

On the Reversibility of Laser-induced Phase-structure Modification of Glass-ceramics

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The possibility of reversible structure modification of two glass-ceramics (photosensitive and in-photosensitive) under CO₂-laser action has been experimentally demonstrated. The virgin glass is converted in to glass-ceramics with use of spontaneous crystallization or photo-thermo-induced one and then under the laser irradiation the glass-ceramics are converted into initial glass state. The rates of such structural modification under laser heating are about 10² – 10³ times higher than under conventional heating in a furnace. The laser technology of structural modification of glass-ceramics is very attractive for development and fabrication of new optical components and devices.

Keywords: laser-induced process, amorphization, crystallization, photosensitive glass, glass-ceramics, heating-cooling rates, optical transparency

1. Introduction

Laser-induced structure modification of glass-ceramic materials (GC) is of high interest among the processes of laser local actions which have been intensively investigated lately^[1-5]. The main reason of such an interest is a possibility to use these phenomena for development of many different kinds of mini- and microoptic devices. It became possible because a structure modification of GC is followed by local alterations of initial material characteristics as optical transparency, chemical solubility, mechanical, etc. It was shown that different mechanisms of phase-structure modification of glass-ceramics can be realized under laser action. The most popular is a laser-induced local crystallization of photosensitive glass, where the crystalline phase of lithium silicates are grown by exposure to UV radiation (for example, nitrogen laser) with a subsequent thermal development^[1-3,5]. The other well-known example is a local amorphization of ST-50 glass-ceramic (TiO₂-SiO₂ type) under photophysical action of CO₂-laser [4, 5].

A possibility of reverse structure modification processes has been recently demonstrated in these two materials^[6]. It is evidently that reverse ability of phase-structure modification could bring many new opportunities for development and fabrication of new micro-devices. That is why we have paid a special attention to this subject, especially to kinetic of reversible phase-structure modification.

2. Reversible IR-laser photophysical amorphization-crystallization of ST-50 (TiO₂ - Al₂O₃ - CaO - MgO - SiO₂) glass-ceramic

Glass-ceramics usually have a glass phase and microcrystalline one that are responsible for main properties: mechanical, chemical, optical etc. Microcrystalline structure

of GC is a consequence of tendency of the initial melted raw materials composition to crystallization (because of the presence of many ions, for example, Ti, Ag and others which play a role of catalysts — as nucleation centers during heating-cooling cycle) which could be hardly avoided in traditional thermal treatments of glass. At the same time it seems that realizing a high-speed cooling after laser melting of GC in definite zone should help to save a high-temperature amorphous (glassy) structure (which is typical for melted GC) till room temperature.

The idea how to provide this fast cooling rate is the following: it is necessary to “switch on” a new more effective mechanism of thermo-conductive cooling in solids instead of the natural air cooling. This “new” mechanism is thermoconductivity because thermoconduction cooling in solids is 2 orders of magnitude higher than cooling rate in air or water. To realize this idea it is enough to irradiate a local zone of material. In this case, after the end of laser action, the heat from the irradiated zone is the most effectively transferred to neighboring zones of solid. This explains the fast cooling kinetics which takes place after laser action. Such an idea has been realized (see Fig. 1) and new amorphous structures at room temperature have been demonstrated [4-6].

The idea to control structure modification by heating-cooling rates can be expended for reverse process – laser-induced crystallization. Opportunity to implement the fast-local reversible amorphization-crystallization process could give a key to development of many new types of micro- and nanocomponents and devices.

The most important information about the kinetic of phase-structural changes can be received from temperature kinetics, especially from heating and cooling rates which are responsible properly for forming of definite phases. Temperature kinetics were investigated by digital micro-

pyrometer and described in more details in previous publications [5]. Movement of the amorphization front, which we identify as a transparent front, was studied by optical methods: optical microscopy of sections, and micro-

video-recording (through the transparent irradiated zone after melting).

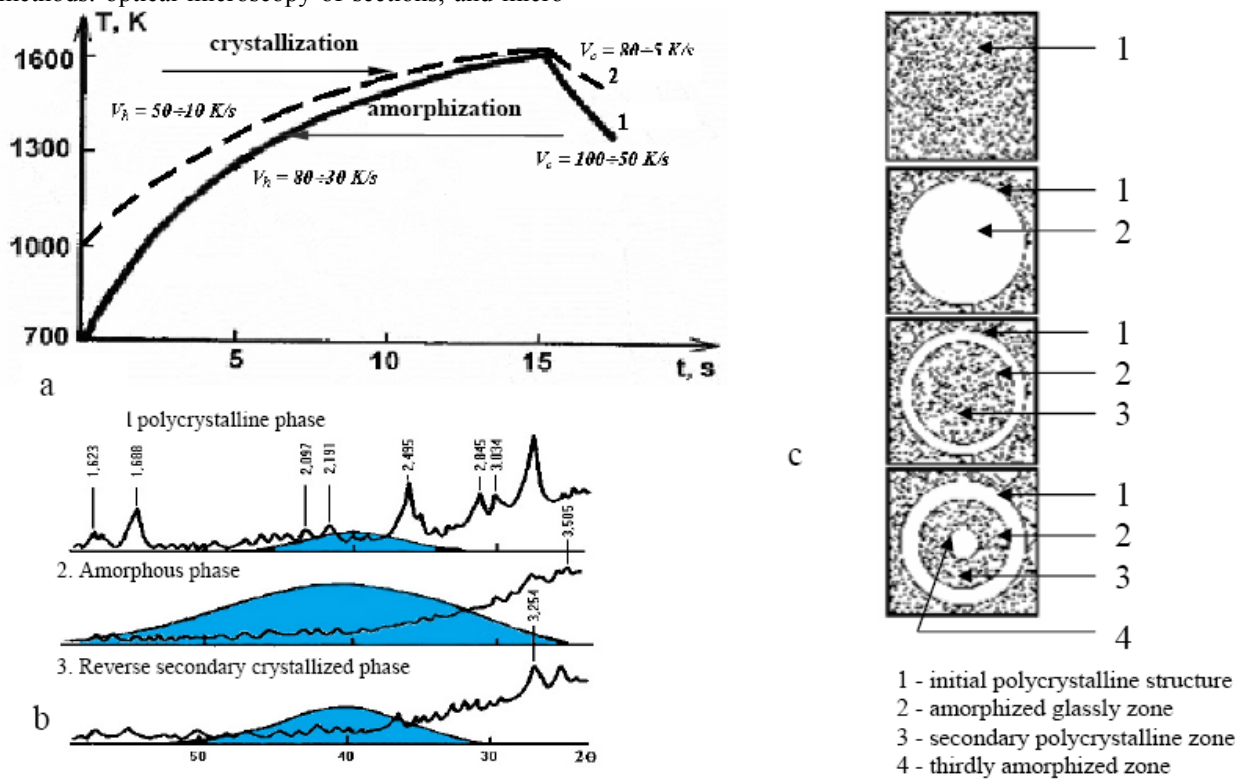


Fig. 1. a) experimental curves of laser heating and cooling of ST-50 GC taken by optical pyrometer for two regimes – amorphization (1) and crystallization (2); b) X-ray diffractograms (XRD) for initial state of ST-50 (1), after laser amorphization (2) and after reverse crystallization (3); c) the general view of irradiated zones in passing light – white-one – transparent amorphous zones, grey-one-non – transparent polycrystalline zones.

A typical view of heating-cooling curves of GC ST-50 under CO₂-laser irradiation at different laser power densities are shown on Fig. 1, a). In all cases, the laser heating should provide a temperature about 1500 K (the vitrifying and melting temperatures of ST-50: $T_{gl} = 1033$ K and $T_m = 1473$ K correspondingly must be in the heating range).

At the region of laser power density about $3 \cdot 10^5 - 1 \cdot 10^6$ W/m² samples plates with thickness of $\sim 0,6$ mm were preliminary heated to temperature of 600–800 K (Fig. 1, a, curve 1). At those conditions amorphization of glass-ceramic with corresponding transformation of optical transparency can be observed (Fig. 1, b, c).

At smaller power densities ($q \leq 10^5$ W/m²) with preliminary heating of plates to temperature 800 – 1000 K (Fig. 1, a, curve 2) in case of irradiation of amorphized (transparent) zones, the other phenomenon, a back crystallization, can be observed (Fig. 1, b, c).

Temperature of heating $T_n^{max} = \frac{2AP}{\sqrt{\pi kS}} \sqrt{a\tau}$ and the temperature rates of heating and cooling

$$V_n^{max} = \frac{\partial T_n^{max}}{\partial t} = \frac{A}{\sqrt{\pi}} \frac{P}{\rho c S} \frac{1}{\sqrt{a\tau}} \quad (T_n^{max} \text{ and } V_n^{max} - \text{the}$$

temperature and temperature heating rate at the center of laser spot of the surface), and controlling laser parameters: P – laser power, A – absorption coefficient, S – laser spot square, τ – time of irradiation, a – thermo-diffusivity coefficient, k – thermo-conductivity coefficient), play a leading role for the choice of the correct regime [8].

The X-ray structural analysis (Fig. 1, b) has proved structural changes in GCs ST-50 after laser irradiation. Initial glass-ceramic materials had microcrystalline structure which resulted in the appearance of peaks in the corresponding XRD (ST-50 has two crystalline phases, rutile of α -TiO₂ and cordierite of 2MgO·2Al₂O₃·5SiO₂) (Fig. 1, b, 1). A different XRD was received for the laser-heated zone in case of temperature kinetic corresponding to the curve 1 (Fig. 1, a) intensities peaks were dramatically decreased which shows evidence of the disappearance (or considerable decrease) of microcrystals, and moreover the increase in intensity of the amorphous halo signals (Fig. 1, b, 2). So, XRD after laser irradiation had exhibited that the laser action resulted in

formation of a new structure, the main part of which was in amorphous phase and the sizes of initial crystallites were noticeably decreased. The transparency picture after laser amorphization corresponds to position 1, central white spot is amorphised ceramic, transparent for visible light (Fig. 1, c).

The second irradiation of new (mostly amorphous) material according curve 2 (Fig.1,a) results in almost initial polycrystalline structure (Fig. 1, b, 3). Corresponding optical view, Fig. 1, c, confirms the returning of non-transparent crystalline structure and realizing of multi-time amorphisation-crystallization process with corresponding structures (Fig.1,c).

3. Photo-thermo-induced crystallization and reverse IR-laser amorphization of photosensitive glass

For photo-thermo-induced crystallization we used a photosensitive glass of FS-1 (Russian analogous of Foturan by Schott or Fotoform by Corning), which consists of $\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and photosensitive dopants of Ce^{3+} , Ce^{4+} , and Ag^+ . The crystalline phase of lithium silicates grows by two-step process in the glass: (1st) - UV exposure and subsequent (2nd)-thermal development [3]. The exposure of the glass sample by UV radiation produces ionization of Ce^{3+} ions. The electrons are released from cerium ions then trapped by silver ions. As a result, silver ions are converted to neutral atoms. This stage corresponds to a latent image formation, and no significant coloration occurs (Fig.2, curve 1). The thermal development includes two stages. The first stage involves the high diffusion rate that silver atoms possess in silicate glass. This diffusion leads to the formation of tiny silver colloidal clusters with band absorption at 420-450 nm under relatively low temperature of 400-450°C (Fig.2, curve 2). The silver colloidal clusters play a role of nucleation centers for growth of crystalline phase of lithium silicates. The microcrystals of lithium silicates precipitate at relatively high temperature of 600-650°C and time treatment more than 10 hours (Fig.2, curve 3).

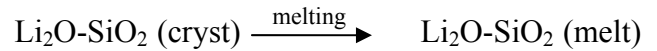
In our experiments, the polished samples of FS-1 were irradiated by He-Cd laser (325 nm). The irradiated samples were thermally treated at temperatures of 400 and 600°C consequently for 2 and 12 hours. Absorption spectrum of initial glass, spectrum after UV exposure and 1st stage of thermal development at 400° C and after 2nd stage of thermal treatment at 600° C are given on Fig 2, a (curves 1, 2 and 3). Such treatment resulted in yellow coloration (effect of silver colloidal clusters) and strong scattering in the sample (effect of crystalline phase). A general view of FS-1 glass sample before and after photo-thermo induced crystallization is shown on Fig. 2, b.

The next stage of our investigation was an amorphization of FS-1 glass-ceramic with use of IR radiation of CO_2 -laser. After the laser radiation, the yellow coloration and strong scattering of the sample have disappeared. The irradiated area became transparent one. Fig. 2,b illustrates such transparent areas. In other words, IR laser-induced treatment resulted in transformation of glass-ceramic into the previous glass. The

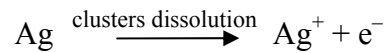
curve 4 on Fig. 2,a illustrates the absorption spectrum after IR radiation. One can see, the band absorption of the silver colloidal clusters totally disappeared and the band absorption of Ce^{3+} appeared again. Thus, the secondary glass has got previous photosensitivity. The spectrum of secondary glass (curve 4) is very close to initial glass (curve 1). We named such transformation as a reversible structure modification, because we transformed the virgin glass into the glass-ceramics and then we converted the glass-ceramics into the secondary glass with spectral properties close to virgin glass and such transformations can be continue.

The mechanism of amorphization can be presented as a consequence of the following steps:

- 1) lithium silicates microcrystals melting:



- 2) dissolution of Ag-clusters



- 3) free electrons trapping by Ce^{4+} ions with partial reduction of cerium ions - Ce^{3+} .

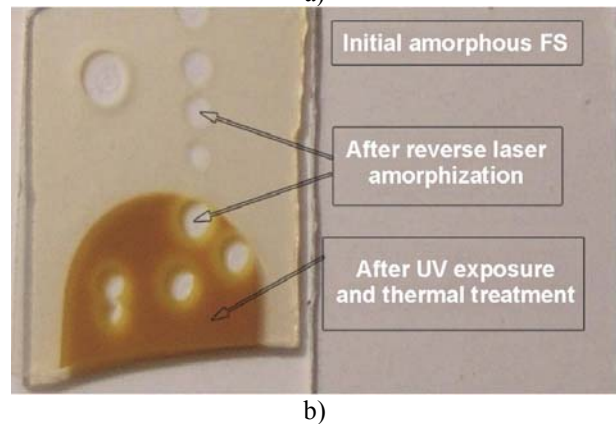
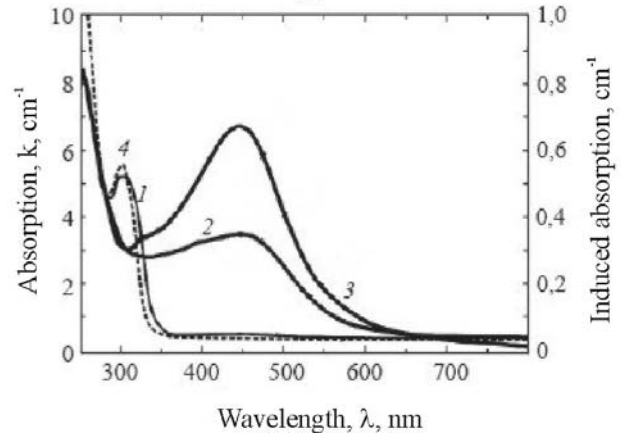
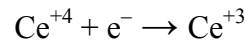


Fig. 2. a - absorption spectra of initial (1), secondary (4) glass, induced spectrum after UV exposure and 1st, at 400° C (2), and 2nd at 600° C (3). b - general view on FS-1 sample

before and after laser crystallization and reverse amorphization.

We have used the same spectra (Fig. 2a) and general view (Fig. 2b) as experimental proof of above explained mechanism: the secondary glass spectrum (Fig. 2a, curve 4) proves the reconstruction of initial-like structure of FS-1 glass with refreshment of photosensitivity to UV radiation at 313 nm absorption peak at the final optical spectrum (Fig 1a, curve 4) due to Ce^{+3} ions restoring.

4. Experimental study of the kinetic of laser-induced structure modification of ST-50 glass-ceramic

Glass-ceramic ST-50 was chosen for further study kinetic of reversible structure modifications because of one step for both-local laser-induced amorphization and crystallization processes. Such structure modifications are accompanied with an instant switching of optical transparency (see initial and laser-induced absorption spectra of ST-50, Fig. 3 and FS-1, Fig. 2).

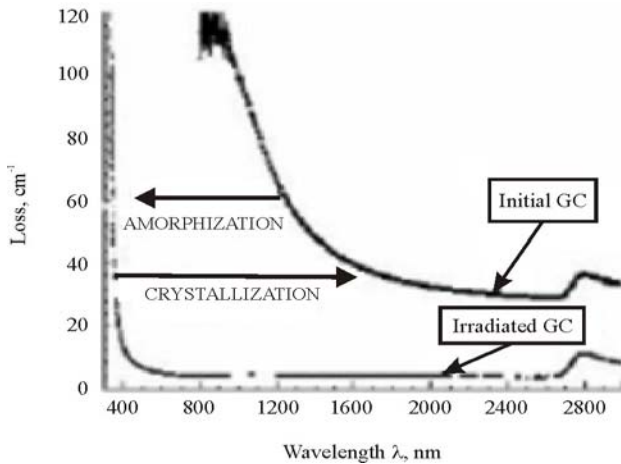


Fig. 3. Initial and laser-induced absorption spectra of ST-50 glass-ceramic.

The most informative parameters of the kinetic of structural modifications under laser irradiation action are: a time-resolved optical transparency and a temperature of restructured zones (both of them directly correspond with structure modification front movement).

The schematic experimental set-up to study kinetic of laser-induced structure modification of ST-50 is shown at Fig. 4. CO₂-laser beam (1) with power about 40 W irradiates the sample (9) though the optical system (2, 4, 5, 8) and produces structure modification. At the same time He-Ne laser (6) illuminates the modified zone of GC, which changes transparency during laser radiation. Pyrometer (7) measures the surface temperature in the laser-irradiated spot.

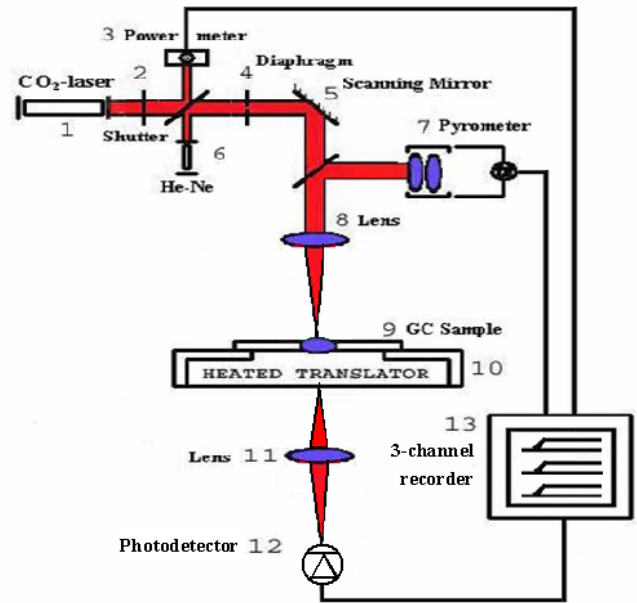


Fig. 4. Scheme of experimental set-up for kinetic studying of laser-induced structure modification.

Most important is that during laser amorphization – crystallization under CO₂ laser action the optical transparency of the modifying areas and the temperature of the surface as well as laser power signal could be recorded together [5, 7].

Typical experimental results are shown at Fig 5. Experimental results show that there is some definite temperatures near by glassing T~1033 K, at which transparency quickly falls, that is a speed at nucleation increases.

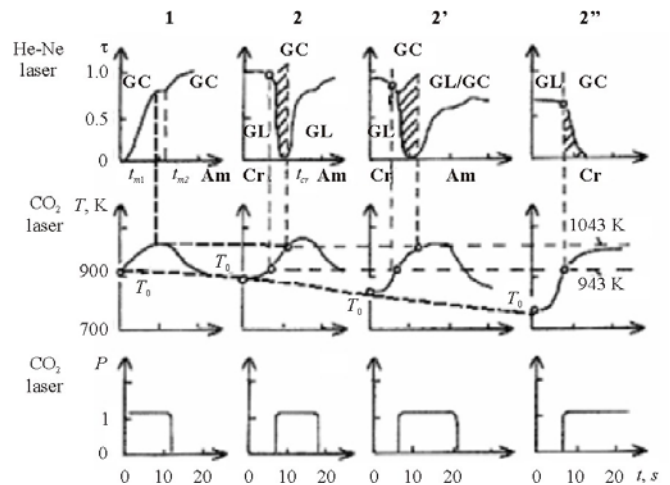


Fig 5. Experimental kinetic of reverse laser-induced structure modification processes. τ – transparency at wavelength of He-Ne laser, T – temperature of exposure zone during CO₂-laser radiation, P – laser power (relative number), t – time, sec. $P \sim 10^6 - 10^5$ W/m², thickness of the sample $h = 0.6$ mm. 1 – laser amorphizations. 2, 2', 2'' –

following crystallization–amorphization cycle during time of irradiation at different preheating temperatures.

Fig. 6 illustrates characteristic times dependences on laser power, P . All the characteristic times are decreased with the increase of P due to heating speed growth up to melting temperature.

There are two key temperatures: $T = 943$ K – beginning of crystallization process and decreasing of transparency, τ . $T = 1043$ K – beginning of melting process (pre-amorphization) and increasing of τ . Also there are three important times: t_{m1} – time of melting through along the laser beam direction, t_{m2} – time of complete melting through at irradiated spot (pre-amorphization). t_{cr} – time of complete crystallization.

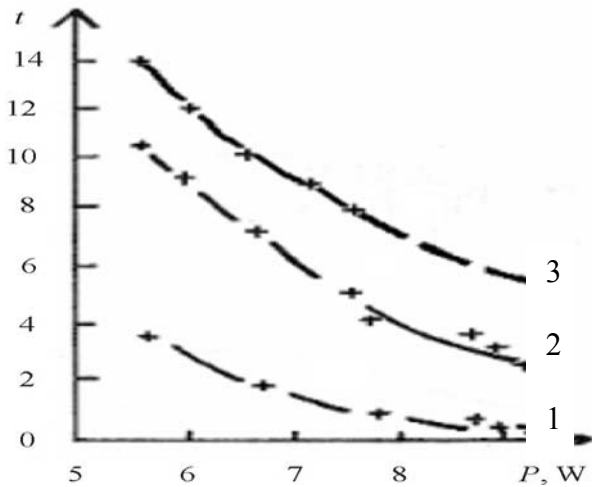


Fig. 6. The dependence of characteristic times: 1 - t_{m1} , 2 - t_{m2} and 3 - t_{cr} from the laser power P .

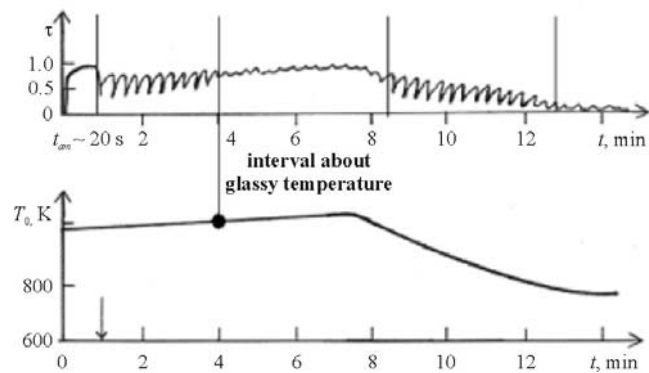


Fig. 7. Kinetic of amorphization – crystallization process under modulated beam of CO_2 -laser ($P = 9$ W, pulses durability – 10 s, repetition rate – 0.05 Hz): τ – transparency of the sample, T_0 – temperature of preheating.

The kinetic of this process is well seen from the next experiment (Fig. 7) done by irradiation of the sample with modulated in time with a small frequency CO_2 -laser light at

relatively small power density with a some drift of a sample preheating temperature. At first, GC ST-50 sample was amorphized during the time $t_0 = t_{am}$, after power modulation began.

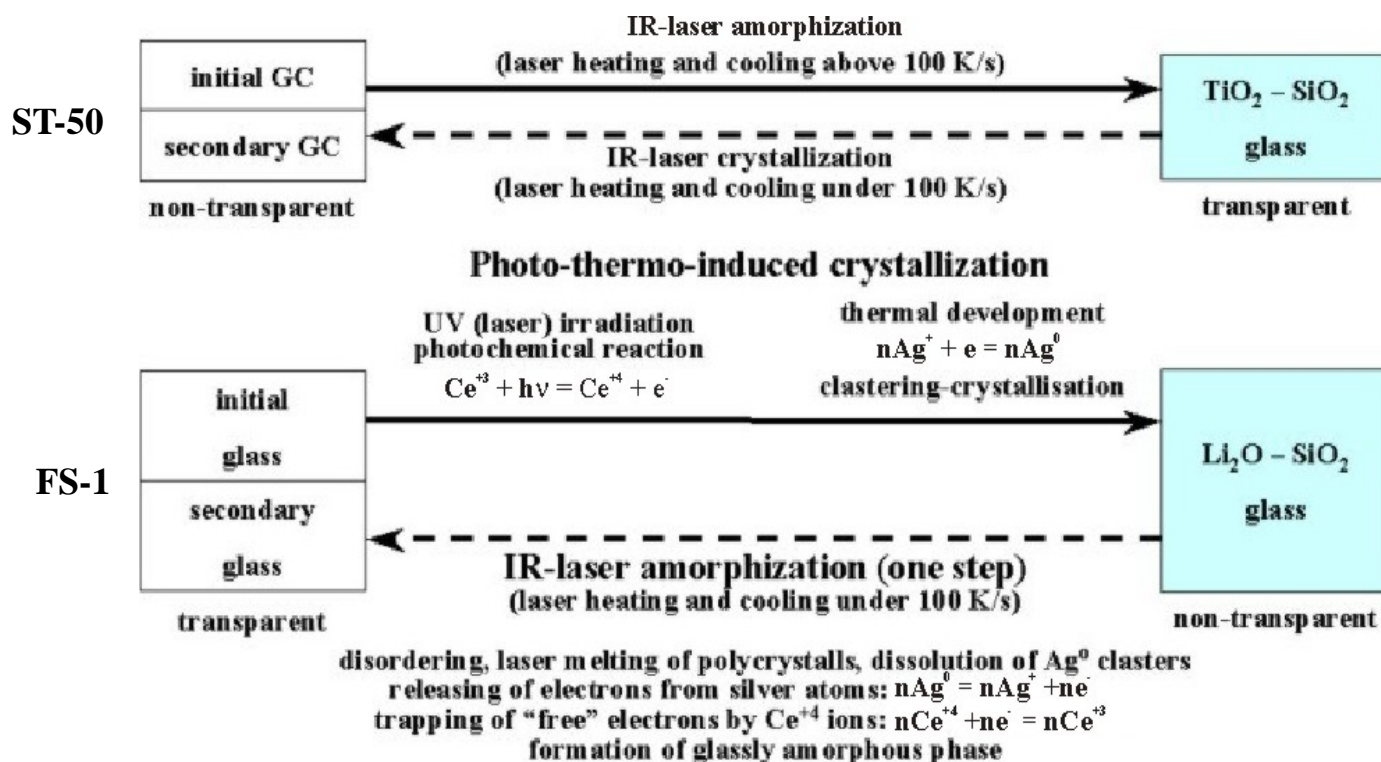
At increasing of T the amplitude of τ decreases due to narrowing of crystallization time interval. When decreasing T till 950 K at about 8,3 min and further the amplitude of τ decreases up to zero. In this case the glass is crystallized in the whole irradiated volume.

One of the most interesting peculiarities of the local laser action on glass-ceramics is a very high speed of amorphization and the same for crystallization of corresponding glasses. X-ray diffraction result shows that at laser crystallization of GS ST-50 a new structure appears after 10 sec, in analogous to that after few hours in furnace. So, the mechanisms of so quick structure modification of ST-50 and ST-1 under the laser heating present a subject to our next research.

5. Conclusion

Based on our experimental results we can make following conclusions:

- The possibility of reversible structure modification of GCs of ST-50 and FS-1 under laser action has been demonstrated. The general scheme of laser-induced reversible structure modification is shown below. It is seen that for ST-50 (TiO_2 - SiO_2 type) glass-ceramic as amorphization as crystallization takes one relatively short (about tens of sec) laser heating operation. Structure modifications of photosensitive glass FS-1 is also reversible at least from glassy state and after crystallization back to glassy state. And this amorphization process take the same short CO_2 -laser irradiation.
- Rates of structure modification under laser heating are about $10^2 - 10^3$ times higher than under conventional heating in a furnace. Characteristic time of laser amorphization-crystallisation cycle for GC of ST-50 is about 10 s in comparison with some hours for heating in a furnace.
- Optical transparency of GC depends on the correlation of volume fraction of crystalline phase and amorphous one.
- It is possible to modify a structure of amorphized or crystallized GC for required thickness of the sample using the dependence of transparency τ on laser power- P , time of irradiation, and pre-heating temperature - T_0 .



The general scheme of laser-induced reversible structure modifications for ST-50 glass-ceramic and FS-1 glass

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