Spectroscopic and photoluminescence properties of MgO:Cr^{3+} nanosheets for WLEDs

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ABSTRACT

This work explores the synthesis of nanocrystalline MgO:Cr^{3+} (1–9 mol%) nanophosphors via solution combustion route at 400 °C. The nanophosphors were well characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infra-Red (FTIR) spectroscopy. PXRD results confirm cubic phase and SEM micrographs indicate that the particles are highly porous and agglomerated. The TEM images show that the powder consists of spherical particles of size ∼5–15 nm. Upon 356 nm excitation the emission profile of MgO:Cr^{3+} exhibits an emission peak at 677 nm due to $^2E_g \rightarrow {}^4A_{2g}$ transition. It was observed that PL intensity increases with increase in Cr^{3+} concentration and highest PL intensity was observed for 3 mol% doped sample and afterward it decreases, attributed to concentration quenching. The resultant CIE chromaticity co-ordinates in the white region make the present phosphor highly useful for display applications and also for white light-emitting diodes (WLEDs).

1. Introduction

Rare-earth doped oxide phosphors have widely been investigated due to their several advantages over other phosphors. These phosphors have excellent thermal stability as a result they were extensively used in a variety of applications, namely lamp industry, color display screens, semiconductor light-emitting diodes, solid state lasers and X-ray medical radiography [1–4]. Even though several studies on rare-earth ions doped oxides were available in the literature [1,5,6], transition metal ions doped oxides were limited. Oxide compounds doped with transition metal ions continue to draw attention in view of their variety of applications. It was well known that impurities play an important role, because they can influence the properties of host materials. Therefore, the interest in achieving new photoluminescent materials and tunable

solid-state lasers were significantly promoted the study of transition metal (Mn, Fe, Cr, Co, etc.) doped phosphors [7–10].

Trivalent chromium (Cr^{3+}) was the most stable oxidation state, therefore widely used as a luminescent dopant and luminescence sensitizer in various host materials. Chromium a low cost activator, which can provide deep color and bright luminescence. For instance, the color of many natural and synthetic gemstones like ruby, emerald, alexandrite, etc. were due to Cr^{3+} ions. On this account, Cr^{3+} was subject of numerous spectroscopic and luminescence investigations. Further, Cr^{3+} doped systems were used in modern technologies, like tunable solid-state lasers [11], high temperature sensors [12] and high-pressure calibrate [13]. Cr^{3+} ions more effectively interact with lattice and have high luminescent quantum efficiency as dopants in several host materials. Recently, significant efforts have been devoted by several research groups on the synthesis and characterization of various Cr^{3+} doped host materials [14,15].

In the development of Cr^{3+} activated luminescence materials, MgO was an excellent host because Cr^{3+} ions can easily substitute Mg^{2+} ions in the host lattices because of crystal field strength

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around Cr^{3+} ions [16]. For red and NIR photoluminescence, trivalent chromium ions (Cr^{3+}) favorable emitting center due to its wide-range emission from 650–1400 nm, including the R-line narrow band emission around 680 nm from the $^2E \rightarrow {}^4A_2$ transition and the broadband emission from the $^4T_2 \rightarrow {}^4A_2$ transition depending on the host lattice and the crystal field strength [17].

The common WLED (white light emitting diode) device composed of chips that emit blue light and phosphors that can be excited by blue light to emit other colors. Since WLED devices were characterized by their high emission intensity, the quality of phosphors was vital to the performance of WLED device. WLEDs can save about 70% of the energy and do not need any harmful component in comparison with the conventional light sources. Therefore, WLEDs have a great potential to replace them and are considered as next generation solid state lighting devices [18]. Further, Light emitting diodes (LEDs) have been a subject of considerable interest due to their quick response time, environmental benefits, lower energy consumption and wide optical and electrical applications [19]. Taking these points into consideration, we have synthesized Cr^{3+} doped MgO through a relatively low-temperature initiated, self-propagating and energy saving solution combustion method. The combustion process has distinguished itself as a safe, instantaneous and capable to produce direct single phase compounds. The structural preparations of the synthesized phosphors have been studied by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) techniques. The optical properties of Cr^{3+} ions in MgO phosphor have been investigated to obtain information about crystal field parameters, and the local site symmetry of the doped ion.

2. Experimental

2.1. Synthesis

The powdered samples of Cr^{3+} (1–9 mol%) doped MgO phosphor was synthesized by via combustion method. For this, metal nitrates were used as the oxidizer, and glycine was employed as fuel. The stoichiometric composition of the mixtures was calculated based on the total oxidizing and reducing valences of the oxidizer and combustion fuel [20]. The molar ratio of the metal nitrates (oxidizers) to glycine (fuel) was controlled at 1:1.75. Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), Chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) and glycine [NH_2CH_2COOH (analar)], were used as starting chemicals and were dissolved in distilled water and the concentration of the Chromium ions was varied in the range 1–9 mol% in relative to Mg content. After mixing the precursors in a Petri dish and then introduced into a pre-heated muffle furnace at $\sim 400 \pm 5\,°C$. The solution underwent dehydration, and finally decomposed with the evolution of gases (oxides of nitrogen and ammonia). The mixture was frothed and swelled, forming foam that ruptured with a flame. The combustion process was completed in not less than 5 min. The voluminous foamy combustion product was grinded well and used for characterization and PL studies.

2.2. Characterization

The crystalline nature of the powder sample was characterized by PXRD using X-ray diffractometer (Shimadzu) (operating at 50 kV and 20 mA by means of Cu Kα (1.541 Å) radiation with a nickel filter at a scan rate of 2 deg min^{-1}). The surface morphology of the product was examined by scanning electron microscopy (SEM) Hitachi table top (SEM) (Model TM 3000). Transmission electron microscopy (TEM) analysis was performed on a (JEOL, JEM 2100) (accelerating voltage up to 200 kV, LaB$_6$ filament). FTIR

studies of the samples were performed with a Perkin Elmer FTIR spectrophotometer (Spectrum-1000). Photoluminescence studies were made using Horiba, (model Fluorolog-3) spectrofluorimeter at RT using 450 W xenon as excitation source and Fluor Essence™ software is used for spectral analysis.

3. Results and discussion

Fig. 1 shows the PXRD patterns of undoped and Cr^{3+} (1–9 mol%) doped MgO samples without any further calcinations. All the X-ray diffraction peaks of the samples at 2θ, 35.57 (1 1 1), 42.59 (2 0 0), 62 (2 2 0), 74.28 (3 1 1), 78.34 (2 2 2) were well indexed to pure single cubic phase and matched with JCPDS card No. 4-829 with space group $fm-3m$ (2 2 5) [21]. The lattice parameter and unit cell volume for cubic MgO was estimated for (2 0 0) plane. The estimated lattice parameter and unit cell volume are found to be 4.3 Å and 79.507 Å^3 respectively. From the analysis of PXRD, it was clear that the introduction of an activator (Cr^{3+}) did not influence the crystal structure but certainly modified the lattice parameters due to the difference in the ionic radius between the dopant and the substituted magnesium ion (the ionic radii of R^{3+}_{Cr} = 0.143 nm and R^{2+}_{Mg} = 0.072 nm). The average crystallite size (D) was estimated from the line broadening in X-ray powder using Scherrer's formula [22] $D = K\lambda/\beta \cos\theta$ [where, 'K'; constant, 'λ'; wavelength of X-rays, and 'β'; FWHM] is found to be in the range 5–15 nm. It was observed that, as the dopant concentration increases, the position of the main diffraction peaks shift to the lower angle side (Fig. 1 (b)) and the PXRD intensity decreases, which indicates that Cr^{3+} ions were strongly capped in to the crystal lattice of MgO. The Cr^{3+} ions doped into MgO matrix causes expansion of the unit cell resulting in tensile stress, as a result the PXRD peaks shifted toward higher angle side [23]. The peak shift and line broadening in PXRD profiles arises due to the presence of micro strain in nanophosphors.

Further, crystallite size was calculated in MgO:Cr^{3+} (1–9 mol%) nanoparticles prepared by combustion method was calculated using the W–H plots. $\frac{\beta \cos\theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\eta \sin\theta}{\lambda}$, where '$\varepsilon$'; the strain associated with the nanoparticles [24]. The above equation represents a straight line between '$4\sin\theta$' (x-axis) and '$\beta\cos\theta$' (y-axis) as shown in Fig. 2(a). The slope of the line gives the strain and intercept of this line on y-axis gives crystallite size (D). Nelson–Riley method [25,26] was also used to study size – strain parameters as shown in Fig. 2 (b). In this method crystallite size was described by a Lorentzian function and the strain profile by a Gaussian function [27]. Accordingly, we have $(d_{hkl}\beta_{hkl}\cos\theta)^2 = \frac{k\lambda}{D}(d_{hkl}\beta_{hkl}\cos\theta) + \left(\frac{\varepsilon}{2}\right)^2$, where k; constant that depends on the shape of the particles; for

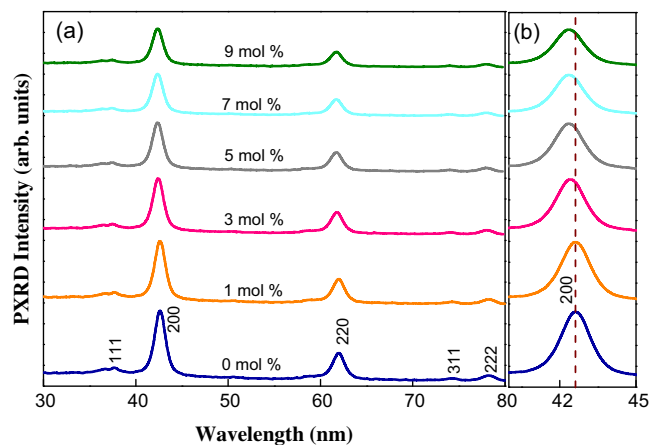**Fig. 1.** PXRD patterns of un-doped and Cr^{3+} doped MgO.