J Mater Sci (2007) 42:4170–4176
DOI 10.1007/s10853-006-0682-7

X-ray irradiation induced optical absorptions in silver and manganese doped soda-lime silicate glass

Jiawei Sheng · Liqiang Jiang

Received: 29 April 2006 / Accepted: 17 July 2006 / Published online: 2 March 2007

Abstract Silver nanoclusters formation was observed in Ag-doped or Ag–Mn-doped soda-lime silicate glasses after X-ray irradiation followed by thermal annealing. Silver nanoclusters were formed with mean-size of about 3 nm after heating at 420 °C for 1 h in Ag-doped glass, and were disappeared after heating at 600 °C for 1 h. Mn^{3+} was formed in Mn-doped glass after X-ray irradiation followed by heating at 400 °C for 1 h, and was reduced to Mn^{2+} upon subsequently heating at 600 °C for 1 h. The presence of Mn^{3+} led to a purple color, while the silver nanoclusters provided a yellow color in the glass. The Ag-doped or Mn-doped glass may be viable as recyclable coloration glasses. In Ag–Mn-doped glass silver nanoclusters were formed only after heating at a high temperature of 600 °C following the irradiation. In addition, manganese showed a similar X-ray-induced behavior in the Mn-doped glass and the Ag–Mn-doped glass. In contrast, silver behaved differently in the Ag-doped glass and the Ag–Mn-doped glass. Unlike those in Ag-doped glass, the silver nanoclusters would not be dissolved in Ag–Mn-doped once they were formed.

Introduction

From ancient times to the present day, the transparentness and colorfulness of glass have remained as perhaps its most attractive physical properties. The following additives have been widely adopted to prepare the color of glass: (1) transition metal ions, (2) rare earth ions and (3) metallic nanoclusters [1, 2]. In general, the change of glass color is achieved by altering the glass composition, such as doping different types of ions. The color of the glass can also be modified by changing the redox of certain metal ions. With the exception of amber glass, colored glasses now present problems in the recycling process, because they must be separated from colorless glass to prevent colorization during re-melting. Apparently, the development of simple techniques for the coloration and equally importantly the decoloration to eliminate the need for the separation in recycling process, (e.g. photoinduced coloration and decoloration by thermal bleaching), should be a great benefit to the industry of glass as a whole [3, 4].

We have previously explored the use of various coloration techniques to develop economically recyclable glasses [4–6]. These techniques which involved in producing silver nanoclusters by X-ray irradiation or changing of the oxidation states of manganese in glass were promising because the coloration and decoloration could be generated reversibly [4, 5]. We have reported that the glass which was colorless turned yellow when doped with small amount of silver. In addition, manganese displayed a purple color after X-ray irradiation and thermal annealing. The yellow or purple color could be bleached after heating at temperature higher than 500 °C [4, 5]. It is possible to produce multiple colors in a glass by controlling the redox of manganese or the formation of silver nanoclusters through annealing under varied annealing conditions [7]. Moreover, X-ray-induced silver

J. Sheng · L. Jiang (✉)
College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Zhaohui No. 6, Hangzhou, Zhejiang 310014, China
e-mail: jw-sheng@zjut.edu.cn

nanoclusters in glass could not be re-dissolved after heating at 600 °C once manganese was co-doped. There have been, however, few studies thus far on silver nanoclusters behavior in the presence or absence of manganese. In the present research, we studied silver nanoclusters formation and manganese redox behavior under X-ray irradiation and thermal annealing. The mechanism and absorption behavior of silver nanoclusters and manganese were investigated by using absorption spectrometry and electron spin resonance (ESR) techniques.

Experimental procedures

Commercial soda-lime glass substrates composed of (wt.%): 74.2 SiO_2, 14.3 Na_2O, 1.9 Al_2O_3, 8.1 CaO, and 1.5 MgO, were used as a base glass. A small amount of Ag_2O, or/and MnO_2, along with SnO, a reductant, were added into the base glass to obtain as-named Ag-doped glass, or Mn-doped glass, and Ag–Mn-doped glass. Analytically pure carbonates and the metal oxides mentioned above were melted in a platinum crucible at 1,400 °C for 3 h under an air atmosphere and then annealed at 560 °C for 1 h. The glass was subsequently ground, polished, and cut into $10 \times 20 \times 2$ mm^3 plates. Irradiation was performed using an X-ray spectrometer (ThermoARL) at room temperature (Rh K_α, $\lambda = 0.061$ nm, 50 kV, 50 mA). The glasses were irradiated for 30 min. Optical absorption spectra were recorded at room temperature using a spectrophotometer (Shimadzu). All optical spectra were referenced to the absorption at $\lambda = 1{,}000$ nm of a non-irradiated sample (blank sample). The fluorescence spectra were measured using a HITACHI F-4500 fluorescence spectrophotometer at room temperature. First-derivative ESR absorption spectra were recorded at room temperature on an electron spin resonance spectrometer (BRUKER 300E), operating at 9.7 GHz. DPPH (1,1-diphenyl-2-piterylhydrozyl) was used to adjust the g-values, in which, the g-value was defined by the relation $h\nu = g\beta H$, where h is the Planck's constant, ν the spectrometer frequency, β the Bohr magneton, and H is the magnitude of the laboratory applied magnetic field at resonance.

Results and discussion

Ag-doped glass

Our results showed that the Ag-doped glass which was initially colorless (as-quenched glass, 0.02 wt.% of Ag_2O) displayed a dark brown color after X-ray irradiation. This is speculated to be due to the formation of induced defects [5, 6, 8]. The brown color was unstable. After heating at 420 °C for 1 h, it turned yellow which was stable at room temperature. When heated at 600 °C for 1 h, the glass returned to colorless. These attractive coloration properties of the Ag-doped glass were depicted in Fig. 1. The absorption band at about 410 nm after heating at 420 °C for 1 h was due to the surface plasmon absorption of silver nanoclusters. In contrast, the unirradiated Ag-doped glass kept colorless after thermal annealing for 1 h at a temperature ranging from 300 to 600 °C.

The silver introduced into glasses contains mainly as Ag^+ with a minor amount of Ag^0 atoms. As shown in Fig. 2, no significant Ag^0 signals were detected in the samples by ESR measurement before irradiation. After excited at 250 nm, a fluorescence emission peak at 335 nm was observed for the Ag-doped sample (Fig. 3), confirming the existence of Ag^+ [9]. Radiation may cause the displacement of lattice atoms or cause electron defects that involve changes in the valence state of lattice or impurity atoms [6, 10–13]. The ionizing radiation produces electron-hole pairs in the glass structure, leading to brown color. Silver ion is a strong electron trapper. When the silver-doped glass was subjected to X-ray irradiation, reduction of silver atoms was induced as

$$\text{Glass} \overset{\text{X-ray}}{\rightarrow} h^+ + e^- \quad (1)$$

$$Ag^+ + e^- \rightarrow Ag^0, \quad (2)$$

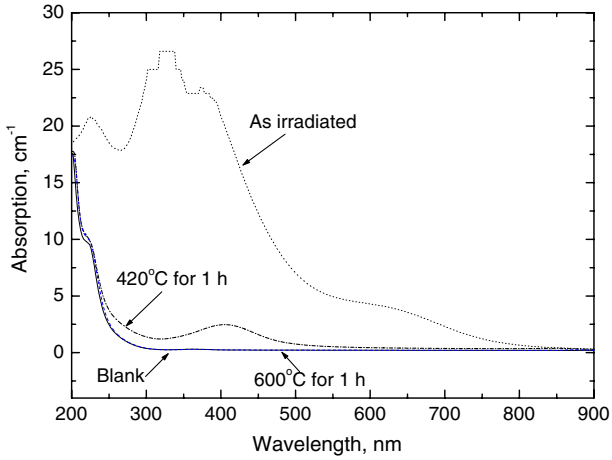

Fig. 1 Optical absorption of Ag-doped glass under different treatments

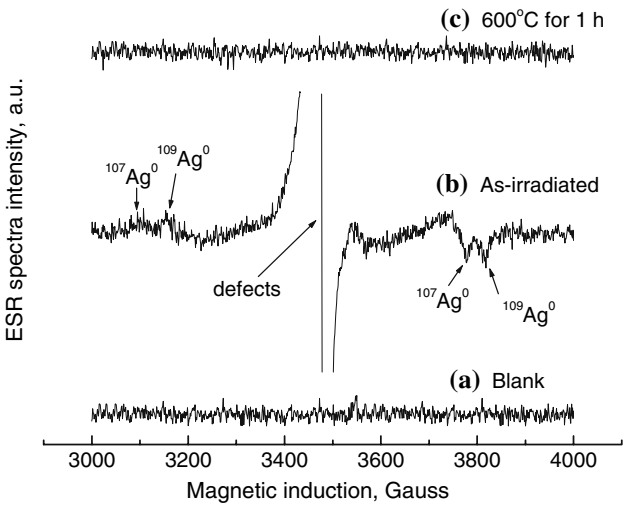

Fig. 2 ESR spectra of Ag-doped glass after varied treatments

where h^+ is a hole center and e^- is an electron. The Ag^0 signal was detected by ESR measurement after irradiation (Fig. 2b) The 335 nm silver ion fluorescence emission disappeared after X-ray irradiation, as shown in Fig. 3, indicating that silver ions have been transferred to silver atoms as in reaction (2). The silver atoms were not yet aggregated to form the cluster immediately after irradiation at room temperature. They aggregated into nanoclusters after thermal annealing

$$n\mathrm{Ag}^0 \rightarrow \mathrm{Ag}_n. \tag{3}$$

The aggregation of the Ag^0 atoms resulted in an absorption band at about 410 nm, leading to a yellow color. The mean size of nanoclusters was estimated to be ~3 nm according to Mie theory [14–16].

In order to understand the silver nanoclusters behavior, we monitored the absorption at 410 nm for the irradiated glass during annealing with a heating rate of 6 °C/min from 300 to 600 °C. The formation and dissolution of silver nanoclusters was shown in Fig. 4. The silver nanoclusters' dissolution was clearly observed at 600 °C. The silver nanocluster dissolution process was attributed to the recombination of electrons in silver atoms with hole centers or dissolution of silver nanoclusters forming silver atoms

$$\mathrm{Ag}^0 \rightarrow \mathrm{Ag}^+ + e^- \tag{4}$$

$$\mathrm{Ag}_n \rightarrow \mathrm{Ag}_m + (n-m)\mathrm{Ag}^+ + (n-m)e^-. \tag{5}$$

Migration and aggregation of silver atoms in glass is sensitive to temperature [7, 15]. Low temperature (such as <300 °C) prevents any large-scale silver movement. Dispersed silver atoms would not produce a surface plasma resonance; the brown color observed in our samples was due to the irradiation-induced defects. Major induced defects are recombined at elevated temperatures (such as 300 °C). The continuous elevation of the glass temperature allows enhanced migration of the silver atoms and thus coalescence into nanoclusters. The formation and dissolution of silver nanoclusters in our tested glass was revisable. Therefore, the silver-doped soda-lime silicate could be developed for a recyclable yellow glass.

Mn-doped glass

Manganese is often added into the soda-lime silicate glass to adjust the redox states. It is known that man-

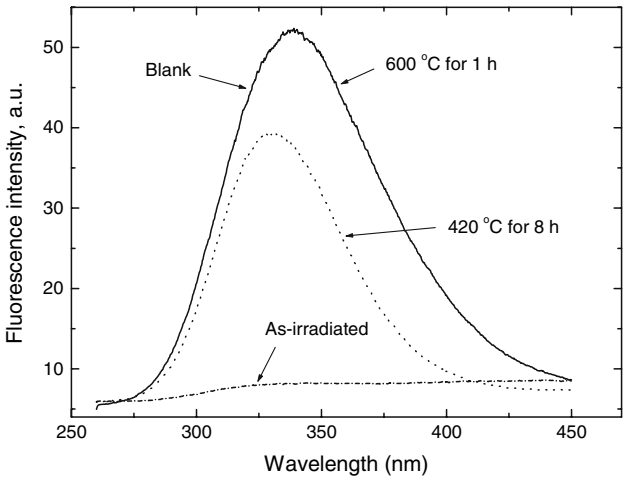

Fig. 3 Fluorescence spectra of Ag-doped glass with the excitation wavelength at 250 nm

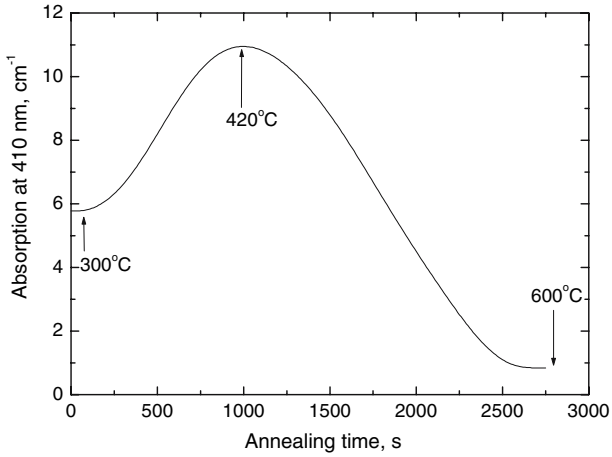

Fig. 4 Absorption of X-ray irradiated Ag-doped glass at various annealing time

ganese in soda-lime silicate glasses exists in the forms of Mn^{2+} and Mn^{3+}. In glass, Mn^{3+} has a very strong absorption around 500 nm, while Mn^{2+} has no visible absorption. Therefore, the presence of Mn^{3+} was detected by absorption at about 500 nm, and Mn^{2+} was measured by ESR in this study. The manganese-only doped glass showed a pink color resulted from Mn^{3+} ions before irradiation. To get a colorless Mn-doped glass, the reductant of SnO was needed. After adding equal amounts (0.05 mol%) of MnO_2 and SnO to base composition, as-quenched Mn-doped glass showed colorless. As depicted in Fig. 5, Mn-doped glass showed a deep purple color right after X-ray irradiation. The deep purple sustained after heating at 400 °C for 1 h. The glass returned to colorless after heating at 600 °C for 1 h. Like Ag-doped glass, unirradiated Mn-doped glass remained colorless after thermal annealing at temperatures ranging from 300 to 600 °C for 1 h.

The Mn^{3+} was reduced to Mn^{2+} by Sn^{2+} at a high temperature

$$Mn^{3+} + Sn^{2+} \rightarrow Mn^{2+} + Sn^{4+}. \quad (6)$$

Both Sn^{2+} and Sn^{4+} are colorless in glass, which provided a colorless as-quenched glass. The presence of Mn^{2+} was detected by ESR measurements, as shown in Fig. 6. The ESR spectrum of Mn^{2+} contained three sets of lines with effective g-factor values of approximately 4, 3, and 2, respectively. The hyperfine components due to ^{55}Mn were also observed for the $g \approx 2$ signal. During irradiation, hole and electron pairs were produced as shown in reaction (1). Induced electrons were captured by Sn^{4+} and hole centers were trapped by Mn^{2+}. Thus, the following overall reaction occurred in glass after irradiation

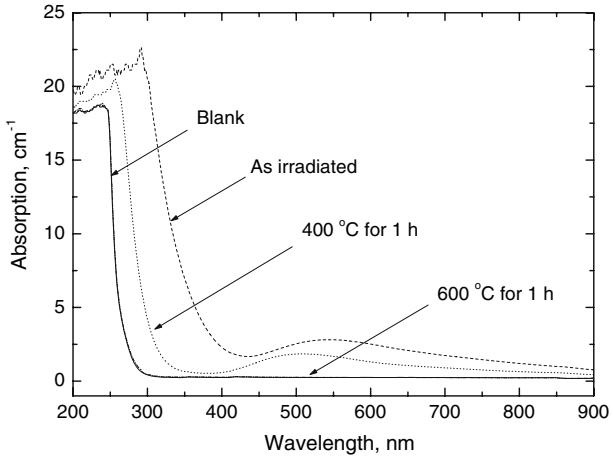

Fig. 5 Optical absorption of Mn-doped glass after varied treatments

$$Mn^{2+} + Sn^{4+} \rightarrow Mn^{3+} + Sn^{2+}. \quad (7)$$

The main absorption band right after irradiation appeared around 550 nm other than 500 nm, as shown in Fig. 5. Band separation using Gaussian resolution revealed that this absorption band resulted from the absorptions of Mn^{3+} (~500 nm) and induced defects (~620 nm) [3, 7]. The defects signals ($g \approx 2$) were clearly detected in the ESR spectrum (Fig. 6b). After heating at 400 °C for 1 h, the induced defects were recovered and the absorption peak was at 500 nm, which led to the purple color. At elevated temperatures, the reaction (6) occurred more readily than (7) according to thermodynamical calculation. Thus, Mn-doped glass became colorless again after heating at 600 °C for 1 h, because manganese completely recovered to Mn^{2+}. These results indicated the coloration of Mn-doped glass was reversible.

Ag–Mn-doped glass

When we added 0.02 wt.% of Ag_2O with equal amount of MnO_2 and SnO (0.05 mol%) into the base glass, the

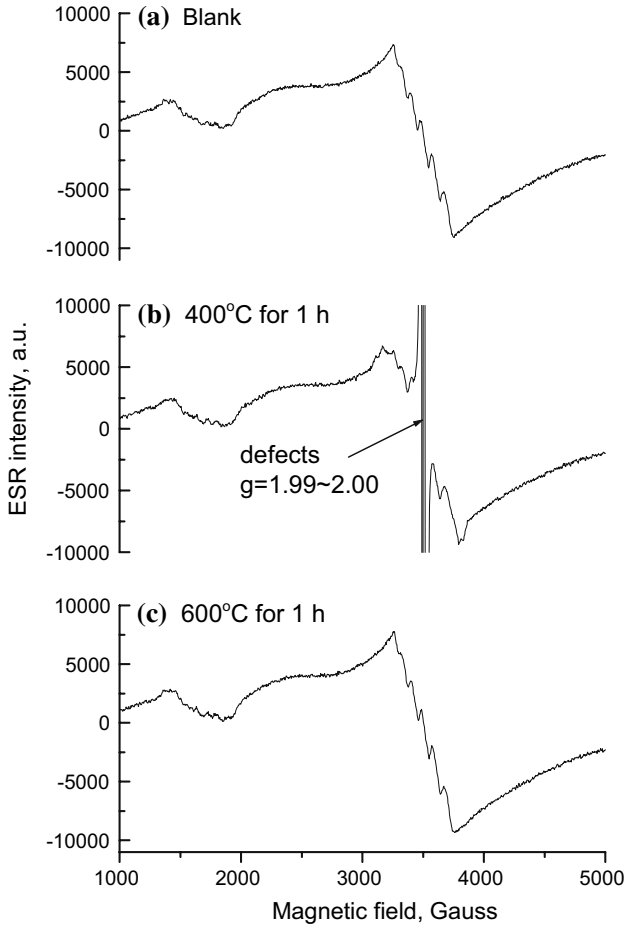

Fig. 6 ESR spectra of Mn-doped glass

colorless as-quenched Ag–Mn-doped glass was obtained. The unirradiated Ag–Mn-doped glass sustained colorless under heat treatment at up to 600 °C for 1 h. A dark brown color appeared after X-ray irradiation. The irradiated Ag–Mn-doped glass showed a purple color after heating at 300 or 400 °C for 1 h, and turned colorless after subsequently heating at 560 °C for 1 h or at 600 °C for about few minutes, and displayed a yellow color after heating at 600 °C for more than 10 min. The color intensity increased with the annealing time at 600 °C. Figure 7 shows the absorption spectra of Ag–Mn-doped glass after irradiation followed by annealing. The absorption band at about 500 nm resulted from the existence of Mn^{3+}, while the absorption band at about 410 nm was due to the surface plasmon resonance of silver nanoclusters. Unlike the Ag- or Mn-doped glass, Ag–Mn-doped glass displayed distinct optical properties. The yellow color sustained after heating at 600 °C. The Ag–Mn-doped glass may be viable as a multicolored glass.

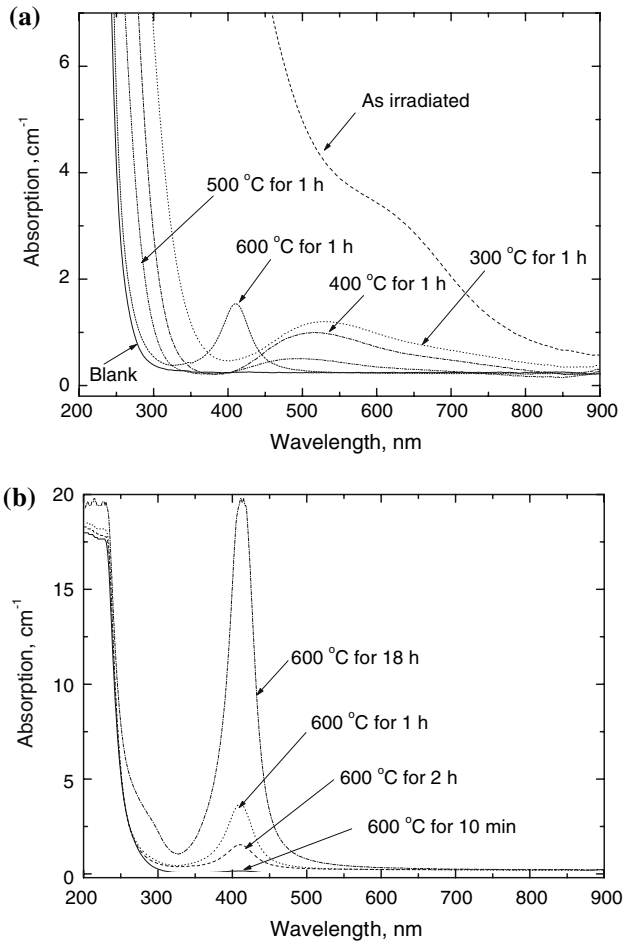

Fig. 7 Optical absorption spectra of Ag–Mn-doped glass after varied treatments

When Ag and Mn were co-doped in glass with the reducing agent SnO, no absorption around 500 nm was observed indicating the amount of Mn^{3+} was very small. Clearly, Mn^{3+} was reduced to Mn^{2+} by Sn^{2+} as shown in the reaction (6). The presence of Mn^{2+} was confirmed by the ESR measurements, as shown in Fig. 8. In addition, silver existed as Ag^{+} ions in the glass which were detected in the fluorescence spectra showing in Fig. 9, where a 355 nm fluorescence emission was observed in the as-quenched sample. Our results indicated that, prior to irradiation, Ag showed similar existing states in either the Ag-doped or Ag–Mn-doped glass. Likewise, the redox states of Mn in the Ag–Mn-doped glass were similar to those in the Mn-doped glass before irradiation.

After X-ray irradiation, the Ag–Mn-doped glass mainly contained induced defects (holes and electrons), Ag^{0}, Mn^{3+}, Mn^{2+}, Sn^{2+}, and Sn^{2+}, resulting from the reactions (1), (2) and (7). A weak absorption band at 520 nm was separated using the Gaussian resolution method, indicating the existence of Mn^{3+}. The absorption of Mn^{3+} was overlapped by the defects. Silver ions were transferred to silver atoms since the 355 nm fluorescence emission totally disappeared after irradiation, as shown in Fig. 9. The ESR signals of silver atoms were weak and were completely overlapped by the Mn^{2+} signals. After heated at 300 °C for 1 h, the glass showed a purple color. The color did not change after further heating at up to 500 °C for 1 h. At temperatures below 500 °C, no silver nanoclusters were formed since no absorption band at 390–420 nm was occurred. The induced defects were recovered after heating at 300 °C for 1 h, as the defects ESR signal completely disappeared (Fig. 8c). The silver was mostly in atomic state after annealing at 300 °C for 1 h based on the fluorescence spectrum shown in Fig. 7. After heating at 560 °C for 1 h or 600 °C for a short period of time such as a few minutes, the glass became colorless. This is because Mn^{3+} was reduced Mn^{2+}. However, silver atoms did not aggregate under this annealing condition. After heating at 600 °C for more than 10 min, the glass showed a slight yellow, due to the surface plasmon absorption (~410 nm) of silver nanoclusters. It should be noted that the intensity of this absorption band increased sharply with heating time while the peak position did not change, indicating that the number of silver nanoclusters was increased but their size did not grow [17, 18]. Analyzed from this bandwidth using Mie theory, the mean size of these nanoclusters was estimated to be ~7 nm, which was much larger than those formed in the Ag-doped glass.

Manganese showed a similar X-ray-induced behavior in either the Mn-doped or the Ag–Mn-doped glass,

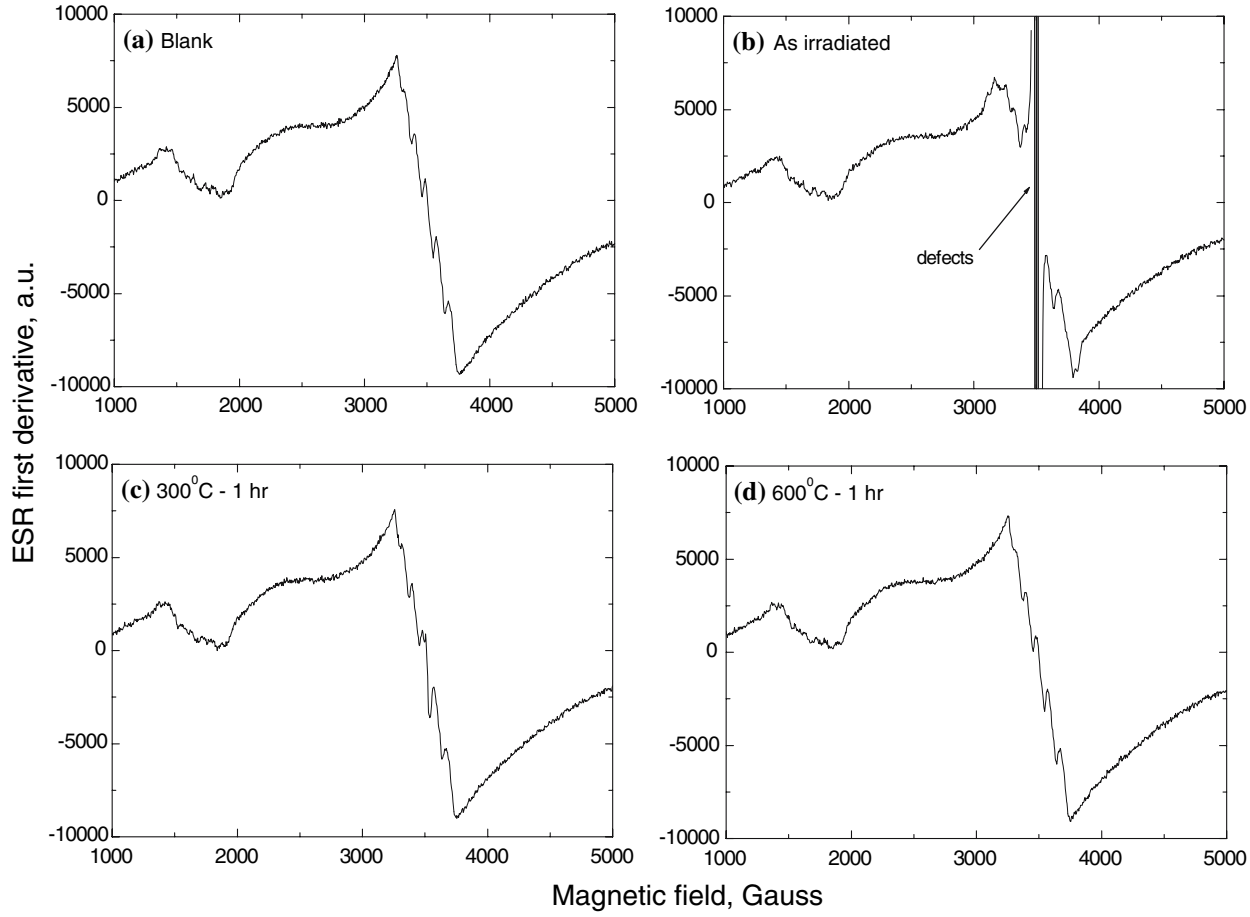

Fig. 8 ESR spectra of Ag–Mn-doped glass

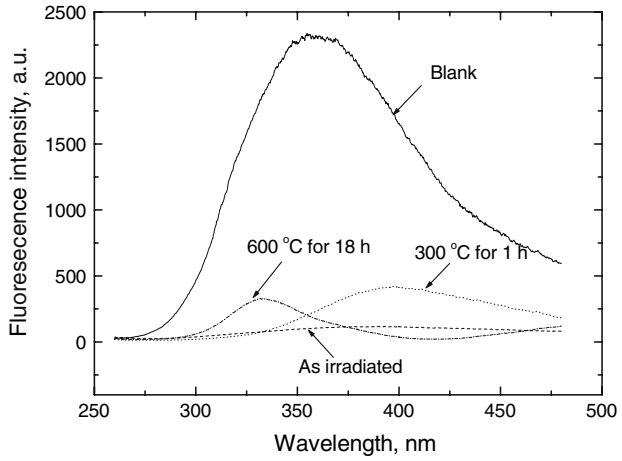

Fig. 9 Fluorescence spectra of Ag–Mn-doped glass with the excitation wavelength at 250 nm

while Ag behaved differently in the Ag-doped glass and the Ag–Mn-doped glass. Silver nanoclusters were dissolved in Ag-doped glass after heating at 600 °C, whereas they sustained in Ag–Mn-doped glass. Although silver atoms formation process had no change, the silver nanoclusters formation was greatly influenced by the addition of Mn_2O or/and SnO. From the experimental data present in this research, it is difficult to fully understand the mechanism of the silver behavior at this point.

Conclusion

Silver nanoclusters formation was observed in Ag-doped or Ag–Mn-doped soda-lime silicate glasses after X-ray irradiation followed by thermal annealing. Silver ions trapped the induced electrons and transferred to silver atoms after irradiation. Silver nanoclusters were formed with mean size of about 3 nm after heating at 420 °C for 1 h in Ag-doped glass, and were disappeared after heating at 600 °C for 1 h. Manganese existed mainly in Mn^{2+} in the as-quenched Mn-doped glass. Mn-doped glass showed a deep purple color after

X-ray irradiation followed by heating at 400 °C for 1 h, due to the formation of Mn^{3+}. Mn-doped glass returned to colorless after subsequently heating at 600 °C for 1 h because Mn^{3+} completely recovered to Mn^{2+}. These results indicated that Ag-doped or Mn-doped glass may be viable as recyclable coloration glasses. In addition, silver nanoclusters were only formed after irradiation followed by heating at much higher temperatures (e.g., 600 °C) in Ag–Mn-doped glass. After irradiation and subsequently heating at 300–500 °C for 1 h, Ag–Mn-doped glass showed purple due to the existing of Mn^{3+}. Silver nanoclusters with mean size of about 7 nm were observed after subsequently heating at 600 °C for 1 h, and the glass showed a yellow color. Unlike that of Ag-doped glass, the formed silver nanoclusters would not be dissolved in Ag–Mn-doped after heating at 600 °C. Without irradiation no change was observed for all three kinds of glasses when heated at up to 600 °C. It is therefore clear that X-ray irradiation played a great role on the redox behavior of silver and manganese.

Acknowledgements The author gratefully acknowledges the financial support for this work from Zhejiang Provincial Natural Science Foundation of China (R404108), Zhejiang Provincial Special Hired Professor Foundation, and Scientific Research Foundation of Zhejiang Provincial Education Department (20040556). Dr Bill X. Huang of NIH/NIAAA were acknowledged for the English improvement.

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