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Effects of dopant concentrations and firing temperatures on decay kinetics of manganese doped willemite nanopowders

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ABSTRACT

Nanocrystallline willemite, $Zn_{2-x}Mn_xSiO_4$ ($0.5 \le x \le 5$ mol%), doped with variable concentration of divalent manganese ions, phosphor powders were prepared using the simple wet-chemical sol–gel method combined with furnace firing at 800, 900, and 1000 °C. X-ray diffraction (XRD) and high resolution X-ray photoelectron (HR-XPS) scans confirm the presence of willemite phase of Zn_2SiO_4. Laser-induced phosphorescence decay measurements of $Zn_{2-x}Mn_xSiO_4$ nanophosphors were investigated using high peak power pulsed UV nitrogen laser ($\lambda = 337.1$ nm). The decay curves show non-single exponential behavior with long term decay rate. Various parameters describing the strength of optical transitions in atoms and molecules such as, Einstein's *A* and *B* coefficients, '*f*', integrated cross-section, and transition dipole moment values have been calculated. The long term decay rate of optical transition parameters was found to be somewhat temperature and concentration dependent.

1. Introduction

Phosphors are widely used in emissive display devices. However, presently used phosphors still need considerable improvement such as, in lower current saturation, high efficiency, and better chromaticity [1]. Ceramic oxide based phosphors, including silicates phosphors, are more chemically stable and environment friendly compared to sulfate or polymer-dye based phosphors. Nanophosphor powders or thin films doped with various transition metals and rare-earth ions have recently been recognized to hold special position in photonic and biophotonic industry [2–7]. Their potential applications are still very much in designing phase. Further, fundamental research in this field remains a challenge [8]. This is very important because the transition metals and rare-earth ions doped nanophosphors have proven to be very difficult and been the subject of debate in the recent years. The important issue will be whether the dopant impurity ions are really been incorporated into the lattice sites of nanophosphors (doping) or adsorbed on the nanoparticles surface (activation) and their effects on optical properties [8]. The phosphor layer serves as a host matrix for various intentional impurities, known as luminescent impurity centers, which ultimately are responsible for emission of light in visible region. Typically, luminescent impurities substitute cationic species in the lattice, for instance Mn^{2+} replaces Zn^{2+} to form Zn_2SiO_4:Mn^{2+}.

Metal silicates have recently been reported [9] as an ideal phosphor host matrix, for various transition metals and rare-earth ions, with magnificent luminescence properties in blue, green, and red spectral regions. Zinc orthosilicate (willemite), Zn_2SiO_4, is used as a chemically stable transparent dielectric host for a number of luminescent dopants [10–13]. For example, manganese doped zinc silicate is a well-known photoluminescent, cathodoluminescent, green light-emitting phosphor with high luminescent efficiency, better chemical stability, and splendid color purity. It has been used in fluorescent lamps, cathode ray tube devices, thin film electroluminescent panels, field emission display panels, plasma devices for lighting, televisions, projection displays, copy machines, flat panel displays, medical imaging, and portable communication equipments [11,14–19]. Recently, zinc silicate is reported to be used as a laser crystal [20] and upconversion luminescent material [21]. Zn_2SiO_4 possesses a rhombohedral structure ($R\bar{3}$, space group) having wide forbidden band gap of ≈ 5.5 eV. Silicate materials are very useful in many applications of technological importance [22]. Zn_2SiO_4:Mn^{2+} was used as a green component in the first tri-color lamp [23]. Additionally, the light emitted by Zn_2SiO_4:Mn^{2+} seems to be compatible with the spectral sensitivity of optical detectors (film, photocathodes, and photodiodes) used in X-ray or nuclear imaging [14]. Photostimulated luminescence in silicates is used for developing X-ray storage phosphors [22]. Traditionally, solid state diffusion method has been employed for the synthesis of Zn_2SiO_4, which involves crushing, grinding, ball milling, and sintering of source materials at very high temperatures. But, nowadays, sol–gel, forced precipitation, pulsed laser deposition (PLD), organometallic complex route, combustion methods, dry reaction, spray-pyrolysis, polymer

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assisted methods, etc. [22,24–29] are widely used to synthesize Zn_2SiO_4 nanophosphor powders or thin films. Zeng et al. [10] synthesized Zn_2SiO_4 using hydrothermal method with possible lowest crystallization temperature. Lukic et al. [30] synthesized polymer assisted Zn_2SiO_4 phosphor powders using the sol–gel method, where polymer polyethylene glycol is utilized to produce gel.

In the present paper, Zn_2SiO_4:Mn^{2+} nanophosphor matrix is synthesized using the wet-chemical sol–gel method [31]. Various phosphorescence decay parameters such as, Einstein's *A* and *B* coefficients, '*f*' values, integrated cross-section, and transition dipole moment values are calculated and reported. These parameters are obtained by laser-induced phosphorescence decay curves, which show non-single exponential decay behavior. Considerable percussion of dopant ion concentrations and firing temperatures are observed in the optical transition parameters.

2. Experimental details

Precursors used for the preparation of Zn_2SiO_4:Mn^{2+} nanophosphor powders are tetraethylorthosilicate (TEOS) $Si(OC_2H_5)_4$, ammonium hydroxide NH_4OH, zinc acetate dihydrated $Zn(OOCCH_3)_2 \cdot 2H_2O$ (99.9%), manganese acetate tetrahydrate $Mn(OOCCH_3)_2 \cdot 4H_2O$ (99.9%), nitric acid HNO_3, and ethanol C_2H_5OH (absolute, 99.99%). All chemicals are of analytical grade and used without further purification. The reaction solutions are prepared in high purity deionized water.

2.1. Preparation of Zn_2SiO_4:Mn nanoparticles

The target gel composition, for preparing the required samples is 60 ZnO:40 SiO_2 (mol%). The precursors used are zinc acetate, $Zn(OOCCH_3)_2 \cdot 2H_2O$, and tetraethylorthosilicate $Si(OC_2H_5)_4$, used as the silica source. At first, silica sol is prepared by hydrolysis and condensation reaction of tertraethylorthosilicates (TEOS). $Si(OC_2H_5)_4$ is hydrolyzed and stirred for 1 h. The molar ratio of TEOS:H_2O:-C_2H_5OH:HNO_3(3N) is 1:1:6:0.0025, used in the experiment. Required amount of $Zn(OOCCH_3)_2 \cdot 2H_2O$ followed by $Mn(OOCCH_3)_2 \cdot 4H_2O$ is dissolved in 40 ml ethanol–water (4:1 v/v). The doping concentration of Mn^{2+} ions varies from 0.5 to 5 mol%, substituting for Zn^{2+} in Zn_2SiO_4. These two solutions are then mixed together and stirred for next 1 h. NH_4OH (35%) solution is slowly added drop-by-drop with continuous stirring for next 1 h. Gelation of the sol droplets resulted due to the controlled addition of base. The resultant solution is left undisturbed for next 3 days till it is gelled properly. It is then dried at 110 °C for 24 h to obtained xerogel. Powder phosphors are prepared by firing the preheated gel particles in an open atmosphere for 1 h at different temperatures ranging from 800 °C to 1000 °C. The basic chemical equation involved is as follows:

$$2ZnO + SiO_4 \rightarrow Zn_2SiO_4 \quad (1)$$

3. Time-resolved phosphorescence decay kinetics

The experimental setup shown in Fig. 1 is used to fully characterize the decay parameters. High peak-power ($\approx$ 10 kW), intense UV pulsed-nitrogen (N_2) laser (337.1 nm) is employed as an excitation source for phosphorescence decay measurements. Luminescence in visible region is observed from doped Zn_2SiO_4 phosphor. The nanophosphor powder is mounted on the sample holder using xylene, placed at a right angle to the laser beam, and the emission in the visible region is recorded by the monochromator. After the selection of the emission wavelength (425 nm and 528 nm) from the sample, the signal is passed through a fast photomultiplier tube [RCA8053PMT]. A glass slab or $CuSO_4$ solution is introduced in the path of emitted visible light to filter out

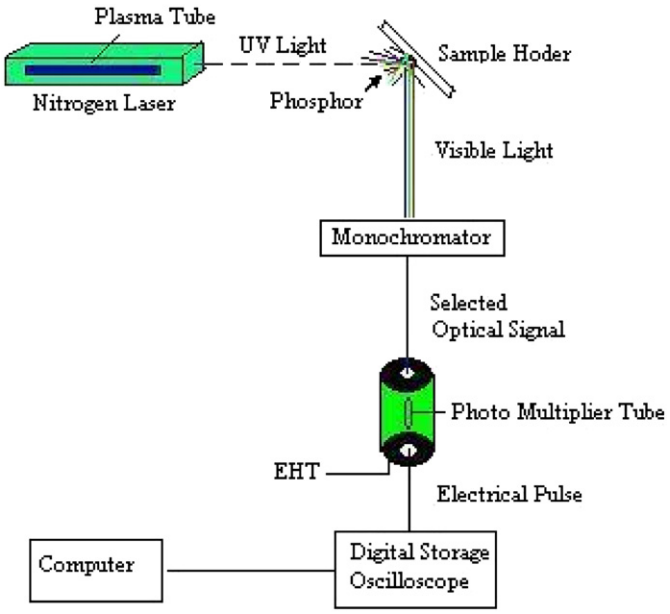

Fig. 1. Experimental setup used for time-resolved laser induced spectroscopy of $Zn_{2-x}Mn_xSiO_4$ ($0.5 \le x \le 5$ mol%).

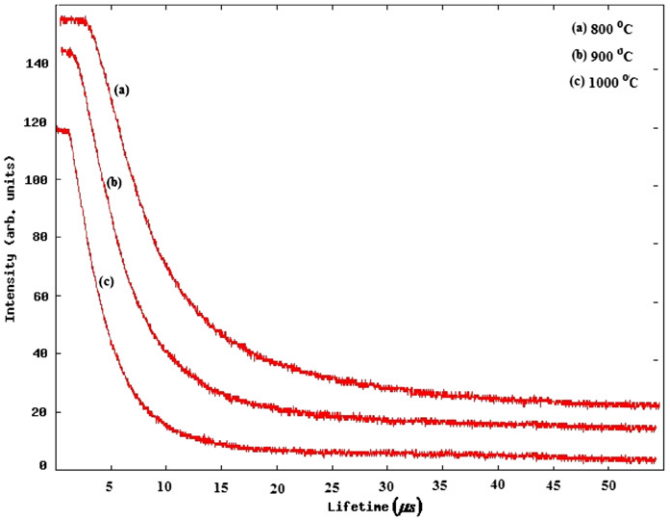

Fig. 2. Decay kinetics of $Zn_{2-x}Mn_xSiO_4$ (0.5 mol%) phosphor particles fired at 800, 900, and 1000 °C (showing three overlapping exponentials).

all scattered UV radiations. The signal is then transmitted to digital storage oscilloscope (DSO) [TektronicsTDS1012] and finally signal is sent to computer assembly to analyze the observed data. Three components of transition probability have been peeled-off from decay curves (Fig. 2) using peeling-off method of Bubes [32–36] to get the average life-time values [31]. Various optical parameters of interest like Einstein's *A* and *B* coefficients, '*f*' (oscillator strength), integrated cross-section, and transition dipole moment values of corresponding radiative transitions are calculated.

4. Theoretical background

When samples are irradiated using high energy laser (UV) beam, the electrons present in the valence band raise to the excited states. On returning back to the valence band, there is an