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Effect of crystallographic phase on green and yellow emissions in Mn-doped zinc silicate nanoparticles incorporated in silica host matrix

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ABSTRACT

Silica host matrix reached by manganese-doped zinc silicate nanoparticles (SiO_2/Zn_2SiO_4:Mn) were in-situ synthesized by a sol–gel process. In our approach, we synthesis ZnO:Mn nanoparticles in supercritical conditions of ethanol. After the incorporation of these nanoparticles in silica host matrix, a heat treatment at 1200 °C and 1500 °C for 2 h was performed for the elaboration of SiO_2/Zn_2SiO_4:Mn nanocomposites. Then, these samples were characterized by various techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and photoluminescence (PL). These samples exhibit broad green and yellow PL bands depending on synthesis temperature. The SiO_2/Zn_2SiO_4:Mn prepared at 1200 °C exhibit a green emission centered at about 525 nm while the yellow emission centered at 575 nm resulted from SiO_2/Zn_2SiO_4:Mn prepared at 1500 °C. These two emissions are originated from internal transition in Mn^{2+} ion doped zinc silicate nanoparticles and the emission wavelength is correlated to the local crystalline field which is fixed by the crystallographic phase.

1. Introduction

Zn_2SiO_4:Mn, in recent years, is being one of the most investigated green emitting phosphors [1]. Important for color rendering, a host lattice of Zn_2SiO_4 containing Ti^{4+}, Tb^{3+} or Eu^{3+} dopant ions covers the blue, green, and red portions of the visible spectrum, respectively [2–4]. However, the luminescent properties of silicate-based inorganic phosphors have been extensively investigated [5]. Manganese-doped zinc silicate (Zn_2SiO_4:Mn^{2+}) is an phosphor widely used in plasma display panels (PDPs), cathode ray tube (CRT), tri-color lamps, color television and thin film electroluminescent devices because of its high luminescence efficiency, the purity of color, chemical stability and large color gamut [6–8]. In addition to the thermodynamically most stable α-Zn_2SiO_4 modification, β-Zn_2SiO_4 has been described as a luminescent material, too. The latter is known for yellow emission with an average wavelength of 570 nm [9]. El Mir et al. [10] showed that the β-phase Zn_2SiO_4:Mn^{2+} shows a yellow emission, and these results are consistent with results reported by Jiang et al. [5]. The crystal system was probably orthorhombic [11]. Pfeiffer and Fonda [12] have synthesized β-phase Zn_2SiO_4:Mn^{2+} which has a strong yellow emission (580 nm) under ultraviolet light, similar to the emission reported by Rooksby and McKeag [9]. In addition, to

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improve its physical, chemical, and photoluminescence properties, El Mir et al. [13] purposed an in-situ synthesis of luminescent nanoparticles of Zn_2SiO_4:Mn in silica host matrix. The mean idea of this protocol is to increase the lifetime of the components and prevent contamination caused by the external environment which gives more stability to β-phase.

2. Experimental details

2.1. Sample preparation

SiO_2/Zn_2SiO_4:Mn nanocomposites were prepared by sol–gel method according to El Mir protocol [10,14].

2.2. Characterization techniques

The crystalline phases of annealed powders were identified by X-ray diffraction (XRD) using a Bruker D5005 powder X-ray diffractometer using a Co K_α source (1.78901 Å radiation). Crystallite sizes (G, in Å) were estimated from the Scherrer's equation [15]:

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

where λ is the X-ray wavelength, θ_B is the maximum of the Bragg diffraction peak (in radians) and B is the linewidth at half maximum. The samples were also characterized using JEM-200CX transmission electron microscope (TEM). The photoluminescence (PL) setup has been described elsewhere [16].

3. Results and discussion

Powder X-ray diffraction (XRD) patterns of the SiO_2/Zn_2SiO_4:Mn nanocomposites were recorded in the range 2θ = 20–70° with a pitch = 0.02°. The XRD analysis of our nanocomposites Zn_2SiO_4:Mn in silica treated at different temperatures (900 °C, 1000 °C, 1100 °C and 1200 °C) for two hours in air, are shown in Fig. 1. We noticed the presence of willemite phase (α-Zn_2SiO_4, JCPDS Card 37-1485) with a particle size deduced from Scherrer's equation of about 74 nm. 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 two other phases of silica that correspond to cristobalite and quartz [6,17]. In addition, these analysis shows that the willemite phase begins to appear from 900 °C, and increasing heat treatment temperature promotes the crystallinity of nanocomposites and the diminution of the width at half height of the diffraction peaks. Otherwise, XRD patterns in Fig. 2 of SiO_2/Zn_2SiO_4:Mn nanocomposite annealed for 2 h at 1500 °C illustrate the presence of β-Zn_2SiO_4 (JCPDS No. 19-1479) as a crystalline phase [5,9,10] with a particle size of about 82 nm.

3.1. Surface morphology

To confirm the results obtained by XRD and to learn more about morphology of our samples, we performed an analysis by transmission electron microscopy (TEM). We conducted an observation (TEM) for the SiO_2/Zn_2SiO_4:Mn nanocomposites. At high temperature, ZnO particles aggregate and Zn and Si spices move and diffuse inside the porous body to form Zn_2SiO_4:Mn

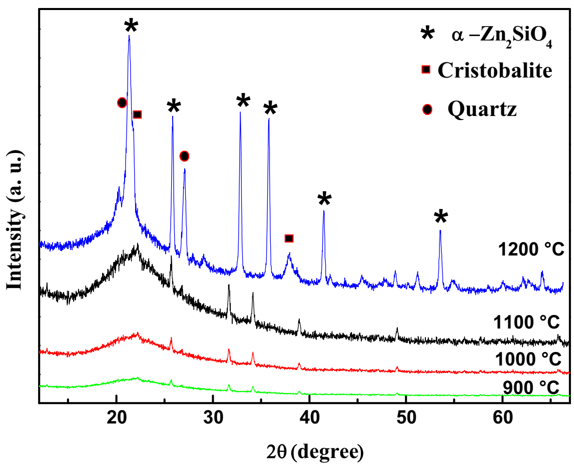

Fig. 1. X-ray diffraction pattern of the SiO_2/Zn_2SiO_4:Mn nanocomposite samples prepared at different temperatures.