



Structural, microstructural, optical, and dielectric properties of Mn²⁺: Willemite Zn₂SiO₄ nanocomposites obtained by a sol-gel method



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ABSTRACT

The synthesis of Zn₂SiO₄ doped with Mn²⁺ ions at different concentrations have been successfully achieved by a conventional sol–gel method. The structure and morphology of the obtained samples were characterized by XRD, FTIR, Raman spectroscopy, EDAX, and FE-SEM, TEM. The XRD results of Zn₂SiO₄ samples with different Mn concentrations showed no obvious differences from the willemite structure. The SEM and TEM results showed the ceramic powders are nanometer sized spherical grains spherical forms and EDAX results confirmed the successful doping of Mn²⁺ ions into Zn₂SiO₄ matrix. The optical and dielectric properties of Mn²⁺ ions doped Zn₂SiO₄ show an appreciable difference between the levels of Mn²⁺ doping. The luminescence spectra showed that 0.25mol% Mn²⁺ in Zn₂SiO₄ gives a maximum intensity *a* in the green emission corresponding to the ⁴T₁ (4G) → ⁶A₁ (6S) transition for tetrahedral-coordinated Mn²⁺ (weak crystal field) and at higher levels of Mn²⁺ doping the green band intensity decreases. The 0.25mol% Mn²⁺ in Zn₂SiO₄ also gives the highest ionic conductivity at 373 K. The dielectric constant (*ε'*), loss tangent (tan *δ*) and AC conductivity (*σ_{ac}*) properties as the function of frequency have also been analyzed and those are strongly dependent on Mn ion concentrations.

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1. Introduction

There has been a great deal of research on the synthesis and analysis of nanostructures inorganic luminescent powder phosphors for their potential applications in electronic display devices, coatings in lamps, cathode ray tubes, flat panel displays, electroluminescent, optoelectronic devices, radiation detectors in medical imaging systems etc. [1–4]. Furthermore, inorganic nanophosphors based on the rare earth and transition metals are receiving considerable attention in potentially novel applications [3–6]. Published results show the photoluminescence spectra of Mn²⁺ doped Zn₂SiO₄ phosphors is a result of 3d⁵ electrons in the Mn²⁺ ion acting as an activation center in the willemite structure. In particular, the transition from the lowest excited state to the

ground state, i.e. ⁴T_{1g} (⁴G) → ⁶A_{1g} (⁶S) transition, is directly responsible for the green light emission [7,8]. It is reported the luminescent intensity depends on the firing temperature and the heating time due to an increase in crystallinity being responsible for the increase in intensity of luminescence [9]. It should be noted that zinc silicate exists in three structural polymorphs. i.e. *α*-, *β*-, *γ*-Zn₂SiO₄ and it is the *α*-Mn-doped willemite, which gives green emission. The *β*-, and *γ*- forms are metastable phases which transform to *α* - (willemite) phase at high temperature [3]. The luminescence from *β*-Zn₂SiO₄: Mn phosphors is in the yellow region has a much longer decay time than that of *α*-Mn-doped willemite in the green emission [9,10]. Consequently synthesizing a pure *α*-Mn-doped willemite phase as the reliable green component to be used in the display devices is necessary.

Besides of these optical properties of Mn²⁺ ion, fundamental electrical properties understanding also very importance, because of conductivity and dielectric properties of ceramics are strongly dependent on frequencies and temperatures. Higher values of electrical resistivity could be achieved by doping suitable host matrices with proper divalent cations or by controlling their

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microstructures. However, the ultrafine particles are predominantly controlled by grain boundaries as barriers for electrons flow and as results of that, there is a reduction in eddy current losses [11]. Hence, study on such properties at different frequencies, temperatures and chemical compositions could provide vital information about the kind of additives required to obtain high quality materials for practical applications [12,13]. Moreover, dielectric properties of ceramics depend upon several factors including the method of preparation method, heat treatment, sintering conditions chemical composition, cation distribution and crystallite structure or size [14]. Hence, preparing homogeneous and nanostructure Mn-doped willemite phosphors by the sol–gel method with a suitably chosen molecular precursor is very significant.

The sol–gel technique has been considered a versatile procedure in the production of a wide variety of optical and dielectric materials. This is because it offers the possibility of controlling not only the size and uniform distribution of particles in host matrices at lower temperature but also their shape and so the sol–gel technique has a clear advantage over the other methods [15]. The properties of sol-gel derived products depend strongly on the precursor used hence preparing homogeneous and nanostructure Mn-doped willemite phosphor powder by sol-gel method with suitably chosen molecular precursor is important. Since, there exists no report in literature so far on the electrical properties of $\text{Mn}^{2+}:\text{Zn}_2\text{SiO}_4$. In the present study, the authors made an attempt to study different properties of $\text{Mn}^{2+}:\text{Zn}_2\text{SiO}_4$ nanocomposites at room temperature using XRD, FTIR, Raman, FE-SEM, EDAX, photoluminescence and dielectric spectroscopy techniques.

2. Experimental studies

2.1. Materials

All the chemicals used in the present work were analytical grade from Merck and Sigma- Aldrich. The precursors were TEOS (SiOC_2H_5)₄ (99% Aldrich) as SiO_2 source, zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) as ZnO source, and manganese nitrate as the source of Mn^{2+} ions, high pure ethanol (EtOH) has been used as the solvent with a 0.2 ml of HCl as the catalyst.

2.2. Preparation of $\text{Zn}_{2-x}\text{SiO}_4:x\text{Mn}^{2+}$ ceramic powders

Powders of $\text{Zn}_{2-x}\text{SiO}_4:x\text{Mn}^{2+}$ with $x = 0.00, 0.05, 0.25, 0.50,$ and 0.75 mol% were prepared by a sol–gel method [16]. Initially tetraethylorthosilicate (TEOS) and ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were weighed to give a 2:1 M ratio and these were separately dissolved in appropriate amounts of ethyl alcohol (EtOH) which each of these solutions were stirred for 15 min. The manganese nitrate was weighed to give 0.05, 0.25, 0.50 and 0.75 mol % and these were dissolved separately in double ionized (D.I.) water and then stirred for about 10 min. Then Zn and Mn nitrate solutions were mixed to give the required molarity and these were added solution were added to TEOS solution. Finally 0.2 ml HCl was added as a catalyst for hydrolysis of TEOS, after a few minutes of stirring, a clear and transparent solution was obtained, which was continuously stirred for about 12 h at a temperature around $\sim 75\text{--}80$ °C after which mixtures were cooled to room temperature and left to evaporate in air for 2 or 3 days to obtain transparent xero-gels. These were then heated in air at 120 °C for 12 h in order to remove any moisture present from the samples, after which the temperature was raised to 1000 °C for 2 h to give samples of $\text{Zn}_{2-x}\text{SiO}_4:x\text{Mn}^{2+}$ with $x = 0.00, 0.05, 0.25, 0.50,$ and 0.75 mol % nano phosphor powders.

2.3. XRD profile measurements

The phase identity of the phosphor powders was examined by X-ray diffraction (XRPD) (3003 TT SEIFERT) with $\text{CuK}\alpha$ ($\lambda = 1.5418$ Å) of radiation, in the 2θ range of $10\text{--}80^\circ$ with a scanning rate of 0.02° . The observed peaks were analyzed by using the appropriate Joint Committee on Powder Diffraction Standards (JCPDS) card. The crystallite size of the samples was calculated using full width at half maxima (FWHM) by using Scherrer's formula [17].

$$D_{\text{crystallite}} = \frac{k\lambda}{\beta(2\theta)\cos\theta} \quad (1)$$

Where D is the crystallite size, k is Scherer's constant which is dependent on shape, here 0.96 is used, $\lambda = 1.5406$ Å (X-ray wavelength), and β was full width at half maxima at diffraction angle 2θ . D is the average diameter of the crystallite size. All the XRD peaks were indexed and lattice constants (a and c) and cell volume of unit cell for each concentration were respectively calculated by the following relations [16,18].

$$\sin^2\theta = \frac{\lambda^2}{3a^2} (hk + k^2) + \left(\frac{\lambda^2}{4c^2}\right) l^2 \quad (2)$$

here λ is the X-ray wavelength, a and c are the lattice constants and (h, k, l) are the corresponding Miller indices.

$$V = a^2c \sin 120^\circ \quad (3)$$

2.4. Raman measurements

Raman spectra were obtained from compacted powder pellets using a Confocal Raman Microscope (LabRAM HR 800, Horiba Jobin Yvon SAS, France) equipped with a 532 nm Nd: YAG laser (Torus Laser, Laser Quantum, France) with laser power 50 mW, 2 scans with a $50\times$ LWD air-dry visible objective (NA = 0.50 WD = 10.6 mm lieu Microsystems of Model BX 41), which eliminates the problem of sample fluorescence and photo-decomposition and attached with a Filetiyar multichannel CCD detector. Each Raman spectra were measured in the range $100\text{--}1200\text{ cm}^{-1}$ and $1200\text{--}1800\text{ cm}^{-1}$, with a spectral resolution of $0.35\text{ cm}^{-1}/\text{pixel}$ with a 1800 gr/mm grating at the confocal pinhole was a set to 400 nm. Lab Spec software was used to control the Raman system and for data acquisition and data storage.

2.5. FT-IR spectral analysis

FTIR was used to obtain information about the bonding coordination of the different compositions, the spectrum of powder sample was recorded on a Thermo Nicotet Avator 360 FT-IR spectrophotometer in the range $400\text{--}4000\text{ cm}^{-1}$ using KBr pellet.

2.6. Morphologies and elemental analysis

Morphologies of the samples were carried out on a field emission scanning electron microscope (JEOL JEM-2100) operating at 200 kV voltage. The grain sizes and structures confirmations were carried out on a Transition Electron Microscopy (Phillips TECH-NAIFE12). The elemental analyses of the samples were determined by EDAX. EDAX was carried out on an Oxford instrument detector on the SEM over the range 0–20 keV.

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