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# Development of silver doped nanocomposite using solgel technique

**Surender Duhan[1]*, Sunita Devi[2], M.Singh[3]**

[1]Materials Science Lab, Department of Materials Science & Nanotechnology Deenbandhu Chhotu Ram University of Science & Technology Murthal, Sonepat-131039, U.P., (INDIA)

[2]Department of Chemistry, Meerut College, Meerut, U.P., (INDIA)

[3]Department of Physics, Amity School of Engineering and Technology, Amity University Sec-125, Noida-201301, U.P., (INDIA)

E-mail : surender6561@yahoo.co.in

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## ABSTRACT

The solgel process was successfully prepared Silver/Silica nanocomposites. In this paper, our aim was to develop the silver based nano composites using sol gel method. This work is mainly focused on to study the synthesis of metal composites by sol gel method. We will also observe the morphologies and dimension of silver nitrate doped nano composites are influenced due to alteration in growth parameters such as different composition or thermal treatment. The structure of the sample prepared was studied using X-ray Diffraction (XRD), Energy dispersive X-Ray Spectroscopy (EDS), High Resolution Transmission Electron Microscopy (TEM).

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## KEYWORDS

Ag nanoparticles;
Silica gel;
Solgel;
Temperature.

## INTRODUCTION

Synthesis and characterization of nano-sized metallic powders have attracted attention of the materials community due to their promising properties[1-3]. Nanomaterials have properties which depend inherently on the small grain size. They show significantly different properties compared to the bulk material. In nanomaterials, the surface forms a sharp interface between a particle and its surrounding atmosphere. Properties of nanocrystallites depend on the preparation methods; molar ratio of the precursor used and post treatment[2]. The surface volume ratio of nanomaterials is very large. Nanotechnology is in the precompetitive stage which means its use is limited; nanoparticles are being used in a number of industries. In the recent past, nanocrystalline silver oxide/silicates have been synthesized by various methods, e.g. precipitation in high-boiling poyalcohol solutions, inverse micro emlusion, co-precipitation, hydrothermal and solgel auto-combustion[4-10]. Nano scale materials are used in electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, catalytic and materials applications[11-14]. Areas producing the greatest revenue for nanoparticles reportedly are chemical-mechanical polishing, magnetic recording tapes, sunscreens, automotive catalyst supports, bio labeling, electro conductive coatings and optical fibers[15-20].There are a number of techniques used to prepare nanomaterials. The solgel process is a method that is used commercially in many

applications, such as forming coatings on window glasses. One can summarize the key advantages offered by the solgel process. There are, it uses relatively low temperatures, can create very fine powders, produces compositions not possible by the solid state fusion. In addition, it allows higher doping concentrations and a more uniform distribution of metal in the host glass matrix to be achieved. The solgel method consists of series of seven steps: mixing, casting, gelation, ageing, drying, dehydration, and densification. Nanomaterials have the structural features in between those of atoms and bulk materials. While most micro-structured materials have similar properties to the corresponding bulk materials, the properties of materials with nanomaterials dimensions are significantly different from those of atoms and bulk materials. Due to nanometer size, many of the mechanically properties of nanomaterials are modified to be different from the bulk materials including, the hardness, elastic modulus, fracture toughness, scratch resistance, and fatigue strength etc. Thermal properties of nanoparticles have only seen slower progress. Recently, it has been shown that silica glasses containing certain amounts of silver, prepared by solgel method, can be crystallized in cristobalite phase at annealing temperatures much lower than $500^0$C predicted by the phase diagrams. Prior to the formation of the cristobalite phase, the silver forms nanocrystalline aggregates when the bulk samples are heat treated at temperatures of $500^0$C or higher.

In the present report, we have studied effect of calcinations temperature with prolonged annealing time that mainly supports the development of the silver silicates nanocrystallites in case of silver-containing-silica. The stem of this study is in the results of our earlier report[21], in which, we demonstrated the effect of temperature and time on silver nanoparticles. We found that the average size of the silver nanocrystallites in a silica matrix was~50 nm. The X-ray diffraction (XRD), Energy dispersive X-Ray Spectroscopy (EDS), High Resolution Transmission Electron Microscopy (HRTEM) data for silver silicates is presented.

## EXPERIMENTAL

Silver oxide/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 samples, the molar ratio of starting solution was taken as TEOS: $H_2O$: $C_2H_5OH$ was 1:11:5. (0.1-1 wt %) of $AgNO_3$ was introduced in the pre-hydrolyzed solution. About 80% of the total water was used for hydrolysis and condensation reaction and rest for the dissolution of $AgNO_3$. The pH of resultant solutions was two. The resultant homogeneous solutions were filled in a mold and placed in drying oven at room temperature. The gelation occured after 17 days. After gelation the samples were still left inside the oven for 30 days, for ageing (which results in a further shrinkage and stiffening of the gel), until no shrinkage appeared. Densification of the prepared samples was obtained by annealing in air, at different temperatures (100, 200, 400, and $500^0$C) and time (1h). 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 $A^0$ at 40KV and 30 mA. Using XRD data approximate crystalline size was also determined via Scherrer formula;

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

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. The particle size and aggregation state of particles were further measured with transmission electron microscope (model -FEI-Tecnai F30 G2 STWIN (300kV FEG)).

## RESULTS

### XRD

Figure 1 shows the XRD patterns of as prepared samples sintered at 100, 200, 400 and $500^0$C. Silver crystalline diffraction peaks were not observed in the sample (0.1 wt % and 0.2 wt %) heat treated at 100 and $200^0$C. It is believed that absence of silver peaks in these samples was due to highly dispersed silver species. Silver crystalline peak that is relatively weak and broad, indexed as (111) appeared at $2\theta = 38.3^0$ in the samples (0.5 wt %) sintered at $400^0$C. No other dif-

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fraction peaks were observed at higher angles in this sample. Diffraction peaks observed at higher angles, in the samples (1 wt %) sintered at $500^0$C may be attributed to polycrystalline growth of Ag particles. Silver peaks indexed as (1 1 1) and (2 0 0) were observed at angles $38.3^0$ and $44.6^0$ in the sample calcined at $500^0$C. These peaks correspond to the formation of nanoparticles in the amorphous silica network after sintering. The diffraction peaks became intense and their FWHM turned suggesting gradually narrow an increase in particle size. The mean size of silver nanoparticles was estimated by Scherer's equation. Mean silver particle sizes (diameters) estimated in the silica matrix varied from about 25 to 45 nm in these composite samples. The results indicate that with the increase in annealing temperature during sintering of samples, mean size of Ag nanoparticles in the amorphous $SiO_2$ matrix increased.

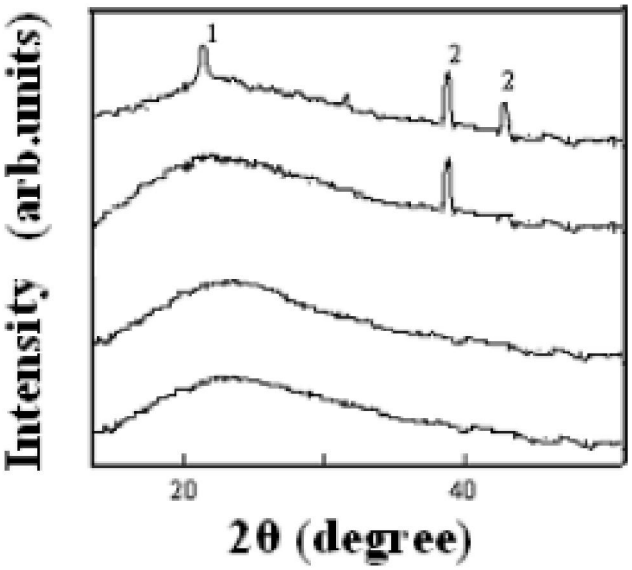
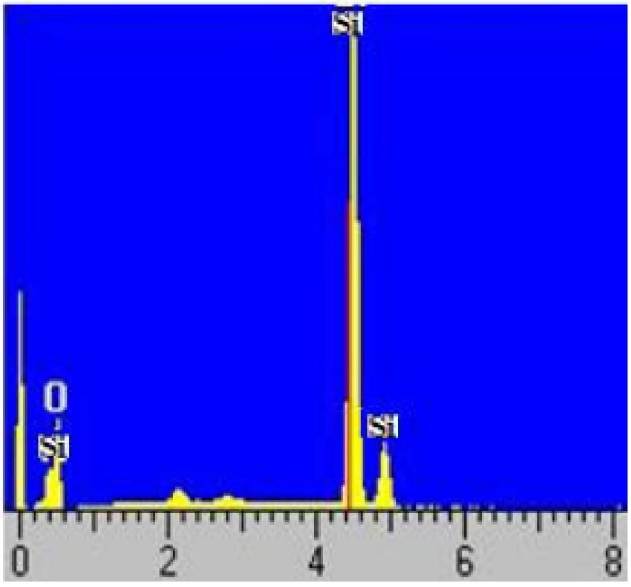



**Figure 1 : XRD pattern of the different amount of silver doped samples annealed at $100^0$C, $200^0$C, $400^0$C and $500^0$C**

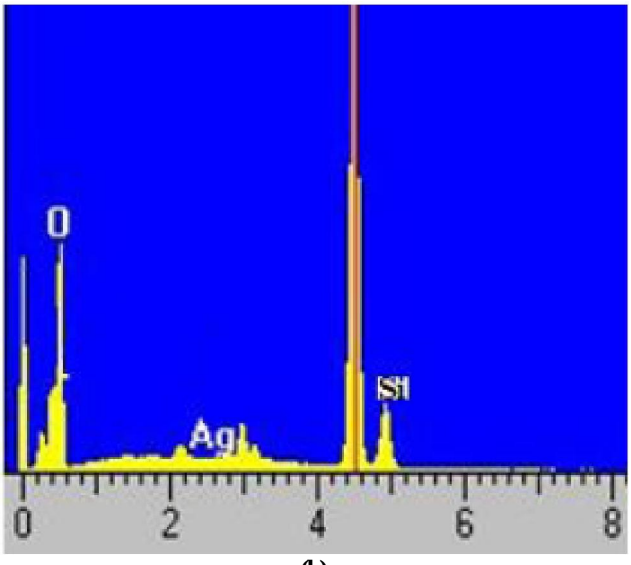
## Energy dispersive x-ray spectroscopy (EDS)

The detailed elemental analysis of Ag doped $SiO_2$ nanoparticles was carried out by using Energy Dispersive X-ray Spectroscopy (EDS), which is shown in Figure 2 (a, b). The spot EDS measurement was performed with reduced beam size and low accelerating potential to enhance signal to noise ratio.

The EDS study revealed that our $SiO_2$ is pure and stoichiometric. The elements Silica and Oxygen are present in exact 1:2 stoichiometric ratio. In the doped case there is a peak showing the presence of silver which is due to silver doping during sample preparation and there is no other element depicted.




**(a)**

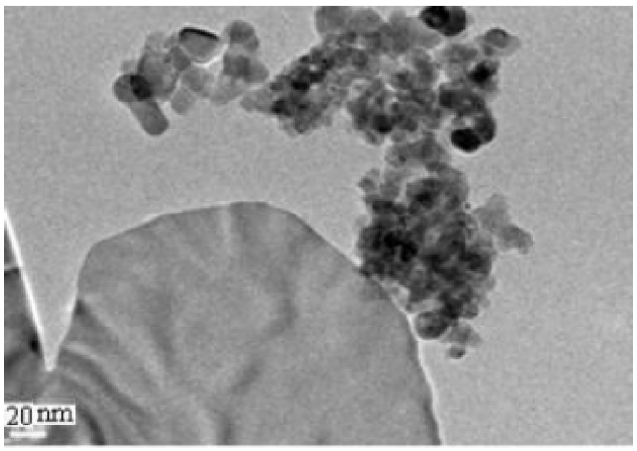



**(b)**

**Figure 2 : Energy dispersive spectra (a) $SiO_2$ (b) 1 wt % $AgSiO_2$.**

## HRTEM micrographs

Figure 3 show the TEM micrographs of the dispersion of silver nanoparticles in $SiO_2$ matrix. The nanoparticles with a mean size close to 13 nm were observed in micrograph. TEM micrograph with a mean grain size of around 20 nm was observed which was also justified by XRD, data. TEM micrograph some flakes of Ag are also shown which is due to the high doping of silver.




**(a)**

**Figure 3 : TEM micrographs showing the dispersion of silver in $SiO_2$ matrix (a) $500^0$C (1 wt%).**

## CONCLUSIONS

The solgel process successfully prepared silver-doped silica samples. The samples were characterized by XRD, EDS and HRTEM, and the formation of Ag/$SiO_2$ nanocomposites was confirmed. It is found that the evolution of the system as a function of the annealing temperature and doping percentage is necessary for obtaining a nanoclusters distribution in silica matrix.

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