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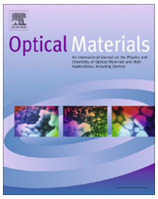

Sol–gel synthesis, structural and luminescence properties of MT-doped SiO_2/Zn_2SiO_4 nanocomposites

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ABSTRACT

The sol–gel method is used for the preparation of undoped, Mn and V-doped Zn_2SiO_4 particles embedded in SiO_2 host matrix. The phase purity and morphological features were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) investigations. The obtained SiO_2/Zn_2SiO_4 nanocomposite, exhibits a strong photoluminescence (PL) band centered at around 760 nm, attributed to energy transfer occurs from Zn_2SiO_4 particles to NBOHs interfaces defects. 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. In the case of SiO_2/Zn_2SiO_4:V, the PL reveals a band centered at about 540 nm attributed to the effect of the V^{5+} in the host matrix nanocomposite.

1. Introduction

In recent years, a great deal of interest has been focused on the fabrication and characterization of zinc orthosilicate (α-Zn_2SiO_4, willemite). Potential fields of application are, for example, optics and optoelectronics, pharmaceutics or biological and medical diagnostics [1–3]. Just like transition metal (TM) doped zinc orthosilicate are highly photostable, exhibit long luminescence lifetimes and narrow emission bands. However, the emission color is dependent on the particle size [4]. It can be adjusted by the choice of the host material and dopants and their combination. The luminescence intensity is dependent on the concentration of doping ions, the crystal structure of the host material, and the degree of crystallinity [5]. The high chemical stability and bright luminescent performance of these nanomaterials make them potentially suitable for biological labeling [3].

Traditionally, this phosphor is prepared by the solid-state reaction method, which involves a pulverizing process and subsequent high-temperature firing. The resulting Zn_2SiO_4:Mn powder phosphors are utilized as paints. However, it is difficult to obtain reliable intensity using such methods, probably because of inhomogeneous distribution of activator ions, phase separation and contamination of impurities. Therefore, recent investigations have addressed development of some alternative synthetic procedures for this phosphor, such as hydrothermal method [6] polymer pyrolysis [7] and sol–gel method [8,9]. Among them 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 [10,11]. Additionally, the sol–gel technology is suitable for deposition of thin amorphous and crystalline films, which have found extensive applications in many fields [12].

At present, Taghavinia et al. [13] used porous silicon as one of the starting materials and impregnated porous silicon layers with luminescent Zn_2SiO_4:Mn^{2+} particles. Porous silicon was directly involved in the reaction responsible for the formation of luminescent Zn_2SiO_4 phosphors. The phosphor particles were obtained inside a transparent porous body, making it possible to activate porous silicon layers with highly efficient phosphors [13]. Kang and Park used the colloidal solution method to fabricate spherical Zn_2SiO_4 phosphors with an optimal emission intensity that was 112% that of commercially available materials [14]. Although these chemical methods can be applied to produce fine particles with good luminescence, they have the shortcomings related to complex processing, difficulties in achieving controllability and mass production, and high cost [15–17].

In this study, the method is applied to prepare Zn_2SiO_4 (SZ), Zn_2SiO_4:Mn (SZM) and Zn_2SiO_4:V (SZV) particles embedded in

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silica monolith by the same protocol of sol–gel method combined with a furnace firing [4,18,19] but using for the first time, manganese and vanadium doped zinc oxide nanoparticles and studied the structural and optical properties of the obtained nanocomposites.

2. Experimental

2.1. Preparation

The preparation of colloid suspension particles in silicate host matrix has been done in three steps. In the first one, nanocrystalline ZnO, ZnO:Mn and ZnO:V aerogels were prepared by a sol–gel method under supercritical conditions of ethyl alcohol (EtOH) based on El Ghoul et al. protocol [4,8,9,20], 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, ZnO:Mn and ZnO:V 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 SZ, SZM and SZV 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 Kα source (1.5418 Å radiation). Crystallite sizes were estimated from the Scherrer's equation [21].

$$G = \frac{0.9\lambda}{B\cos\theta_B} \qquad (1)$$

where λ is the X-ray wavelength (λ = 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. 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 pixels). The photoluminescence excitation (PLE) measurements were performed on a Jobin–Yvon Fluorolog 3–2 spectrometer. The decays were analyzed by a PM Hamamatsu R928 and a scope Nicolet 400 with a time constant on the order of 1 ns. The low temperature experiments were carried out in a Janis VPF-600 Dewar with variable temperature controlled between 78 and 300 K.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows X-ray diffraction spectra obtained from the SZ (a), SZM (b) and SZV (c) nanocomposites treated at 1200 °C for 2 h in air. These spectra show the X-ray diffraction pattern corresponding to a well-developed willemite structure (α-Zn_2SiO_4, JCPDS No. 37-1485) [8,22]. The lattice constants calculated from the XRD pattern for the three samples are about a = 13.939 Å and c = 9.301 Å, which are very close to willemite α-Zn_2SiO_4 [4,18,23]. The peak signatures of hexagonal wurtzite ZnO were also observed. Therefore, the hexagonal ZnO and willemite Zn_2SiO_4 may coexist in the composite. However, at high temperature, the surface mobility of Zn and Si species is high enough, so they move and diffuse inside the porous body and contribute to the formation of zinc silica phase. The sharpness of the diffraction peaks indicates that the size of the crystalline particles is about 80 nm [8,18]. This result indicates that α-Zn_2SiO_4 has a rhombohedral structure [4]. It is clear that the crystalline phase is the most dominant one corresponding to the α-phase Zn_2SiO_4, in parallel we note the appearance of three other phases that correspond to ZnO, cristobalite and quartz [4]. Therefore, the hexagonal zinc oxide and willemite Zn_2SiO_4 coexist in the composite, this means that the solid reaction at higher temperature is not complete and the obtained composite is formed by very small ZnO nanoparticles covered by willemite Zn_2SiO_4 as a shell supported by SiO_2 as a host matrix. Average grain size (G) of the crystallites Zn_2SiO_4 varies from 50 nm to 80 nm, has been estimated using Scherrer's formula (1). However, Jiang et al. [22] predicted that the particle average size for the Zn_2SiO_4 nanopowder was 100 nm.

The TEM micrographs, HRTEM image and EDX analyzes of the SiO_2/Zn_2SiO_4 nanocomposites treated at 1200 °C for 2 h in air are shown in Fig. 2. The morphology of the sample is found to be nearly spherical in nature with the diameters ranging from 40 to 90 nm. It clearly shows that the average particle size is nanoscale and it is in accordance with the results of the XRD.

EDX analysis showed the presence of the elements Zn and Si. At high temperature at 1200 °C, Zn and Si species, move and diffuse inside the porous body to form Zn_2SiO_4 phase. In parallel, the HRTM image and the corresponding EDX analysis showed the presence of nanoparticles that correspond to ZnO in sample, such results is confirmed that the results obtained by XRD.

The TEM images corresponding to SZM (Fig. 3a) and SZV (Fig. 3b). The Zn_2SiO_4 colloid suspension is formed in silica host matrix with a particle size of about 70 nm. The EDX spectrum of the doped sample showed signals directly related to the dopants. Zn, Si and O appeared as the main components with low levels of Mn and V (Fig. 3). This confirmed the formation of SZM and SZV phases.

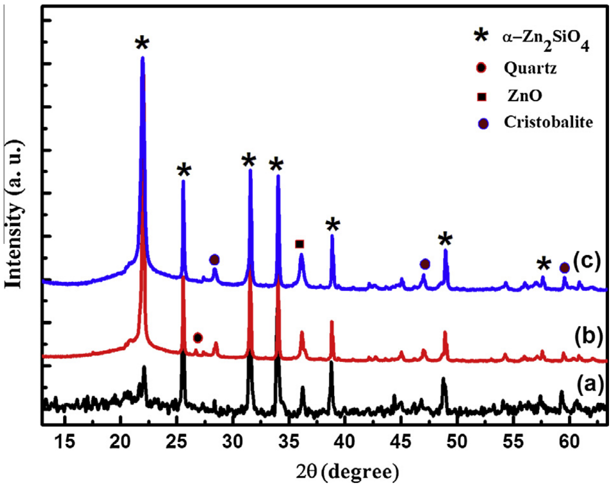

Fig. 1. X-ray diffraction pattern of the (a) Zn_2SiO_4, (b) Zn_2SiO_4:Mn and (c) Zn_2SiO_4:V nanocomposite.