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Synthesis, photoluminescence and mechanoluminescence properties of Eu^{3+} ions activated $Ca_2Gd_2W_3O_{14}$ phosphors

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Abstract A new series of Eu^{3+} ions-activated calcium gadolinium tungstate [$Ca_2Gd_2W_3O_{14}$] phosphors were synthesized by conventional solid-state reaction method. The X-ray diffraction patterns of the powder samples indicate that the Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors are of tetragonal structure. The prepared phosphors were well characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL), and mechanoluminescence (ML) spectra. PL spectra of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ powder phosphors have shown strong *red* emission at 615 nm ($^5D_0 \rightarrow {}^7F_2$) with an excitation wavelength $\lambda_{exci} = 392$ nm ($^7F_0 \rightarrow {}^5L_6$). The energy transfer from tungstate groups to europium ions has also reported. Mechanoluminescence studies of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors have also been explained systematically.

Introduction

In recent years, many efforts have been paid to the white LEDs because of their advantages such as high efficiency, low power consumption, lack of toxic mercury, long lifetime, fast response, energy saving, and environment friendliness [1]. The white LEDs can be fabricated by using red, green, and blue light emitting phosphors coated on the near-UV LED chip [2]. Therefore, it is required to prepare novel and superior red phosphors for WLEDs. Calcium tungstate is an excellent and interesting phosphor for its strong visible luminescence and could be utilized in plasma display panels, quantum electronics, scintillators, solid-state optoelectronic devices, lasers, optical fiber components, and also used as a phosphor, scintillation counter, laser material, and in the ceramics industry [3]. Development of high quality devices such as cathode ray tubes, plasma displays, field emission displays, high definition projection television, and light emitting diodes needs to prepare high quality phosphors. Among different phosphors, the phosphors containing gadolinium and tungsten have attracted much attention for their interesting properties such as ferroelectricity, laser hosts, phosphors and catalysis [4]. Based on the above applications, we have chosen the new host lattice containing Ca, Gd, and W elements as $Ca_2Gd_2W_3O_{14}$ phosphors.

Rare earth activated phosphors have potential technological applications in solid-state lasers, color TV monitors, fluorescent lamps, lighting, imaging, display applications, illuminations, cathode ray tubes, field emission displays, plasma displays, and in the development of white light emitting diodes (WLEDs) due to their potential luminescent properties such as high brightness, high efficiency, and long working time [5, 6]. Basically these rare earth ions have been considered as the important optical activators for luminescent devices [7]. Among the different rare earth ions Eu^{3+} ions are one, which have been extensively used as active ions of red phosphors for different reasons such as the characteristic emission band at ~613 nm in the red

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region and these ions can also be used to detect the crystal symmetry. The red luminescence of Eu^{3+} ion has been extensively used in the lighting and displays because of its 4*f*–4*f* transitions. Trivalent Eu ion is one of the promising species which exhibits strong visible emission in red color regions and can be used in fluorescent lamps and color lighting [8].

Mechanoluminescence is a type of luminescence where an emission of light is observed due to the mechanical deformation of materials when they are subjected to mechanical stress like compressing, rubbing, cutting, cleavage, grinding, and shaking etc., ML has also been termed as elasticoluminescence, plasticoluminescence, fractoluminescence, and triboluminescence in the literature depending upon the nature of mechanical stress. Recently ML materials, whose ML emission is observed with naked eye have been prepared and such materials are having important applications in stress imaging devices, wireless fracture sensor systems, self-diagnosis systems, optical stress sensors, damage sensors, and in fuse system for army warheads [9, 10].

Compared with many studies on different host lattices rare earth ions doped tungstates have been less studied. So far, there are no reports on the rare earth ions activated $Ca_2Gd_2W_3O_{14}$ phosphors, therefore, we have undertaken the present work. In this article, we report the energy transfer from tungstate groups to europium ions, the effect of Eu^{3+} ion concentration on the photoluminescence (PL) and mechanoluminescence (ML) properties of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ novel phosphors.

Experimental

Chemicals used

Starting materials $CaCO_3$, Gd_2O_3, WO_3, and Eu_2O_3 are purchased from Sigma Aldrich and are used as received without any further purification.

Solid-state synthesis

$Ca_2Gd_{2-x}W_3O_{14}$: Eu_x^{3+} (where $x = 0.5$, 1, 5, 10, 15, and 20 mol%) phosphors were prepared by solid-state reaction method. The starting materials $CaCO_3$, Gd_2O_3, WO_3, and Eu_2O_3 were blended in appropriate stoichiometric ratio. These powders were ground thoroughly in an agate mortar, and then the mixtures were put into an alumina crucible. They were heated in an electric furnace at a temperature 1,000 °C for 2 h. The final samples were white powders. The chemical reaction of the synthesis of $Ca_2Gd_2W_3O_{14}$ powder phosphors is as follows:

$$2CaCO_3 + Gd_2O_3 + 3WO_3 \rightarrow Ca_2Gd_2W_3O_{14} + 2CO_2$$

Characterization

Structural characterization of these samples has been carried out from the X-ray powder diffraction measurements on a XRD 3003TT Seifert diffractometer with CuKα radiation ($\lambda = 1.5406$ Å) at 40 kV and 20 mA and the 2θ range was varied between 20° and 60°. Morphology of the powder phosphors were examined on a ZEISS-EVO-MA15 ESEM. The scanning electron microscopy (SEM) image was obtained for samples by using a 35 m camera attached to a high resolution recording system. The elemental analysis has been carried out by energy dispersive X-ray analysis (EDAX) using an X-ray detector attached to the SEM instrument. The FT-IR spectrum (4,000–450 cm^{-1}) was recorded on a Perkin Elmer Spectrum1 spectrometer with KBr pellets.

PL characteristics were studied for 2 mg of sample each time using a RF-5301PC SHIMADZU spectrofluorophotometer, at room temperature, using 1.5 nm spectral slit width in the range of 200–700 nm. To study the effect of gamma irradiation on their photoluminescent properties of the prepared phosphors, the samples were exposed to gamma rays from a ^{60}Co source at room temperature at the rate of 0.995 kGy/h.

The ML was excited impulsively by dropping a load onto 1 mg gamma-irradiated phosphor placed on the Lucite plate (surface area 2.826×10^{-3} m^2), from various heights, using a guiding cylinder (area of cross section 1.256×10^{-3} m^2). The ML was monitored using a RCA 931 photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope. The ML spectrum was recorded using a series of optical band pass filter. Seven different filters were used and all the filters had bandwidth in the range 15–30 nm and transmission from 40 to 60%.

Results and discussion

X-ray diffraction patterns

The X-ray diffraction profiles of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors prepared by traditional solid-state reaction method are shown in Fig. 1. The diffraction peaks are well consistent with the standard JCPDS card no. 41-0186. This indicates that the prepared phosphors exist in a tetragonal phase and the doping concentration of Eu^{3+} ions does not influence the intensity as well as the crystal structure of the phosphors.

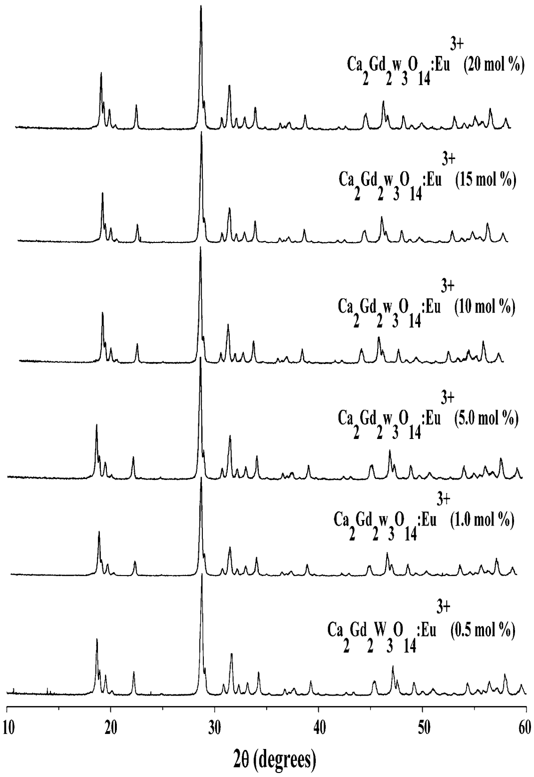

Fig. 1 XRD Profiles of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors

SEM and EDAX analysis

The size and the shape of the prepared products were measured by SEM images. Figure 2 shows the SEM image of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ powder phosphor. From the SEM image, it is observed that, the particles are randomly distributed having various shapes and sizes, and the average grain size is expected to be around 300–500 nm. EDAX spectrum of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor is shown in Fig. 3, which confirms the presence of the Eu^{3+} ions.

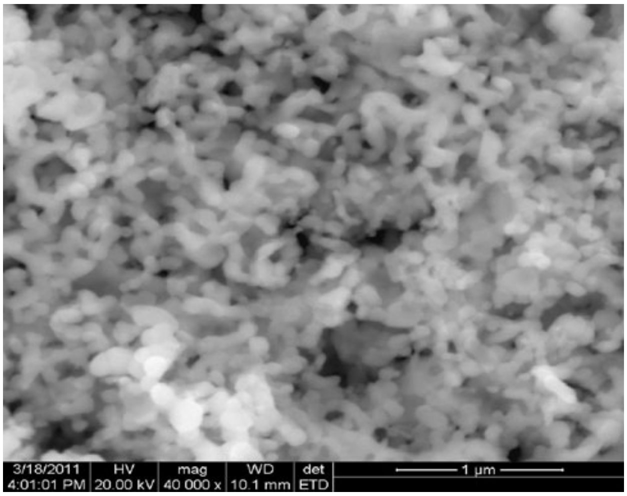

Fig. 2 SEM image of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor

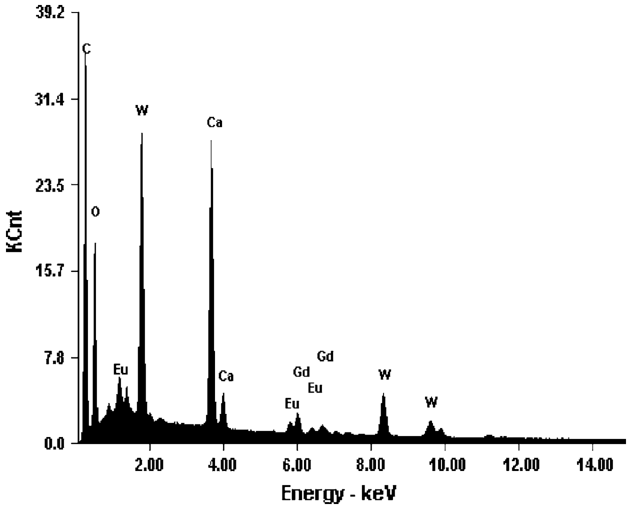

Fig. 3 EDAX spectrum of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor

FTIR analysis

FTIR spectrum of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor is shown in Fig. 4. From the FTIR spectrum, it is observed that the bending vibration of H_2O molecule and O–H stretching vibrations are present at about 1,480 cm^{-1} and in the range from 3,800 to 2,700 cm^{-1} [11]. The band at 809 cm^{-1} can be assigned to the stretching mode of W–O bonds and the band at 607 cm^{-1} in the range from

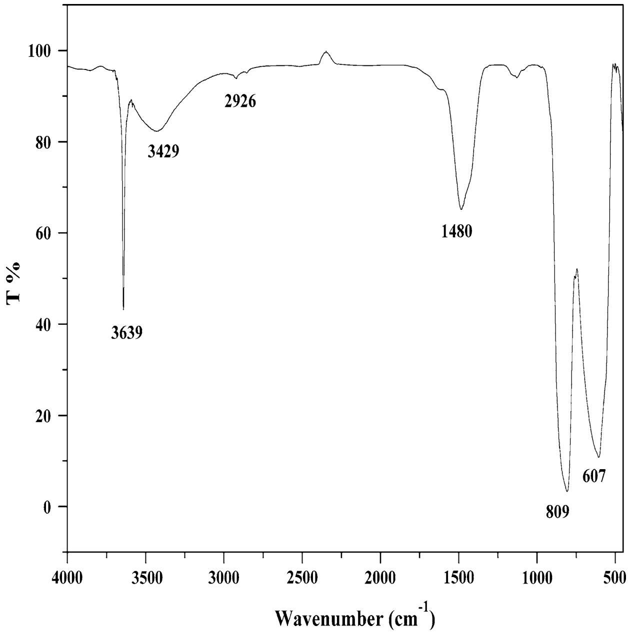

Fig. 4 FTIR spectrum of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor

800 to 600 cm^{-1} corresponds to the W–O vibrations, respectively [4].

Photoluminescence studies

The excitation spectrum of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ powder phosphor monitored by the emission at 615 nm is shown in Fig. 5. It contains an intense broad band centered at 304 nm in the wavelength region 250–350 nm, which is attributed to the charge transfer band (CTB) between $O^{2-} \rightarrow W^{6+}$ and $O^{2-} \rightarrow Eu^{3+}$ [12]. The presence of the most intense broadband of $WO_{24}{}^{2-}$ in the excitation spectrum of Eu^{3+} indicates that there is an efficient energy transfer from the tungstate groups to Eu^{3+} ions in $Ca_2Gd_2W_3O_{14}$ phosphors [4]. In the wavelength region 350–450 nm, several excitation peaks are observed and are located at 359 nm ($^7F_0 \rightarrow {}^5D_4$), 379 nm ($^7F_0 \rightarrow {}^5L_7$), 392 nm ($^7F_0 \rightarrow {}^5L_6$), 414 nm ($^7F_0 \rightarrow {}^5D_3$), 463 nm ($^7F_0 \rightarrow {}^5D_2$), and 533 nm ($^7F_0 \rightarrow {}^5D_1$) which are attributed to *f–f* transitions of Eu^{3+}. Moreover, the charge transfer band is very sensitive to the changes in the crystal field compared to the *f–f* transitions of Eu^{3+} ions [13]. The most intense peak in the longer wavelength region was located at 392 nm and has been chosen for the measurement of emission spectra of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors. From the excitation spectrum, it was found that the intensity of *f–f* transition at 392 nm in the longer wavelength region (350–450 nm) is low compared with the intensity of the charge transfer band at 304 nm as reported in Y_2O_3: Eu^{3+}, this indicates that absorption of light is mainly due to the charge transfer transition only but not due to the *f–f* transitions [11, 14]. Figure 6 shows the emission spectra of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors. The emission spectra contain an intense emission peak at 615 nm which is assigned to the electric dipole transition of $^5D_0 \rightarrow {}^7F_2$, while the weak emission peaks are located at 579, 591, 645, and 702 nm and are assigned to the transitions $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$, respectively. Luminescence originating from transitions between 4*f* levels is predominant due to electric dipole or magnetic dipole interactions [15]. The intense red emission with the transition $^5D_0 \rightarrow {}^7F_2$ is the dominant only when Eu^{3+} occupies the symmetry local site without an inversion center and also this transition is known as hypersensitive transition since its intensity is easily affected by the local environment of Eu^{3+} and its surrounding ligands. On the contrary, if Eu^{3+} occupies an inversion symmetry site the transition $^5D_0 \rightarrow {}^7F_1$ is the dominant with orange-red emission. The $^5D_0 \rightarrow {}^7F_1$ transition is purely magnetic dipole allowed and is usually taken as a reference transition because the crystal field does not considerably alter the intensity of this transition. It is very clear that, we can observe all the characteristic transitions of Eu^{3+} with red emission as the dominant one. This indicates that the energy has been transferred from $W_4O_{24}^{-24}$ to Eu^{3+} [4]. From the emission spectra, it is observed that the $^5D_0 \rightarrow {}^7F_1$ and the $^5D_0 \rightarrow {}^7F_2$ emission bands split in two Stark components, this depends on the local environment of Eu^{3+} ions in the crystalline structure. In other words, the local environment of the rare earth ions plays an effective role on the luminescence performance.

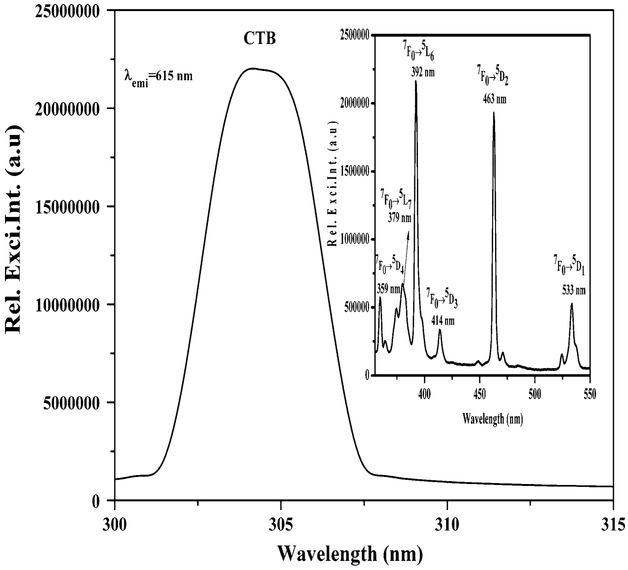

Fig. 5 Excitation spectrum of (10 mol%) Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor

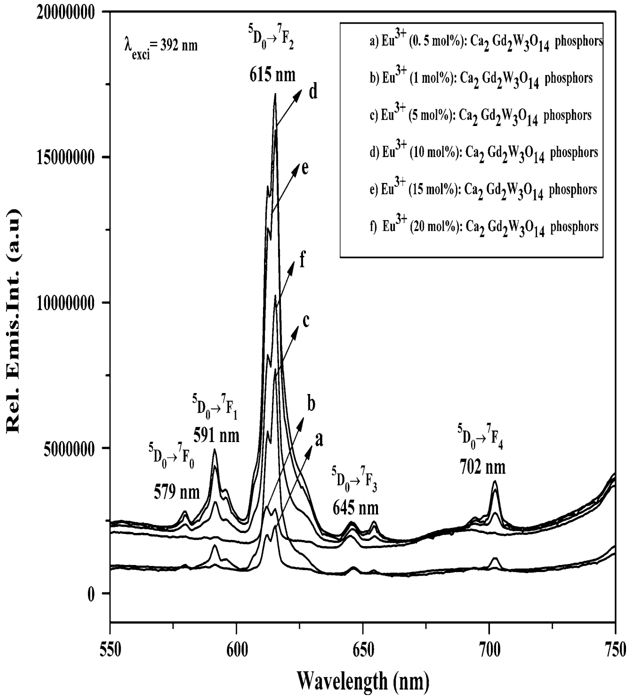

Fig. 6 Emission spectra of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors

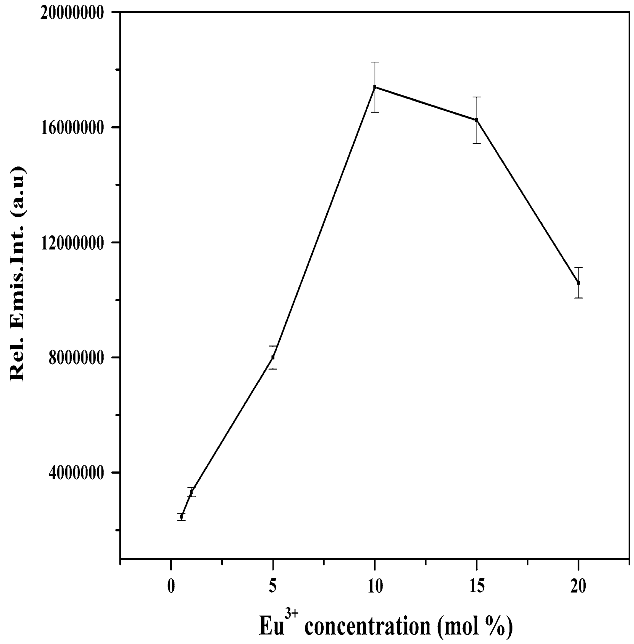

Fig. 7 Emission intensity of Eu^{3+} as a function of its doping concentration of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors

Particularly, the $^5D_0 \rightarrow {}^7F_2$ transition is very sensitive to the variations in the local crystal field, which causes the splitting and shifting of the emission band than for the other transitions [16, 17]. It is well known that the luminescence performance of the powder phosphors depends mainly on the concentration of activator ions, thus the identification of optimum dopant concentration is necessary. It is also observed from the emission spectra that by increasing the dopant (Eu^{3+}) concentration the PL intensity was also increased up to 10 mol% beyond that concentration, the PL intensity was decreased. This is known as the concentration quenching, in general by increasing the dopant concentration, number of Eu^{3+} ions will increase and the distance between activator ions will decrease which causes the interaction between Eu^{3+} ions and also energy migration among rare earth ions which bring the excitation energy to defect sites in the crystal lattice [18]. Thus, 10 mol% is the optimized concentration. Figure 7 presents the emission intensity of Eu^{3+} as a function of its doping concentration (mol%).

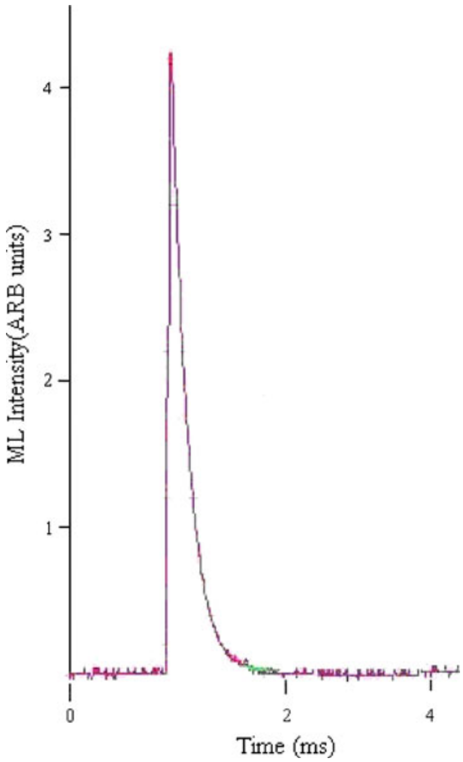

Fig. 8 Mechanoluminescence of Eu^{3+} activated $Ca_2Gd_2W_3O_{14}$ phosphor (5 mol%) for 30 min irradiation time

Mechanoluminescence studies

Figure 8 shows the ML of γ-irradiated $Ca_2Gd_2W_3O_{14}$:Eu^{3+} (5 mol%) phosphor for 30 min irradiation time. It is observed that initially the ML intensity increases with time attains a maximum and then it decreases with time and finally disappeared. On the impact of the load the dislocation in the crystal starts moving. The moving dislocation interacts with Vk centers and capture holes. The ML intensity is due to radiative recombination of dislocation holes with the recombination centers (defect centers containing electron), ML process can be explained by following equations.During irradiation

$$Eu^{3+} + e^- = Eu^{2+}$$

$$\text{Positive ion vacancy} + \text{hole} = \text{Vk}$$

During deformation

$$\text{Vk} + \text{D} = \text{D}^+ + \text{Positive ion vacancy}$$

$$Re^{2+} + D^+ = Re^{3+} + D$$

$$Re^{3+*} = Re^{3+} + h\nu$$

where Vk and D represent Vk center and dislocation, respectively, D$^+$ is the dislocation containing hole.

Figure 9 shows the ML of γ-irradiated $Ca_2Gd_2W_3O_{14}$:Eu^{3+} phosphor for different concentration of Eu^{3+}. It is seen that ML intensity initially increases with increasing concentration of dopant and then it is maximum at 10 mol% concentrations. And after that ML intensity decreases with increasing concentration of dopant. This is due to concentration quenching at higher concentration. The ML characterization shows that the ML intensity increases up to 10 mol% of impurity concentration and saturated at 1 kGy/h due to aggregation of color centers which are formed by irradiation, these results show that the

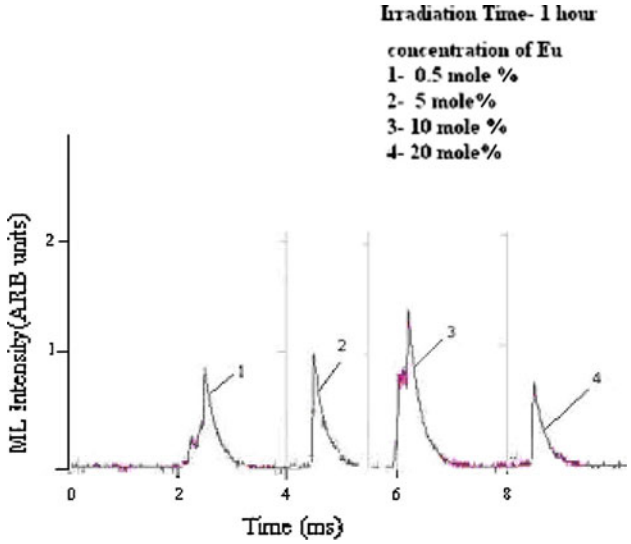

Fig. 9 Dependence of ML intensity of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor on different concentration of dopants for 1 h irradiation time

prepared materials can also be used as a ML dosimetry phosphor for radiation measurement up to higher exposure i.e. 1 kGy.

From the measurements of PL and ML spectra of $Ca_2Gd_2W_3O_{14}$: Eu^{3+} phosphors, it is observed that in both the cases the luminescence intensity attains its maximum at 10 mol% and then decreases by increasing the impurity concentration. Thus, 10 mol% is the optimized concentration and these phosphors [$Ca_2Gd_2W_3O_{14}$: Eu^{3+} (10 mol%)] found the applications in WLEDs and also used as a ML dosimetry phosphors for radiation measurements up to higher exposure i.e. 1 kGy.

Conclusions

It is concluded that Eu^{3+} ions-activated $Ca_2Gd_2W_3O_{14}$ powder phosphors have been synthesized by using a solid-state reaction method. The excitation spectrum of the Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphor shows the energy transfer from WO^{2-} group of the host lattice to the Eu^{3+} ions. Emission spectra of Eu^{3+}: $Ca_2Gd_2W_3O_{14}$ phosphors have shown a strong red emission and may be promising candidates as red-emitting phosphors for WLEDs. The ML characterization shows that the ML intensity saturated at 1 kGy/h due to aggregation of color centers are formed by irradiation, this results show that the prepared materials can also be used as a ML dosimetry phosphor for radiation measurement up to higher exposure i.e. 1 kGy.

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