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Preparation and characterization of sol–gel derived silver-silica nanocomposite

Surender Duhan[a,*], N. Kishore[b], P. Aghamkar[c], Sunita Devi[d]

[a] Materials Science Lab, Department of Materials Science & Nanotechnology, Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Sonepat131039, India
[b] Materials Science Lab, Department of Applied Physics, Guru Jambheshwar University of Science & Technology, Hisar 125001, India
[c] Department of Physics, Chaudhary Devi Lal University, Sirsa 125055, India
[d] Department of Chemistry, Lajpat Rai College, Sahibabad (Ghaziabad), UP, India

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ABSTRACT

Composite silver silicate nano-particles were prepared by sol–gel method to investigate the effect of annealing temperature and time durations. The prepared samples were subjected to heat treatment in the temperature range 100–350 °C for different time durations. Characterization of heat treated samples was carried out by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), (UV–vis–NIR) spectroscopy and scanning electron microscopy (SEM). The effect of sintering temperature and time durations on the structural changes of Ag-doped silica has been discussed in detail. The sample sintered at 350 °C for 4 h shows the formation of silver nanocrystallites in silica matrix with average grain size ~17.8 nm.

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1. Introduction

Synthesis and characterization of nano-sized metallic powders have attracted attention of the materials community due to their promising properties. Nano-binary oxide system containing Ag, Nd, Cu and SiO_2, with controllable size and properties has applications in miniaturized optical devices, catalysts [1–4], photonics [5], advanced high temperature superconductors/ceramics [6] and integrated optics [7]. Particularly nano-silver-oxide powders show good catalytic properties in several reactions including synthesis of Cu and oxidative coupling of methane [8], while thin film of Al oxides are of interest for many purposes such as optical antireflection coating, gas insulator, and protective coating [9]. For the above mentioned specialized applications, mostly silica has been preferred as host matrix due to its higher softening temperature, higher thermal shock resistance, lower index of refraction etc. in comparison to other oxide glasses [7,10]. Recently nanocomposites and nanocrystallites containing glasses have attracted a great deal of interest due to their macroscopically properties such as high mechanical resistance, chemical stability and heat resistance etc. Moreover, their optical and magnetic properties justify the wide use of these glasses as optical amplifiers in telecommunication fibers network, as new miniature optical devices and as components for laser technology [11]. Such materials are particularly promising for optoelectronics and photonics applications. Glasses that contain crystallites of metals, obtained by sol–gel method, exhibit effective third-order susceptibilities several hundred times larger than those of colloidal melt glasses, making them potential candidates for all optical switching devices. Materials containing metal nanoclusters have traditionally been prepared by a variety of chemical or physical methods. Among various methods, sol–gel has been largely used for the preparation of inorganic oxide, due to its versatility and low cost. Moreover this method allows the incorporation of different species such as atoms, molecules or ultrafine particles into dried glass. These species are added in the precursor solutions producing characteristic properties in solid-glasses. Metal crystallites embedded in a transparent glass matrix produce a special coloration due to the presence of characteristic absorption bands in the visible spectrum and the spectrum of absorption band can be utilized in optoelectronics [5–7]. Prior to the formation of the crystoballite phase, the silver forms nanocrystallites aggregates when the bulk samples are heat treated at temperatures of 350 °C or higher.

The focus of the present work is to studied effect of calcinations temperature with prolonged annealing time mainly supports the development of the Ag silicates nanocrystallites in case of silver-containing-silica. The stem of this study is in the results of our earlier report [12,13], in which, we demonstrated that the effect

* Corresponding author. Tel.: +91 9813170944.
E-mail address: surender6561@yahoo.co.in (S. Duhan).

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of temperature and time on Nd_2O_3–SiO_2 nanocomposites. It was observed that the annealing temperature and time dependences of the formation of Nd_2O_3 nanocrystallites as well as their distribution in fused silica matrix. We found average size of the silver nanocrystallites in a silica matrix was ~17.8 nm. Characterizations have been made by the X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV–vis–NIR spectroscopy and scanning electron microscopy (SEM) data are of the prepared samples.

2. Experiment

Silver silicates were prepared by mixing high purity reagents $(CH_3CH_2O)Si$ (TEOS) tetraethoxy silane (Aldrich 99.999), ethanol (Aldrich 99.9995), and deionized water. To prepare the Ag/SiO_2 molar ratio of $TEOS:H_2O:HNO_3:C_2H_5OH$ was 1:11:0.2:5. 0.5 wt% of $AgNO_3$ was introduced in the pre-hydrolyzed solutions. About 85% of the total water was used for hydrolysis and condensation reaction and rest for the dissolution of $AgNO_3$. The resultant homogeneous solutions were filled in a mold and placed in drying oven. The gelation acts after 21 days. After gelation the samples were still left inside the oven for 15 days, for ageing (which result in a further shrinkage and stiffening of the gel), until no shrinkage appear. The optical absorption spectra (in the wave length range 200–700 nm) were obtained at room temperature using a dual beam spectrometer (PerkinElmer, model lambda-19). A silica glass was used as a reference sample. The X-ray diffraction (XRD) patterns of the prepared samples were recorded with a Philips X-ray diffractometer PW/1710; with Ni filter, using monochromatised CuKα radiation of wavelength 1.5418 Å at 40 kV and 30 mA. Using XRD data approximate crystalline size was also determined via Scherrer formula:

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta}, \quad (1)$$

where k is a constant which is taken as 0.9 for calculation, β is full width at half maximum (FWHM) in radians; θ is the Bragg angle at which the peak maximum occurs. λ is the wave length of X-ray radiation used for the study. Infrared spectra were collected from with a PerkinElmer 1600 (spectrophotometer) in 2000–500 cm^{-1} range. The microstructure of the prepared samples was studied by a scanning electron microscope (Hitachi Model No. S3400).

3. Results and discussion

3.1. XRD

The XRD pattern for the sample annealed at 100 °C (1 h) (not shown in Fig. 1) broad hump, centred at 2θ ~23° indicating its amorphous nature. The sample annealed at temperature 200 °C (1 h) also

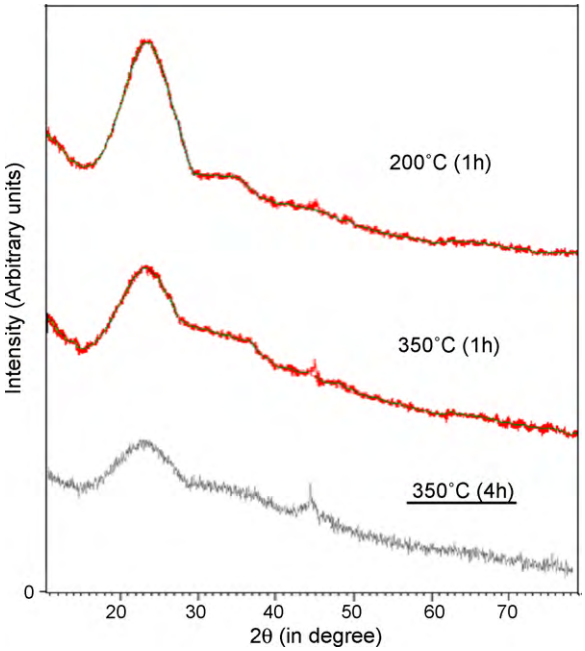

Fig. 1. XRD pattern of the silver-doped samples annealed at 200 °C (1 h), 350 °C (1 h) and 350 °C (4 h).

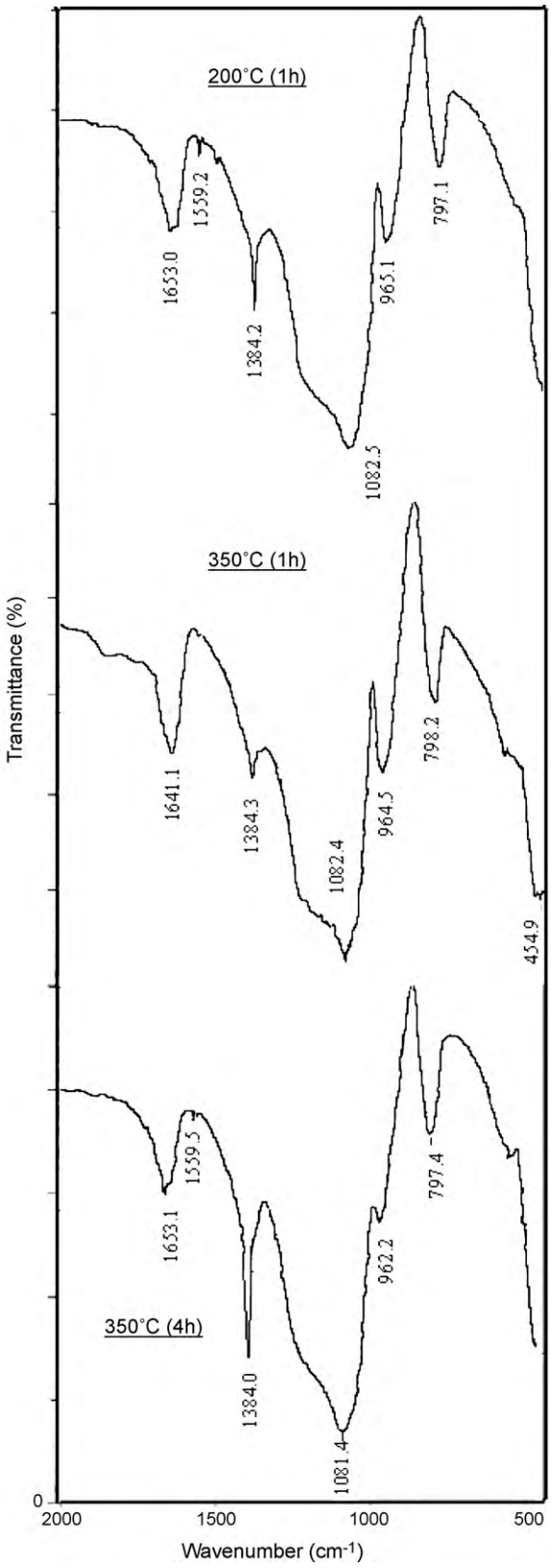

Fig. 2. Absorption spectrum of sample annealed at 350 °C at 4 h.

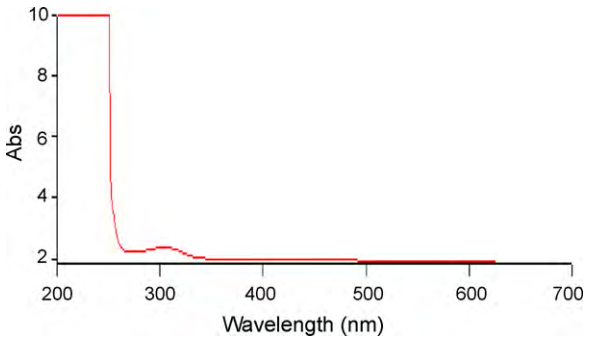

Fig. 3. Infrared spectra of a silver-doped silica matrix heated at 200 °C (1 h), 350 °C (1 h) and 350 °C (4 h).

as evidenced by absence of sharp peaks in its XRD (Fig. 1) pattern. It is believed that absence of silver peaks in these samples was due to highly dispersed silver species.

The diffraction pattern corresponding to the sample heated at 350 °C (1 h) presented silver crystalline peak that is relatively weak corresponding to index as (2 0 0) and appeared at 2θ ~44.6°. No other diffraction peaks were observed at higher angles in this sample. With increasing annealing time, it is also observed that hump centred at 2θ ~23° became narrower. These changes can be attributed to an increment in the structural order of the amorphous SiO_2 towards the crystoballite phase, one of the crystalline forms of the SiO_2 [14,15].

Finally, the XRD pattern heat treated at 350 °C (4 h), exhibits diffraction peak, at around 2θ ~44.6° (JCPDS File No.03-0921) which suggests the initial development phase of silver. It is interesting to notice in silica glasses containing silver, prepared by the sol–gel route, the crystoballite phase also appears in this last pattern. The diffraction peaks became intense and their FWHM turned gradually narrow suggesting an increase in particle size. Mean silver particle sizes (diameters) estimated in the silica matrix is ~17.8 nm in these composite samples. The results indicate that with the increase in annealing temperature, mean size of silver nano-particles in the amorphous SiO_2 matrix increased. The broad background contribution from the amorphous silica network was observed in the X-ray diffraction patterns due to the presence of small volume fraction of silver.

3.2. FTIR

Fig. 2 shows the FTIR spectra of the samples annealed at different temperatures in the region 500–2000 cm^{-1}. In all of the IR spectra, water bands observed at around 1640 cm^{-1} corresponding to bending vibrations indicate hygroscopic character of the powdered samples [16]. The spectra of samples heat treated at 200 °C show the deconvoluted bond-stretching vibration of the Si–O–Si units [17,5]. Strong bands observed at 1082, 965, and 798 cm^{-1} have been attributed to Si–O–Si and Si–OH absorptions [18]. However, when the sample was sintered for 350 °C (1 h), discrete bands appeared between 500 and 800 cm^{-1}. Small absorption due to metal–oxygen (M–O) stretching is also seen at around 600 cm^{-1}. As the heat treatment time increases for the, specimens with equal amount of Ag, the sharpening of bands and slight shift to higher frequency have been observed. This exhibits the occurrence of the band shortening and reduction in the mean Si–O–Si bond angle

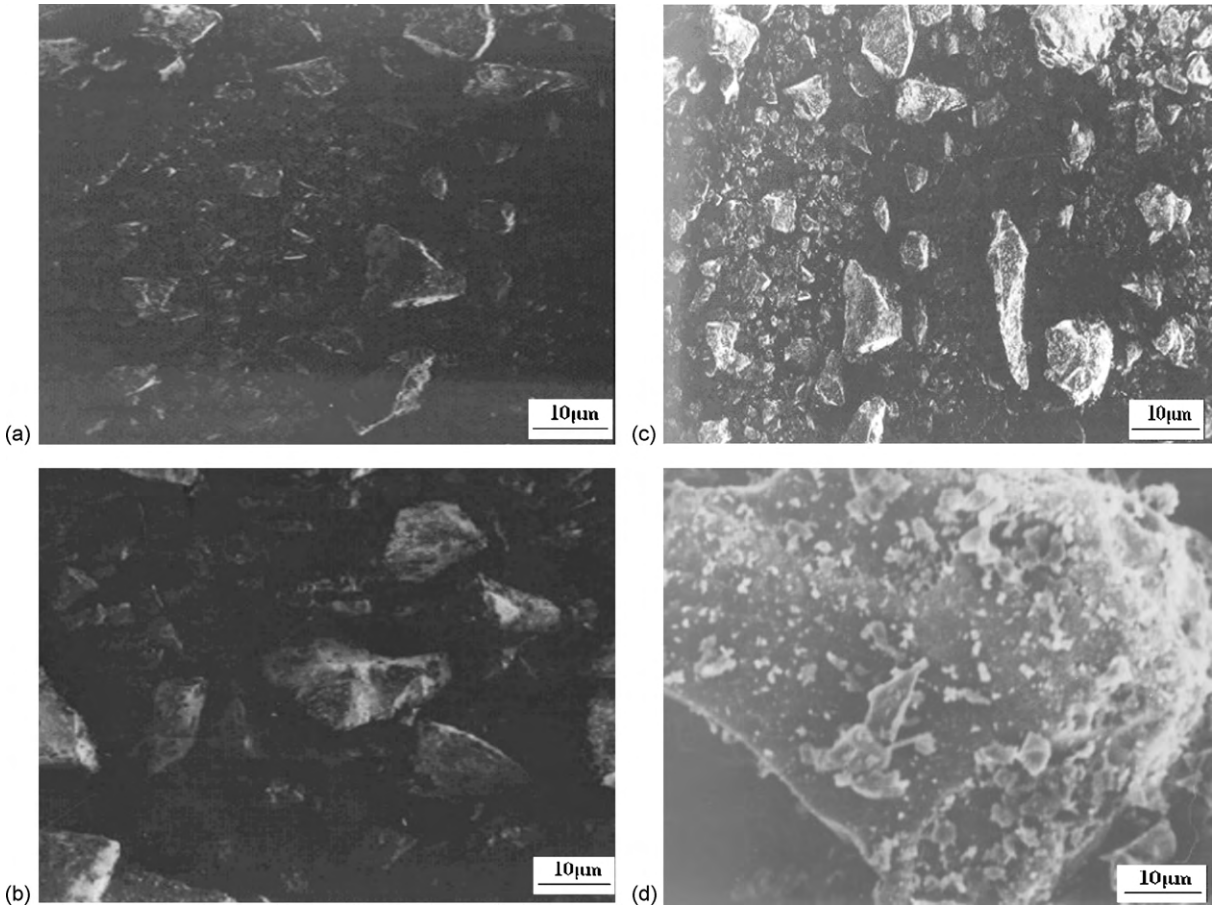

Fig. 4. SEM photographs of silver-containing silica powder samples heated at (a) 100 °C (1 h), (b) 200 °C (1 h), (c) 350 °C (1 h) and (d) 350 °C (4 h).

with increasing heat treatment time. However, when the sample was sintered for 350 °C (3 h), elimination of bands corresponding to water molecules, Si–OH and volatiles in FTIR spectra, confirm densification of the binary system [19] and also makes the system almost transparent for spatial frequency 2000 to 1800 cm^{-1} [20]. During preparation of the samples it was noted that the sols as well as gels remain colourless transparent materials. However, after drying of the aged gels, there were visible changes in colour along with lowering of transparency. It was found that this change of colour was predominant in the humid condition even at room temperature if the samples were exposed to air for a few days. However, if the samples with changed colours are heat treated above 350 °C (4 h) the samples regain the transparency. Alternate exposure to humid air and heat treatment repeat the cycle. Such activities are believed to be due to the presence of oxide compounds of Ag which are opaque in the visible band, in present samples, as have been found by analysis of X-ray diffraction.

3.3. Optical

Fig. 3 shows typical optical absorption spectra of the silver-doped-silica sample annealed at 350 °C for 4 h. The optical absorption at 300 nm may be attributed due to silver [21]. At this stage, the sample was grey in colour. This absorption peak was low in intensity and broader because we believe that nano-particles were smaller in average size and have relatively wide size distribution.

3.4. SEM

The samples were examined by the SEM to investigate the morphology of the nano-particles. Fig. 4 shows the SEM micrographs of silver nano-particles formed in the samples heat treated at 100–350 °C for different durations.

The morphology of the sample calcined at 100 °C (1 h) (i.e. amorphous Ag-doped silica). On raising the annealing temperature at 200 °C (1 h), change in grain sizes is observed. SEM image shows broad size distribution of particles having diameter in the range of less than 10 μm.

The microstructure changes from coarse scale to good ones by increasing the sintering temperature to 350 °C of sample. The SEM observation confirmed the advantages of the sol–gel process for obtaining amorphous materials at lower temperature while dense and more homogeneous materials were obtained at higher temperature. When the sample annealed at 350 °C (4 h), the silver nano-particles can be clearly seen embedded in the SiO_2 matrix. Their dispersion in glass matrix is high and homogeneous. The particles are well separated from each other and their shape is essentially semispherical rather than spherical. Occasionally, ellipsoidal shape particles are also observed by SEM technique. The sintering of the thick semispherical structures was intended to roughly spherical shape with size between 350 and 500 nm. These particles were, in general, spherical in shape, isolated with adequate spacing and well distributed in the amorphous silica matrix. The electron microscopy also revealed an increase in particle size and improvement in distribution with increase in annealing temperature as observed in XRD. However, the bigger size particles observed in the SEM indicates that there may be some agglomeration in some cases. Ag nano-particles organize themselves in extended three dimensional amorphous silica networks. The growth of Ag particles is likely to occur as a result of temperature dependent diffusion and coalescence processes. The excess surface area of the coalescing of small spherical particles provided driving force for interdiffusion of smaller particles. SEM studies reveal that the average size of the silver nano-particles increases as the annealing temperature is increased, which suggests that thermal treatment is an important parameter to control the size distribution.

4. Conclusions

Using the sol–gel method for $AgNO_3$:SiO_2 (binary oxide), different structures were successfully obtained upon heat treatment in air. At 100–350 °C intermediate Ag silicates grow depending on the annealing temperature and annealing time duration. During annealing, the aggregation in powders is due to solid-state bonds formed between nano-particles and the gel. The sizes of silver nano-particles increase with increasing annealing temperatures. Mean size of silver particles (diameters) estimated in the silica matrix is ~17.8 nm for these composite samples. The results indicate that with the increase in annealing temperature, mean size of Ag nano-particles in the amorphous SiO_2 matrix increased. It was found that change of colour was predominant in the humid condition even at room temperature if the samples were exposed to air for a few days. However, if the samples with changed colours are heat treated above 300 °C the samples regain the transparency. This indicates that the samples are suitable candidates for making humidity sensors. The particles are well separated from each other and their shape is essentially semispherical rather than spherical. The largest part of silver remains in an atomic state (as shown by the optical absorption band at 300 nm), with the increase of temperature, the densification of silicate network followed by elimination of residual organics mainly carbon and water formed by condensation reaction. It is also noticed that silver particles formed at 350 °C are stable and do not show any degradation of their optical properties with ageing. Controlled heat treatment process plays important role to develop silver silicate phase in glass.

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