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Effect of gamma rays absorbed doses and heat treatment on the optical absorption spectra of silver ion-exchanged silicate glass

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ABSTRACT

Samples of a commercial silicate glass have been subjected to ion exchange at 320 °C in a molten mixture of $AgNO_3$ and $NaNO_3$ with molar ratio of 1:99 and 5:95 for 60 min. The ion exchange process was followed by gamma irradiation in the dose range of 1–250 kGy and heating at the temperature of 550 °C for different time periods ranging from 10 to 582 min. The spectral absorption in UV–Vis range of the Ag–Na ion exchanged glass was measured and used to determine the states of silver prevailing in the glass during the ion exchange, the gamma irradiation and the heat treatment. The gamma irradiation induced holes and electrons in the glass structure leading to the creation of a brown colour, and silver ions trapped electrons to form silver atoms. We observed the first stage of aggregation after irradiation, as well as after heating. The silver atoms diffused and then aggregated to form nanoclusters after heating at 550 °C. A characteristic band at about 430 nm was induced. The surface Plasmon absorption of silver nanoclusters in the glass indicated that the nanoclusters radius grew between 0.9 and 1.43 nm with increasing of annealing time from 10 to 242 min and then saturated. We also found that the size of aggregates depends on the value of gamma radiation absorbed dose. Contrary to what was expected, we found that 20 kGy is the optimal absorbed dose corresponding to the larger size of the aggregates which decreases for absorbed doses above 20 kGy.

1. Introduction

Small silver particles embedded in glass matrix are widely studied because of their potential applications for glass colouration [1,2] for ionizing radiation dosimetry [3] and recently for fabricating optical devices [4]. The ion exchange has been considered one of the most important techniques to introduce noble metals in glass surface. This technique is simple, and does not require sophisticated equipments. Combined with a heat treatment, the ion exchange technique has received an increase attention as it can be used to introduce metallic nanosize particles such silver, gold and copper into glass matrix [5–7]. Recently ionizing radiation such as gamma rays, electrons, heavy ions, X-ray or laser beam, has been used, with or instead of the heat treatment, to produce silver colloids after the ion exchange in glass [8–11]. Ionizing radiation produces in insulating materials electron hole pairs (excitons) which lead to the production of stable defects and changes of the valence state of doping and impurities ions in the glasses. The production of irradiation defects cause preferential light absorption and consequently these defects are called "colour centres". These centres are of many types and depending on the glass composition and can be analyzed using optical absorption bands and EPR lines.

Gamma irradiation effects in silicate glass have been studied in our previous papers [12,13].

Only few works have been reported in the literature about the combined role of gamma irradiation and heat treatment on the formation of silver nanoparticles in ion exchanged glass.

Further investigations will be necessary to shed light on the relationship between the absorbed dose of gamma radiation and the properties of UV–visible spectra of silver ion-exchanged silicate glass. Our observations indicate that the first stage of aggregation can occur after irradiation before the heat treatment. We have

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observed that gamma irradiation followed by the heat treatment of an ion exchanged silicate glass can effectively promote silver migration and aggregation of metallic nanocluster. The effect of absorbed dose variation on the size of the aggregates has also investigated. In our knowledge, this effect had not been reported in previous work.

2. Experimental

2.1. Glass composition

The glass samples were obtained from the same glass sheets purchased from the local market and were cut into pieces of $11 \times 30 \times 1.5\ mm^3$ dimensions for optical measurements. The chemical composition of the glass samples were determined by the Prompt Gamma Activation Analysis technique [14] in the Budapest Neutron centre (constituents in wt%: 68.52 SiO_2, 13.77 Na_2O, 8.19 CaO, 4.34 MgO, 1.003 Al_2O_3, 0.588 K_2O, 0.105 Fe_2O_3 and about 3.5% of other components).

2.2. Procedure of ion exchange

Glass samples were dipped in a molten salt bath formed by a mixture of $AgNO_3$ and $NaNO_3$ with molar ratio of 1:99, 5:90 and 10:90 for 60 min in crucible of Al_20_3. The ion exchange has been carried out at a temperature of 320 °C for 1 h. During this step, the silver ions of the salt bath diffuse inside the glass matrix. The ion exchange samples are cleaned with distilled water and acetone to remove any silver nitrate adhering to their surface.

2.3. Gamma irradiation and heat treatment

Glass samples were irradiated at the Tunisian pilot plant ^{60}Co gamma irradiation facility [15] at a dose rate of 8.5 kGy/h and at room temperature with doses varying from 1 to 250 kGy.

Thermal annealing was performed in electrical furnace in air at the temperature of 550 °C for different time periods ranging from 10 to 582 min.

2.4. Optical absorption spectra

Optical absorption spectra of the glass samples were measured in the range of 300–700 nm with a Shimadzu UV–VIS spectrophotometer (model PharmaSpec UV-1700). The measurements were carried out against a glass sample subjected neither to ion exchange nor to gamma irradiation.

3. Results and discussion

3.1. Effect of ion-exchange

Glass samples were subjected to ion exchange procedure, with molar ratio of 5:95, at a temperature of 320 °C for 1 h. After ion exchange, the absorption spectrum showed significant difference from that before the ion exchange. As illustrated in Fig. 1, the spectrum is characterized by a sharp asymmetrical absorption band located at 305 nm. The asymmetric shape of this band may be due to the fact that the maximum measured does not match the maximum of the band but only to the loss of sensitivity of the spectrophotometer below 300 nm.

When samples of silicate glass are immersed in molten silver nitrate, sodium ions diffuse from the glass surfaces to the molten salt, and silver ions diffuse from the molten salt to the glass surfaces where they replace sodium ions. The exchanged glass is colourless or very faint yellow state. Accordingly, changes in the

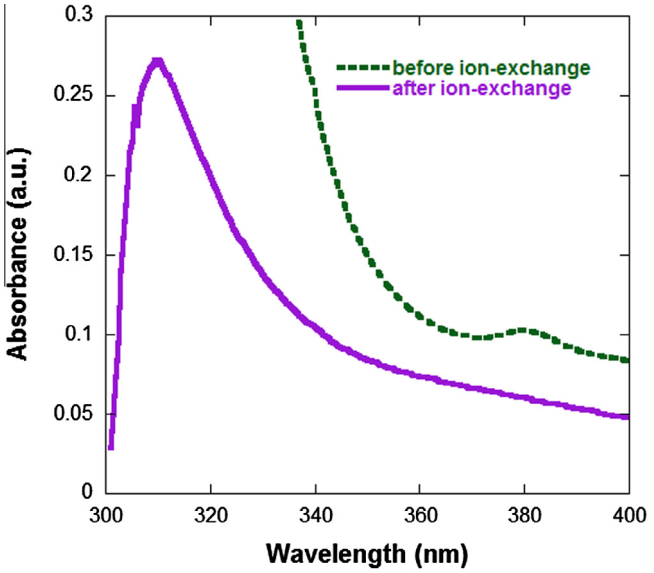

Fig. 1. Absorption optical spectra of silicate glass before and after ion-exchange.

spectrum of glass after ion exchange could be ascribed to modification of the composition of the glass surface by replacement of sodium ions by silver according to the reaction:

$$\equiv Si{-}O{-}Na^{+} + Ag^{+}NO_3^{-} \rightarrow \equiv Si{-}O{-}Ag^{+} + Na^{+}NO_3^{-} \quad (1)$$

The absorption band having a maximum at 305 nm was assigned to Ag^{+} ion. The information available in the literature about the origin of this band was reviewed in details by Ahmed et al. [16] and Paje et al. [17].

3.2. Effect of gamma irradiation

Silver exchanged as well as non-exchanged silicate glass samples were gamma-irradiated to 250 kGy. Optical absorption spectra were measured several days after irradiation are shown Fig. 2. The

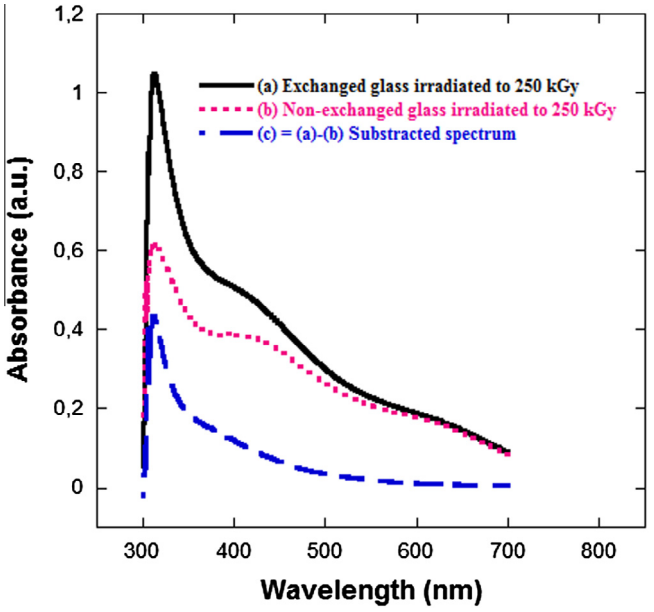

Fig. 2. Absorption spectra of the glass irradiated with γ rays at 250 kGy (a) spectrum of a 10% $AgNO_3$ exchanged glass; (b) spectrum of non-exchanged glass; (c) = (a) – (b).