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Sol-Gel synthesis and optical characterization of Lead-Silicate nanocomposite monolithic xerogels

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Abstract: Nanocomposite binary systems of $PbO\text{-}SiO_2$ monolithic xerogels were synthesized via sol-gel method. TG-DTA, FT-IR, UV-DRS and solid PL techniques were used to characterize the nanocomposite xerogels. The results indicated lower defect levels arising due to oxygen vacancies and interstitial occupation of dopent atoms
Keywords: Sol-gel process; Lead-Silicate; nanocomposites; monolithic xerogels; diffuse reflectance; PL emission.

Introduction and Experimental

Lead can play the multiple roles such as a network former (Pb^{4+} replacing Si^{4+}) or as a network modifier. The content of PbO as a network modifier of glass network can be introduced at larger molar ratio (upto 50%) so as to obtain desired structure of $PbO\text{-}SiO_2$ glasses [1]. Addition of Lead (II) oxide lowers melting point and viscosity of the melt while it increases the refractive index thus yields glasses with appreciable brilliance. The chemical resistance of lead crystal glass with respect to corrosion by aqueous solutions is an important property [2]. The higher ionic radius of the Pb^{+} ion (~0.119 nm) is a steric hinderance to the mobility in the matrix and also hinders the mobility of other ions. As a result lead glasses exhibit high electrical resistance ($10^{8.5}$ ohm.cm) nearly twice that of soda-lime glass.In physical terms, nano-composites differ from conventional composites due to their distinguishing property of high 'aspect ratio' (surface to volume ratio) of the reinforcing nano-phase components. Sol-gel process is an attractive method to synthesize nanocomposite xerogels and glasses of high homogeneity and purity with specific compositions, functions and shapes that are difficult to obtain using conventional methods[3].

Tetraethylorthosilicate (TEOS) [$Si(OC_2H_5)_4$] and Lead acetate trihydrate [Pb $(CH3COO)_2.3H_2O$] were used as precursors for the sol-gel synthesis of $PbO\text{-}SiO_2$ nanocomposite xerogels. For pre-hydrolysis of TEOS the initial solution was prepared by mixing TEOS, ethanol and water in the molar ration of 11:11:14 respectively and magnetically stirred at 60ºC. A dilute solution of 2 drops of HCl in 5 ml of water was drop-wise added during stirring till the pH was in the range 2 to 3. The second solution was prepared by mixing 0.1M of lead acetate trihydrate in 50 ml of water and separately stirred at 50ºC for 90 minutes. 10 ml of water was added to the initial solution to make the pH in the range 4 to 5. Finally, the two solutions were mixed and stirred for 1hr at 60ºC. The reacted mixture was poured into a plastic mould, sealed and aged for two days and allowed

to slowly evaporate for 15 days. The dried xerogels was then heat treated in a PID controlled furnace according to a schedule derived from TG-DTA curve shown in figure 1. The absence of any characteristic peak in the XRD pattern (not shown) implies the glassy nature of the xerogels.

Results and Discussion

The UV-Vis Diffuse Reflectance Spectra and the plot of reflectance versus band gap energy are shown in Figure 2. The estimated values of band gap energies are 4.9 eV and 5.2 eV for the xerogels calcined at 120ºC and 500ºC respectively as shown in figure 2. Considering the average value 5.1 eV it can be observed that this band gap energy of the nanocomposites is lower than that SiO_2 (11.8 eV) and higher than that of PbO (2.2 eV). The decrease in band gap energy of SiO_2 matrix is due to 'shrinkage effect'. This shrinkage of band gap happens due to the introduction of shallow level donor impurities creating a continuum of energy levels near the conduction band and/or a continuum of acceptor energy levels of impurities created near the valence band edge [4].

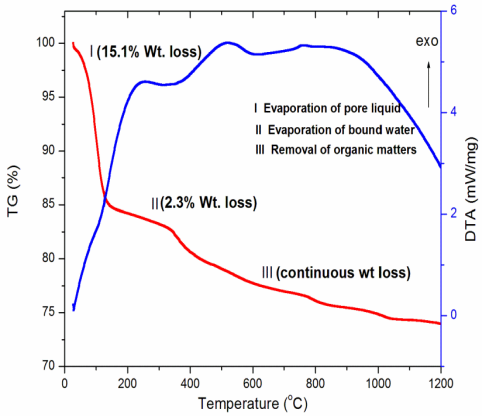

Figure 1. TG—DTA curve of xerogels heated to 120 °C

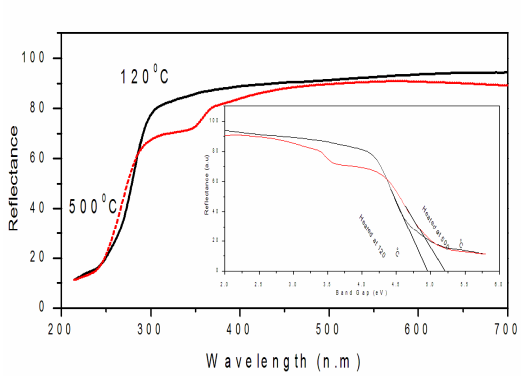

Figure 2. UV-DRS spectra and band gap plots of PbO-SiO_2 xerogel powders heat treated to 120 and 500°C

The FT-IR spectra of the nanocomposite xerogels heat treated to 120ºC and 500ºC are shown in figure3. The peaks exhibited at 796 and 466 cm^{-1} are due to the presence of lead and can be assigned to the Pb-O vibrations [5, 6]. It can be observed in the spectrum of the xerogels heated to 500ºC that the absorption bands at 3469 and 1631 cm^{-1} corresponding to the OH group and surface silanols respectively, have diminished intensity implying their removal from the sample. However, the peaks corresponding to siloxane and lead oxide vibrations are present.

Figure 4.displays the PL emission spectra of PbO-SiO_2 xerogels heated to 120ºC and 500ºC (λ excitation = 300 nm). The weak emission peak appearing at 344 nm is attributed to the vibronic fluorescence band. The intense PL emission peak appearing at 400 nm is the result of excitonic recombination. The green band occurring at 527 nm is related to the surface level oxygen vacancies which are considered as defect states of the matrix having sublevels in energy band gap [7]. The intensity of this band is more for the sample sintered at 500ºC and may be the result of increased number of non-bridging oxygen in the PbO doped SiO_2 matrix structure. Very week band representing yellow emission above 575 nm implies less significant levels of interstitial defects, present in both PbO and SiO_2 nanoparticles.

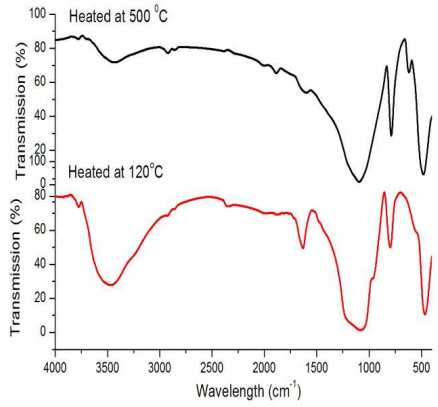

Figure 3. FT-IR spectra of the nanocomposite xerogels heat treated to 120ºC and 500ºC

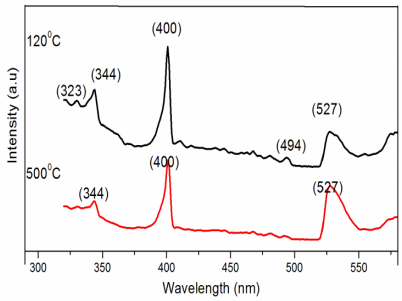

Figure 4. PL emission spectra of PbO-SiO_2 xerogels heat treated to 120ºC and 500ºC

Conclusively, UV-Vis-DRS characterization of the synthesized PbO-SiO_2xerogelrevealed band gap shrinkage effect of the SiO_2 matrix due to incorporation of the PbO nanoparticles which implies easier and fine tuning possibilities of SiO_2 band gap. The FT-IR analysis indicated the sintering effects on the xerogels and the presence of low levels of surface and interstial defects were observed in the PL emission spectra.

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