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Cadmium silicate nanopowders for radiation dosimetry application: Luminescence and dielectric studies

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ABSTRACT

Pure cadmium silicate ($CdSiO_3$) nanophosphor was prepared by a low temperature solution combustion technique. In this technique, meso-structured silica was used as silica source. The prepared compounds were well characterized by powder X-ray diffraction (PXRD), scanning electron microscopy, high resolution transmission electron microscopy, Fourier transform infrared and UV–vis spectroscopic techniques. The PXRD peaks of as-formed sample are broad and amorphous in nature. The compound calcined at 800 °C shows pure monoclinic phase, which is the lowest temperature reported so far to obtain in this phase. The average crystallite size for phase pure compound was found to be ~31 nm. The optical energy band gap of ~5.6 eV was observed for the compound. Raman spectrum of the sample showed the all possible states of vibrational motions of the prepared samples. The UV irradiated samples with different dose and time with constant heating rate exhibit the thermoluminescence (TL) with a well resolved glow peak at ~160 °C. The variation of TL intensity with dosage time results that the material was found to be quite useful in radiation dosimetry. The frequency dependent dielectric constant of the prepared sample exhibits high value at low frequency and vice versa.

1. Introduction

Phosphors with highly stable, good morphology and better yield were in great demand for energy saving applications such as display, lasers, scintillators, safety indicators and dosimetry [1,2]. In this regard, rare earth's doped silicates based phosphors exhibit multi-color phosphorescence and are stable against acid, alkali and oxygen environments [3]. Various silicate hosts were well studied by doping with rare earth and transition metal ions such as $CdSiO_3:In^{3+}$, $CdSiO_3:Mn^{2+}$, $CdSiO_3:Sm^{3+}$, $CdSiO_3:Tb^{3+}$, $CaSiO_3:Eu^{3+}$, $Ba_2SiO_4:Eu^{2+}$, $Sr_2SiO_4:Pr^{3+}$, $Mg_2SiO_4:Tb^{3+}$, $Zn_2SiO_4:Mn^{2+}$, $Mg_2SiO_4:Eu^{3+}$, $Mg_2SiO_4:Dy^{3+}$, and $Sr_2SiO_4:Pr^{3+}$ [4–13]. Among the various silicates $CdSiO_3$ as a host exhibits remarkable optical and luminescent properties. Due to the presence of Cd^{2+} ions and strong interaction between Si–O of SiO_3 group, $CdSiO_3$ shows combined nature of ionic and covalent bonding. The crystal structure of $CdSiO_3$ shows one dimensional chain of edge-sharing SiO_4 tetrahedron helping in replacing the Cd site by transition metal ions. However in order to maintain the charge neutrality, the charge compensation of Cd^{2+} and O^{2-} was tuned by rare earth ions as a dopant. These dopants were responsible for the creation of traps at appropriate depths, which stores the excitation energy and emit the light in the visible range after some time [14,15].

Thermoluminescence (TL) is a phenomenon of emission of light caused by thermal stimulation by the ionizing radiation on the

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material induces electrons from the traps of the semiconductors or insulators. A TL glow curve provides the information about the defect centers induced due to ionizing radiations in the material. TL study mainly depends on particle size, type of dopant, morphology, crystallization, growth mechanism, local symmetry, host matrix and synthesis methods. Further, TL finds wide range of applications in the field of archeology, radiation dosimetry and defect studies [16,17]. Therefore, to improve the structural properties of the luminescent materials, the exothermic reaction based solution combustion technique was developed [18]. The reported work in this paper is the first time synthesis of $CdSiO_3$ nanopowder using oxalyldihydrazide (ODH) as a fuel and meso-structured silica as silica source during solution combustion. The prepared samples were well characterized by powder X-ray diffraction (PXRD), scanning electron microscope (SEM), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR) and UV–vis spectroscopy (UV–vis). Thermoluminescence (TL), dielectric and ac conductivity studies were discussed in detail.

2. Experimental

2.1. Synthesis of meso-structured silica

Meso-structured silica was prepared by taking appropriate quantities of hexadecyltrimethyl ammonium bromide (CTAB, Sigma Aldrich), KOH and distilled water. The mixture was heated at 80 °C for 30 min. After uniform mixing of solution for about 30 min, 3.0 mL of tetraethyl orthosilicate (TEOS, Sigma Aldrich) was added to the mixture dropwise under fast stirring to obtain a suspension. The obtained suspension was kept at 80 °C for 2 h to complete the precipitation process. The decomposition of the prepared precipitate was controlled by allowing it to cool at room temperature. Further thoroughly washed with deionised water and dried for 12 h at 80 °C [19].

2.2. Synthesis of $CdSiO_3$ nanopowder

The materials used for synthesis of $CdSiO_3$ were cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) and freshly prepared meso-structured silica (Section 2.1) was used as the source of Cd and Si respectively. The stoichiometric quantity of the redox mixture was taken in Petri dish in the ratio of 1:1 and dissolved in deionised water [20]. Then the required amount of ODH was added to the mixture and stirred well for 15–20 min using magnetic stirrer. The mixture was placed in a preheated Muffle furnace maintained at 500 ± 10 °C. The reaction took place within few seconds by heating the redox mixture followed by decomposition. During this process initially large amount of gases (usually CO_2, H_2O and N_2) liberate followed by a spontaneous ignition occurred and then the solution underwent flame type combustion with swelling. After combustion, the product was cooled and grinded well using mortar and pestle. The fine powder was calcined at various temperatures such as 600, 700, 800 and 900 °C for 2 h.

2.3. Measurements

Powder X-ray diffraction (PXRD) analysis was performed using Philips analytical X-ray diffractometer with CuK_α radiation (λ = 1.5405 Å) along with a nickel filter. The data were collected in 2θ range from 10° to 60°. Morphology of the sample was analyzed by using Hitachi table top scanning electron microscope (SEM – TM 3000). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) pattern were done using JEOL 2100 HRTEM. Fourier transform infrared (FTIR) spectra were recorded in absorption mode with Perkin Elmer spectrometer (Spectrum 1000) along with KBr pellets. UV–vis spectrum of the sample was recorded with the Elico SL 159 spectrometer by dispersing the powder in liquid paraffin. Raman spectra are recorded on a Raman Horiba Jobin yvon-labram-HR 800 Raman spectrometer in the frequency range of 50–1200 cm^{-1}. For TL studies, samples were exposed to UV-source of wavelength 254 nm and power of 15 W. Samples were filled in the sample holder of squares with area approximately 1 cm^2 by keeping the distance between the source and sample at constant distance of 1 cm where the intensity was 0.028 W m^{-2}. The samples were exposed in varied times such as 5–40 min at room temperature (RT). After the desired exposure, the TL glow curves were recorded using Nucleonix TL reader consisting of a small metal planchet (72% Fe, 23% Al and 2% Cr or Nichrome) heated directly using a temperature programmer. During TL measurements, each time ~30 mg of the samples were taken and heating rate was set to 5 °C s^{-1}. Highly polished pellets with a thin layer of silver paste on either side of the pellets (for ohmic contacts) were used for dielectric measurements. Measurements were carried out at room temperature (RT) using LCR meter model HIOKI 3532-50 LCR HiTESTER version 2.3, in the frequency range of 50 Hz–5 MHz.

3. Results and discussion

3.1. Investigations from PXRD

Fig. 1 shows the PXRD patterns of mesoporous silica (Fig. 1(a); JCPDS card No. 47-0715), CdO (Fig. 1(b); JCPDS card No. 78-0653) and $CdSiO_3$ (Fig. 1(c)–(f)). The diffraction peaks of $CdSiO_3$ were well matched with the JCPDS card No. 35-0810 [21] confirming the formation of cadmium silicate. Among the prepared silica, the sample calcined at 800 °C for 2 h shows better crystallinity and single monoclinic phase [22–24]. To the best of our knowledge, this is the best possible lowest temperature for the synthesis of

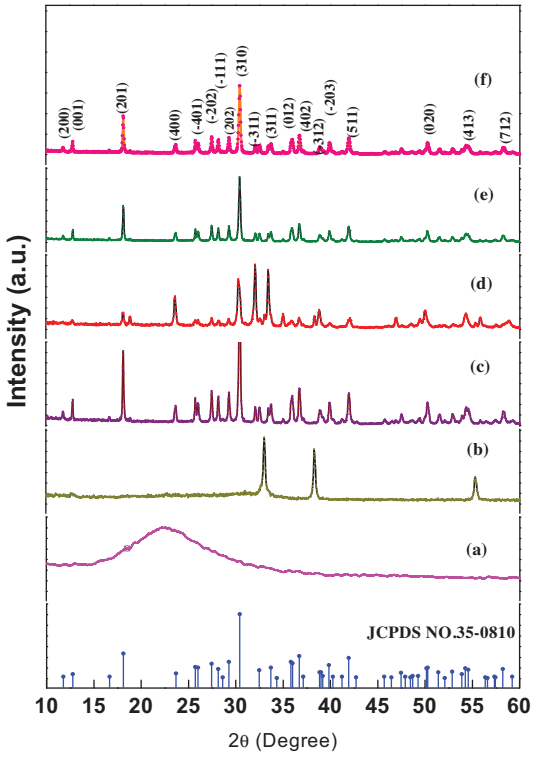

Fig. 1. PXRD of mesoporous silica, CdO and $CdSiO_3$: (a) mesoporous silica, (b) as formed sample contains CdO and amorphous silica. Further, samples were calcined at (c) 600 °C, (d) 700 °C, (e) 800 °C and (f) 900 °C for 2 h.