Structural & Thermal Investigation Studies of Synthesized Cerium Doped Akermanite Phosphor

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Abstract:
Here, we reported that the TL characteristics of rare earth Ce doped $Ca_2MgSi_2O_7$ phosphor using conventional high temperature solid-state reaction technique at the constant furnace temperature 1200^0C. It was further characterized by XRD (x-ray diffraction), for confirmation of phase purity, and also characterized by Thermoluminescence reader for thermal properties. The synthesized material has shown tetragonal crystal structure with single phase. We have observed the TL glow curve situated at 131.25^0C which reveals that the TL intensity is maximum for 15 minutes UV-irradiation time for Ce dopant ions. The synthesized phosphor displays potential application as a long persistent phosphor as well as better TL material.

Keywords: X-ray diffraction (XRD), Solid-State Reaction, $Ca_2MgSi_2O_7:Ce^{3+}$, Thermo-luminescence (TL).

INTRODUCTION

Each day, technological advances at an astounding pace that may people find consider beyond understanding. Research in the material sciences has risen in the modern era of technological advancements. The level of competition as well as curiosity is rising as increasing investigators and researchers endeavour to broaden and develop novel concepts related to societal benefits and environment protection. We are to demonstrate that the most rapid growing domains of material science as a luminescent tool to great support for efficient technologies. In modern times, every aspect of technological advancement in these fields such as search for novel thermoluminescent material and long persistent phosphor applications indicate the fast track towards achievement. An intriguing and significant role for long persistent materials is played in the rapid development of the lighting industries and technologies.

Mellites are a diverse group of substances with a typical structural formula: $A_2X^1Y_2^2O_7$ [where A = Ba, Sr, Ca; X^1 = Mg, Zn, Cu, Mn, Co; and Y^2 =Ge, Si] [1]. Different rare earth doped $Ca_2MgSi_2O_7$ was prepared by solid-state reaction technique under weak reduction atmosphere [2]. $Ca_2MgSi_2O_7$ phosphor have been broadly investigated from the manufacturing purpose because it is clearly indicating to better qualities of product sample, stability, energy consumed, abundant and relatively inexpensive [3,19]. Over the last 15 years, silicate-based rare earth (RE)-ion-doped phosphors have attracted a great deal of interest [4] because of their excellent properties, e.g., high thermal and chemical stability in natural surroundings, cheaper, excellent water resistance and strong absorption in the near UV region [5] high brightness, long persistency, non-toxic and environmental capability. Ce^{3+} ions are expected to substitute Ca^{2+} lattice site in the host crystal lattice ($Ca_2MgSi_2O_7$) because the ionic radii of Ce^{3+} and Ca^{2+} ions are 1.034Å and 1.12Å, respectively, and match closely. Ce^{3+} does not replace Mg^{2+} and Si^{4+} ions because the ionic radius

of Mg^{2+} (0.89Å) & Si^{4+} (0.40Å) are far smaller than that of Ce^{3+} ions [6]. Cerium [Ce^{3+}] rare-earth ions could not only be trap centre but also perform as luminescence-centre. In this present work, the result of XRD study, this phosphor revealed its tetragonal, akermanite structure with a space group P$\overline{4}$2$_1$m. In this TL study, the sample exposed for 15minutes produces the best TL intensity at 131.25°C temperature and exhibits a single TL glow curve peak. The synthesized $Ca_2MgSi_2O_7$: Ce^{3+} (CMS: Ce) phosphor is a more effective and superior TL phosphor for long persistent applications. In this work, high temperature solid state reaction technique was used to prepare CMS: Ce phosphor using H_3BO_3 as a flux. The structural property of CMS: Ce powder sample was characterized by powder X-ray diffraction (XRD) and thermal property was also performed on the basis of thermo-luminescence (TL) glow curve peak.

EXPERIMENTAL PROCEDURE

Solid-State Synthesis

Traditionally, phosphors are synthesized in powder form by different procedures involving crushing, grinding, ball milling, sol-gel, microwave process, combustion synthesis, co-precipitation and high temperature conventional solid-state reactions, Thermal decomposition and Flame synthesis technique etc. Among these methods, the most popular method is solid state reaction technique. This method has shown their potential as an important route for material synthesis, because sample prepared using this technique have good luminescence and very better morphology also. This technique can provide superior luminescent intensity and better long-persistent features in comparison of the same phosphor synthesized via other synthesis techniques.

Material Synthesis

The $Ca_2MgSi_2O_7$: Ce^{3+} sample was prepared by conventional high temperature solid-state reaction technique. The initial chemical reagents were utilized as $CaCO_3$ (99.99%), MgO (99.99%), $SiO_2.H_2O$ (99.99%) and rare earth oxide CeO_2 (99.99%) and boric acid (H_3BO_3) was also utilized as a flux in very small quantity. The raw chemical reagents were weight stoichiometrically and mixed thoroughly grind in an agate mortar pestle, then sintered under a weak reducing atmosphere (i.e., using activated charcoal) at 1200°C for approximately 3.30 hours after being held in a programmable muffle furnace. The furnace's heating and cooling rates were both set at 5°C per minute. Additional grinding, which produces fine powder, was used to create the final $Ca_2MgSi_2O_7$: Ce^{3+} phosphor. For further characterization study, the synthesized phosphor was placed in a sealed container.

The reagents' chemical reaction is,

$$2CaCO_3 + MgO + 2SiO_2.H_2O + CeO_2 \rightarrow Ca_2MgSi_2O_7: Ce + 2H_2O (\uparrow) + 2CO_2 (\uparrow) + O_2 (\uparrow) (1)$$
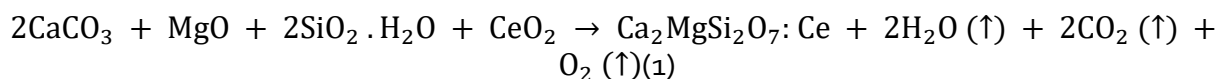
Material Characterization

Samples are weighed using Shimadzu ATX 224 single pan analytical balance and the samples are synthesized in a high temperature digital muffle furnace. The crystalline structure, size and phase composition of the sample are examined by Bruker D8 advanced X-ray diffractometer and Cu − K_α radiation with a wavelength of (λ =1.5405 Å), where X-rays are generated and operated at 40KV/40mA voltage and current values respectively. The TL spectra are recorded using Nucleonics make TL reader (model I 10091). All tests were carried out under the same conditions, and it was found that the outcomes were repeatable. Every measurement was made at room

temperature.

RESULT AND DISCUSSIONS

X-Ray Diffraction (XRD) Analysis

This material characterization technique was widely utilized to identify the phase composition, structure and their crystallinity. In Fig.1, the XRD-pattern of synthesized $Ca_2MgSi_2O_7$: Ce^{3+} phosphor have well matched from standard JCPDS data file (#77-1149) [7]. The XRD pattern were collected in the range of 10°<2θ<60°.
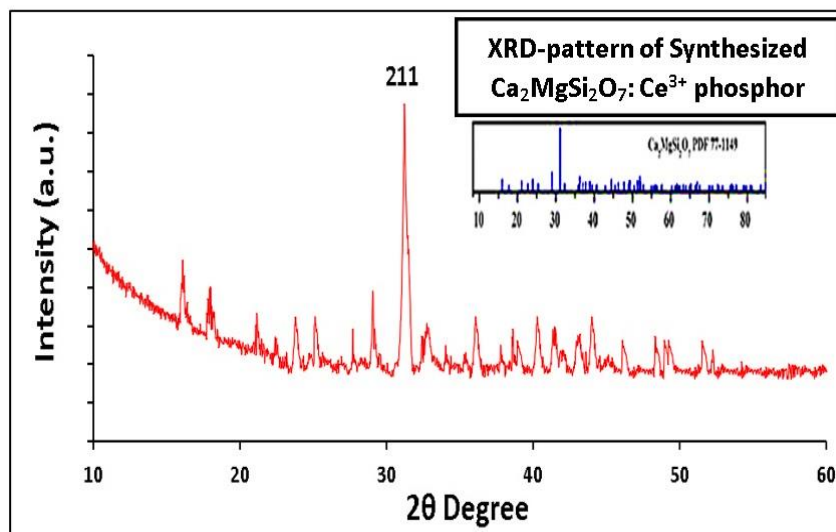

Figure 1: XRD-pattern of synthesized $Ca_2MgSi_2O_7$: Ce^{3+} phosphor

The layered compound formed by this crystal structure, which belongs to the melilite group. The cell parameters were a = b = 7.8071 Å, c = 4.9821 Å & α = β = γ = 90° [8]. Therefore, Cerium [Ce^{3+}] ions have expected to occupy the Ca^{2+} sites in the host. We note that the structure of this phosphor was not altered by the addition of rare earth doped ions. The doped Ce^{3+} ions did not change significantly the lattice structure of the host. XRD analysis also confirmed the produced phosphors' phase development. Here, the phase structure of the synthesized sample are exhibits akermanite type structure which belongs to the tetragonal crystal symmetry with space group $P\bar{4}2_1m$.

Crystallite/Particle Size (D) & Crystal Lattice Strain (ε)

The crystallite size (D) of the synthesized $Ca_2MgSi_2O_7$: Ce^{3+} phosphor is calculated as 44.26 nm, for (211) peak using Debye-Sherrer equation. Debye–Scherrer formula [9] is represented as: $D = k\lambda/\beta Cos\vartheta$. The crystal lattice strain of the synthesized $Ca_2MgSi_2O_7$: Ce^{3+} phosphor is calculated as 0.28nm. The crystal lattice strain induced broadening in the powder material were calculated via the following mathematical relation as: $\varepsilon = \beta/4 tan\vartheta$. Where K is the Scherrer constant having value 0.94, k is wavelength of incident X-ray, β is the FWHM of the peaks and θ is the corresponding Bragg's diffraction angle as well as **ε** is the crystal lattice strain.

Thermoluminescence (TL) Analysis

Thermo-luminescence (TL) is the phenomenon of light emission upon heating a material, which has been previously excited. All types of radiations, such as gamma rays, X-rays, alpha rays, beta rays and light rays can 'excite' a material, but to widely different extents [10]. The long afterglow characteristics of thermo-luminescence phosphor, also known as persistent luminescence, are

extremely useful in a variety of applications, including emergency signs, bio- imaging, and brightness on dark roads. The development of novel TL materials demonstrates a brand-new and rapidly expanding field of application for research in the fields of physics, medicine, mineral production, archaeological dating, forensic science, and radiation dosimetry [11].
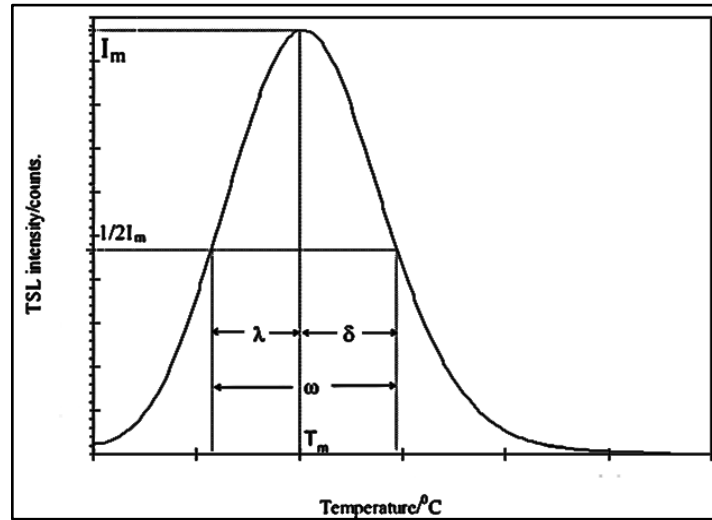

Figure 2: An illustration of a typical thermoluminescent light curve utilizing the peak shape approach.

Calculation of Kinetic Parameters

The TL glow peaks is highly isolated from the others, the experimental technique such as peak shape method [Fig.2] is appropriate to determine kinetic parameters. The TL kinetic parameters such as activation energy [E], order of kinetics [b], and frequency factor [S] for the prominent glow peak of sintered phosphors were calculated with the help the peak shape method. In order to determine the kinetic parameters of TL glow curves, Chen's empirical formula was used. It is clearly depending on the peak shape of TL glow curve [12].

Fig. 3 shows the TL glow curve of $Ca_2MgSi_2O_7$: Ce^{3+} phosphor for fixed 15min UV radiation times. In the present case, the TL intensity increases with increasing irradiation time up to 15min and then decreases over time because, at a particular time, the population of trapped charge carriers in a metastable state reaches a maximum value. From the TL glow curve of synthesized $Ca_2MgSi_2O_7$: Ce^{3+} phosphor, it was observed that single broad peak exists at 131.25°C temperature. The mechanism of recombination of de-trapped charge carriers with their counterparts is called as the order of kinetics [b]. The order of kinetics for glow peak of $Ca_2MgSi_2O_7$: Ce^{3+} phosphor can be determined via calculating geometrical factor μ_g from the mathematical relation as follows:

$$\mu_g = \frac{\delta}{\omega} = \frac{T_2 - T_m}{T_2 - T_1} \tag{2}$$

where T_m is the optimum peak temperature, T_1 and T_2 are temperatures at half intensity on the ascending and descending parts of the glow peak, respectively, [$\omega = T_2 - T_1$], the high temperature half width [$\delta = T_2 - T_m$] maxima (FWHM). The geometric factor is to differentiate between first and second order TL glow peak. [μ_g = 0.39-0.42] for the first order kinetics; [μ_g = 0.49-0.52] for the second order kinetics and [μ_g = 0.43-0.48] for the mixed order kinetics [13-15].
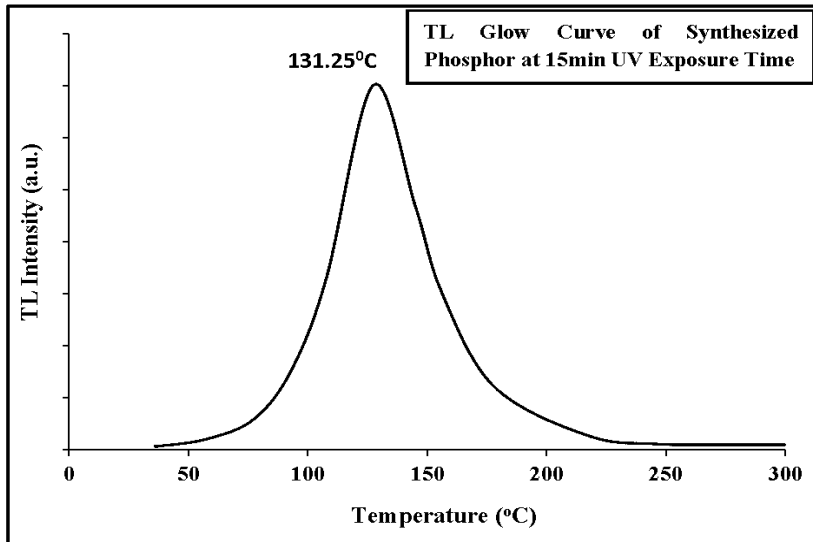
Figure 3: TL glow curve of synthesized $Ca_2MgSi_2O_7$: Ce^{3+} phosphor

The μ_g of the single peak was calculated and found to be 0.49, respectively, which are close to the value for the second-order peak (0.49-0.52). This shows that the single band is second-order peak. The result indicates that, after the carriers from the traps corresponding to the band was released, the probability of retrapping carriers is increased in comparison with that of the first-order case [14].

We used the following equation to estimate the depth of the traps, E:

$$E_\alpha = C_\alpha \left(\frac{kT_m^2}{\alpha}\right) - b_\alpha(2kT_m) \tag{3}$$

where k is the Boltzmann constant. The relationship between the frequency factor s and the depth E of the trap is given by

$$\frac{\beta E}{kT_m^2} = s \left[1 + (b-1)\frac{2kT_m}{E}\right] \exp(-E/kT_m) \tag{4}$$

where β is the heating rate, b is the order of the kinetics, which is 2 in this case. The trap parameters of depth E, and frequency factor S at the temperature of room temperature are given in the Table 1, calculated according to eqns 2–4.

Table 1: TL kinetic parameters of Synthesized $Ca_2MgSi_2O_7$: Ce^{3+} Phosphor

UV Exposure Time	Peak temperature T_m/°C	Trap Depth E(eV)	Frequency factor (S/s)
15min	131.25	0.66	3.80×10^{10}

Fig 3. represent that the effect of 15min UV exposures on the $Ca_2MgSi_2O_7$: Ce^{3+} phosphor and all TL parameters are calculated in Table 1. Corresponding the Activation Energy (E) and Frequency factor (s⁻¹) were calculated is 0.66eV and 3.80×10^{10}s⁻¹ respectively. Trap depth/Activation energy calculated as 0.66eV, which supports the fact that the sample show higher amount of persistency in its thermoluminescence property [15]. Sakai et al. and Mashangva et al. were reported that an appropriate trap depth (0.65-0.75 eV) is necessary for materials to display long persistence characteristics [16,17]. So, the trap density of synthesized materials is

appropriate for long afterglow properties. In our case of phosphor, the activation energy is found 0.66eV respectively, which indicates that a better long persistency and superior thermoluminescent intensity. It is highly favorable properties for application as long persistency.

CONCLUSIONS

$Ca_2MgSi_2O_7$: Ce^{3+} phosphor was well synthesized using the conventional high temperature solid-state reaction technique under a weak reducing atmosphere (i.e., using activated charcoal). Crystal phase structure was identified by XRD and the thermal properties were investigated by TL reader. The XRD analysis revealed that the compound is single crystalline phase $Ca_2MgSi_2O_7$: Ce^{3+} phosphor with tetragonal, akermanite structure with a $P\bar{4}2_1m$ phase group, which is confirmed through JCPDS #77-1149. The particle size of synthesized phosphor varies between 35 and 52 nm with an average value of 44.26 nm and crystal lattice strain is calculated as 0.28nm. In TL analysis, single broadband glow curve peak was observed at 131.25°C. It is very clear from TL spectra that second order kinetics, which supports the probability of re-trapping released charge carriers before recombination process. The value of the activation energy or trap-depth was found to be 0.66eV. Thus, it is concluded that this phosphor exhibits excellent thermal stability, indicating that it is highly favourable properties for application as long persistent properties and as a better TL material.

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