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Sol–gel synthesis and luminescence of undoped and Mn-doped zinc orthosilicate phosphor nanocomposites

J. El Ghoul [a,*], L. El Mir [a,b]

[a] Laboratoire de Physique des Matériaux et des Nanomatériaux Appliquée à l'Environnement, Faculté des Sciences de Gabès, Cité Erriadh Manara Zrig, 6072 Gabès, Tunisie
[b] Al Imam Mohammad Ibn Saud Islamic University (IMSIU), College of Sciences, Departement of Physics, Riyadh 11623, Saudi Arabia

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ABSTRACT

Zn_2SiO_4 and Zn_2SiO_4:Mn particles embedded in SiO_2 host matrix prepared by sol gel method under supercritical conditions of ethyl alcohol in two steps. Were prepared by a simple solid-phase reaction under natural atmosphere at 1200 °C after the incorporation of ZnO and ZnO:Mn nanoparticles, respectively, in silica monolith. In the case of SiO_2/Zn_2SiO_4 nanocomposite, the powder with an average particle size of 80 nm shows a strong luminescence band centred at around 760 nm in the visible range. In addition, the PL spectrum for the SiO_2/Zn_2SiO_4:Mn nanocomposite showed that a dominant peak at 525 nm appeared, which originated from the $^4T_1$–$^6A_1$ transitions of Mn^{2+} ions. The luminescence properties of nanocomposites were characterized by emission and excitation spectra as well their dependencies of upon temperature and power excitation density.

1. Introduction

Over the last decade, the luminescent properties of silicate based inorganic phosphors have been extensively investigated [1–4]. Among the silicates, one of the promising candidates so far is manganese doped zinc silicate (Zn_2SiO_4:Mn) phosphor [5–8], which has been used in cathode ray tubes, fluorescent lamps, and plasma display panels due to its high luminescence efficiency and chemical stability. Although researches about the effect of Mn^{2+} ions on luminescent properties have been performed, most of the studies concerning the amount of Mn^{2+} ions substituting for Zn^{2+} ions have chemically focused on the quantities of Mn^{2+} ions in Zn_2SiO_4. Since the amount of Mn^{2+} ions doped into the crystal lattice of Zn_2SiO_4 is closely related to the performance of $Zn_2SiO_4:Mn^{2+}$ phosphor such as decay time, color shift and concentration quenching, the determination of the quantities of Mn^{2+} ions in the crystal lattice is more essential. Furthermore, the site preference of Mn^{2+} ions is indispensible to advance the luminescent properties of green or yellow color-emitting phosphor.

It is well known that the luminescence properties of phosphor depend on its synthesis process. Usually, $Zn_2SiO_4:Mn^{2+}$ phosphors are prepared by solid-state reactions [9]. In solid-state reaction, it requires high-temperature process with long period of time. Therefore, agglomerated particles with irregular shape and large size are produced by the solid-state reaction method. Accordingly, grinding and milling process, which is harmful to the luminescent properties, are necessary to reduce the particle size desired for the application [10]. In recent years, many new preparation approaches have been proposed, including spray pyrolysis route, sol–gel method, chemical vapor synthesis and hydrothermalmethod [11–14]. Among these methods, the hydrothermal synthesis has great advantage, such as better distribution of metal ions, controllable morphology and lower cost [15–18]. Therefore, it is imperative to develop a simple synthesis route in order to potentially overcome most of these difficulties in commercialization [19]. It is in this context that are situated the work of our team. It comes to new protocols find nanoparticle synthesis by the sol–gel technique for various chemical and physical applications [20,21]. Our objective in this work is, in a first step the in-situ synthesis of luminescent nanoparticles of Zn_2SiO_4:Mn in a silica matrix whose objective is to increase the life of components and prevent contamination caused by the external environment. The sol–gel method has been confirmed to have more advantages in lowering the firing temperature, distributing the activator ions homogeneously and improving the emission efficiency for the powder phosphors [22,23].

In this study, the method is applied to prepare Zn_2SiO_4 and Zn_2SiO_4:Mn particles embedded in silica monolith by the same protocol of sol–gel method combined with a furnace firing [3,9] but using for the first time, manganese doped zinc oxide nanoparticles

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[*] Corresponding author. Tel.: +216 97 86 35 99; fax: +216 75 39 24 21.
E-mail address: ghoultn@yahoo.fr (J. El Ghoul).

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and studied the structural and optical properties of the obtained nanocomposites.

2. Experimental

2.1. Synthesis

The preparation of colloid suspension particles in silicate host matrix has been done in three steps. In the first one, nanocrystalline ZnO and ZnO:Mn aerogels were prepared by a sol–gel method under supercritical conditions of ethyl alcohol (EtOH) based on Omri et al. protocol [9,24], where the water for hydrolysis was slowly released by esterification reaction to control the size of the formed nanoparticles. In the second step, we have prepared ZnO and ZnO:Mn confined in silica aerogel according to the following process: 0.5 ml of TEOS was first dissolved in EtOH. Then, with constant stirring of the mixture of TEOS and EtOH, 0.44 ml of water and 30 mg of nanoparticles powder prepared in the first step were added. The whole solution was stirred for about 30 min, resulting in the formation of a uniform sol. The sols were transferred to tubes in ultrasonic bath where 100 ml of fluoride acid was added. The wet gel formed in few seconds. Monolithic and white aerogel was obtained by supercritical drying in EtOH as described in the first step. Finally, silica glasses containing Zn_2SiO_4 and Zn_2SiO_4:Mn particles were obtained after firing aerogel at 1200 °C for 2 h.

2.2. Characterizations

The crystalline phases of annealed samples were identified by X-ray diffraction (XRD) using a Bruker D5005 powder X-ray diffractometer using a Cu*K*α source (1.5418 Å radiation). Crystallite sizes were estimated from the Scherrer's equation [25].

$$G = \frac{0.9\lambda}{B\ \cos\ \theta_B} \tag{1}$$

where λ is the X-ray wavelength ($\lambda = 1.5418$ Å), θ_B is the maximum of the Bragg diffraction peak (rad) and B is the line width at half maximum.

Transmission electron microscopy (TEM, JEM-200CX) was used to study the morphology and particle size of the phosphor powders. The specimens for TEM were prepared by putting the as-grown products in EtOH and immersing them in an ultrasonic bath for 15 min, then dropping a few drops of the resulting suspension containing the synthesized materials onto TEM grid. The optical absorbance of the powders was determined using a Schimadzu UV-3101 PC spectrophotometer with integrating sphere in the wavelength range 200–2000 nm. For photoluminescence (PL) measurements, the 450-W Xenon lamp was used as an excitation source. The emitted light from the sample collected by an optical fiber on the same side as that of excitation was analyzed with a Jobin-Yvon Spectrometer HR460 and a multichannel CCD detector (2000 pixel). The photoluminescence excitation (PLE) measurements were performed on a Jobin-Yvon Fluorolog 3-2 spectrometer. The low temperature experiments were carried out in a Janis VPF-600 Dewar with variable temperature controlled between 78 and 300 K.

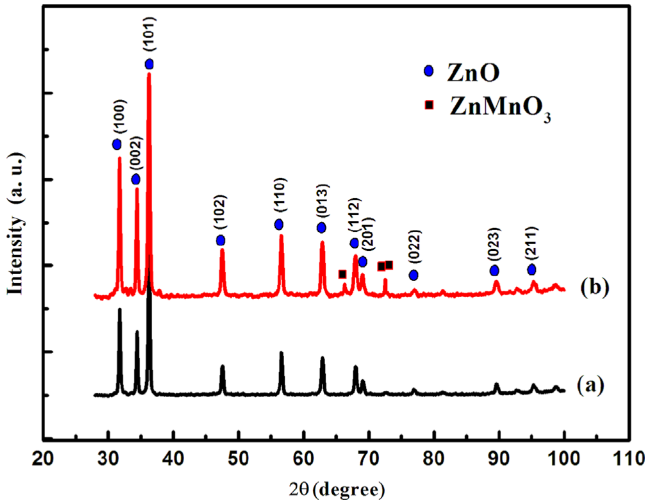

Fig. 1. X-ray diffraction pattern of the (a) undoped ZnO and (b) ZnO:Mn nanopowder.

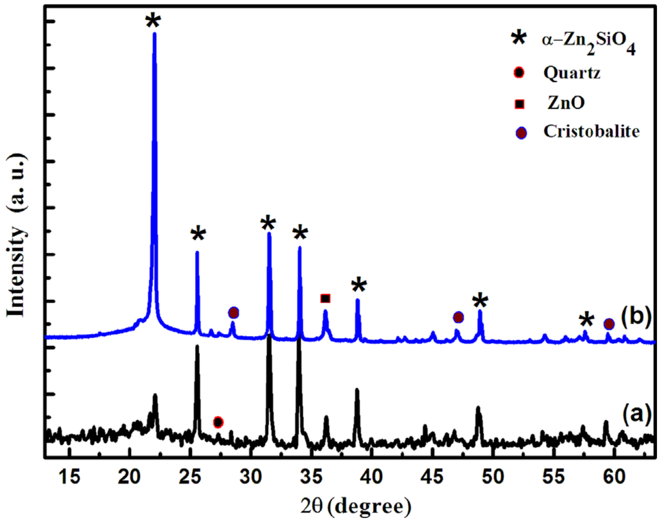

Fig. 2. X-ray diffraction pattern of the (a) SiO_2/Zn_2SiO_4 and (b) SiO_2/Zn_2SiO_4:Mn nanocomposite.

3. Results and discussion

3.1. Structural studies

The XRD spectra of undoped and Mn doped ZnO nanopwder have been presented in Fig. 1. In the case of undoped ZnO, we noticed the appearance of nine pronounced diffraction peaks at $2\theta = 31.50°$, 34.19°, 36.15°, 47.39°, 56.44°, 62.79°, 67.93°, 68.91°, 72.33°, 76.97°, 89.41° and 95.31° which can be attributed to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (0 1 3), (1 1 2), (2 0 1), (0 2 2), (0 2 3) and (2 1 1) planes of ZnO, respectively [26]. The obtained XRD spectra matched well with the space group $P6_3mc$ (1 8 6) (No. 36-1451) of wurtzite ZnO structure [24,26]. After doping of ZnO with manganese, in addition to the peaks corresponding to ZnO, one secondary additional phase were detected which can be attributed to $ZnOMn_3$, (JCPDS Card 37-1485). The lattice constants calculated from the XRD pattern, which are very close to ZnO ones, i.e., $a = 3.2498$ Å and $c = 5.2066$ Å. These results are in a good agreement with those obtained by El Ghoul et al. [26–28]. Due to the small size of the crystallites in the aerogel, the diffraction lines are broadened and are further found to depend on the Miller indices of the corresponding sets of crystal planes. For our samples, the (0 0 2) diffraction line is always narrower than the (1 0 1) line and the latter is narrower than the (1 0 0) line. After a correction for the instrumental broadening, an average value of the basal diameter of the cylinder-shape crystallites was found to be 14–22 nm, whereas the height of the crystallites was 23–30 nm.

Fig. 2 shows the X-ray diffraction patterns of SiO_2/Zn_2SiO_4 and SiO_2/Zn_2SiO_4:Mn nanocomposites treated at 1200 °C for 2 h in air. It is clear that all the diffraction peaks are in good agreement with