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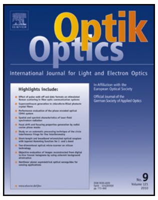

Original research article

Photoluminescence properties of green emitting $CaY_2Al_4SiO_{12}:Tb^{3+}$ garnet phosphor

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ABSTRACT

The photoemission properties of a microcrystalline-powder Tb^{3+}-doped $CaY_2Al_4SiO_{12}$ garnet phosphor were studied. The microcrystalline materials were obtained using the sol–gel method that yields chemically homogeneous and microparticle-sized powders. X-ray powder diffraction (XRPD) and scanning electron microscope (SEM) analyses were used to reveal the crystallinity, crystal structure, and surface morphology of the prepared $CaY_2Al_4SiO_{12}:Tb^{3+}$ garnet phosphor. The samples showed a green-emission characteristic at around 544 nm with an excitation at 271 nm. A concentration quenching was observed with the increasing of the Tb^{3+} concentration. The effect of the Tb^{3+} doping and the photoluminescence properties were also investigated, leading to the proposal of a feasible interpretation by the authors.

1. Introduction

Presently, tricolor (red/green/blue)-emitting phosphors that are excited by near-ultraviolet (NUV) light-emitting diode (LED) chips have become the center of attention. Moreover, rare-earth-doped phosphors have attracted immense attention due to their excellent luminescent properties and corresponding applications in the lighting industry [1–5]. The notable narrowband-emission properties of lanthanides like dysprosium (Dy^{3+}), terbium (Tb^{3+}), europium (Eu^{3+}), and thulium (Tm^{3+}) ions have been utilized in the development of energy-efficient phosphors [6]. Among these, the Tb ions with the $^5D_4$–$^7F_5$ transition are used as the activator in particular hosts because their characteristic intense-green emission is suitable for many industrial lamp applications [2]. In commercial-phosphor devices, the most common way to obtain white light is by combining blue gallium nitride (GaN)-based LED chips with the yellow phosphor of yttrium aluminum garnet ($Y_3A_{l5}O_{12}$):cerium (Ce^{3+}), or YAG:Ce^{3+} [7]. Thousands of researchers throughout the world are working on the YAG:Ce^{3+} phosphor due to its efficiency and garnet-type crystal structure.

The general stoichiometric formula of the garnet structure is $\{A\}_3\,[B]_2\,(C)_3O_{12}$, where A, B, and C are the dodecahedral, octahedral, and tetrahedral coordinates, respectively [8]. The crystal chemical formula for the $CaY_2Al_4SiO_{12}$ garnet can be written as $\{CaY_2\}$ sites that are the dodecahedrons, $[Al^{3+}]$ sites that are the octahedrons, and (Al_2Si) sites that are

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

Sample compositions	Sample code	Starting materials					
$CaY_2Al_4SiO_{12}$:$Tb_{0.005}$	CYA1	Ca = 0.2361 g	Y = 0.7660 g	Al = 1.5 g	Si = 0.0600 g	C.A = 3.0736 g	Tb = 0.0021 g
$CaY_2Al_4SiO_{12}$:$Tb_{0.015}$	CYA2	Ca = 0.2361 g	Y = 0.7660 g	Al = 1.5 g	Si = 0.0600 g	C.A = 3.0736 g	Tb = 0.0065 g
$CaY_2Al_4SiO_{12}$:$Tb_{0.03}$	CYA3	Ca = 0.2361 g	Y = 0.7660 g	Al = 1.5 g	Si = 0.0600 g	C.A = 3.0736 g	Tb = 0.0130 g
$CaY_2Al_4SiO_{12}$:$Tb_{0.05}$	CYA4	Ca = 0.2361 g	Y = 0.7660 g	Al = 1.5 g	Si = 0.0600 g	C.A = 3.0736 g	Tb = 0.0217 g
$CaY_2Al_4SiO_{12}$:$Tb_{0.07}$	CYA5	Ca = 0.2361 g	Y = 0.7660 g	Al = 1.5 g	Si = 0.0600 g	C.A = 3.0736 g	Tb = 0.0304 g
$CaY_2Al_4SiO_{12}$: $Tb_{0.09}$	CYA6	Ca = 0.2361 g	Y = 0.7660g	Al = 1.5 g	Si = 0.0600 g	C.A = 3.0736 g	Tb = 0.0391 g

(Ca = $Ca(NO_3)_2{\cdot}4H_2O$), Y = $Y(NO_3)_3{\cdot}6H_2O$), Si = SiO_2, Al = $Al(NO_3)_3{\cdot}9H_2O$), C.A = Citric acid, Tb = $Tb(NO_3)_3{\cdot}5H_2O$).

the tetrahedrons [9]. As host compounds, garnet-type structures are sound host-structure candidates due to a number of favorable qualities such as low synthesis temperatures and high chemical- and physical-stability values. Nevertheless, a dearth of attention remains in terms of the luminescent property of the Tb^{3+}-doped $CaY_2Al_4SiO_{12}$ garnet-type phosphor. This paper investigates a green-emitting $CaY_2Al_4SiO_{12}$:Tb^{3+} phosphor that is excited by ultraviolet (UV) LEDs. The structure and photoluminescence (PL) properties of the $CaY_2Al_4SiO_{12}$:Tb^{3+} were explored extensively. In addition to this, the Tb^{3+} concentration was optimized to obtain a highly efficient phosphor. The results show that $CaY_2Al_4SiO_{12}$:Tb^{3+} may be considered as a potential green-emitting phosphor for UV-based white LEDs.

2. Materials preparation and analysis

A series of $CaY_2Al_4SiO_{12}$:Tb (CYA1–CYA6) phosphors were prepared by using the sol–gel method. All of the starting materials were of a high purity and were used without further purification. The details of the sample compositions, sample codes, and starting materials are given in Table 1. In accordance with the typical synthesis, the stoichiometric quantities of the starting materials such as calcium nitrate tetrahydrate ($Ca[NO_3]_2{\cdot}4H_2O$), yttrium nitrate hexahydrate ($Y[NO_3]_3{\cdot}6H_2O$), aluminum nitrate nonahydrate ($Al[NO_3]_3{\cdot}9H_2O$), silicon dioxide (SiO_2), terbium nitrate pentahydrate ($Tb[NO_3]_3{\cdot}5H_2O$), and citric acid, where the citric-acid/metal-ion molar ratio is 2:1, were firstly dissolved in 10 ml of deionized water under stirring at 500 rpm. A transparent aqueous solution was obtained after a 1-h stirring. The resultant transparent solution was kept at 110 °C in an oven until homogeneous dried gels had formed. Then, the obtained dried gels were ground and sintered at 400 °C for 2 h in air. Finally, the resultant brown residual samples were fully ground and annealed at 1100 °C for 3 h in air.

The X-ray powder diffraction (XRPD) patterns of the samples were recorded using the Miniflex-II diffractometer (Rigaku, Japan), with the use of Cu-Kα radiation (λ = 1.5406 Å) as the X-ray source. 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) instrument (Hitachi, Japan). Photoluminescence (PL) measurements were carried out at room temperature using the RF-5301PC spectrofluorophotometer (Shimadzu, Japan) equipped with a xenon-flash lamp.

3. Results and discussion

3.1. Crystal-structure and particle-size analyses

The structure type and the phase purity of the synthesized samples were characterized using the conventional X-ray powder diffraction (XRPD) technique. The XRPD patterns of the $CaY_2Al_4SiO_{12}$:Tb (CYA1-CYA6) samples are shown in Fig. 1, along with a reference pattern of the $Y_3Al_5O_{12}$ (Joint Committee on Powder Diffraction Standards [JCPDS] File No. 33-0040). Most of the diffraction peaks that were observed for the samples are effective matches for the standard $Y_3Al_5O_{12}$ data, showing that the sample had crystallized into the garnet phase along with some of the secondary minor phases. The secondary minor phases belong to $Ca_2Al_2SiO_7$, as reported in the Ref. [10]. All of the XRPD patterns of the synthesized samples were indexed with the lattice constants.

It should be noted that the coupled heterovalent substitution of calcium (Ca^{2+}) + silicon (Si^{4+}) → yttrium (Y^{3+}) + aluminum (Al^{3+}) on the two sites led to only a number of insignificant changes of the $CaY_2Al_4SiO_{12}$ parameters. The XRPD analysis confirmed that all of the synthesized compounds containing the garnet phase. Furthermore, a minor amount of the Tb^{3+} doping did not significantly change the crystal lattice. The ionic radius of the Tb^{3+} (0.104 nm) is close to that of the Y^{3+} (0.119 nm), because the Tb^{3+} can be easily doped into the host lattice and substituted to the site of the Y^{3+} ions. The crystallite sizes of the samples were calculated from the XRPD data using the well-known Scherrer equation, as follows: $d = 0.9\lambda/\beta\cos\theta$, where d is the average grain size of the crystallites, λ is the incident wavelength, θ is the Bragg angle, and β is the full width at half maximum (FWHM) of the strongest diffraction (420) peak. The average crystallite size that was obtained using this method is in the range of 25–29 nm. The crystallite size and the FWHM for all of the samples are given in Table 2.

3.2. Scanning electron microscopy analysis

With the aim of investigating the morphology of the phosphors, SEM images of the $CaY_2Al_4SiO_{12}$:$Tb_{0.07}$ (CYA5) sample were taken. Fig. 2(a)–(d) portrays the highly agglomerated structure of the phosphor display, further confirming its perfect