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Effects of TiO_2 and P_2O_5 on solarization and crystallization of photosensitive lithium silicate glass

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ABSTRACT

In this study, the parent photosensitive glass and glass-ceramic in the system of lithium silicate containing AgCl under radiation of ultraviolet (UV) light were successfully prepared by melting process. Besides, the effects of adding TiO_2 and P_2O_5 as nucleating agents on the solarization and crystallization of lithium silicate photosensitive glass were studied. The characteristics of the samples were identified by ultraviolet-visible absorption spectroscopy (UV-Visible), simultaneous thermal analysis (STA-TG/DTA), X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). The results showed that adding P_2O_5 in the amount of 2 wt.% to this system could be an acceptable nucleating agent, while adding 4 wt.% TiO_2 to it resulted in shielding behavior against the UV light. Therefore, this amount of TiO_2 is not successful in both solarization improvement and nucleation process. In addition, lithium disilicate crystalline phase formed only in the samples containing P_2O_5.

1. Introduction

Nowadays, applications of glasses in various fields are wide spread. One of the most attractive types is photosensitive glass which possesses the capability of precipitation manipulating in soluble ceramic phase from the base glass. Typically, adding a photoactive compound and metal ions as nucleating agent to the glass matrix can take the control of the local precipitation process. Hence, it brings possibility of micro-shaping and micro-structuring on photosensitive glass ceramics through optical lithographic patterning and chemical etching processes. The most common dopants such as Sb_2O_3, Ag_2O, SnO_2 and CeO_2 within the glass matrix are able to emerge photosensitivity feature. Technically, UV radiation can release electrons from Ce^{3+} and Sn^{2+} and result in Ce^{4+} and Sn^{4+}. The Ag^+ ions would absorb these electrons and agglomerate to Ag clusters through the heat treatment then. All the mentioned processes are based on succeeding Equations.

$$2Ce^{4+} + Sb^{3+} \leftrightarrow 2Ce^{3+} + Sb^{5+}, \quad (1)$$

$$Ce^{3+} + h\nu \rightarrow Ce^{4+} + e, \quad (2)$$

$$Sn^{2+} + h\nu \rightarrow Sn^{4+} + 2e, \quad (3)$$

$$Ag^{+} + e \rightarrow Ag^{o}, \quad (4)$$

$$xAg^{o} \xrightarrow{\text{heat-treatment}} \left(Ag^{o}\right)_x \quad (5)$$

where x is the number of silver atoms aggregated into clusters. Considering the observations, Ce^{3+} ions are stabilized in presence of Sb^{3+} based on Eq. (1) during the photosensitive glasses melting process. Particularly for lithium silicate systems, the lithium-metasilicate crystallizes would be appeared around the Ag clusters; therefore, grain formation and growth will happen [1–5].

On the other side, introducing some suitable nucleating agents to the glasses may help to have an appropriate glass ceramics through heat treatment. Admittedly, precipitated crystals and their microstructures can play an important role in many properties of glass ceramics. Both TiO_2 and P_2O_5 as influential nucleating agents could provide a fine-grained interlocking microstructure in lithium disilicate glass ceramics and fortify mechanical properties [6,7]. More specifically, P_2O_5 in the range of 1.5–2.5 mol% can be a successful nucleating agent for lithium silicate glass ceramics. In practice, it boosts heterogeneous nucleation and forms a fine-grained interlocking morphology after heat treatment. It is noteworthy that manipulation of both composition and heat treatment schedule would be able to bring desirable properties [7–9]. Another nucleating agent in the preparation of glass ceramics can be TiO_2 a member of 3d transition metal oxides [10–12].

Titanium can be found in forms of trivalent (Ti^{3+}) and tetravalent valence (Ti^{4+}) in glasses but the proportion of each type might be varying depending on the glass type, composition and condition of melting [11,12].

Although it is known that P_2O_5 and TiO_2 are used as nucleating agents in various glass systems, there is only few publications about

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this glass system in which these oxides used as nucleating agents [13]. Therefore, the role of these nucleating agents in presence of the photosensitive elements Ce, Sb, Sn and Ag under radiation of UV light in solarization, crystallization temperature, and the microstructure for various glasses is worthy of more attention.

In this work, the parent photosensitive glass and glass-ceramic in the system of lithium silicate containing AgCl under radiation of UV light were successfully prepared by melting process to reveal the effects of adding P_2O_5 and TiO_2 as nucleating agents on the crystallization and solarization of lithium silicate photosensitive glass.

2. Experimental procedure

2.1. Sample preparation

The study was conducted for parent glass of lithium silicate system (G_B) with regard to several publications based on the following chemical composition (wt.%): 75.00% SiO_2, 5.00% Al_2O_3, 12.00% Li_2O, 4.00% K_2O, 4.00% Na_2O, 0.15% AgCl, 0.30% Sb_2O_3, 0.05% CeO_2, and 0.07% SnO_2 [1,2,4]. The employed substances here are extra pure supplied by Merck Co. except silica obtained after acid washing of a commercially grade silica powder. The purity of resulted silica powder might go further than 99.8 wt.%. Two other glasses containing all above-mentioned materials are called G_T and G_P when 4.00 wt.% TiO_2 and 2.00 wt.% P_2O_5 are added respectively.

The glasses were prepared in an electric furnace at 1450 °C for 1 h. The heating rate was 10 °C/min and the crucible was alumina. It should be noted that the crucible were covered with an alumina lid to minimize the volatilization of volatile components like phosphorous, alkali oxides, and silver. Indeed, covering the melt can increase the partial pressure of the volatile components above the melt and set a dynamic equilibrium between the dissolved and vaporized species to prevent significant losses [14,15]. Besides, in the case of silver, the volatilization loss can be controlled by introducing a small amount of tin to the composition. It is believed that tin ions can participate in the glass as a network former; and at the same time can exert forces on the noble metal by their residual valencies. These forces make a condition under which the noble metal cannot volatilize from the melt [16,17]. On the whole, since photosensitivity is observable in the final glasses, it can be concluded that these two factors have provided a suitable situation to keep sufficient amounts of some volatile components like Ag, Sb, P, and alkali oxides in compositions. It is noteworthy that interactions between glass compositions and the alumina crucible will inevitably happen during melting and increase Al_2O_3 content of the resulting glass. According to previous studies and our experiments, this reaction is negligible and has no negative effects on glass properties [2,4,18]. The prepared glasses were annealed at 500 °C, close to their glass transition temperatures for 2 h. After cutting and polishing, rectangular cube samples are formed in dimensions of $10 \times 10 \times 2$ mm. Then the samples got radiated for 2 h by a 1000-W UV-ray lamp. This source, invented in the local lab, includes UV lamp, cooling fans, radiation cylindrical shield, refractory fibers, etc. Here the distance between lamp and sample is 7 cm in this structure. After that, the G_B, G_P and G_T irradiated glasses were named $G_{B(UV)}$, $G_{P(UV)}$, and $G_{T(UV)}$, respectively. Finally, heat treatment of all the samples was carried out at DTA crystallization peak temperature for 2 h at the heating rate of 10 °C/min.

2.2. Characterization methods

The UV-Visible absorption spectra of the glasses were measured via UV-VIS double beam spectrophotometer (SHIMADZU UV-2501PC model) in the wavelength range of 300–700 nm. The standard sample was G_B silver free. Besides, the simultaneous thermal analysis was performed on a NETZSCH STA 409 PC/PG at the heating rate of 10 °C/min under air atmosphere. The curve was acquired in the temperature range of 30–1100 °C. The reference material in these experiments was α-Al_2O_3 powder. In addition, the X-ray powder diffraction patterns were examined on a JEOL JDX-8030 with Cu K_α radiation in the 2θ range of 10–80° at 40 kV and 40 mA. Finally, The microstructures of the heat treated samples were observed by scanning electron microscope (Philips XL30) working at 30 kV after polishing and chemical etching in 0.5% HF solution for 3 min. The samples were coated with a thin layer of gold before imaging.

3. Results and discussion

Fig. 1 shows UV–Visible absorption spectra of the lithium silicate glasses G_B, G_P, and G_T before and after irradiation. In the case of G_B, there is a small peak around 360 nm that can be referred to colloidal silvers which precipitates via redox reactions during melting. It is believed that some ionic silvers can be reduced to their colloidal form due to redox conditions during melting. As a matter of fact, the equilibrium between ionic silver and colloidal one is affected by oxidation-reduction conditions (batch composition, furnace atmosphere). For example, small amount of tin compounds in silicate glasses can be existed in both states of Sn^{2+} and Sn^{4+}. These stannous and stannic ions can participate in the reactions during the glass melting as oxidizing or reducing agents, respectively [16–18]. After UV radiation, the small peak of G_B widened and continued to 600 nm which confirmed that UV radiation can reduce ionic silver to colloidal one. Additionally, the absorption peak height arose after irradiation. This might indicate further ionic silver reduction into colloidal form during irradiation. On the other hand, the result of UV-Visible absorption spectrum of G_P indicates that there is no peak around 360 nm before irradiation; thus, ionic silver reduction

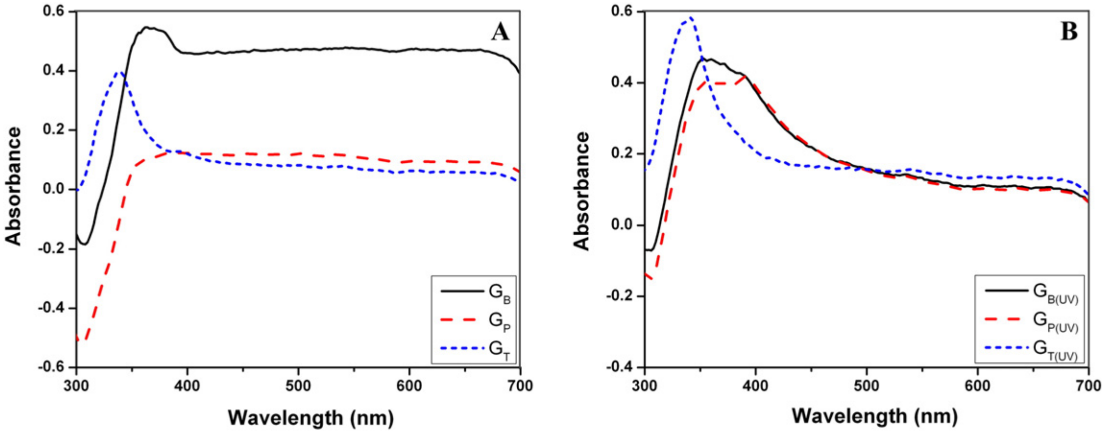

Fig. 1. UV–visible absorption spectra of the lithium silicate glasses G_B, G_P, and G_T. (A) before irradiation, (B) after irradiation.