PHOTOLUMINESCENCE AND THERMOLUMINESCENCE PROPERTIES OF Ce^{3+} DOPED $Ca_2MgSi_2O_7$ PHOSPHOR

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The novel alkaline earth silicate based phosphor $Ca_2MgSi_2O_7$ activated with the trivalent rare earth Ce^{3+} ion (4 mol%) was synthesized by solid state reaction method and their characterization and luminescent properties were investigated. The emission and excitation spectra, and TL glow curves were employed to study the luminescence properties. The kinetic parameters were calculated using TL glow curve. The calcined powders of the Ce^{3+} emits ultraviolet light. In the photoluminescence investigations, there is a single and highly symmetric site for activator ions in the $Ca_2MgSi_2O_7$ host lattice. The sharp emission properties show that the $Ca_2MgSi_2O_7$ is a suitable host for rare-earth doped laser crystal and phosphor material.

INTRODUCTION

The most efficient long-lasting phosphors are still based on alkaline-earth aluminates and sulphide, for example $SrAl_2O_4 : Eu^{2+}, Dy^{3+}$ produced green colour, $CaAl_2O_4 : Eu^{2+}, Nd^{3+}$ produced deep blue colour and $Y_2O_2S : Eu^{3+}, Ti^{4+}, Mg^{2+}$ produced red colour (Matsuzawa, 1986). Aluminates based phosphors have been replacing sulphide base. This is due to the aluminates had provide interesting and useful result such as no radiation, high brightness and long afterglow. But the properties of these phosphors may be decreased greatly when soaked in water for several hours (Aitasalo, 2005). Nowadays, alkaline earth silicate are regarded as suitable host with stable crystal structure, water-resistant property, high physical and chemical stability compared to sulphide phosphorescent phosphors and strontium aluminates phosphor (Yamazaki, 1986). It is also easy in preparation and low cost. Therefore, silicate host was attracting more attention in the application of long afterglow phosphor (Bo Liu *et al.*, 2005) and considerable attention had been paid because of its multi-colour phosphorescence and resistance to acid, alkali and oxygen. Glasses doped with Ce^{3+} ions that emit optical transitions in the 300-500 nm wavelength range due to electric dipole allowed 5d-4f transitions, are useful in many applications including fiber optics, scintillators and tunable lasers [1]. Currently, much interest has emerged in the Ce^{3+} ion for its application in high energy physics, because of fast and efficient luminescence in the UV and blue spectral region. The emission of the Ce^{3+} ions produced by the electron transition of 4fn-1 5d-4fn, can be blue/red shifted depending on the type of co-doping solids [2, 3]. Also other factors such as modification of the ligand field around the Ce^{3+} ions in silica, presence of hydroxyl ions, energy transfer by

cross-relaxation and the concentration of the co-dopants have significant effect on the luminescent wavelength and intensity. An important aspect of this study was the accurate characterization of Ce^{3+} doped $Ca_2MgSi_2O_7$ phosphor.

EXPERIMENTAL

$Ca_2MgSi_2O_7$ doped with 4 mol % Ce^{3+} phosphor was prepared by solid state reaction method by mixing stochiometric amounts of compounds calcium carbonate ($CaCO_3$) and magnesium oxide (MgO), SiO_2 and CeO_2. The prepared phosphor $Ca_2MgSi_2O_7$ is weighed and grounded into a fine powder using agate mortar and pestle about an hour. The grounded mixture was placed in an alumina crucible and heated from room temperature to 1200°C in a muffle furnace with a heating rate of 5°C/min. After reaching 1200°C the phosphor heated for 3 hours and the furnace was allowed to cool to room temperature along with the samples, resulting in a white powder.

The basic reaction is as follows:

$$CaCO_3 + MgO + SiO_2 * H_2O = Ca2MgSi_2O_7 + 2CO_2 + 2H_2O$$
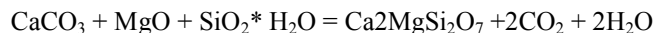
The photoluminescence emissions (PL) of the powder were measured using the spectro flurophotometer (SHIMADZU, RF5301PC) xenon lamp as excitation source. Phosphorescence lifetime measurements were achieved by irradiating the sample for 10 minutes using a mercury lamp, and immediately after switching the lamp off, a PMT was allowed to measure the phosphorescence signal at room temperature, with an approximated delay time of 1 second. The phase and surface morphology were identified using a Bruker AXS D8 Advance X-ray diffractometer (XRD) and Scanning electron microscopy (SEM) with EDX(Model: QUANTA 200F-FEI), respectively. The glow curves were acquired by thermoluminescence spectroscopy (TLD Nucleonix TL 10091), after irradiating the phosphor using mercury lamp. The luminescence detection for the TL system consists of a photomultiplier (PMT) with a U340 Schott filter that is effective in the 340 – 380 nm wavelengths.

RESULTS AND DISCUSSION

The SEM micrograph of $Ca_2MgSi_2O_7$: Ce^{3+} is presented in figure 4.1 and it shows an agglomeration of small spherical particles, which is a unique trace of particles prepared at very high temperatures [11]. The XRD pattern of $Ca_2MgSi_2O_7$: Ce^{3+} that matches that of a standard pattern of orthorombic $Ca_2MgSi_2O_7$ referenced in JCPDS 35-592 file number are shown in figure 2. This suggests that a single phase was crystallized. The crystallite sizes were approximated to be 19.69 nm using the diffraction peaks measured and Scherrer's equation (Eq. 4.1) [4]:

Here, **d** calculated by Bragg's equation $n\lambda = d \sin\theta$ here $\lambda = 1.54$ Å

and Crystalline size D_P calculated by Scherrer's formula $D_p = K \lambda / \beta_{1/2} \cos \theta$

where K scherrer's constant = 0.94 , $\beta_{1/2}$ FWHM = $2\Delta\theta = 0.44°$ = 0.00768 radian

Crystalline size $D_P = (0.94 \times .154056)/ 0.00768 \times \cos (16.7)$

$$= 19.69 \text{ nm}$$
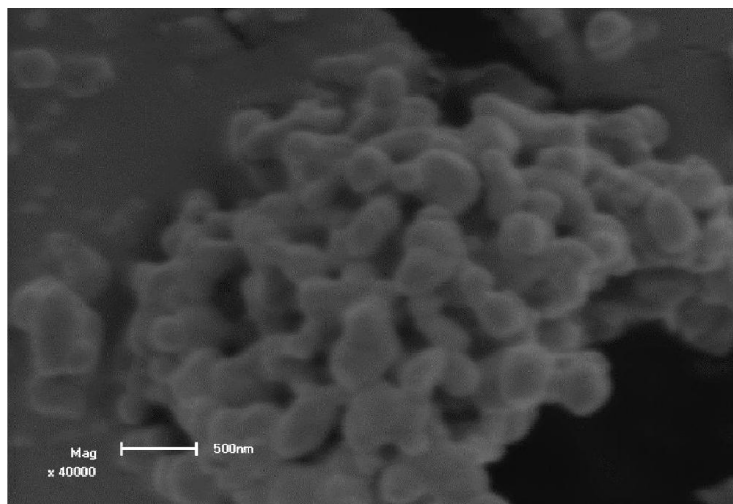
Figure 4.1: The SEM micrograph with 500 nm field view.
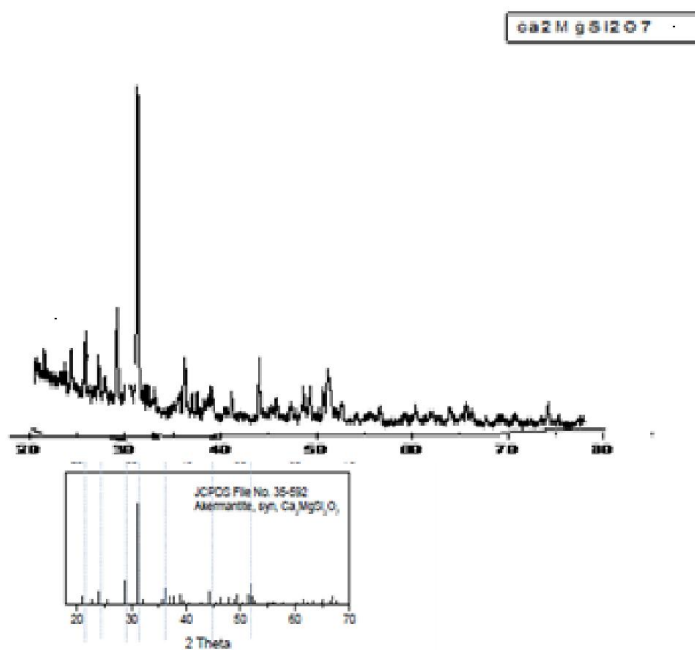
Figure 4.2 : The XRD patterns of Ca$_2$MgSi$_2$O$_7$: Ce^{3+}

PHOTOLUMINESCENCE PROPERTIES

Fig. 5a. Presents the photoluminescence emission spectra of 0.4 mol% Ce^{3+} doped Ca$_2$MgSi$_2$O$_7$ phosphor. A broad emission with maximum peak at 381nm was detected in the ultraviolet region of the visible spectrum. Fig. 5b shows the excitation spectrum of 0.4 mol% Ce^{3+} doped Ca$_2$MgSi$_2$O$_7$ phosphor. From the fig. indicated a excitation band in the region

from 220 nm -350 nm. This band is attributed to allowed transitions from the ground state to the crystal field splitting of the 5d level. Excitation spectra consist of several bands. From Fig. 5b, in excitation spectra, there are two excitation peaks at 267 and 315 nm were observed which is due to $4f^1$–$4f^0 5d^1$ transition. Usually, Ce^{3+} in one specific lattice site shows two emission bands corresponding to the transition from the lowest 5d excited state to $^2F_{5/2}$ and $^2F_{7/2}$ spin orbit split 4f ground states. Therefore, this spectrum is probably produced by the overlap of the emission bands from different emission Ce^{3+} Centers.
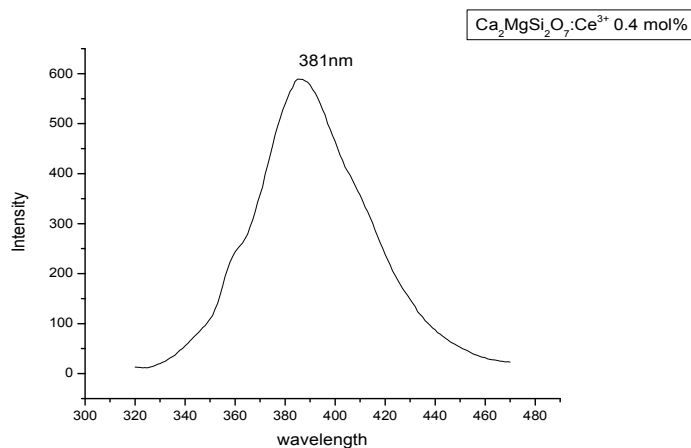
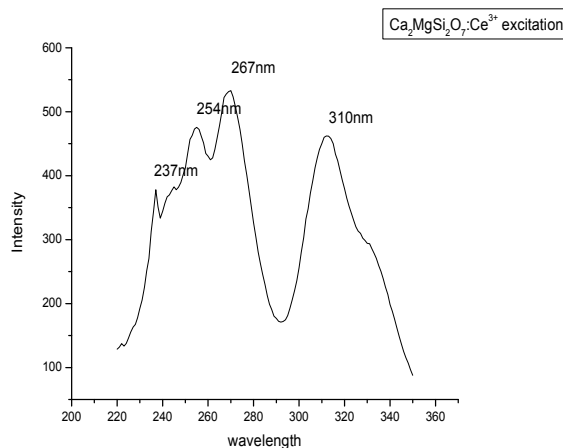

Fig. 5a : Emission Spectra of Ce³⁺ Ca₂MgSi₂O₇ phosphor.

Fig. 5b : Excitation Spectra of Ce³⁺ Ca₂MgSi₂O₇ phosphor.

Thermo-luminescence studies

Thermoluminescence anaylsis was used to investigate the electron trap distribution within the material, from which the energy required to thermally stimulate the electrons from an electron traps is used to determine the depth of the electron traps [24]. Fig 6 . Shows the TL

glow curve of $Ca_2MgSi_2O_7$ with 0.4 mol% Ce^{3+} for 1, 3, 5, 7 and 10 min UV irradiation. Prominent glow peaks found at 293.87°C respectively for all the UV exposure time. Here TL intensity increases with increasing the UV exposure time and the optimized time of UV is 5min UV exposure where maximum TL glow curve intensity was found. The calculation of kinetic parameters such as activation energy (E) in eV as well as the frequency factor in s^{-1} was determined by initial rise method. The trap depth and frequency factor were calculated for optimized UV exposure (5min) of Ce^{3+} doped $Ca_2MgSi_2O_7$ phosphor come out to be 0.27 eV and 0.19 H_Z .
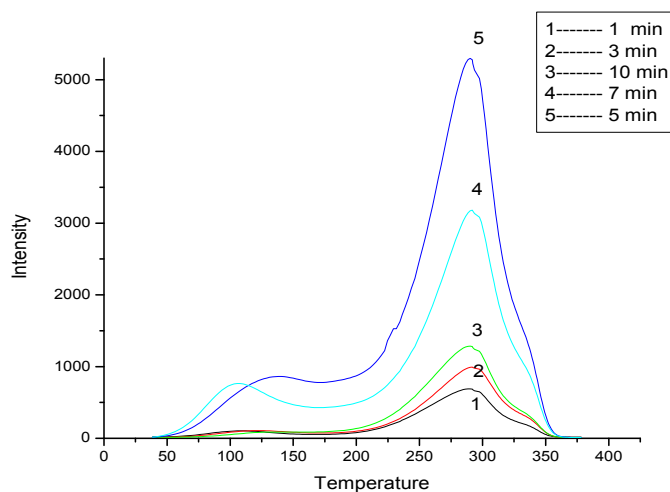
CONCLUSION

A new ultraviolet long after glow phosphor was prepared by doping $Ca_2MgSi_2O_7$ with 4 mol% Ce^{3+}. The XRD characterization shows that the prepared phosphor has crystalline size $\approx$ 20nm. It was observed that the akermanite $Ca_2MgSi_2O_7$ host promotes blue emission due to presence of a single emission center. The depth of the electron trapping centers and frequency factor that lead to phosphorescence were approximated to be 0.27 eV and 0.19H_Z .

ACKNOWLEDGEMENT

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