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Grazing incidence small angle X-ray scattering study of silver nanoparticles in ion-exchanged glasses

Weidong Cheng [a,*], Zhaojun Wu [b], Xiaohua Gu [a], Xueqing Xing [c], Guang Mo [c], Zhonghua Wu [c,*]

[a] College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China
[b] Department of Practice Teaching and Equipment Management, Qiqihar University, Qiqihar 161006, China
[c] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

The size and distribution of silver nanoparticles in ion-exchanged silicate glass induced by thermal treatments in air at different temperatures were investigated by means of grazing incidence small angle X-ray scattering technique, X-ray diffraction and optical absorption spectra. Silver–sodium ion exchange of soda-lime silicate glasses was done at 350 °C for 240 min, then the samples were treated by thermal annealing in air at different temperatures 400, 500 and 550 °C, respectively, for 1 h. After the annealing treatment above 400 °C for 1 h, smaller Ag nanoparticles occurred, together with bigger ones. Both dissolution of smaller Ag nanoparticles and diffusion of larger ones are discussed in these stages of annealing in this contribution.

1. Introduction

Noble silver nanoparticles embedded in ion-exchange glasses are one of the most intensively studied materials due to their unique properties, such as their specific optical absorption, large third-order nonlinear susceptibility, as well as therapeutic and antibacterial potential [1–4]. These properties of silver nanoparticles are strongly dependent on the structural and geometric parameters of the particles (e.g. size, shape, distribution), which are determined by the specific preparation conditions [5]. Ion exchange is intrinsically a non-equilibrium process, where at least three phenomena contribute to give the ion-exchanged glass system, namely, diffusion, nucleation and aggregates growth. In the preparation process of Ag ion-exchange glass, silver ions coming from a molten salt penetrate into an alkali glass matrix following an inter-diffusion process. The concentration of diffused Ag^+ ions and their diffusion depth in the glass matrix depend considerably on the temperature, the duration time of ion-exchange process, the silver ions concentration in the molten salt, and the sort of glass matrix. The Ag ion-exchanged glass contains primarily Ag ions but also few nanoclusters. The nanocluster formation indicates that part of the Ag ions have been reduced during the ion-exchanged process [6]. A maximum exchange depth around 17 μm has been obtained in EDS configuration for the ion-exchanged sample at 320 °C for 120 min. After an annealing at 450 °C for 390 min the silver penetration reaches about 100 μm for the sample [7]. Structural rearrangements of the matrix often take place with the possible formation of either silver oxide complexes or silver nanoparticles [2,8,9]. Previous researches reveal that the annealing of sample promoted the formation of the silver nanoparticles, and the increase of size and penetration depth [1,10–14]. Annealing in air leads to oxidation of Ag nanoclusters and the formation of Ag–Ag_2O core–shell nanoparticles [8]. When the annealing temperature is higher than 575 °C, the smaller particles dissolve and bigger ones coarsen easily by Ostwald ripening in the surface layer [1].

A comprehensive characterization for the nanostructures of Ag-doped materials during a thermal process is crucial from both fundamental and technological standpoints. For this purpose, it demands the experimental information about particle size, concentration and distribution at the different stages of synthetic procedure. Small angle X-ray scattering (SAXS) technique is quite suitable for the nondestructive study of nanoscaled structures. For example, SAXS technique has been employed successfully to investigate the formation and growth mechanism of silver nanoparticles embedded in an ion-exchange glass matrix by annealing [6,15]. Grazing incidence small angle X-ray scattering (GISAXS) method has also proved to be a valuable tool in studying the size

* Corresponding authors. Tel.: +86 18704521820 (W. Cheng), +86 10 88235982 (Z. Wu).
E-mail addresses: 57399942@qq.com (W. Cheng), wuzh@ihep.ac.cn (Z. Wu).

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and distribution of silver nanoparticles in the superficial layer of ion-exchange glasses during a thermal treatment. Although the nanoparticles and nanostructures in the Ag nanocomposite glasses have been studied extensively in the thermal processes, the reports on the nanostructural studies of Ag nanocomposite glasses with the GISAXS method are still limited. In this framework, the use of GISAXS technique is expected to give novel contributions in the understanding of the mechanisms underlying the formation of Ag nanoparticles. The purpose of this paper is to clarify the size and distribution changes of Ag nanoparticles in the ion-exchanged glass specimen annealed at different temperatures 400, 500 and 550 °C for 1 h through an observation of GISAXS features, and further to obtain the information on the silver nanoparticles behavior in a diffusion and growth of non-equilibrium process.

2. Experiments details

Ag^+–Na^+ ion-exchanged glass samples were obtained by immersing commercial soda-lime slides (Sail brand, Cat. No. 7101, 25.4 × 76.2 × 1 mm, composed (wt%) of 72SiO_2, 14.5Na_2O, 0.7K_2O, 7.0CaO, 4.0MgO, 1.7Al_2O_3 0.1Fe_2O_3, and manufactured by Yancheng Huida medical instruments Co. Ltd.) into a molten salt bath of $AgNO_3$/$NaNO_3$ with mass ratio of 1:25 at 350 °C for 240 min. After cooling down to room temperature (RT), the ion-exchanged slide was washed subsequently with deionized water. Then, thermal annealing was performed in electrical furnace in air at the different temperature of 400, 500, 550 °C, respectively, for 1 h.

The ion-exchanged glass degradation characteristic was determined by thermogravimetric analysis (TG) using a TA Q5000IR type instrument. Measurement were carried out in air in the temperature range from RT to 1100 °C. The XRD measurements were performed on a Bruker-AXS D8 ADVANCE diffractometer operating in the Bragg–Brentano configuration with Cu Kα radiation (λ = 0.154 nm). Optical absorption spectra of the ion-exchanged samples were measured in the range of 300–800 nm with a PE Lamda35 type spectrophotometer.

The GISAXS experiment was manipulated at beam line 1W2A of Beijing Synchrotron Radiation Facility (BSRF) with incident X-ray wavelength of 0.154 nm. The storage ring was operated at 2.5 GeV with current about 200 mA. A Mar 165 two-dimensional charge couple device (CCD) detector with 2048 × 2048 pixels was positioned perpendicularly to the incident beam with a detector-sample distance of 5200 mm which was calibrated with a standard sample. The angle of grazing incidence was set to be 0.3°. These measured GISAXS patterns were transformed into one dimensional curves with the software Fit2D.

3. Results and discussion

TG curve of the Ag^+ ion-exchanged glass sample is shown in Fig. 1. There are three main stages of Ag^+ ion-exchanged glass degradation. The first stage of thermal decomposition occurred from about 100–300 °C; the second stage-from 400 to 700 °C; and the third stage-from 900 to 1020 °C. Thermal decomposition of Ag^+ ion-exchanged glass occurred in the three stages with a maximum decomposition rate at 200, 500 and 970 °C, respectively. The TG complexity of Ag^+ ion-exchanged glass suggests that Ag-containing nanoparticles and nanoclusters influence especially the decomposition. In this paper, the size and distribution of Ag-containing nanoparticles and nanoclusters in annealing samples are investigated in the second decomposition stage 400–550 °C.

The recorded X-ray diffraction patterns are shown in Fig. 2. According to the XRD analysis, each diffractogram contains only a broad hump at around 2θ = 20–35° and no obvious diffraction

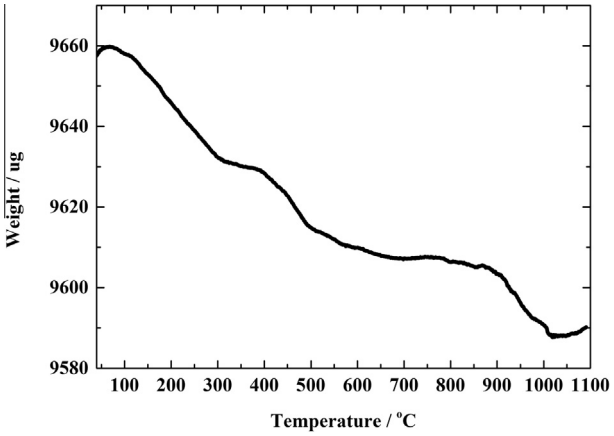

Fig. 1. TG curve of the Ag^+ ion-exchanged glass sample.

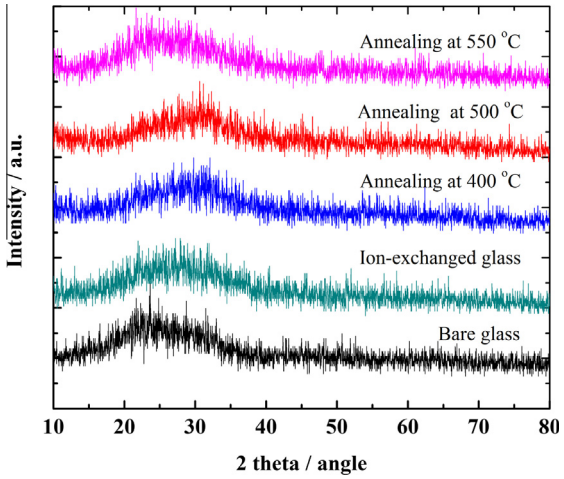

Fig. 2. XRD pattern of the Ag^+ ion-exchanged glass samples after 1 h annealing in air at different temperatures.

peaks corresponding to Ag-containing crystals were observed, which reveals the amorphous character of all glass samples. However, the broad hump shifts to bigger 2θ value, which is probably associated with the existence of very small (a few nanometers), metallic silver nanoparticles inside the glass matrix.

However, the broad hump of XRD annealed at 550 °C for 1 h moves to smaller 2θ value again. It's suggested that the structure of sample might occur a drastic change in annealing at 550 °C for 1 h.

Absorption spectra were recorded for the samples annealed for 1 h at the different temperatures in Fig. 3. For the Ag^+ ion-exchanged sample, the absence of a significant absorption band around 429 nm conforms that silver nanoclusters, if present, have very small size. During annealing for 1 h at temperature above 400 °C the absorbance at around 429 nm emerges. With increasing annealing temperature, this absorption band around 429 nm continuously increasing. At 550 °C annealing for 1 h, this absorption band is increased significantly and can clearly be assigned to the silver nanoparticle plasmon resonance. According to the literatures, the absorption band could present in the spectral regions 400–500 nm due to silver surface plasmon resonances of Ag_2O and 250–330 nm due to electronic transitions of Ag^0 metallic species [15]. A broad band is observed between 300 and 330 nm together with a new broad signal identified in the spectral region