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Solarization of silver-doped soda-lime silicate glass containing X-ray induced color centers

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X-ray irradiation induced color centers and silver atoms in silver-doped soda-lime silicate glass at room temperature. After natural solar irradiation, the intensities of induced absorptions were greatly decreased; and the induced color was much unstable than sample without solarization. The induced absorption band at 330 nm was disappeared after solar irradiation, because silver atoms dissolved into ions during solarization.

1. Introduction

From ancient time to the present day, the various transparencies and colors of glass have remained perhaps its most attractive physical properties. In general, the change of glass color is achieved by changing the glass composition, such as doping different types of ions. Changes in color of glass may be obtained by changing the redox of certain ions either. On the other hand, it is widely known that the high-energy ionizing radiation (X-ray, gamma rays, and electrons, etc.) may produce visible coloration on the glass [1–3]. Although the study of the high-energy ionizing radiation on glass has been carried out for many decades, the emphasis of research is being on the preventing the darkening in glasses used in reactor or hot-cell windows and optical-fibers. Since the induced color is easily bleached by heat treatment, therefore, the application of the irradiation induced color of glass is prompting a renewed interest in Japan. We are developing the recyclable coloration of glass based on the X-ray induced color centers and have found that a small amount of silver (~0.02 wt%) greatly improved the induced coloration [4, 5]. The induced color is unstable at room temperature. We invested the durability and bleaching behavior of induced color when samples are stored in a dark place [6]. Since the glass will be practically applied in the open environment in future, its solarization behavior is of great interest. In this paper, we investigated the X-ray irradiation induced coloration of a silver-doped commercial soda-lime glass in the open environment. The solarization mechanism was studied. Optical absorption and electron spin resonance (ESR) measurements were made.

2. Experimental procedures

Commercial soda-lime silicate glass substrates composed of (wt%): 73.2 SiO_2, 15.3 Na_2O, 1.3 Al_2O_3, and 10.2 CaO with 0.02 wt% of silver were used. Analytically pure carbonates and oxides of the elements mentioned were melted in a platinum crucible at 1400°C for 3 h under an air atmosphere and then annealed at 550°C for 1 h. The glass was then ground and polished and cut into $10 \times 20 \times 2$ mm^3 plates. Irradiation was performed using a RIGAKU X-ray Spectrometer at room temperature (Rh K_α, $\lambda = 0.061$ nm, 50 kV, 50 mA). The glass was irradiated for 30 min. After irradiation, one sample was stored in an untransparent bag (Dark-sample, hereafter), and the other was kept open to air outside (Open-sample, hereafter), which received natural solar irradiation for about 2 h everyday. Natural solar irradiation was started in spring and then continued to full seasons. Optical absorption spectra were recorded using a HITACHI U4100 Spectrophotometer at room temperature. The optical spectra of non-irradiated sample were measured referenced to air. All optical spectra of irradiated samples were referenced to non-irradiated sample in order to obtain the net radiation induced absorption. Samples for ESR measurements were obtained at the dimensions of about $20 \times 2 \times 2$ mm. The first-derivative ESR absorption spectra were recorded at room temperature on a BRUKER 300E, operating at 9.7 GHz. Data were collected at 0.1 mW microwave power and 1.0 G amplitude of magnetic-field modulation at 100 kHz. DPPH (1,1-diphenyl-2-piterylhydrozyl) was used to adjust the g-values. Here, 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.

3. Results and discussion

The glass is colorless and has no measurable absorption in the region from 350 to 900 nm prior to irradiation, both under dark keeping and under solar irradiation for

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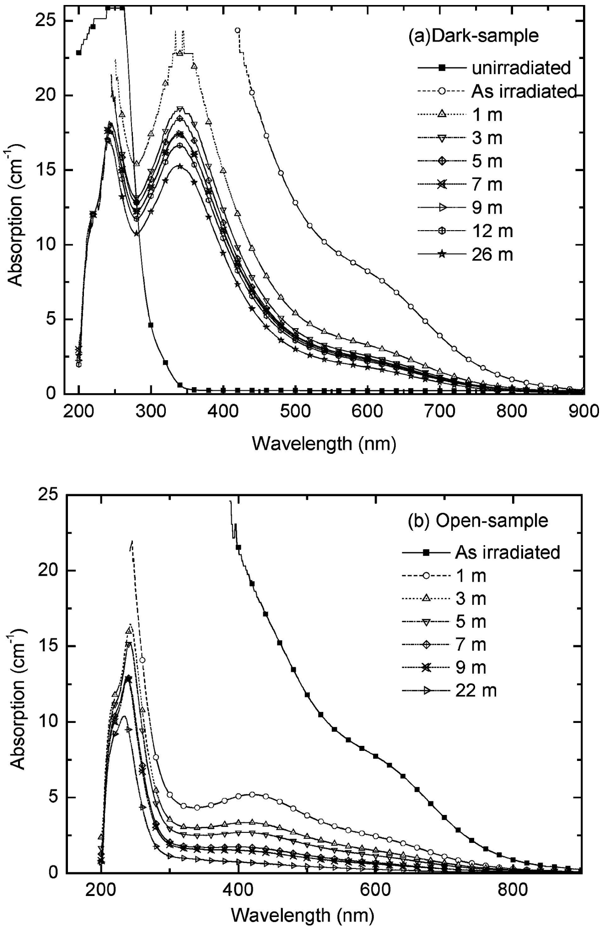

Figure 1 Optical spectra of glasses after X-ray irradiation.

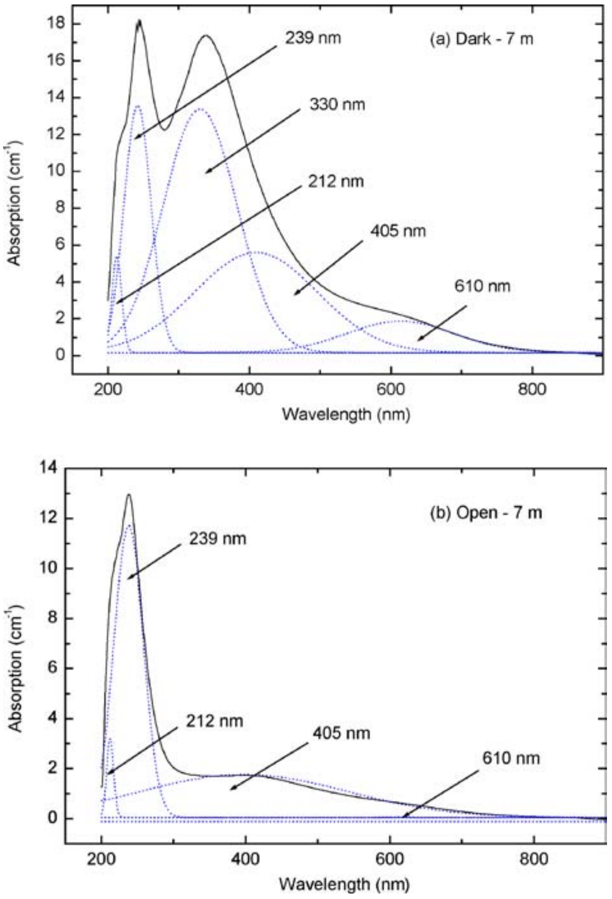

Figure 2 Induced optical absorption (thin lines) with band separation (dot lines).

a long time (>1 year). Since the iron impurity in glass was very low (<50 ppm), the absorption exists below 350 nm is mainly due to the glass absorption edge. The silver ions in glass without halogen are not easy to form silver atoms or clusters under solar irradiation. It was dark brown in color after X-ray irradiation. The net irradiation induced absorptions were shown in Fig. 1. Some additional absorption bands were developed as a result of irradiation. A noticeable bleaching of induced color at room temperature was observed in both samples. Both samples bleached fast at the first month, then bleached slowly after about 3 months. The Dark-sample showed a more stable color than the Open-sample, subsequently, showed a more dark color after irradiation. Two samples showed a great difference in absorption around 330 nm. The induced absorption around 330 nm of the Open-sample was almost disappeared after 1 month. The spectra have the same form during bleaching after 1 month in both samples, which is the same as glass without doping silver [7].

By the band separation with Gaussian resolution of the induced optical absorption spectra, the induced optical absorption for the Dark-sample was well modeled with five bands, having their peak positions at about 610, 405, 330, 239 and 212 nm. On the other hand, the induced absorption of Open-sample was modeled with only four bands, having their peak positions at about 610, 405, 239 and 212 nm. The absorption band at 330 nm was disappeared after solarization. Fig. 2 gives a result of the band separation of absorption spectrum. The induced absorption appears to be due to the superposition of a number of individual absorption bands corresponding to the different defects. The X-ray radiation produces electron-hole pairs which individually become trapped at various defect sites in the glass structure. Accordingly, new optical absorption bands may develop. The most fundamental radiation-induced defects in glasses are the nonbridging oxygen hole center (NBOHC: ≡Si—O*), the E' center (≡Si*), the peroxy radical (POR: ≡Si—O—O*), and the trapped electron (TE), where the notation "≡" represents three bonds with other oxygens in the glass network and "*" denotes an unpaired electron [2, 3, 8]. According to current knowledge and other research [2, 3, 8–11], the absorption bands near 610 and 405 nm were attributed to NBOHCs, the TE has the absorption at 305 nm, the E' center has an absorptions at about 239 and 215 nm, and the POR has an absorption band near 239 nm in both samples. Although no paramagnetic signals were detected in the glasses before irradiation, our ESR measurement clearly detected the signals of induced defects after irradiation, as shown in Fig. 3. As expected, the ESR spectra in Fig. 3 identified NBOHCs (g = 2.001), POR ($g = 1.995$), E' center ($g = 1.992$), and TE ($g = 1.95$) [11–13]. These defects existed in both samples even after keeping for about 2 years. Table II shows the relative ESR intensities of absorption bands after irradiation obtained from Fig. 3, where the E' center was much stable than NBOHCs.

On the other hand, Ag^0 atoms were clearly detected after irradiation (Fig. 3b). It is well known that Ag^0 atoms give an absorption at 330–360 nm in soda-lime

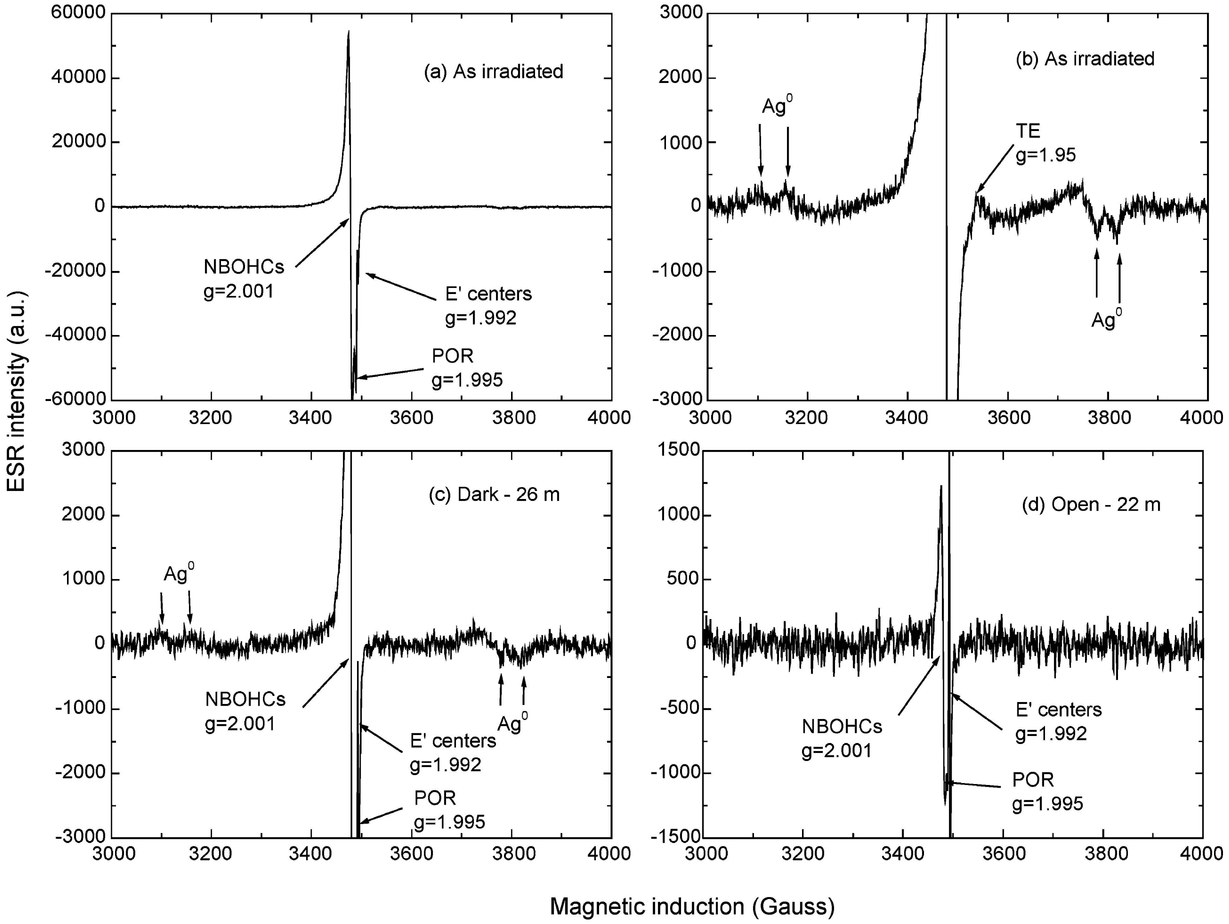

Figure 3 ESR spectra of glasses after X-ray irradiation.

silicate glasses. Therefore, the absorption at 330 nm in Dark-sample was due to not only the TE but also the formation of Ag^0 atoms. It is interesting to find that Ag^0 atoms were detected in Dark-sample after keeping for 26 months, but not detected in Open-sample after 22 months. When the Ag-containing glass was subjected to X-ray, reduction of Ag^0 atoms was induced according to the reaction $Ag^+ \xrightarrow{h\nu} Ag^0$. Table I summrized the induced absorption difference between two samples after keeping for 7 months. The absorption of Dark-sample is much strong than the Open-sample. The disappearance of 330 nm band was mainly due to the disappearance of Ag^0 atoms in the Open-sample. This is because of the solarization reaction $Ag^0 \xrightarrow{h\nu} Ag^+$, accordingly, many free electrons were generated. The induced hole defects easily trapped free electrons from Ag^0 atoms, subsequently, the induced absorption was rapidly bleached down.

TABLE I Intensities of absorption bands after irradiation

Peak position (nm)	Dark−7 m (cm^{-1})	Open−7 m (cm^{-1})	Assignments
610	1.70	0.02	HC2
405	5.42	1.72	HC1
330	13.21	–	Silver atoms, TE
239	13.42	11.67	E' centers, POR
212	5.23	3.15	E' centers

TABLE II Relative ESR intensities of absorption bands after irradiation

	NBOHC ($g = 1.99$–2.00)	E' centers ($g = 1.992$)
As irradiated	100	45.2
Dark–1 m	32.7	20.1
Dark–7 m	24.0	16.0
Dark–26 m	18.5	13.7
Open–22 m	22.3	3.2

The bleaching behavior of induced color, at least in the long-term range, showed a first-order kinetics. It is commonly known that the decay of the paramagnetic defects is the correlated recombination, thus it obeys first-order or second-order kinetics [14–16]. When the induced defects were of a fairly low concentration in the long-term range, the decay process would correspond closely to a diffusion-limited chemical reaction. Therefore, the recombination of induced defects was controlled by the hole or electron diffusion. Accordingly, we considered that the long-term bleaching of the induced color might obey a first-order kinetics, which can be expressed as [14]

$$\frac{dN_i}{dt} = -\lambda_i t \tag{1}$$

or on integrating

$$\ln N_i = A - \lambda_i t \tag{2}$$

where N_i is the induced defect number, λ_i the bleaching constant of induced defect, and A a constant. The

TABLE III Bleaching constants and half-life times of the silver-doped glass

	Absorption (nm)	Bleaching constant	Half-life time (nm)
Dark	610	0.013	53.7
	405	0.011	62.7
Open	610	0.131	5.2
	405	0.129	5.3

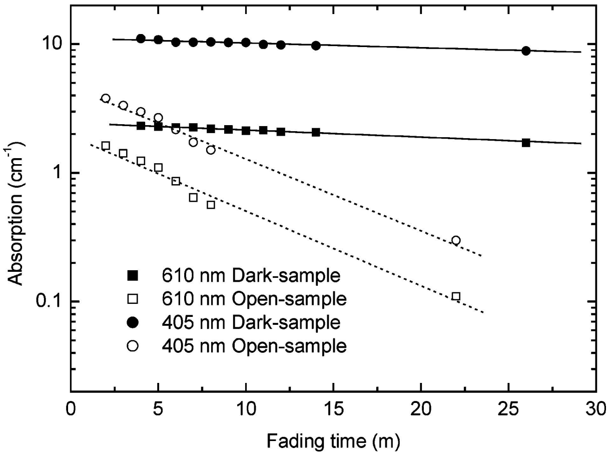

Figure 4 Bleaching behavior of induced absorptions at room temperature.

half-life time of defect τ is calculated from the following relation

$$\tau = \frac{0.69}{\lambda} \tag{3}$$

We calculated the bleaching constant and half-life time of both samples by fitting the experimental data in Fig. 4 using the least-square method. The fitting result was shown in Table III, where a fast decay process was observed for the Open-sample.

4. Conclusions

Solarization of silver-doped soda-lime silicate glass containing X-ray induced color centers was studied by the terms of optical absorption and ESR measurements. The induced optical absorption was due to the generation of defects induced by irradiation and formation of silver atoms. Five induced absorptions, having their peak positions at about 610, 405, 330, 239 and 212 nm, were observed. The induced coloration was much unstable after solar irradiation than keeping at dark place. The induced absorption band at 330 nm was disappeared after solar irradiation, because of the dissolution of silver atoms into ions as $Ag^0 \xrightarrow{h\nu} Ag^+$. In the Open-sample, the induced hole defects easily trapped free electrons from silver atoms, which rapidly bleached down obey a first-order kinetics. A fast decay process was observed for the Open-sample than the Dark-sample.

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