Journal of the European Ceramic Society 21 (2001) 2015–2018
www.elsevier.com/locate/jeurceramsoc

Formation of thick glass-ceramics films by ion-exchange

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Received 4 September 2000; received in revised form 30 November 2000; accepted 5 December 2000

Abstract

The formation of thick sodium-niobate glass-ceramic films on the substrate of lithium-silica-niobate glass was induced by the sodium-lithium ion exchange performed in the glass plates at the temperature exceeding the glass transition temperature. Used conditions of the ion-exchange processing allowed producing glass-ceramic films with the thickness up to 0.5 mm, and the choice of the processing temperature and duration allowed varying optical properties and thickness of the ceramic films. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion; Films; Glass ceramics; Ion exchange; Niobates

1. Introduction

The properties of glass-ceramics are known to depend on both physico-chemical properties of the crystals grown in glass-ceramics formation and composition of the glassy medium, into which these crystals are embedded. However, the properties of the crystalline phase, which are its total volume fraction, crystal composition and symmetry, as well as average crystal size and size dispersion, are most important and practically define the essential properties and the type of the ceramics (electroceramics, piezoceramics, electrooptical ceramics, heat-proof one, and others). It should be noted that the technologies of those ceramics production do not differ and do not depend on the type of the ceramics to be fabricated. As a rule, glass-ceramics are produced by heat treatment of glasses, and corresponding properties of the crystalline phase are controlled by the thermal-temporal conditions of the treatment and depend on the composition of the initial glass used. This conventional technology enables one to produce only bulk pieces of glass-ceramics.

Recently,[1–4] it has been shown that a high-temperature (above T_g) alkali–alkali ion exchange can cause different phase transformations in alkali-contained glasses. Here we present a new technique of the glass-ceramics formation, which is based on the results of those studies. A specific feature of the technique is the possibility to form glass-ceramics films on the substrate of the initial glass. In this report, this possibility is demonstrated by the formation of sodium-niobate glass-ceramics films on the substrate of a lithium-niobate silicate glass.

2. Basis of the technique

In our recent works,[1–4] the phase transformations in glasses, which were induced by a high-temperature alkali–alkali ion exchange, were interpreted in terms of the theory of phase equilibria in heterogeneous liquid solutions. In that interpretation, a glass above its transition temperature was considered a metastable equilibrium liquid or glassy solution. In that case phase equilibria fully depend on the glass composition and temperature. For almost all the glass-forming systems it is typical to have a temperature–concentration range, in which either system crystallization or system homogenization can take place. In our study on the ion-exchange-induced glass decrystallization (homogenization of crystallized glass),[2] the observed vitrification was interpreted as a crystal dissolution resulting from the ion-exchange-induced dilution of the vitreous part of the glass-ceramics with respect to the alkali ions incorporated in the crystals. In other words, the glass-forming system tended towards the phase equilibrium in accordance with the solubility

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PII: S0955-2219(01)00163-7

product of the precipitates. Within the frames of that approach, one can expect the ion-exchange-induced crystallization of the diffused layer if at processing temperature bulk region of the glass sample keeps stability but the ion exchange leads to the supersaturation in the diffused layer. Thus, a high-temperature ion exchange opens a way to form glass-ceramics films on glassy substrates. It is obvious that the thickness and properties of those glass-ceramics films will depend on the compositions of the initial glass and that of the salt melt used and can be controlled by the temperature and duration of the ion exchange process.

3. Experimental

As was mentioned above, we intended to demonstrate the possibilities of the designed technique by the formation of sodium-niobate glass-ceramics films. The set of special experiments showed that sodium-niobate glass-ceramics demonstrated both high transparency and electrooptical sensitivity. The sodium-niobate silicate glasses used in those experiments allowed only bulk crystallization, and, therefore, we had to use another glass system to form the films. The initial glass was a lithium-niobium-silicate one (exact glass composition is shown in Table 1). Being heat-treated at different temperatures (from 630 to 700°C) and for different times (from 2 to 16 h), the glass has been found to crystallize at temperatures higher than 660°C and for the time longer than 8 h. X-ray diffraction (XRD) patterns (see Fig. 1) of the glass upon heat treatments under different temporal–thermal conditions have shown that $LiNbO_3$ microcrystals precipitated. (X-ray diffractometer DRON-2 with Cu (K_α) X-ray source and Ni filter was used.) All the diffraction peaks in Fig. 1 belong to crystalline $LiNbO_3$. This result gave us a chance that the chosen glass would not crystallize in ion exchange if the processing temperature and time did not exceed 660°C and 8 h, correspondingly.

The glass was synthesized by melting an appropriate 180-g batch for 2 h at 1450°C accompanied with 20-min stirring. Upon quenching on a thick brass plate, a clear, homogeneous glass ($80\times50\times10$ mm^3) was yielded. The glass was annealed for 2 h at 580°C, which corresponded to the glass transition temperature ($\log \eta = 12$, where $\eta =$ the glass viscosity in Pa s) determined from the viscosity–temperature dependence of the glass. The attempts to synthesize the same glass with sodium instead of lithium failed. It was possible to replace only 5 mol% Li_2O with the same amount of Na_2O. This evidenced crystallization non-stability of the sodium prototype of the chosen glass (which we called the initial glass), and indicated that the chosen glass was a prospective candidate to form sodium-niobate glass-ceramics films by the high-temperature Li–Na ion exchange.

Table 1
Composition of the initial glass

Oxides	Ta_2O_5	TiO_2	ZrO_2	BaO	Nb_2O_5	Li_2O	Na_2O	GeO_2	SiO_2
mol%	5	7	1	1	20	26	3	5	32

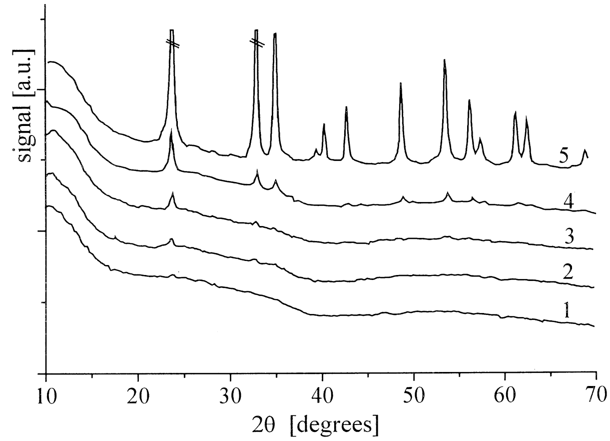

Fig. 1. XRD patterns of the glass heat-treated at 660°C for (1) 4 h, (2) 660°C for 16 h, (3) 680°C for 8 h, (4) 680°C for 16 h and (5) 700°C for 8 h. All the peaks belong to the crystals of $LiNbO_3$.

The typical sizes of the glass samples were about $5\times6\times10$ mm^3 (big samples) or $2\times3\times5$ mm^3 (small samples). Big and small samples underwent the ion exchange in a steel crucible filled with a $NaNO_3$ salt melt. The temperatures and the processing times used were 620 and 650°C, and 2, 4, 8, and 16 h. The salt melt was stirred during the process. The glass viscosity in the temperature range used was equal to $10^{8\pm0.5}$ Pa s.

After processing, all the samples were washed in warm water, and the big faces of each big sample were polished till the diffused layers from those faces were removed. The thickness of those layers was evaluated by the product $(Dt)^{1/2}$, where D is the interdiffusion coefficient at the processing temperature and t is the processing time. The magnitudes of the interdiffusion coefficient were found by linear extrapolation of the $\ln D$ vs. $1/T$ dependence, which had been determined by the ion exchange experiments within the temperature range (600–620°C), where the sodium prototype of the initial glass still kept crystallization stability. The ion-exchanged layers adjacent to the unpolished faces were studied with an optical microscope, and the pictures of those layers were taken with a digital camera. The small samples were powdered for the phase analysis by XRD.

To anticipate a little, it should be noted that the diffused layers after ion exchange could become non-transparent or translucent. The thickness of those layers was measured with an optical microscope equipped with an ocular-micrometer. The accuracy of those measurements was not higher than 15% because of the presence of the twilight zone between the homogeneous transparent glass in the sample bulk and the nontransparent under-surface layers.

4. Results

Typical pictures of the polished big glass samples are presented in Fig. 2 (similar pictures are obtained in all the experiments described below, but we do not present them here). One can see that the layers adjacent to the sample surfaces become either nontransparent or opalescent while the sample bulk remains transparent and homogeneous. It was discovered that those layers appeared only after the ion exchange at 650°C, the sample bulk remaining practically transparent up to the 16-h processing. When processing time exceeded 16 h, the bulks demonstrated weak opalescence. After the ion exchanges at 620°C, such layers appeared only after additional 2-h annealing at temperatures higher than 650°C.

XRD analysis performed using small samples (see Fig. 3) showed that all the samples with nontransparent or opalescent layers contained a crystalline phase, which was quasicubic sodium niobate ($NaNbO_3$). In this analysis we used small samples because in those samples the volume fraction of the under-surface layers, which were supposed to contain sodium niobate microcrystals, was higher, and this could increase the sensitivity of the measurements. In Fig. 3, the results of XRD analysis of the small samples after the ion exchange processing at 650°C for 4, 8, and 16 h are presented. From this figure, one can see that the intensities of the peaks increase with a rise in processing time, that corresponds to the increase in the volume fraction of the crystalline phase. At the same time, our observation showed that thickness of the under-surface non-transparent layers increases with time as well (in our experiments the thickness of the layers achieved about 0.5 mm). All this allow us to state that the used ion exchange processing (and additional annealing, if any) led to the formation of sodium niobate glass-ceramics films under the surfaces of the initial glass.

The thickness of those films can be easily controlled. Fig. 4 demonstrates time dependence of the thickness of the glass-ceramics film obtained at 620°C ion exchange and after additional 2-h annealing at 650°C. One can see that the thickness of the film is directly proportional to $t^{1/2}$. It should be noted that in case of the ion exchange at 650°C, when glass-ceramics films appeared during the ion exchange, the film thickness did not increase directly proportional to $t^{1/2}$.

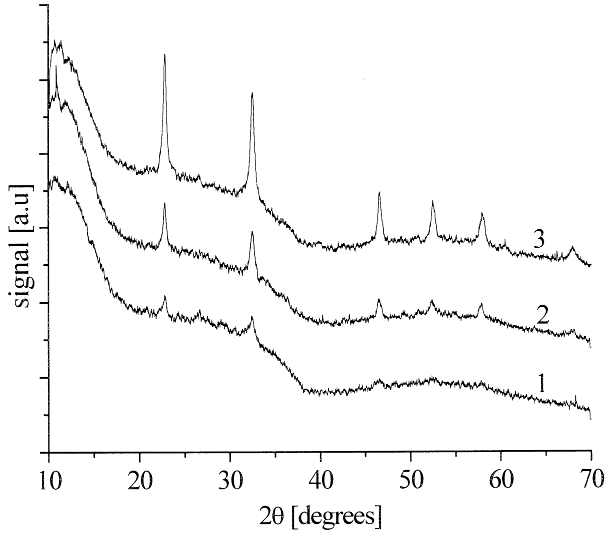

Fig. 3. XRD patterns of the small glass samples exposed to a $NaNO_3$ salt melt at 650°C for (1) 4 h, (2) 8 h, and (3) 16 h. All the peaks belong to quasicubic $NaNbO_3$.

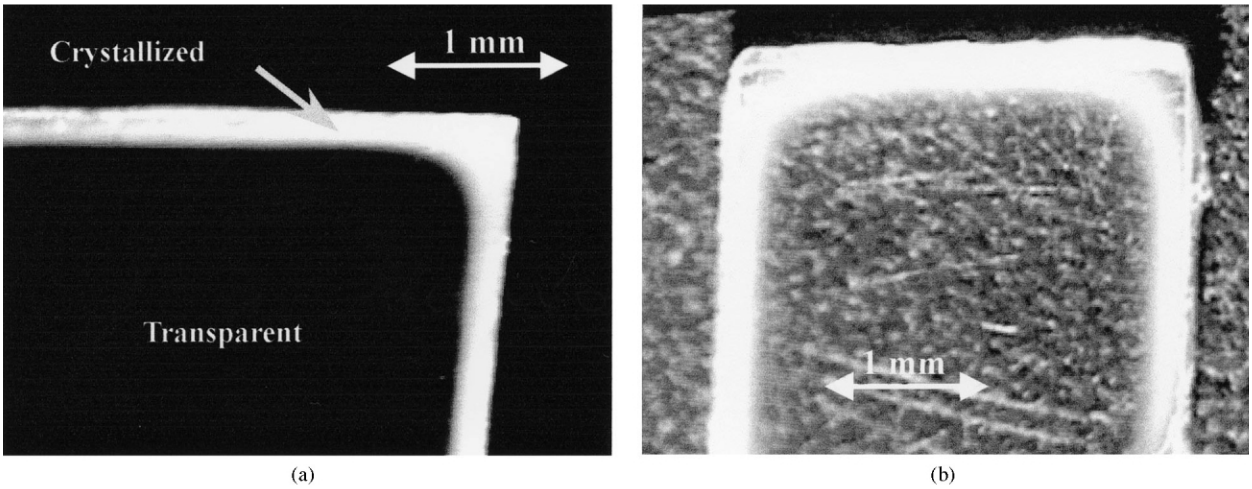

Fig. 2. Pictures of glass samples exposed to a $NaNO_3$ salt melt at 650°C for (a) 4 h and (b) 8 h. One can see (a) the non-transparent layer and (b) the opalescent one under the sample surfaces, although the bulk regions of the samples are transparent.

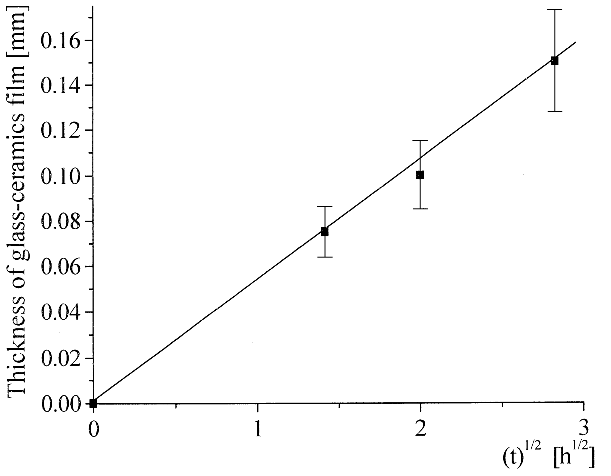

Fig. 4. Time dependence of the thickness of the glass-ceramics film obtained at 620°C ion exchange and after additional 2-h annealing at 650°C.

5. Discussion

In this section, we would like to discuss only one point, namely how to control film thickness.

Our measurements showed that linear $d(t^{1/2})$ dependences of the thickness, d, of the glass-ceramics films could be observed only in case of the films being formed at the 620°C ion exchange with additional 2-h annealing. In case the films are being formed during the ion exchange (at 650°C), those dependences are not linear. This difference comes from the difference in the media, in which diffusion takes place. In ion exchange processing at 620°C, diffused layers remain vitreous and homogeneous during all the process, and, therefore, one can expect the diffusion process to obey the Fick equation.[5] In this case the depth, where the dopant ion concentration coincides with the critical one and satisfies the solubility product of the crystals (therefore, it is equal to some fixed value), must increase linearly with $t^{1/2}$. The edge of the crystallized layers formed in additional annealing should coincide with the depth where glass composition coincides with the critical one. As a result, the thickness of the glass-ceramics film linearly increases with $t^{1/2}$. In ion exchange processing at 650°C, diffused layers crystallize during the process and this can cause a disturbance of the Fickian character of diffusion, that is, the law $t^{1/2}$ will be disturbed. Thus, to control the thickness of glass-ceramics films, the temperature of the ion exchange should fall within the range where the ion exchanged layers do not crystallize for the processing time. Additional annealing at higher temperatures will allow not only forming glass-ceramics film but also controlling its physico-chemical properties by fitting thermal-temporal conditions of that annealing.

6. Conclusion

In this work, the applicability of high-temperature ion exchange has been demonstrated for the formation of surface glass-ceramics. The thickness and the properties of such films can be controlled by temperature and time of the ion exchange processing.

Acknowledgements

This work is partially supported by International Science and Technology Center, project No. 979.

References

1. Tagantsev, D. K., Decrystallization of glass-ceramics under ion exchange diffusion. *Journal of the European Ceramic Society*, 1999, **19**(6–7), 1555–1558.
2. Tagantsev, D. K. and Karapetyan, G. O., Decrystallization of crystallized glasses by ion exchange. *Journal of Non-Crystalline Solids*, 1999, **255**(2–3), 185–192.
3. Karapetyan, G. O., Loboda, V. V. and Tagantsev, D. K., A method of formation of the surface phase-separated layers of a controlled thickness. *Glass Phys. and Chem.*, 1999, **25**(3), 288–290.
4. Karapetyan, G. O., Loboda, V. V. and Tagantsev, D. K., Influence of ion exchange on phase separation in alkali borosilicate glasses: effect of ion exchange induced metastable glass homogenization. *Journal of Non-Crystalline Solids*, 2000, **270**(1–3), 154–162.
5. Boltzmann, L., Zur Integration der Diffusiongleichung bei variablen Diffusioncoefficient. *Ann. Phys. Chem.*, 1894, **53**(12), 959–964.