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Development and properties study of microstructure silver-doped silica nanocomposites by chemical process

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ABSTRACT

A silver-doped silica nanocomposite has been prepared from a sol–gel solution. The physical and optical properties of the prepared material were investigated by several characterization techniques such as X-ray diffraction (XRD), surface area by BET method, UV–Vis Diffuse Reflectance Spectroscopy (DRS) techniques and Photoluminescence (PL). Different silver contents (corresponding to 0.05, 0.5, 5.0, 10 wt% Ag) and reaction temperatures were investigated. XRD results revealed structural evolution in all samples, and the photoluminescence spectrums were studied with respect to the different microstructures and chemical compositions.

1. Introduction

In the recent years, metal and oxide nanoparticles have been the subjects of many researchers due to the unique properties that are significantly different from those of larger grains/crystals [1]. The characterization of nanomaterials has generated not only new sciences in reduced dimensions, but also the possibility of synthesizing radically novel materials and properties [1,2]. This is especially true in the field of optics because of the quantum confinement effect which leads to unusual optoelectronic properties. Emission lifetimes, luminescence quantum efficiency and quenching concentrations are found to depend strongly on the particle-size in the nanometer range [3–5].

Luminescent nanoparticles have attracted increasing technological and industrial interest which has primarily to do with novel photonics applications – arising from unusual optical properties, and several investigations have dealt with the optical properties of metal-doped oxide nanomaterials [6–10]. Investigation of such materials is not only of academic interest but also of future technological importance in the case of many advanced applications and devices [9–11]. In addition, binary systems containing nanomaterials and glass matrix is important in various fields of technology, including laser, opto- and micro-electronics and optical fiber, etc. [12,13]. Especially for photonics applications, silica with its higher softening temperatures, higher thermal shock resistance, and lower index of refraction than the other oxide glasses, may be an ideal host matrix for metal elements and their oxides. In addition, silica (SiO_2) can be useful in humidity sensors due to its resistance to swelling, shrinkage, and peeling off after adsorbing water vapor [14,15]. In particular, among the various materials, silver nanomaterials have attracted increasing technological and industrial interest. This purpose has mainly to do with their novel optical properties such as: it was found that noticeable change of color occurred in humid conditions even at room temperature if the nano-Ag samples were exposed to humid air for a few days. This indicates that the samples may be suitable candidates for making humidity sensors, at least in some humidity range [16].

The successful synthesis of metal-oxide nanoparticles can be achieved by a number of processes, including sputtering, ball milling, co-precipitation techniques, chemical vapour deposition (CVD), gas phase condensation methods or colloidal-chemistry techniques [17–21]. Among these techniques, the sol–gel method has been widely used for the synthesis of inorganic oxides, due to its versatility and low cost. In the sol–gel technique, the preparation of materials begins with precursors and an oxide-network is obtained via hydrolysis, condensation and poly-condensation reactions that occur in solution [22]. This method is useful for the incorporation of different species such as atoms, molecules or ultrafine particles into the silica-glass network. These additions can be made in the precursor solutions subsequently producing additional characteristic properties in silicate glasses.

The optical properties of silica-based nanocomposites, prepared by using chemical routes, depend greatly on the type and amount of the incorporated species [23,24]. It has been reported that silicate glasses containing certain amounts of silver, prepared by the solgel method, can be crystallized in the Cristobalite phase by annealing at temperatures much lower than 475 °C predicted by

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the phase diagrams, and the preliminary results of some optical investigations have been reported by other researchers [25,26]. A study of the available literature suggests that this synthesis route has not been fully studied for the preparation of colloidal suspensions of nano-metal-oxides systems.

Our investigation here was aimed at the synthesis of metal nanoparticles and incorporating these in nano-silicate glasses, for eventual use in various applications. Fundamental research is still required in order to optimize the spectroscopic properties of sol–gel synthesized silver-doped silica glasses. The present work is aimed at improving the knowledge in this particular area of research.

Ag-doped samples were prepared using a base-catalyzed reaction. Several experimental conditions were studied and, different variables that control the sample preparation and nanocomposite formation were identified. In the following sections, these variables are described and discussed in the context of optical and spectroscopic properties. The stem of this study is in the results of our earlier report [22], in which, we demonstrated the effect of temperature and time on Nd_2O_3–SiO_2 nanocomposites. The average size of the silver nanocrystallites in a silica matrix was found to be ~15 nm. The X-ray diffraction (XRD), surface area (BET), UV–Vis Diffuse Reflectance Spectroscopy (DRS) and Photoluminescence data for silver-silicate nanocomposites are presented.

2. Experimental

2.1. Preparation of bulk samples

The principles and the basic technique of the sol–gel process are described in detail elsewhere [22]. Silver silicates were prepared by mixing high purity reagents $(CH_3CH_2O)_4Si$ (TEOS – Tetraethoxy Silane, Aldrich 99.999), ethanol (Aldrich 99.9995), and de-ionized water. To prepare the samples, different amount of silver was introduced in the pre-hydrolyzed solutions in the form of silver-nitrate under heating. The hygroscopic nature of the $Ag(NO)_3$ salt makes its exact weighing difficult to measure. The pH of the resultant solutions was measured at 3. The resultant homogeneous solutions were filled into a mold and stored at room temperature. The onset of gelation occurred after about 5 days. After gelation, the samples were kept inside the oven for 20 more days for ageing, until no further shrinkage was detected.

2.2. Characterization

The crystallographic measurements were carried out using an X-ray Diffractometer (D-8 advanced X-ray diffractometer of M/s Bruker make) with Cu Kα wavelength (λ = 1.54059 Å). The DRS Studies were performed using SHIMADZU 3101 Spectrophotometer. The Photoluminescence investigations were performed using a Perkin–Elmer LS-55 fluorescence spectrophotometer having a standard Xe source. The physical characteristics of these samples were determined by nitrogen gas adsorption–desorption experiments carried out for surface area and pore size analysis using Quanta Chrome Analyzer (NOVA 2000e) at liquid nitrogen temperature. For this purpose, the samples were degassed at 150 °C for 3 h before each analysis. Specific surface area, pore-volume and pore-diameter were obtained by the BET equation and BJH methods respectively [2].

3. Results

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of 0.05 wt% Ag–SiO_2, 0.5 wt% Ag–SiO_2, 5 wt% Ag–SiO_2 and 10 wt% Ag–SiO_2 samples. For all the samples, the diffraction peaks match well with the standard SiO_2 diffraction pattern and the identification is anchored by the peak corresponding to miller indices Quartz [101] (JCPDS File No. 46-1045). The other diffraction peaks match well with the standard diffraction pattern of Ag_2O_3 with miller indices [111], [420] and [331] corresponding to $2\theta \sim 26.6°$, 32.6° and 41.4° (JCPDS File No. 40-0909) respectively. It can be seen that initial crystobalite phase of SiO_2 appears at 21.5° and quartz phase 26.6°. The pure SiO_2 sample shows SiO_2 as the only constituent of the materials,

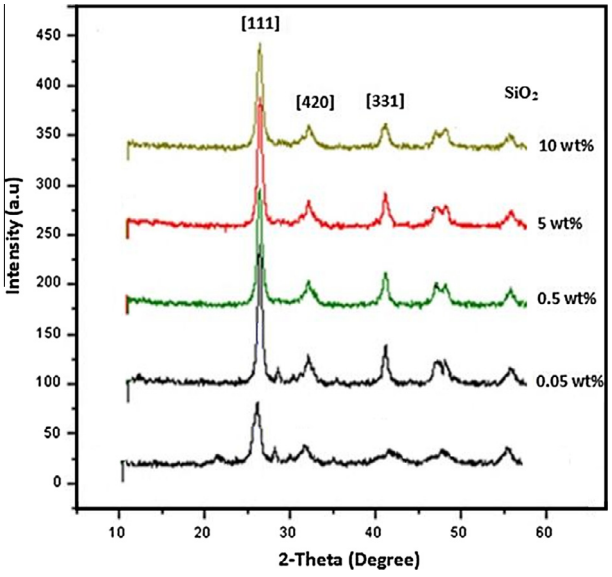

Fig. 1. X-ray Diffraction (XRD) of (a) SiO_2 (b) 0.5 wt% Ag doped SiO_2 (c) 5 wt% Ag doped SiO_2 (d) 10 wt% Ag doped SiO_2.

but as we doped with increasing quantities of silver, phase transformations take place and the silver oxide phase appears.

The crystallite size of these particles, as determined from the broadening of the XRD peaks corresponding to their 2-theta angles employing the Scherer's formula, and the corresponding lattice planes have been tabulated in Tables 1 and 2 by matching the *d*-values with the standard SiO_2 diffraction pattern. Silver doping has promoted phase transformation as clearly recorded in all cases. This can lead to increase in PL intensity.

Thus while the doping of low concentration of Ag (0.05 wt%), resulted in decrease in average crystallite size (15.44–12.35 nm) but as we increase the concentration of Ag to 10 wt% average crystallite size increased up to 23.30 nm.

3.2. BET surface area and pore size analysis

For surface area analysis of silica and Ag doped silica samples, a set of nitrogen (N_2) gas adsorption/desorption isotherm tests were carried out and the experimental results are presented in Fig. 2 (scans a–e). As seen from the nitrogen adsorption–desorption data, all isotherms show an increase of adsorbed volume up to P/P_0 values very close to 1, probably due to capillary condensation in the voids between powder particles and not due to the presence of large pores in the material itself. Volume adsorbed at very small P/P_0 values exhibits a deviation, which is characteristic of the presence of micropores or mesopores. The specific surface area (S_{BET}), total pore volume (V_P) and the average pore diameter (d_P) for the SiO_2 and Ag doped SiO_2 samples were measured by the BET method and the results are listed in Table 3. It can be seen that the specific surface area increased owing to Ag doping. All samples show identical isotherms of type IV and H2 hysteresis loop characteristic of mesoporous materials as classified by IUPAC classification [6]. The BET equation used is

$$\frac{1}{W((P_0/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right)$$

where *W* is the weight of gas adsorbed, P/P_0 the relative pressure, W_m the weight of adsorbate as monolayer, and *C* is the BET constant.

The inserted pore size distribution of these samples is also determined from BJH desorption isotherms shown in Fig. 3(a–e). We can see wide pore size distribution ranging from 26 to 41 nm