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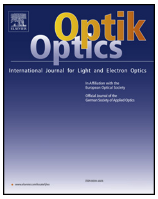

Original research article

Investigation of ultraviolet emitting Gd doped $Sr_2MgSi_2O_7$ phosphors

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ABSTRACT

This article deals with the ultraviolet (UV)-emitting gadolinium (Gd)-doped strontium magnesium disilicate ($Sr_2MgSi_2O_7$) phosphors. A series of the Gd-doped $Sr_2MgSi_2O_7$ phosphors were prepared using a sol-gel method. The powders were well characterized using the X-ray powder diffraction (XRPD) and scanning electron microscope (SEM) techniques. The emission measurements upon a specific UV-light excitation (273 nm) showed the emission characteristics of the Gd^{3+} that are due to the ${}^6P_{J/2} \rightarrow {}^8S_{7/2}$ transition. EPR spectra of the prepared samples indicated the presence of Gd^{3+} ions in low symmetry sites in this sample.

1. Introduction

In the last several years, ultraviolet (UV) radiation has been widely used in a variety of applications such as the production of vitamin D3, insect traps, induction sterilization and disinfection, photochemical reactions, and psoriasis treatment [1–4]. UV radiation is generally divided into the following three categories: UVA, UVB, and UVC. For the preparation of UV-emitting phosphors, the most suitable activators reported are Ce^{3+}, Gd^{3+}, Pr^{3+} and Pb^{2+} ions [5–8]. Among the UV radiations, the narrowband (NB) UVB (311–315 nm) is known to be effective in the treatment of skin diseases and disorders [9,10]. The Gd^{3+} ion has been extensively studied in a number of host lattices [11–14]. The emission of the Gd^{3+} in the range of 311–315 nm is due to the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition, and it is useful as an activator in a variety of the host lattices that can be used as the NB-UVB-emitting phosphor for phototherapy applications. Singh et al. [15] reported a new UVB emission from a Gd^{3+}-activated barium zirconate ($BaZrO_3$) phosphor. Shimizu et al. [16] studied the phase formation and UV luminescence of Gd^{3+}-doped perovskite-type yttrium scandium oxide ($YScO_3$). Huang et al. [17]'s report describes luminescence investigation on UV-emitting rare-earth (RE)-doped phosphors for which synchrotron radiation was used. Pathak et al. [18] studied the NB-UVB emission from Gd-activated yttrium gallate ($Y_3Ga_5O_{12}$) nanogarnets.

Further during the last decade, phosphors based on the alkaline earth silicates and doped with RE ions and transition metal ions (TMIs) have attracted much attention in the photoluminescence (PL) research due to their excellent thermal and chemical stability and high brightness values [19–22]. $Sr_2MgSi_2O_7$ belongs to the melilite family and its crystal structure is the tetragonal-akermanite type [23]. The melilites form a large group of compounds that are characterized by the general formula $A_2BSi_2O_7$, (A = calcium [Ca],

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strontium [Sr], barium [Ba]; B = magnesium [Mg], zinc [Zn]), where A is the alkaline earth and B is the transition metal, and the tetragonal-akermanite-type crystal structures of both are the most common [24,25].

The divalent europium (Eu^{2+}) and trivalent dysprosium (Dy^{3+}) doped $Sr_2MgSi_2O_7$ is well known as an afterglow phosphor and has been reported by several research groups [26–28]. Li et al. [29] reported two-color emissions regarding the codoped $Sr_2MgSi_2O_7$:Eu^{2+}, Tb^{3+} with respect to UV light-emitting diodes (LEDs). Zhai et al. [30] investigated the properties of a red-emitting $Sr_2MgSi_2O_7$:Eu^{3+} phosphor that had been prepared using a gel-combustion method, with the assistance of microwave. Tam et al. [31] reported on the synthesis and optical properties of red/blue-emitting $Sr_2MgSi_2O_7$:Eu^{3+}/Eu^{2+} phosphors for a white LED. Sahu et al. [32] studied the luminescence properties of the $Sr_2MgSi_2O_7$:Eu^{2+}, Ce^{3+} phosphor that had been prepared using the solid-state-reaction method.

The powerful electron paramagnetic resonance (EPR) technique provides information on the nature of systemic electron spins. The EPR investigations of Gd^{3+} ions in the host lattices are very interesting and have received much attention due to the Gd^{3+} EPR signals, which are very sensitive to the local symmetry. The EPR spectrum of the Gd^{3+} can easily be recorded at room temperature, and this spectrum provides useful information about the oxidation state and the site occupancy of this ion in the host structure.

The sol-gel process is one of the versatile methods for the preparation of phosphor materials. This technique does not require very high temperatures for the synthesis of phosphor materials. An organic component that is involved in the sol-gel process influences the reaction kinetics and physical properties of the resultant hybrid materials. Considering these points, UVB-emitting $Sr_2MgSi_2O_7$:Gd^{3+} was prepared in the present study using a sol-gel method. A detailed investigation of the $Sr_2MgSi_2O_7$:Gd^{3+} phosphors was then carried out using spectroscopic methods such as X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), electron spin resonance (ESR), and photoluminescence (PL).

2. Material preparation and analysis

A series of $Sr_2MgSi_2O_7$:Gd_x ($x = 0.01 \le x \le 0.11$) samples were prepared using a citrate-based sol-gel method. For the synthesis, Sr nitrate ($Sr[NO_3]_2$), Mg nitrate hexahydrate ($Mg[NO_3]_2 \cdot 6H_2O$), silicon dioxide (SiO_2), citric acid, and Gd nitrate hexahydrate ($Gd[NO_3]_3 \cdot 6H_2O$) were used as the raw materials. The details of the sample composition and the starting materials are given in Table 1. The stoichiometric amounts of the $Sr(NO_3)_2$, $Mg[NO_3]_2 \cdot 6H_2O$, fumed silica, and $Gd[NO_3]_3 \cdot 6H_2O$ were dissolved in 10 ml of distilled water under stirring. After a few minutes, 10 mol of the citric acid (molar ratio of the citric acid/metal ion = 2:1) was added to the previously mentioned solution and the stirring was continued for 1 h to produce a complete homogeneous solution. The obtained transparent homogeneous solution was dried in an oven to obtain a dried gel. Then, the resultant gel was sintered in a furnace at 400 °C for 2 h. Finally, the obtained black-color residual powder was ground using a mortar and pestle, and then it was annealed at 1000 °C for 3 h to obtain the final white-color powder. The resultant white-color powder was used for further characterization.

The X-ray powder diffraction (XRPD) patterns of the samples were recorded using the Miniflex-II diffractometer (Rigaku, Japan), Cu-Kα radiation ($\lambda = 1.5406$ Å) was used as the X-ray source, and the XRPD patterns were taken with the scan rate of 5°/min in the 2θ range of 10–80°. The morphological details were obtained using the S-3400 scanning electron microscope (SEM) of Hitachi (Japan). The PL measurements were carried out at room temperature (RT) on the RF-5301PC spectrofluorophotometer (Shimadzu, Japan) equipped with a xenon-flash lamp. The EPR spectra of the sample were recorded using the FE1X ESR spectrometer (Jeol, Japan) in the X-band frequencies with a field modulation of 100 kHz.

3. Results and discussion

3.1. Crystal-structure and crystallite-size analyses

The XRPD patterns of the $Sr_2MgSi_2O_7$:Gd_x ($x = 0.01 \le x \le 0.11$) samples are shown in Fig. 1, where most of the diffraction peaks are in accordance with those of $Sr_2MgSi_2O_7$ in terms of the Joint Committee on Powder Diffraction Standards (JCPDS-card no. 75-1736), thereby confirming the tetragonal structure. A small number of peaks were not identified and are indicated by "*." The XRPD patterns of the Gd^{3+}-doped $Sr_2MgSi_2O_7$ show that the dopant did not affect the main structure, and this is probably due to their relatively low concentrations in the host lattice. The crystallite size was calculated from the main XRPD diffraction peak through the application of the well-known Scherrer equation, as follows:

Table 1
Detailed information of the sample composition and the starting materials.

composition	Starting materials				
$Sr_2MgSi_2O_7$:$Gd_{0.01}$	Sr = 0.8464 g	Mg = 0.5128 g	Si = 0.2400 g	C.A = 3.8420 g	Gd = 0.0090 g
$Sr_2MgSi_2O_7$:$Gd_{0.03}$	Sr = 0.8464 g	Mg = 0.5128 g	Si = 0.2400 g	C.A = 3.8420 g	Gd = 0.0270 g
$Sr_2MgSi_2O_7$:$Gd_{0.05}$	Sr = 0.8464 g	Mg = 0.5128 g	Si = 0.2400 g	C.A = 3.8420 g	Gd = 0.0451 g
$Sr_2MgSi_2O_7$:$Gd_{0.07}$	Sr = 0.8464 g	Mg = 0.5128 g	Si = 0.2400 g	C.A = 3.8420 g	Gd = 0.0631 g
$Sr_2MgSi_2O_7$:$Gd_{0.09}$	Sr = 0.8464 g	Mg = 0.5128 g	Si = 0.2400 g	C.A = 3.8420 g	Gd = 0.0812 g
$Sr_2MgSi_2O_7$:$Gd_{0.11}$	Sr = 0.8464 g	Mg = 0.5128 g	Si = 0.2400 g	C.A = 3.8420 g	Gd = 0.0992 g

Sr = $Sr(NO_3)_2$, Mg = $Mg(NO_3)_2 \cdot 6H_2O$, Si = SiO_2, C.A = Citric acid, Gd = $Gd(NO_3)_3 \cdot 6H_2O$.