Original Paper

Study of structural modification in extruded and heat-treated lithium disilicate glasses by the method of radiation color centers chronospectroscopy[1)]

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Samples of extruded and non-extruded lithium disilicate glasses were studied. Extruded glass samples were cut out along and across the extrusion axis of finished cylindrical rods. For all the samples, spectra of radiation-induced absorption, $\Delta a(E)$, were measured for various time instants after the cessation of X-irradiation. On the data basis obtained, kinetic dependences, $\Delta a = f(t)$, were plotted and analyzed. In the diagram "Δa versus $\lg t$", they are represented by straight lines. Each of them is falling down with its own constant slope α. These α's are rate parameters of the decay of radiation color centers (CCs). They appear to be functions of average distances between recombinating electron and hole CCs. The above α-parameter decreases when passing from the longitudinal cut extruded glass sample to the sample of the non-extruded glass and finally to the transversely cut extruded glass sample. These data mean that, in the course of extrusion, the glass structure becomes less dense in the axial direction of extruded glass rods and more dense in the radial one. A 4-hour heat treatment at 465 °C (≈5 °C above the glass transformation temperature, T_g) eliminated the above anisotropy of radiation properties in extruded glasses and forced their anisometric structures to return to the isometric state characteristic of the non-extruded glass.

Untersuchungen zur Strukturmodifikation bei stranggepreßten und getemperten Lithiumdisilicatgläsern mit Hilfe der Chronospektroskopie strahlungsinduzierter Farbzentren

Untersucht wurden polierte Längs- und Querproben von strenggepreßten Lithiumdisilicatgläsern und Proben des nichtstranggepreßten Ausgangsglases. Die Längs- und Querproben wurden aus zylindrischen, stranggepreßten Stäben parallel und senkrecht zur Strangpreßachse ausgeschnitten. Für alle Proben wurden die Spektren $\Delta a(E)$ der strahlungsinduzierten Absorption zu verschiedenen Zeitpunkten t nach dem Ende der Bestrahlung mit Röntgenstrahlen aufgenommen. Ausgehend von den erhaltenen Spektren wurden die Abhängigkeiten $\Delta a = f(t)$ grafisch dargestellt und analysiert. Es zeigte sich, daß diese Abhängigkeiten bei Darstellung von Δa gegen $\lg t$ Geraden ergeben. Jede Gerade besitzt einen bestimmten Anstieg α. Dieser Anstieg entspricht dem Ratenparameter des Farbzentrenzerfalls und scheint eine Funktion der mittleren Abstände zwischen den rekombinierenden Elektronen- und Lochfarbzentren zu sein. Die α-Werte verringern sich in der Reihenfolge Längsprobe, Probe des Ausgangsglases und Querprobe. Diese Ergebnisse zeigen, daß die Glasstruktur offensichtlich durch das Strangpressen in radialer Richtung verdichtet und in axialer Richtung aufgelockert wird. Eine Wärmebehandlung bei 465 °C (≈5 °C oberhalb T_g) für 4 Stunden führt zu einer Relaxation der Glasstruktur und damit zu einer Beseitigung der Anisotropie bei den Farbzentren der stranggepreßten Gläser.

1. Introduction

Extrusion of lithium disilicate based glasses below their temperatures of crystal growth and subsequent heat treatment of extruded glass rods at these temperatures form one of the ways of producing glass-ceramics with rather high degree of $Li_2Si_2O_5$ crystal orientation relative to the extrusion axis [1 and 2]. As a result, spatial anisotropy of mechanical properties is observed in the final glass-ceramic rods [1 and 2]. Unlike this, in the case of non-extruded glasses, their similar heat treatment leads only to the formation of randomly oriented $Li_2Si_2O_5$ crystals. Glass-ceramics produced from non-extruded glasses do not exhibit any spatial anisotropy. It is not excluded that, due to extrusion, an isometric structure characteristic of non-extruded glass is modified to an anisometric state. Moreover, exactly this extrusion-induced structural anisometry can be one of the main conditions which facilitate the crystal orientation in the course of the crystallization process in extruded rods. It means that extruded glasses themselves, like glass-ceramics made from them, can also demonstrate spatial anisotropy of some properties. To reveal such properties, to find their anisotropy for two mutually perpendicular observation directions, and, on this basis, to make quantitative estimations of the extrusion-induced glass structure in samples of extruded lithium disilicate glasses was one of the aims of the work. Further, the heat treatment

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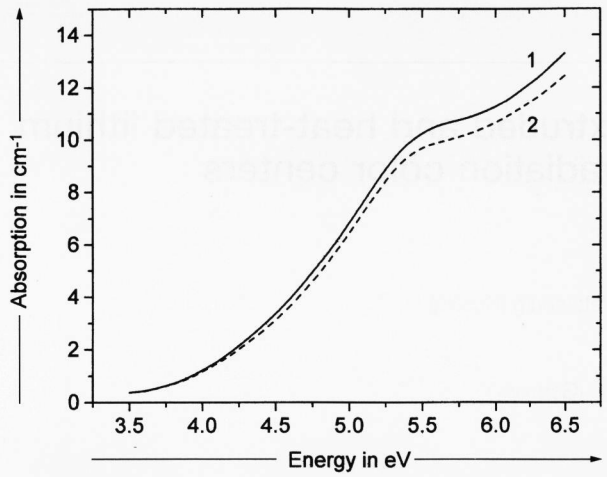

Figure 1. Initial absorption spectra; curve 1: LS; curve 2: TS.

of extruded glasses under consideration at temperatures only slightly above the glass transformation temperature, T_g, was known to reduce the degree of $Li_2Si_2O_5$ crystal orientation in the subsequent crystallization process [1]. Therefore, it was advisable as well to investigate if such a treatment eliminates potential structural anisometry and anisotropy of any properties in extruded glasses.

To achieve these aims, a study of the formation and decay of radiation color centers (CCs) was carried out. The reason for such a choice was as follows. Due to radiation-induced ionization of nonbridging oxygen atoms of main glass structure configurations, ionizing radiation creates free electrons and holes in the glass matrix [3]. Their localization at corresponding traps leads to the formation of intrinsic CCs of electron and hole types. The CCs absorption bands are situated in the range from the UV to the near IR regions of the spectrum [3]. The rates of CCs formation and their post-radiation decay must depend on distances between CCs precursors and between recombinating electron and hole CCs, respectively. Therefore, if the structure of extruded glasses in the direction of extrusion and in the perpendicular one is really anisometric, then the above distances can differ in these two directions. In other words, in samples of extruded glasses, rates of CCs formation and decay can depend on the direction of observation.

2. Experimental

Extruded and non-extruded $Li_2O \cdot 2SiO_2$ glasses served as objects of investigation. Glass extrusion was executed at 540 °C and corresponding viscosity of about $10^{7.5}$ Pa s by means of traditional technique with an electrographite die and pressures varying up to 45 MPa [1 and 2]. Glass rods produced by this method had a cylindrical shape with a diameter of 4 mm. They did not have any crystal inclusions in their volumes and were transparent. Samples under study were polished plates 1 mm thick. They were cut out both from non-extruded glass [initial samples (ISs)] and from extruded rods along [longitudinal samples (LSs)] or across [transverse samples (TSs)] the extrusion axis. Such a preparation of extruded glass samples enabled the measurement of their absorption spectra in directions both parallel (TSs) and perpendicular (LSs) to the extrusion axis.

Subjects of investigation were: sample absorption spectra before $[a_0(E)]$ and after $[a_i(E)]$ the X-irradiation (copper anode with a nickel filter; $U = 40$ kV; $I = 30$ mA) for 5 hours; spectra $\Delta a(E) = a_i(E) - a_0(E)$ of radiation-induced absorption; kinetic curves, $\Delta a = f(t)$, of post-radiation relaxation of CCs absorption. These curves were measured before and after the heat treatment of extruded glasses at 465 °C ($\approx$ only 5 °C above T_g). The treatment was executed in four steps. The first and the second steps had duration of 0.5 hour, the third and fourth ones lasted 1 hour.

3. Results and discussion

Initial absorption spectra of extruded samples are represented in figure 1. From this figure, both samples show a wide band with a maximum at approximately 5.7 eV which is overlapped with the low-energy tail of the fundamental absorption spectrum of glass. This band proved to be caused by iron impurities in glasses under study (approximately 80 ppm). It is noteworthy that the intensity of this impurity absorption in extruded glasses depends on the direction of observation or, in other words, on the sample type. Actually, intensity of spectrum 1 (LS) is $\approx 5\,\%$ higher than that of spectrum 2 (TS). This difference in iron absorption in extruded glasses speaks for distinctions in the iron distribution in regard to the rod extrusion axis. Effective iron concentration in the axial direction of extruded glass rods, C_a, is a little lower than that in the radial one, C_r. Such a situation is only possible if, after the extrusion, average "iron-iron" distances in glasses becomes a little longer in the axial and a little shorter in the radial direction.

Irradiation of glasses under study by X-rays creates CCs which absorb light in a wide spectral range from the ultraviolet to the near infrared regions of the spectrum (figure 2). From this figure, the spectrum of radiation-induced absorption exhibits maxima at approximately 2.1, 2.8, 3.8 and 5.4 eV caused by different types of intrinsic CCs. Both initial glass sample and samples of extruded glasses demonstrate nearly the same spectrum of CCs absorption. It means that the CCs nature remains unchanged during glass extrusion. But it should be noted that, after 5 h of irradiation, the intensity of radiation-induced absorption in the LS is approximately 10 to 12 % higher than in the TS. In other words, extruded glasses show not only spatial anisotropy of iron ions distribution and their absorption, but also the anisotropy in rates of CCs formation.

After the cessation of irradiation, CCs decay takes place (figure 3). As it can be seen from this figure, rates of CCs decay for three represented sample types differ rather strongly. For instance, 15 % decrease of radiation-

induced absorption in the series "LS-IS-TS" takes approximately 11, 26 and 98 h to complete. An attempt to describe kinetic curves 1 to 3 in figure 3 by exponencial functions failed: it proved to be impossible to characterize any relaxation curves by some constant rate parameter. Figure 4 shows that current slopes of relaxation curves in the diagram "$\ln \Delta a$ versus t", or, in other words, rates of CCs decay decrease gradually with observation time. Such a behaviour of kinetic curves of CCs decay supports the conclusion that some relaxation phenomena in glasses can not be described by exponential functions [4]. The relaxation with gradually decreasing rate speaks for the necessity of using the Kohlrausch's stretch exponential function [5 and 6] to analyze experimental $\Delta a = f(t)$ curves. In the present case, this function can be represented by a relation $\Delta a(t) = \Delta a(0) \cdot \exp(-t/\tau_K)^{\beta}$, where $\Delta a(t)$ is the induced absorption at any current time instant t, $\Delta a(0)$ is the induced absorption at the very end of irradiation, τ_K is the Kohlrausch's relaxation time, and β is a constant parameter which lies between 0 and 1. The relation means that it is possible to describe any relaxation curve by means of $\Delta a(0)$ and two Kohlrausch's parameters: τ_K and β. But it turned out that, when dealing with prolonged irradiation durations and restricted observation times, the rather complicated Kohlrausch's function could be transformed satisfactorily to a more simple approximate equation $\Delta a(t) = \Delta a(t_1) \cdot (1 - \log t^{\alpha})$ [7]. In this expression, $\Delta a(t_1)$ is the radiation-induced absorption at the given moment t_1 at which post-radiation observation starts, and α is the constant rate parameter of CCs decay. In the diagram "Δa versus $\lg t$", experimental $\Delta a = f(t)$ dependences are represented usually by straight lines falling approximately linearly with the observation time. At that, the α-parameter is valid at least for the period of about several months and lies in limits from 0 to 1 [7]. The greater the value of this parameter, the faster the relaxation of radiation-induced absorption.

In this case, in the above "Δa versus $\lg t$" diagram, $\Delta a = f(t)$ curves are represented by straight lines rather accurately (figure 5). This circumstance corroborates that, for all the glasses under study, application of the Kohlrausch's function in its approximate form [7] to the analytical description of experimental kinetic curves of CCs decay was correct. It turned out that the α-parameter decreased from (0.146 ± 0.002) to (0.112 ± 0.002) and (0.078 ± 0.002) when passing from the LS to the IS and finally to the TS, respectively. This difference in α's or, in other words, in rates of CCs decay in samples of both non-extruded and extruded glasses shows that the glass structure was really modified in the course of extrusion as it had been expected. At that, the fact that CCs decay in the LS proceeds faster and in the TS slower than in the IS means that distances between recombinating electron and hole CCs in extruded glasses became longer in the direction of extrusion and shorter in the perpendicular direction as compared with similar

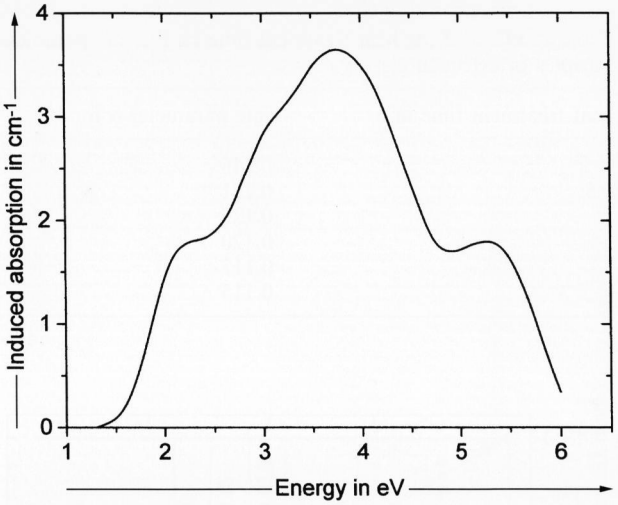

Figure 2. Spectrum of radiation-induced absorption of the LS.

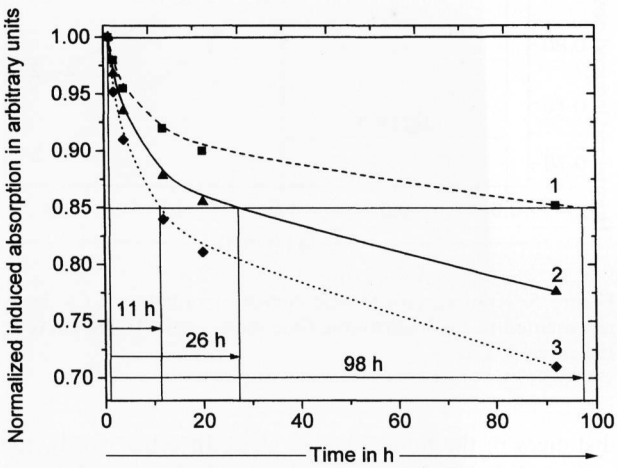

Figure 3. Kinetic curves of radiation CCs decay represented in the real time scale; curve 1: TS; curve 2: IS; curve 3: LS.

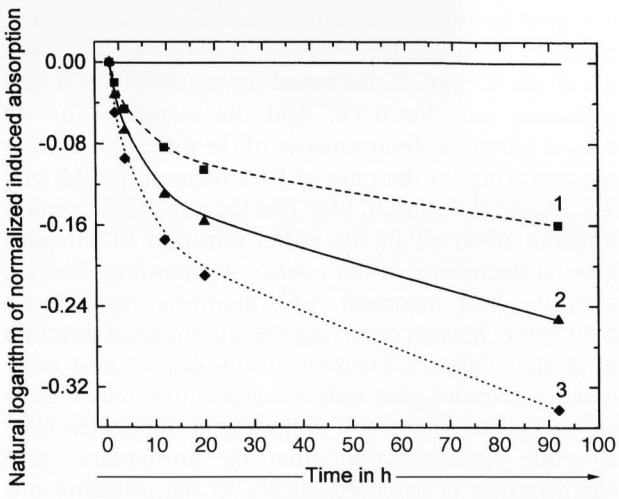

Figure 4. Kinetic curves of radiation CCs decay represented in the exponential amplitude scale; curve 1: TS; curve 2: IS; curve 3: LS.

Table 1. Effect of the heat treatment time an the rate parameters α ($\Delta\alpha = \pm 0.002$) of CCs decay in the longitudinal and transverse samples of extruded glasses

heat treatment time in h	rate parameter α for LS	rate parameter α for TS	$\Delta\alpha = \alpha(\text{LS}) - \alpha(\text{TS})$
0	0.146	0.078	0.068
0.5	0.131	0.091	0.040
1	0.125	0.099	0.026
2	0.120	0.108	0.012
3	0.117	0.113	0.004
4	0.115	0.115	0

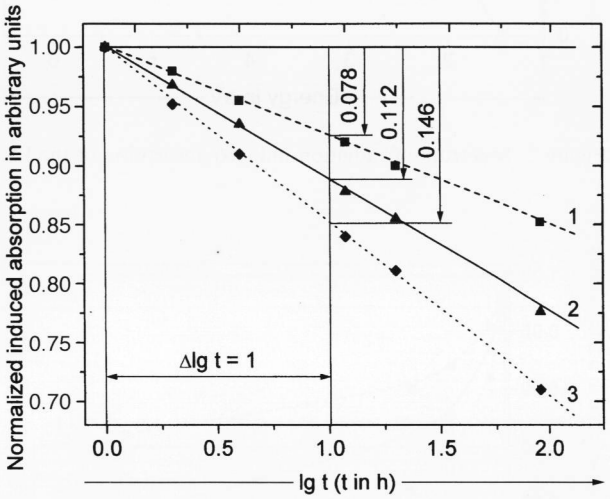

Figure 5. Kohlrausch's kinetic curves of radiation CCs decay represented in the logarithmic time scale; curve 1: TS; curve 2: IS; curve 3: LS.

distances in the non-extruded glass. In other words, the extruded glass structure is anisometric: it is less dense in the axial direction and more dense in the radial one.

After the heat treatment at 465 °C, the α-parameter for the LS became smaller than before the treatment (table 1). In the TS case, the picture is quite inverse: the executed heat treatment caused an increase of the α-parameter. From this table, the initial difference (0.068) in α's of the LS and TS decreased up to 0.040 after a heat treatment only for 0.5 h. And the treatment for 4 h caused complete disappearence of the difference both in α's, and, thus, in the rates of CCs decay in the LS and TS. These results mean, first, that the rate of CCs recombination observed in the radial direction of extruded glass is decreasing in the course of annealing. Second, after the heat treatment, CCs disappear much faster than before it when observing them in the axial direction of extruded glasses. Therefore, in the case of heat treatment of extruded glass rods at temperatures only slightly above T_g, one may speak of the thermostimulated glass structure transformation from the anisometric state characteristic of extruded glasses to the isometric one inherent for the non-extruded glass. In other words, average distances between recombinating electron and hole CCs in any extruded glass which were different in its axial and radial directions before heat treatment demonstrate a tendency to become equal in the course of annealing. End structure configurations $\equiv Si-O^-...R^+$ (where R^+ is the network modifier atom) are known to be responsible for CCs formation in alkali silicate glasses [8 and 9]. Besides, they appear to be main structural fragments in these glasses. For these reasons, in the case of lithium silicate glasses, exact end configurations $\equiv Si-O^-...Li^+$ can be involved in processes of the extrusion-induced modification of the glass structure and its thermostimulated reconstruction.

The above difference in iron absorption in the nonirradiated longitudinal and transverse samples can, obviously, make it possible to estimate distinctions in average distances between iron ions in two mutually perpendicular directions of extruded glasses. Indeed, as a first approximation, the third power of average distances between neighbouring iron ions in axial, D_a, and radial, D_r, directions of extruded rods are in inverse proportion to the mentioned effective concentrations C_a and C_r. Then, a ratio D_a/D_r is approximately equal to 1.016, because the ratio C_r/C_a is about 1.05. This result means that relative deviations of the D_a and D_r values characteristic of extruded glasses from corresponding distances in the non-extruded glass do not exceed ±1 %. It is not excluded that this estimation is also valid for the whole anisometric structure of extruded glasses.

The results represented in this paper show convincingly that the described method of postradiation chronospectroscopy appears to belong to the structure sensitive methods of glass investigation. Therefore, it would be advisable to apply this method to other glass systems which are used for the production of glass-ceramics with high degree of crystal orientation.

4. Conclusions

In the course of extrusion of lithium disilicate glasses, main glass structure configurations which are responsible for the formation of radiation color centers (CCs) seem to move away from each other in the direction of extrusion and approach each other in the perpendicular one. In extruded glass rods, relative deviations of average distances between these configurations in the above directions from corresponding distances in the non-extruded glass do not exceed 1 %.

The above structural transformation causes differences in the rates of CCs formation and decay in extruded glasses in regard to the corresponding rates in the non-extruded glass: these rates become faster while observing the processes in the radial direction and slower when measuring them in the axial one.

The 4-hour heat treatment of extruded glass rods at 465 °C (≈5 °C above the glass transformation temperature, T_g) eliminates the anisotropy of radiation properties in samples of extruded glasses and forces their anisometric structure to transform to the isometric state which is characteristic of the non-extruded glass.

5. References

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