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Influence of doping and annealing temperature on the structural and optical properties of $Mg_2SiO_4:Eu^{3+}$ synthesized by combustion method

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ABSTRACT

This paper presents the structural and optical properties of europium doped magnesium orthosilicate nanophosphor prepared by combustion method and further annealed at varying temperatures. The structural and optical properties were investigated by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscope (FESEM), High resolution Transmission electron microscope (HRTEM), Diffuse Reflectance Spectra (DRS) and Photoluminescence spectra (PL) together with decay time. The XRD results confirmed the phase formation of Mg_2SiO_4. FESEM and TEM results indicated spherical particles in nanometer size. Photoluminescence spectra of $Mg_2SiO_4:Eu^{3+}$ nanophosphors exhibited five groups of peaks $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions. Intensity parameters (Ω_2 Ω_4) and other radiative properties such as radiative transition probability, total radiative transition probability, radiative life time, branching ratio and stimulated emission cross-section were calculated using Judd- Ofelt theory. The lifetime measurement indicates a decreasing trend up to 5 mol% of Eu^{3+} concentration.

1. Introduction

Silicate based materials play a mandatory role in terms of fundamental and technological importance owing to their special characteristics such as water and chemical resistivity and visible light transparency. Silicate family has been widely used as a host due to several merits, such as facile synthesis, stable crystal structures, excellent long term stability and environment friendly characteristics [1]. Among the silicate family Forsterite (Mg_2SiO_4) is a member of olivine family with orthorhombic crystal structure with Mg^{2+} on an octahedral site [2]. The Forsterite has been received attractive material due to some important properties such as high melting point, good mechanical properties, massive electrical and refractory characteristics, chemical stability even at high temperature, bioactivity, biocompatibility, low electric conductivity, low dielectric constant, low dielectric loss, high surface area, low thermal expansion and excellent insulating temperature even at high temperature [3–7]. Therefore, the Forsterite has entered into the merchant application in variety of industrial areas e.g. refractory industry, advanced technologies such as solid oxide fuel cells (SOFC), electronics as insulator working at high frequencies, microwave integrated circuits (MIC) biomedicine and luminescent technology [8–11].

From the last many decades the trivalent rare earth doped materials have been a great deal of attraction as the luminescent materials due to their various optical applications such as in photonic devices, optical displays, site specific bio analysis, broad absorption solar cells and white LEDs [12]. Among rare earth ions, Eu^{3+} has been a tremendous choice as a dopant ion owing to its abundant transition from the excited level $^5D_0$ to the ^7F_J (J = 0,1,2,3 and 4) levels of the $4f^6$ configuration which are used in colour television display and mercury free lamp [13,14]. The electric – dipole transition ($^5D_0 \rightarrow {}^7F_2$) at 617 nm are highly hypersensitive, which is highly sensitive to the symmetry of Eu^{3+} ions in the host lattice while, the magnetic – dipole transition ($^5D_0 \rightarrow {}^7F_1$) at 593 nm are allowed, which is insensitive to the symmetry environment of rare earth ion. Moreover, it has been a great candidate for red phosphors; materials inclusive with Eu^{3+} ions demonstrate superior colour purity than those with **a** broad emission band. Because of the spin and parity forbidden *f-f* transition of the Eu^{3+} ion, exciting through sensitizer other than Eu^{3+} may be a great expected way to increase the energy absorption efficiency [15]. It is

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well known that Eu^{3+} has a $4f^6$ configuration, only one more electron needs to achieve half field $4f^7$ configuration, which is relatively stable half field compared to partially filled configuration. When Eu^{3+} is connected to the O^{2-} ligand, there is a probable chance of electron transfer from O^{2-} to Eu^{3+} to form $Eu^{2+} - O^-$ (Simply Eu − O). Under this, a broad absorption band between 240 and 270 nm depending on the host is created which is called charge transfer band, and this band shifted depending on the particle size of the host material and environment of Eu^{3+}. Rare earth doped Mg_2SiO_4 phosphors existing some attractable applications such as X-ray imaging, long lasting phosphors, light emitting display and environment monitoring etc.

Variety of synthesis routes such as solid state, sol-gel, co-precipitation and hydrothermal have been employed for synthesizing the silicate phosphors. So far all the silicate phosphors have been synthesized above 1200 °C by solid state reaction route [16]. Further sol-gel route requires longer duration and expensive precursors. Among all above mentioned routes low temperature combustion has found a growing attention owing to the wide range of advantages such as the choice of a wide variety of fuel, high purity product, simple experimental set up, low temperature and shorter reaction time. Further, this route makes use of heat energy liberated by the redox exothermic reaction at a relatively low igniting temperature between oxidizer and fuels.

In the new millennium, there has been renaissance in the study of nanomaterials, which has found wide range of applications owing to their unique physical, chemical, electrical, mechanical, magnetic and optical properties. In recent years, researchers have been attracted towards silicate based phosphors due to their stable crystal structure, and high physical and chemical stability. Rare earth activated silicate based compounds have been highly explored as the optical materials in WLED application due to their full spectrum of blue lighting and excitation in the near UV range. White light emitting diodes (WLEDs) are the promising candidates to be the next generation lighting device as a substitute to conventional incandescent and fluorescent lamps due to its various advantages such as high energy efficiency, durability, reliability and environmental friendly. Operating efficiency has been improved regularly by the researchers where they are replacing halogen lamp in traditional mono-chrome lighting application such as traffic light and taillights and incandescent lamps [17].

In the present study, we have successfully synthesized Mg_2SiO_4:Eu^{3+} by low temperature combustion method. Structural and optical characterization of Mg_2SiO_4:Eu^{3+} samples were done for 1–7 mol% of Eu^{3+} doping. The samples were annealed at 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C and 1200 °C to systematically investigate the effect of annealing temperature and different doping concentration of Eu^{3+} ion on the structural, morphological and optical properties of the prepared samples. The changes in luminescence behaviour with doping concentration and varying annealing temperature have been discussed in length. Further, we have calculated the intensity parameters and various other radiative properties such as transition probabilities, radiative life time, branching ratio, stimulated emission cross-section, asymmetric ratio using Judd-Ofelt theory from the luminescence data for optical applications. The photoluminescence emission intensity of $^5D_0 \rightarrow {}^7F_2$ transition of Mg_2SiO_4: Eu^{3+} is compared to those of commercial Y_2O_2S: Eu^{3+} red phosphors.

2. Experimental details

2.1. Material synthesis

In the present study the Eu^{3+} doped Mg_2SiO_4 samples have been prepared by Low temperature combustion method using magnesium nitrate hexahydrate [$Mg(NO_3)_2 \cdot 6H_2O$], silicon dioxide [SiO_2], urea [NH_2CONH_2] and Eu_2O_3 as starting materials. The stock solution of europium nitrate [$Eu_2(NO_3)_3$] was prepared by dissolving Eu_2O_3 in HNO_3. Undoped Mg_2SiO_4 samples were prepared by mixing all raw materials $Mg(NO_3)_2 \cdot 6H_2O$, SiO_2, and NH_2CONH_2 in a molar ratio of 1:0.5:0.25 with the proper amount of deionised water. The complete solution was taken in a 100 ml beaker and stirred at temperature 80 °C till the gel is formed. After that gel was taken in alumina crucible and introduced into the preheated muffle furnace maintained at 500 °C for 5 min. For Eu^{3+} doping, $Eu_2(NO_3)_3$ solution was mixed in different molar concentration with the mixture of $Mg(NO_3)_2 \cdot 6H_2O$, SiO_2 and NH_2CONH_2 before stirring. The obtained powder was further annealed at different temperatures from 600 °C to 1200°C.

2.2. Experimental techniques

X-ray Diffraction patterns of prepared samples were recorded at room temperature in the wide range of Bragg-angle 2θ (10°–80°) using BRUKER D8 FOCUS XRD measuring instrument with Cu-K_α target (λ = 0.15406 nm) at the scanning rate 0.3 **S**ec per step. Fourier transform infra-red spectroscopy (FTIR) of samples were carried out in the range of 400–4000 cm^{-1} by using the measuring instrument spectrum RXI spectrometer made by Perkin Elmer in KBr pellet technique. Field emission scanning electron microscope (FESEM) measurements were done with the help of 55 Supra (Germany) FESEM measuring instrument. High resolution transmission electron microscope (HRTEM) studies of prepared samples were carried out using JEOL JEM -2100 HRTEM measuring instrument to examine the particle size and surface morphology. The photoluminescence studies of prepared samples were carried out using Hitachi Fluorescence spectrometer F-2500 in the range of 220–800 nm while the Ultra Violet Visible studies of the samples were done via CARRY 5000 Spectrophotometer. The decay kinetics were studied using Cary Eclipse Fluorescence Spectrophotometer.

3. Results and discussions

3.1. Structural properties

3.1.1. XRD studies

The XRD patterns for the confirmation of the formation of undoped and doped Mg_2SiO_4 compounds are depicted in Fig. 1(a). All the peaks are well in agreement with the standard JCPDS card no. 85-1364 and is found to have orthorhombic crystal structure having space group P_{bnm}-62. There was an additional peak at 2θ = 43 °C which is periclase (MgO) phase indicated by the star mark in the XRD patterns. The periclase phase is in agreement with the JCPDS card no. 75-1525. R naik et al., A. saberi et al. and M. Ghahari et al. also discussed the periclase phase in the XRD pattern [14,18,19]. The values of hkl of the most prominent peaks are shown in the XRD graph. The lattice parameters of the unit cell of the material are shown in Table 1. The strongest peak found at 2θ = 36.78° corresponds to the plane (112) for all samples. There was no diffraction peak found for Eu_2O_3 (2θ = 29.49°) or other impurities for different concentration which indicates that Eu^{3+} ions are perceptibly uniformly mixed and doped in the host lattice in Mg^{2+} sites. The percentage difference between doped and substituted ions should not exceed 30% for a perfect doping, which was calculated by using the formula:

$$D_r = \frac{R_m(CN) - R_d(CN)}{R_m(CN)} \quad (1)$$

where CN is co-ordination number (9 for both Eu^{3+} and Mg^{2+}), R_m