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Cross-sectional Raman micro-spectroscopy study of silver nanoparticles in soda–lime glasses

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The growth and distribution of silver nanoparticles in ion exchanged glasses induced by thermal treatments in air at different temperatures were studied by means of cross-sectional Raman micro-spectroscopy analysis. Silver–sodium ion exchange of commercial soda–lime silicate glasses was done at 320 °C for 20 min, then the samples were treated by thermal annealing in air at temperatures in the range between 400 and 550 °C for 1 h. During the post-exchange thermal treatment, a further diffusion of silver from the surface toward the bulk occurred, together with the progressive formation of silver nanoparticles, whose fractional amount increased with an increase of the annealing temperature. Their average size and the related evolution as a function of the depth and of the treatment temperature were determined by Raman micro-spectroscopy analysis of the sample cross-section. Both aggregation of silver species and growth of silver nanoclusters are discussed on the basis of the theory of homogeneous nucleation in solids.

1. Introduction

In spite of the considerable amount of experimental research performed in the last two decades, the controlled doping of silicate glass waveguides with metal nanoclusters is still a challenging task for applications in several fields, such as photonics, catalysis and sensor technology, and for the preparation of superparamagnetic materials [1–4]. Furthermore, metal nanoclusters can induce a significant enhancement of the luminescence properties of rare earths in glasses, due to the widening of the excitation bandwidth [5,6], which is of crucial importance in telecommunication technology. In order to get the control of the size and distribution of nano-aggregates in the glass matrix, the precipitation of metal or oxide nanoparticles in glasses has been studied from more basic viewpoints, with specific concern for the cluster nucleation and growth kinetics, stability, and structure in terms of composition, crystalline phase, size, and size distribution [7–11].

In particular, for most applications it is of outmost importance to obtain optical waveguides containing nanoclusters with concentration and size sufficiently small to prevent significant attenuation of the transmitted light signal intensity. In this respect, the ion exchange process (either thermally or field-assisted driven) has demonstrated to be a peculiarly effective technique for doping silicate glasses well beyond the dopant solubility limits, thus producing glass light waveguides in which the formation of nanoparticles may be subsequently promoted by suitable energetic treatments, like irradiation with light ions [12,13], heat treatments in a reducing atmosphere [14,15] or by means of laser irradiation [16,17].

Silver has been the most studied element as metal dopant for these systems, since it is used for the production of several passive and active waveguiding glass-based devices, and its aggregation in the waveguides can be induced by means of several — possibly combined — procedures.

In spite of this great deal of studies, a complete phenomenological description of the nucleation and growth of metal clusters upon ion exchange and thermal annealing for silver-containing waveguides is still lacking, due to several factors. Indeed, ion exchange is intrinsically a non-equilibrium process, where at least three phenomena contribute to give the final system, namely, diffusion, nucleation and aggregates growth. These processes exhibit different regimes, that can be somewhat competing. This happens when dynamic feedbacks are triggered, either weakening or enhancing one process upon small changes of the involved variables like for example the local silver concentration, the temperature, the glass composition, or even the local stoichiometry.

The literature on the aggregation of silver in glass highlights in turn different aspects. The combination of diffusion, aggregation and growth phenomena was first faced by Berger [7], neglecting the diffusion of Ag^0 in the glass matrix, while several other works [8–11] studied the behavior of silver in ion exchanged systems taking into account both the diffusion and the reduction mechanisms, considering also the diffusion coefficient of reduced silver. In this case, the problem is quite complex due to the additional contribution of hydrogen. Nonetheless, the growth

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of nanoparticles within an ion-exchanged glass induced only by thermal treatments is still a rather unexplored task [18,19]. It is worth noting that the reduction of silver in silicate glasses can occur even without reducing agents, owing to the presence in the silica network of loosely bound electrons in reducing defects [20]. In fact, the formation of silver nanoparticles in as-exchanged glasses has been recently experimentally revealed by micro-Raman analysis of ion exchanged waveguides [19].

In this framework, the use of spectroscopic techniques in a configuration that allows a cross-sectional analysis is expected to give novel contributions in the understanding of the mechanisms underlying the formation of metal nanoparticles. In this paper, micro-Raman spectroscopy analyses are presented for silver–sodium ion-exchanged silicate glass slides. To this aim, both front-face and cross-section measurements were performed on the samples after the ion exchange process, as well as after thermal treatments in air at different temperatures. The particle size was calculated from the position of the maximum of low-frequency Raman peak. Then, the growth mechanism of the nanoparticles was described for different silver concentrations and as a function of both the temperature and the involved activation energies, estimated in the frame of the homogenous nucleation model.

2. Experimental

Commercial optical soda–lime glass (SLG) slides, of atomic composition O 60%, Si 24%, Na 10%, Mg 2.3%, K 2.0%, Ca 1.0%, Al 0.7% plus impurity traces, were immersed for 20 min in a molten salt bath of $AgNO_3$:$NaNO_3$ (1.0 mol%) at 320 °C. Some samples were then annealed in air for 1 h, at fixed temperatures in the range between 400 and 550 °C with steps of 50 °C.

Cross-polarized micro-Raman spectra were taken at room temperature in backscattering geometry using a triple-axis monochromator (Horiba-Jobin Yvon, model T64000), set in double-subtractive/single configuration, and equipped with three holographic gratings of 1800 lines/mm. The spectra were excited by the 514.5 nm line of a mixed Ar–Kr ion gas laser. The laser beam was focused onto the sample surface over a region of about 1 μm in size, and the scattered radiation from this region was collected in confocal mode exploiting the same objective used to focus the incident laser beam.

The sample characterization was performed in confocal mode by analyzing both the exchanged glass surface and the sample cross-section for in-depth investigation of the exchanged layer.

For the first type of measurements, the laser beam was focused onto the sample surface through the lens of a 100× microscope objective (N.A. = 0.90). In this configuration, the size of the spot was set in order to focus the laser light on the outermost part of the glass slide.

As for in-depth resolved micro-Raman profiling of glass layers, a cross-sectional cut of as-exchanged and thermally treated samples was first performed, and then confocal Raman microspectroscopy (CRM) was adopted for the lateral scanning throughout the cross-section of the glass layers. An 80× microscope objective (N.A. = 0.75) was used to excite and collect the Raman spectra for in-depth profiling measurements.

Sample positioning under the microscope objective was achieved by a manually operated X–Y translator, with sub-micrometric resolution. In-depth profiling analyses were performed by recording the low frequency Raman scattering spectra along the section perpendicular to the surface of the glass slide, starting from its edge by steps of few microns toward the inner region. The laser power on the sample surface was kept below 1 mW, to avoid heating effects. The scattered radiation, filtered by a double-monochromator, was detected by a liquid nitrogen cooled CCD detector and the final resolution was better than 0.6 cm^{-1}/pixel. In order to accurately determine the low frequency peak wavenumber, different emission lines from the neon lamp were used as reference. Repeated micro-Raman measurements on different sample regions, lying at the same depth beneath the sample surface, were run under the same experimental conditions, verifying that the recorded spectra exhibit a very good reproducibility.

3. Results

After the ion exchange process, the glass samples were colorless, without exhibiting absorption features in the visible region. After the thermal annealing at temperatures higher than 400 °C, the glasses turned yellowish, with color density increasing with the temperature.

Low-frequency cross-polarized micro-Raman spectra acquired for the surface of bare, as-exchanged and thermally treated glasses are reported in Fig. 1.

As it can be observed, the bare glass exhibits the so-called boson peak, which is characteristic of the disordered systems, in the form of a broad bump with maximum at about 60 cm^{-1}. After Ag^+ ion exchange, a distinct low-frequency Raman band peaking at about 32 cm^{-1} clearly grows up. The samples annealed up to 400 °C (not shown in the figure) exhibit the same features of the as-exchanged sample, along with a progressively enhanced luminescence background extending to the high wavenumber side. At annealing temperatures higher than 400 °C, the low-frequency Raman band increases in intensity, sharpens and progressively shifts toward lower wavenumbers.

The observed low-frequency Raman scattering is due to the acoustic vibrational modes of metal silver nanoparticles embedded in the soda–lime silicate glass matrix. In particular, within the approximation of spherical particle shape, the peak frequency ω_p can be related to the particle diameter d by the relationship [21]:

$$d = 0.85\frac{v_t}{\omega_p c} \tag{1}$$

where v_t is the transverse sound velocity in silver (1660 m/s) and c is the light speed. A shift to lower wavenumbers of this peak can be therefore ascribed to an increase of the mean particle size, while its intensity is proportional to particle volume.

Hence, the low-frequency Raman spectra suggest that just beneath the surface of the as-exchanged glass a low concentration of small silver nanoparticles is present, whose average size increases with the annealing temperature. The width of the peaks and the tail toward higher wavenumbers indicates the presence of small particles with a broad size distribution in the sample annealed at 450 °C. The size distribution becomes narrower on further increasing the annealing temperature. The average dimension of the particles on the surface of the glass, as calculated from Eq. (1), ranges from 1.5 nm for the as-exchanged

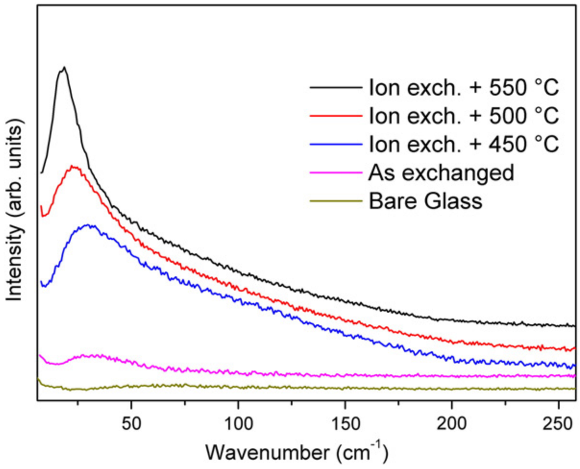

Fig. 1. Low-frequency cross-polarized micro-Raman spectra of the bare soda–lime silicate glass, as-exchanged glass, and ion exchanged glass after annealing in air for 1 h at different temperatures. for 1 h.