDs) for solid-state lighting application. Phosphors converted WLEDs with their superior performance in optoelectronic devices and display fields have attracted much attention due to their benefits over the existing of traditional incandescent and fluorescent lamps such as long lifetime, energy saving qualities, high luminescence efficiency, high color rendering index (CRI) and environmentally friendly [2]. White light is achieved by using blue InGaN blue chip combined with the yellow emitting (YAG: Ce^{3+}) phosphor, which is commercially available and exhibits high efficiency and chemical stability. But it produces a deviated natural white light emission due to the surroundings effect of the ratio of blue and yellow separation and lower color rendering index of $\leq$ 80 due to lack of red emission [3]. The above drawbacks could be resolved by the single-phased white light emitting phosphors via energy transfer from a sensitizer to an activator ion in the same host matrix. On the basis of energy transfer mechanisms, many researchers have successively obtained white emission in single phase phosphors such as $BaGdF_5$:Dy^{3+}, Eu^{3+} [4], YVO4:Dy^{3+}/Eu^{3+} [5], $SrLaMgTaO_6$:Dy^{3+}/Eu^{3+} [6], $Ca_{20}Al_{26}Mg_3Si_3O_{68}$:$Ce^{3+}$,$Dy^{3+}$ [7], $Ca_2La_8(GeO_4)_6O_2$: Tb^{3+}/Sm^{3+} [8] and $LiSrPO_4$: Ce^{3+}, Tb^{3+}, Mn^{2+} [9]. Hence, the search for new phosphors and understanding the energy transfer mechanisms between the trivalent rare earth ions are necessary for finding a single composition white light emitting phosphors.

Among all the trivalent rare earth ions, dysprosium (Dy^{3+}) ion has been studied extensively in luminescent materials due to its potential application for WLEDs [10]. Generally, Dy^{3+} doped phosphors exhibit two intense emission peaks; the first one is blue emission ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and another one is yellow emission ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) [11]. To date, a large number of researchers have investigated on Dy^{3+} doped phosphors such as, $BaGd_2ZnO_5$:Dy^{3+}, Ca_2PO_4Cl:Dy^{3+}, $LiBaPO_4$:Dy^{3+}, $Ba_3Lu(PO_4)_3$:Dy^{3+}, $CaMoO_4$:Dy^{3+}, $Li_4CaB_2O_6$:Dy^{3+}, $M_2Si_5N_8$ (M = Ca, Sr, Ba): Dy^{3+}, $LaGdSiO_5$:Dy^{3+} [12–19]. Furthermore, the lack of red emission of the Dy^{3+} ions was compensated by co-doping with Eu^{3+} ions, since Eu^{3+} ions can be widely used as a luminescence center for various phosphors which exhibits red color emission corresponding to the transition of $^5D_0 \rightarrow {}^7F_2$. Generally, the trivalent Eu^{3+} ion exhibits four emission peaks due to transitions $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4). Many Eu^{3+} doped phosphors exhibit a strong red emission of the wavelength

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615 nm owing to the electronic transition $^5D_0 \rightarrow {}^7F_2$. Hence, the single-phased white-emitting phosphors can be obtained by introducing the Eu^{3+} ion in the Dy^{3+} doped phosphors. Recently, research works have been carried out to develop single-phase white light emission via the energy transfer mechanisms from sensitizer to activator such as, $CaLaP_3O_{10}$: Dy^{3+}, Eu^{3+}, $NaLa(MoO_4)_2$: Dy^{3+}, Eu^{3+}, $Ca_2Gd_8Si_6O_{26}$:Dy^{3+}, Eu^{3+} $Sr_3Y(PO4)_3$:Dy^{3+}, Eu^{3+}, SrMoO4: Eu^{3+}, Tb^{3+}, $Sr_3Lu(PO_4)_3$:Ce^{3+}, Tb^{3+} phosphors [20–25].

Silicate family has caught much more attention owing to their special characteristics such as rigid crystal structure, abundant crystalline phase, good physical and chemical stability, low cost, water resistance, high brightness, long lifetime, multicolor emission and high luminous efficiency [26]. Among silicate family the $Ca_2ZnSi_2O_7$ constituent of the melilites group having general formula $X_2MY_2O_7$ (X = Ca, Sr, Na; M = Mg, Zn; Y = Si, Al, B). These materials have crystallized in tetragonal structure. Due to this comfort of incorporation, melilites are currently widely used as a host material for rare earth dopant and transition metal ion to prepare phosphors which can be used in many potential applications such as light emitting diodes, flat panel display, plasma display panels, cathode ray tubes, solar cell and many other varieties of light emitting devices [27]. A variety of research works have successively done by the researchers in $Ca_2ZnSi_2O_7$ host matrix such as Jiang et al. reported luminescence properties of yellow long-lasting phosphor $Ca_2ZnSi_2O_7$: Eu^{2+}, Dy^{3+} [28]. Kamioka et al. reported photo-induced properties of $Ca_2ZnSi_2O_7$: Eu^{2+} phosphor [29]. Zeng et al. reported green long-lasting phosphor $Ca_2ZnSi_2O_7$: Eu^{2+} [30].

In this study, we have prepared CZS: Dy^{3+} phosphors by solid-state reaction method and systematically investigated their crystal structural, morphology, UV–Vis and photoluminescence properties. In order to improve the red emission of CZS: Dy^{3+} phosphor, Eu^{3+} ions were also co-doped and the energy transfer mechanism between Dy^{3+} and Eu^{3+} ions was studied. A novel luminescence behavior was observed between Dy^{3+} and Eu^{3+} ions in CZS host.

2. Experimental section

2.1. Phosphors preparation

Undoped, Dy^{3+} doped and Dy^{3+}, Eu^{3+} co-doped $Ca_2ZnSi_2O_7$samples were prepared using conventional solid state reaction technique. The starting chemicals were calcium carbonate ($CaCO_3$ 99.90%), zinc oxide (ZnO 99.90%), silicon dioxide (SiO_2 99.99%), dysprosium oxide (Dy_2O_3 99.99%) and europium oxide (Eu_2O_3 99.99%). All of the chemicals were analytical grade (A.R.) deputed in this experiment. Initially, the raw materials were weighed according to the stoichiometric composition of $Ca_{2\text{-}2x}ZnSi_2O_7$:2xDy^{3+}(x = 0.5–2.0 mol%) and $Ca_{2\text{-}2(x\text{-}y)}ZnSi_2O_7$:2xDy^{3+},2yEu^{3+} (x = 1 mol%, y = 1, 1.5, 2, 2.5, 3 mol%) phosphors after that the powders were mixed homogeneously in an agate mortar and pestle using AR grade ethanol as the mixing medium. The chemical reaction which is used for stoichiometric calculation is as follows:

$2CaCO_3 + ZnO_2 + 2SiO_2 + Dy_2O_3 \rightarrow Ca_2ZnSi_2O_7\text{: }Dy^{3+} + 2CO_2\uparrow + 2O_2\uparrow$

$2CaCO_3 + ZnO_2 + 2SiO_2 + Dy_2O_3 + Eu_2O_3 \rightarrow Ca_2ZnSi_2O_7\text{:}Dy^{3+}\text{,}Eu^{3+} + 2CO_2\uparrow + 3O_2\uparrow$

The obtained samples taken in 30 ml alumina crucibles are introduced in a programmable furnace which is heated at the rate of 4 °C per minute and finally, the samples were fired at 1200 °C for 3 h in the air. The final products were obtained after cooling the sample to room temperature by natural cooling.

2.2. Characterization techniques

The phase purity and structural properties of undoped $Ca_2ZnSi_2O_7$ phosphors were checked by using XRD diffractometer recorded in the range of Bragg's angle 2θ (10° to 80°) using a Bruker D8 Focus X-ray diffraction (XRD) with Cu-Kα radiation. The surface morphology of the prepared phosphors was examined by using field emission scanning electron microscopy (FESEM) with the help of 55- Supra (Germany) FESEM measuring instrument. The photoluminescence studies were examined using Hitachi Fluorescence spectrometer F-2500 with a 150 W Xe lamp in the wavelength range of 220–800 nm while the UltraViolet Visible (UV–Vis) Diffuse reflectance studies of prepared samples were done using CARRY – 5000 spectrophotometers. The decay kinetics were studied using Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer. The temperature dependent photoluminescence studies were carried out using Optistate DN2 (Oxford Cryostat). The quantum efficiency was carried out by using Horiba Acton 2500 spectrophotometer excitation with a xenon arc lamp.

3. Results and discussion

3.1. XRD studies

The structural study is an important tool to estimate the crystallinity and crystallite size which have the strong effect on the PL properties of the phosphors materials. The XRD patterns of the undoped, single doped (1 mol% Dy^{3+}) and co-doped (1 mol% Dy^{3+}, 2 mol% Eu^{3+}) of CZS samples are shown in Fig. 1. According to the standard XRD pattern of CZS phosphor having JCPDS card no 75–0916., the prepared phosphors have received the tetragonal structure with the space group $P\bar{4}2_{1m}(113)$ with lattice parameters a = b = 7.830 Å and c = 4.99 Å and volume = 305.93 Å^3. From Fig. 1 it can be seen that the prepared CZS: Dy^{3+} phosphors are found to be isostructural. All the observed intense diffraction peaks (0 0 1), (1 1 1), (2 0 1), (2 1 1), (3 1 0), (3 1 2) are well indexed with to the tetragonal Akermanite structure. There were three additional peaks at 2θ = 34°, 56° and 40.96° coming due to $CaSiO_3$ phase (JCPDS card no. 80-0654) which indicated in XRD plot. The small amount of $CaSiO_3$ impurity phase will not affect the luminous properties of the material.

The ionic radius percentage difference between the dopants Dy^{3+}, Eu^{3+} and substituent ion (Ca^{2+}) is determined using the following equation [31].

$$D_r = \frac{R_m(CN) - R_d(CN)}{R_m(CN)} \times 100\% \tag{1}$$

where D_r is the ionic radius percentage difference, CN is the co-ordination number, R_m is the ionic radius of host cation, R_d is the radius of the doped ion. The CN and atomic radius (r) of Dy^{3+} are 6 and 0.0912 nm respectively and that of Eu^3 are 6 and 0.095 nm respectively. The CN and the atomic radius of Ca^{2+} ion are 6 and 0.099 nm respectively. The radius percentage differences were found to be 7.8 for Dy^{3+} and 4.0% for Eu^{3+} ions respectively. The radius percentage difference between doped and substituted ion should not exceed 30% for a perfect doping. The charges of two Dy^{3+} or Eu^{3+} ions may substitute three Ca^{2+} sites to remain the charge balance. The above two properties indicates that the Dy^{3+} and Eu^{3+} ions are perfectly substituted to Ca^{2+} sites in the $Ca_2ZnSi_2O_7$ host lattice. The Ca^{2+} ions with site symmetry m are located between the layers and coordinated by eight oxygen ions in $Ca_2ZnSi_2O_7$ [32,33].

The average crystallite size of the prepared samples was calculated using Debye-Scherrer formula and Williamson-Hall equation [32,33]. The calculated average crystallite size of the samples is summarized in Table 1. The average crystallite size of the samples was found to be decreasing trend with increasing the Dy^{3+} doping concentration in the CZS host lattice due to increase in the strain introduced due to the replacement of Ca^{2+} ions by Dy^{3+} ions of smaller ionic radii. The crystallite size calculated from Williamson-Hall equation was higher than those calculated from Debey-Sherrer formula. This variation was coming due to the fact that in the Debey-Sherrer formula the