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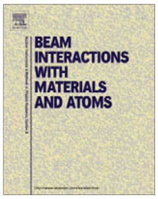

Effect of additive ions on the optical density and stability of the color centers induced by X-ray irradiation in soda-lime silicate glass

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ABSTRACT

To apply radiation-induced coloration of glasses as a reversible glass-coloring technique, we studied the influence of various additive ions incorporated into a soda-lime silicate glass on the optical density and stability of the color induced by X-ray irradiation. Absorption spectra before and after irradiation are discussed in the comparison with those of the undoped soda-lime silicate glass. Additive ions were incorporated as metal oxides, namely TiO_2, V_2O_5, Fe_2O_3, ZnO, Ga_2O_3, GeO_2, ZrO_2, Nb_2O_3, MoO_3, Ag_2O, In_2O_3, SnO, SnO_2, CeO_2, Eu_2O_3, Ta_2O_5, WO_3 and Bi_2O_3. Among them, TiO_2, GeO_2, Nb_2O_3, MoO_3, Ag_2O, In_2O_3, Eu_2O_3, Ta_2O_5, WO_3 and Bi_2O_3 have a large effect on optical density. The optical densities in the visible region for glasses doped with these oxides were much stronger than for undoped soda-lime silicate glass. On the other hand, incorporation of Fe_2O_3, SnO and CeO_2 reduced the optical density. Over longer periods the coloration of the undoped glass was one of the most stable while those of the Fe_2O_3, SnO and CeO_2-doped glasses soon faded.

1. Introduction

High energy electromagnetic radiation such as γ-rays, X-rays and ultraviolet induces various types of defects in glasses [1–3]. These defects have strong and broad absorption from the ultraviolet to the visible region. For instance, non-bridging oxygen hole centers are formed by irradiation through the following reaction in multicomponent glasses with non-bridging oxygen,

$$\equiv\text{Si—O}^- \rightarrow \equiv\text{Si—O}^{\cdot} + e^-.$$

Here, $\equiv$Si—O$^-$ and $\equiv$Si—O$^{\cdot}$ represent the non-bridging oxygen (NBO) and non-bridging oxygen hole center (NBOHC), respectively. The e^- represents the electrons released from the NBOs, which may be trapped at various sites in the glasses. The NBOHCs in the multicomponent glasses have broad absorption in the visible region and make the glasses brownish. These defect-forming reactions are reversible by thermal activation and then the coloration due to the defects disappears.

Photo-induced defects or color centers and their absorption deteriorate the optical performance of glass products in many cases [1,3]. Therefore, studies on defects in glasses have mainly focused on the assignments of the defects and their precursors in order to prevent such defect formation. Intensive studies on the photo-induced defects have been performed not only for silica glass [1,3,4] but also for phosphate and fluorophosphate glasses which are used as optical elements in the ultraviolet region [5–8].

On the other hand, we have proposed the practical application of the absorption due to the defects as a glass-coloring technique. This proposal is based on the concept in which the recycling of glasses becomes easier and is promoted using the reversible coloring and bleaching reactions by photo-irradiation and heat-treatment [9–11]. Colorless glasses are colored by photo-irradiation inducing defects and are used as colored glasses. Then, the colored glasses are recycled together with colorless glasses. Any processes to separate the colored glasses from the colorless ones are not necessary because the color of the glasses can be removed through the

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recycling process, i.e. heat-treatment or remelting. For instance, the brownish color due to the NBOHCs in soda-lime silicate glasses can be applied as the umber color which is widely used for bottle containers. This color will be also applicable to UV-cut windows used in vehicles.

Since the thermal stability of the defects is not sufficient, the color gradually disappears even at room temperature. Thus, more dense and stable coloration by photo-irradiation is indispensable in the practical application as umber glasses. The formation and stability of the photo-induced defects are well affected by the incorporated ions and these effects have been investigated, particularly for the transition metal ion-doped glasses [12–30]. However, there are few studies on the comparison of the optical density of the photo-induced color and its stability for long term period under the same condition for glasses with various dopants. In this paper, we investigated the effect of small amounts of additive ions on the optical density and its stability of the photo-induced absorption assigned to the NBOHCs in soda-lime silicate glasses.

2. Experimental procedures

2.1. Preparation of glasses

Reagent grade SiO_2, Na_2CO_3, $CaCO_3$ and oxides of additive ions were used as raw materials. Batches for 100–150 g glass having the desired compositions were mixed in alumina mortar and melted in Pt crucibles at 1400 °C for 2 h. The glass melts were cast in graphite moulds. The glasses were annealed at 500 °C and cooled to room temperature. The obtained glasses were cut into 2 mm thickness and the both sides were optically polished. Sheet glasses with 2 mm thickness were also used for comparison. Table 1 shows the compositions of the undoped soda-lime silicate glass referred to as base glass, and the sheet glass. The additives were introduced as oxides into the 100 wt% of the base glass. The incorporated oxides and the amounts are shown in Fig. 2. These oxides were chosen because they have no intense absorption in the visible region when incorporated into glasses at low concentration. The amounts of the additive ions were 0.26 mol for the cations in 100 mol of the base glass except for some ions, i.e. Ti; 0.30 mol, Fe; 0.44 mol, Zr; 0.30 mol, Ce; 0.21 mol.

2.2. X-ray irradiation and UV–visible absorption spectroscopy

X-ray irradiation of the glasses was performed using an X-ray source with Mo target ($\lambda = 0.7107$ Å for Kα line) operated at 50 kV and 50 mA without any monochrometers. The irradiation time was 10 min. Absorption spectra were obtained using a spectrophotometer, Hitachi U-4100.

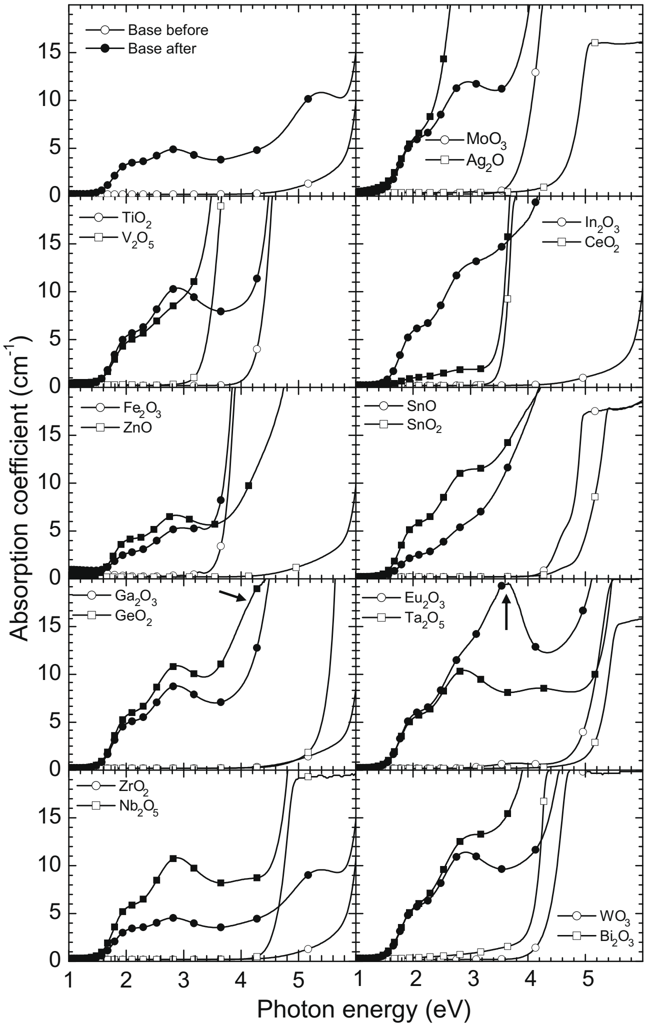

Fig. 1. Absorption spectra of the base and the various oxide-doped glasses before (open symbols) and after (closed symbols) X-ray irradiation.

Table 1
Composition of glasses used in the experiments (wt% and mol% in parenthesis).

	SiO_2	Na_2O	CaO	Al_2O_3	MgO
Base glass	74.1 (74)	16.5 (16)	9.4 (10)	0	0
Sheet glass[a]	71.1 (70.4)	13.1 (12.6)	8.9 (9.5)	1.5 (0.9)	5.4 (6.6)

[a] The sheet glass usually contains some impurities; the most important one is iron which comes from raw silica sands. Typical content in the glass of the iron impurity is 0.07 wt% as Fe_2O_3.

3. Results

In Fig. 1, the absorption spectra before and after the X-ray irradiation are shown for the undoped base glass and all the glasses doped with additive oxides investigated here. The absorption peaks at 1.98 and 2.74 eV for the irradiated base glass are assigned to the non-bridging oxygen hole centers HC_2 and HC_1, respectively [3]. These absorption bands in the visible region make the glass brownish. The absorption bands at 4.1 and 5.37 eV in the UV region are assigned to the trapped electron and hole (E′ center), respectively [3]. The absorption edges for most of the doped glasses before irradiation shifted to the lower photon energy side compared with that of the base glass because of the intra and inter ionic charge transfer transition relevant to the additive ions. For the ZnO, Ga_2O_3, ZrO_2 and In_2O_3 doped glasses, however, absorption shifts were scarcely observed. This is partly because of the low concentration of the additive ions. The absorption spectra of all the doped glasses after the irradiation showed two peaks or shoulders in the visible region, which are assigned to the NBOHCs. One exception was shown in the spectrum of the Ag_2O-doped glass, in which only one shoulder was observed because the absorption at the high photon energy side was extremely intense. For most of the doped glasses, since the absorption edges shifted to the low photon energy side after irradiation compared with those before irradiation, no specific absorption bands were observed in the UV region. However, some absorption bands other than the defect absorptions as the same as those of the X-ray irradiated base glass were observed for the X-ray irradiated GeO_2-doped and Eu_2O_3-doped glasses (see arrows in Fig. 1).

Fig. 2 summarizes the difference in the absorption coefficients at 1.98 eV before and after irradiation of the base, sheet and additive ion-doped glasses. This figure shows that they were strongly