Optica Applicata, Vol. XVII, No. 4, 1987

Interaction of low energy radiation ($E < 6$ eV) with the quartz glasses. Part 2. Mechanism of the processes*

STANISŁAW GĘBALA

Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland.

This is the second work of a series concerning the interaction of low energy radiation with the quartz glass. Thermoluminescent effects appearing in the quartz glasses after their irradiation from the sources of different spectra are presented. The quartz glasses were produced by melting the Brasilian quartz of Bahia and Red Telequartz types in electric furnaces. Also the thermostimulated electric effects and the EPR spectrum appearing in these glasses after similar irradiations are presented. The following conclusions are formulated: i) there exists a state of chemical equilibrium between all own defects and the dopings, ii) the changes in any component cause the changes in the whole system, and iii) the changes made exclusively in the doping result automatically in changes in the whole system. An example of creating the centre E' by irradiating with a visual light is presented. This explains many effects connected with glass irradiation.

1. Introduction

The real quartz glasses melted of natural quartz are defected due to the presence of technological dopings and material impurities. The dopings may replace isomorphically Si^{+4} (most frequently there appear Ga^{4+}, Al^{3+}, Ti^{4+}). The others may create the final groups in disrupted lattice as follows: $SiO_{3/2}O^-R^+$, $SiO_{3/2}OH$, $SiO_{3/2}Cl$, $SiO_{3/2}H$ (where R = Li, Na and K).

The own defects of the SiO_2 lattice occur mainly when the quartz glass is melted under the reducing or neutral conditions. The oxygen vacances as well as the Si–O bond breaking belong to this kind of defects. Si–O bond having been broken, a homological distribution of electrons may occur so that one electron is attributed to Si and the other on to O creating thus two paramagnetic groups, i.e., free radicals of $O_{3/2}\dot{S}i$ and $\dot{O}SiO_{3/2}$ types, respectively, where $O_{3/2}\dot{S}i$ is called centre E', while $\dot{O}SiO_{3/2}$ – centre on nonbridged oxigen atom (the corresponding notations in the GREAVES work [1] – Si^o and O^o). This type of SiO_2 bond breakage occurs also for nuclear irradiation. New structures may recombine with each other recreating the defectless structures or combine with dopings to create new structures $SiO_{3/2}H$, $O_{3/2}SiOH$. The participation of the new radicals in reactions is not identical. When

*Sponsored by the Polish Ministry of Science and Higher Education Project CPBP 01.06.

both the valence electrons remain with the oxygen atom during the Si–O bond breakage two charged defects: positive $O_{3/2}Si^+$ and negative $O_{3/2}SiO^-$ are created. These are diamagnetic centres. (The respective notations in the GREAVES work [1] are: Si^+ and Si^-). They appear also due to nuclear interaction.

The energy needed to break the Si–O band amounts to 420 kJ/mol and the probability of occurrence of the process in the liquid state is very low. The number of the own defects starts to increase with the increase of doping concentration. In the liquid state (> 1970 K) SiO_2 reacts easily with the materials coming from the crucible, furnace or gas medium (H_2, H_2O, and so on). These materials act as reducers and, in effect, reduced forms of silica $Si^{3+}O_{3/2}$, $Si^{2+}O_{2/2}$, etc. are produced in the glass. This diminishes the content of oxygen and in reality we have SiO_{2-x}, where x – decrement of the oxygen. The more of the reduced forms of silica the greater the x and the higher the reduction degree of the glass. Some examinations have been carried out in order to determine the oxygen deficit. Nowadays it is assumed that this deficit is comparable with the quantity of dopings in the glass. The reduced forms of silica are chemically active and for a given temperature the equilibrium state with the dopings is established. Incomplete forms of silica are stable at higher temperatures. When passing to lower temperatures they oxidize at the cost of dopings reduction, often to the atomic form. By rapid cooling a high temperature equilibrium state may be established. The frozen state of equilibrium may be shifted by thermal processing of the glass in the region of its softening. The thermal processing may change the equality of the lattice defects as well as the structural state of the dopings [2].

In the examinations of the irradiation influence on the quartz glasses, the nuclear irradiation is mainly used to evoke the changes of optical properties and the like. This is conditioned by the quantities of dopings. In addition to A(550 nm) and B(300 nm), also C(215 nm) connected with E' centre belongs to colour centres. The light from the visual and UV regions was used only to diminish the concentration of colour centres. The thermal processing of irradiated glasses is accompanied by light emission (thermoluminescence). It was believed that in order to examine the defects in quartz glass they must be produced, and for that purpose the nuclear irradiation is needed. According to [3] the energy needed to create a defect ranges from 17 to 33 eV.

The author of this work suggested in [4] another approach to the examination of defects in quartz glasses. In these glasses all the changes introduced earlier were removed by heating up to the temperature of 870 K. After annealing no thermoluminescence effects, among others, were observed. Only so prepared glasses were exposed to irradiation by lamps of the visual and UV spectrum ($E < 6$ eV). It turned out that in the quartz glasses the thermoluminescence was evoked without necessity of applying the nuclear radiation. Interesting thermoluminescence effects may be obtained after irradiation with the sun light. It has been also stated, that the irradiation by light creates the possibility of selective influence on particular thermoluminescence maxima and by the same time – on dopings.

The purpose of this paper is to widen the examination methodology. An explanation of this phenomena will be offered as well.

2. Description of the defects

The quartz glasses examined in this work were melted of the Brasilian quartz of Bahia and Red Telequartz types. These glasses contain dopings amounting to 10^{-2}–10^{-3}%, to which belong Al^{3+}, Ge^{4+}, Ti^{4+}, Li, and Na as well as the hydrogen (H_2, H_2O). These glasses were produced in the form of tubes which were next cut to produce plates to be examined. The starting point of the processing of each sample was the annealing in a furnace up to the temperature 870 K in order to remove the existing centres. Such samples after thermal processing gave no thermoluminescence effects.

In Figures 1 and 2 the curves of the thermoluminescence after irradiation by deuter lamp, mercury lamp, and with the window sun light are presented. Each of the used light sources is of different light spectrum. So, the deuter lamp has a continuous spectrum in UV region while the Hg lamp has a linear spectrum both in UV and in visible interval. The sun light is of continuous spectrum and contains the whole visible interval as well as near infrared. After the earlier annealing the quartz glass

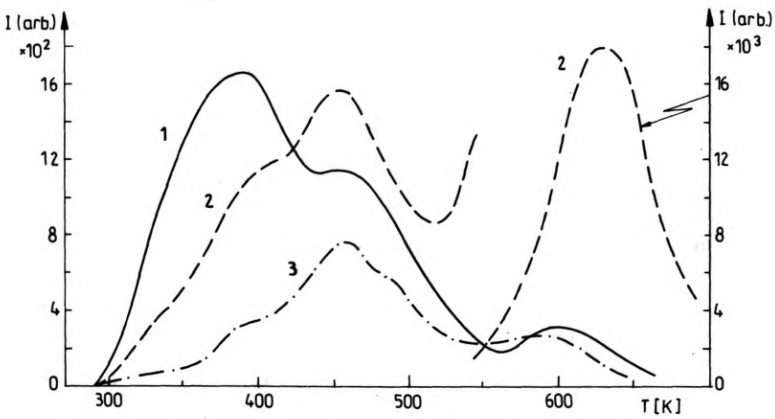

Fig. 1. Thermoluminescence in quartz glass of Bahia type irradiated with: 1 — deuter lamp, 2 — Hg lamp, 3 — sun light

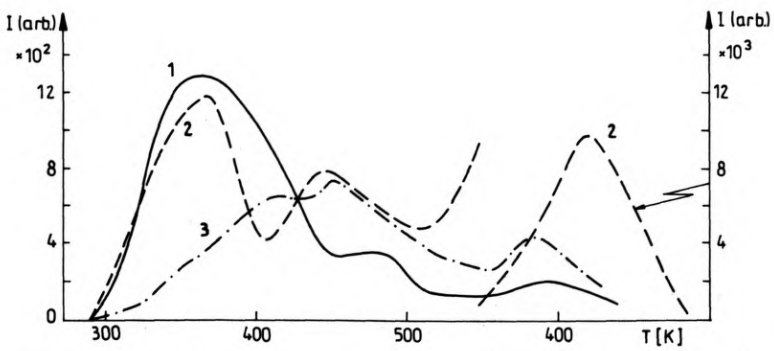

Fig. 2. Thermoluminescence of quartz glass of Red Telequartz type irradiated with: 1 — deuter lamp, 2 — Hg lamp, 3 — sun light,

plate was irradiated to produce the thermoluminescence spectra. The main maxima corresponds to the temperatures: 370 K, 450 K, 620 K, respectively. The other maxima may be attributed to the temperatures 410 K, 490 K and 580 K. The deuter lamp excites, above all, the band at 370 K. On the other hand, this band almost disappears when irradiating the sample with the sun light. For the quartz glass of Bahia type the luminescence intensity is stronger than that for the Red Telequartz type. This indicates that in the first glass there are more dopings while in the Red Telequartz glass there are more hydrogen compunds (H_2, OH^-).

In Figure 3 the comparison curves are shown for the thermoluminescence of quartz glass (Red Telequartz) after γ irradiation — curve 1. There appear two bands

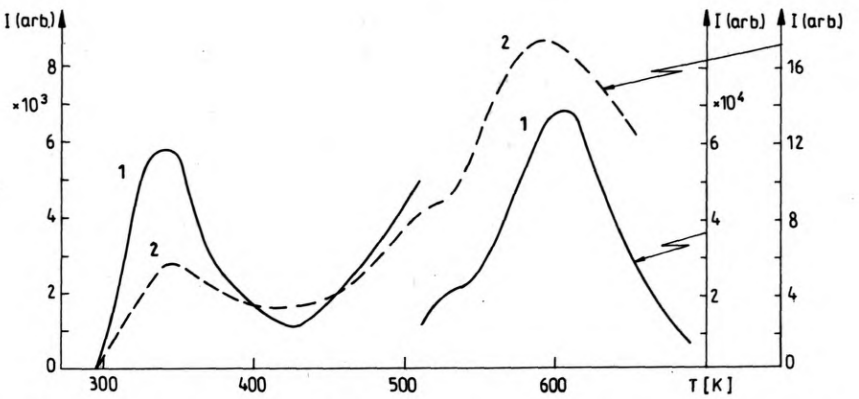

Fig. 3. Thermoluminescence of quartz glass of Red Telequartz type irradiated with γ radiation — 1. Thermoluminescence in crystal quartz Red Telequartz irradiated with a mercury lamp — 2

corresponding to 345 K and 590 K, respectively. On the other hand, the curve 2 shows the thermoluminescence of quartz of the same sort, in the form of powder, exposed to irradiation with a mercury lamp. The similarity of bands is visible. This result is interesting because no examinations seem to be reported in literature concerning thermoluminescence in the crystal glass after irradiation by mercury lamp.

In Figure 4 the thermoluminescence of the Red Telequartz glass after irradiation by monochromatic light has been shown. The plates of glass were irradiated with the Hg lamp via a SMP–2 monochromator with a quartz prism. A regularity is observed in the positioning of the thermoluminescence curves: the shorter the wavelength of the irradiating radiation the greater the bands at 370 K.

Additionally, the thermostimulated electric conductivity is shown as well as the thermally excited electric discharge in the Red Telequartz glass sample irradiated with the Hg lamp. This kind of examinations is known [5]. Thermostimulated electric conductivity reflects approximately the thermoluminescence distribution. Here, a shift of the maxima in the direction of lower temperatures is observed. The thermostimulated electric discharge of the sample appears due to the fact that an electret is produced in the first stage as a result of irradiating with the Hg lamp (Fig.

5). At room temperature the direction of the current flow is negative in our plot. Both a change of direction and an increase of current intensity result from the increase of the temperature. The maxima of these intensities are obtained at the same places as the thermoluminescence maxima.

The change back to the negative direction appears at the 700 K temperature. In this process free electrons, as well as hydrogen and alkali metal ions, take part. In Figure 6 the EPR spectrum is shown for the quartz glass with the visible signal of the centre E' (339 mT) [6] after the sample irradiation with the Hg lamp and the halogen lamp. Both the irradiation and the measurements were performed at room temperature (traditionally for the recovery of the centre the nuclear radiation is

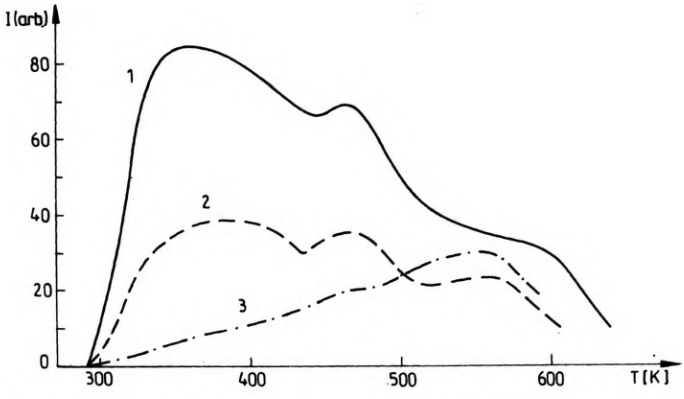

Fig. 4. Thermoluminescence of quartz glass of Red Telequartz type irradiated with monochromatic light: 1 – 247 nm, 2 – 265 nm, 3 – 546 nm

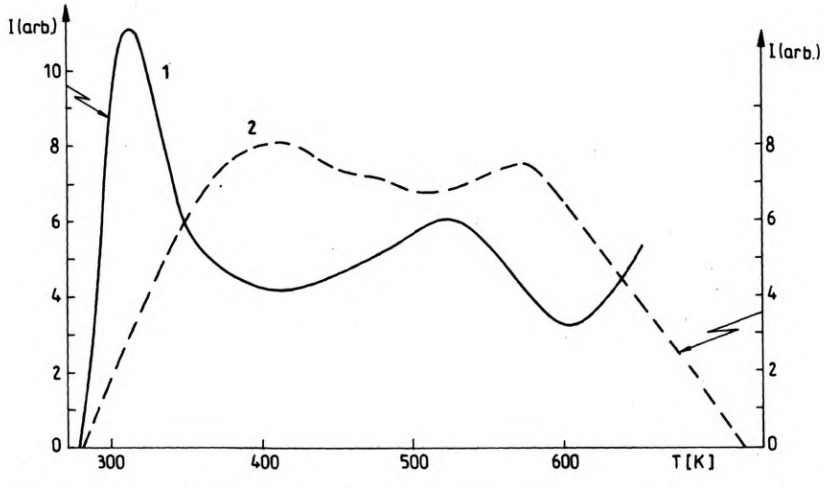

Fig. 5. Thermostimulated electrical conductivity of the quartz glass sample (Red Telequartz) after irradiation with mercury lamp – 1. Thermostimulated electric discharge of the sample of the same sort after irradiation with mercury lamp – 2

used). This signal comes from unpaired electrons located at $Si(O_{3/2}Si^{\bullet})$. The stable glasses give no signal. Only after damaging of the structure a signal appears which fades during the thermal annealing or when the sample is left in the open air for a while. The samples before the irradiation had been annealed in the furnace.

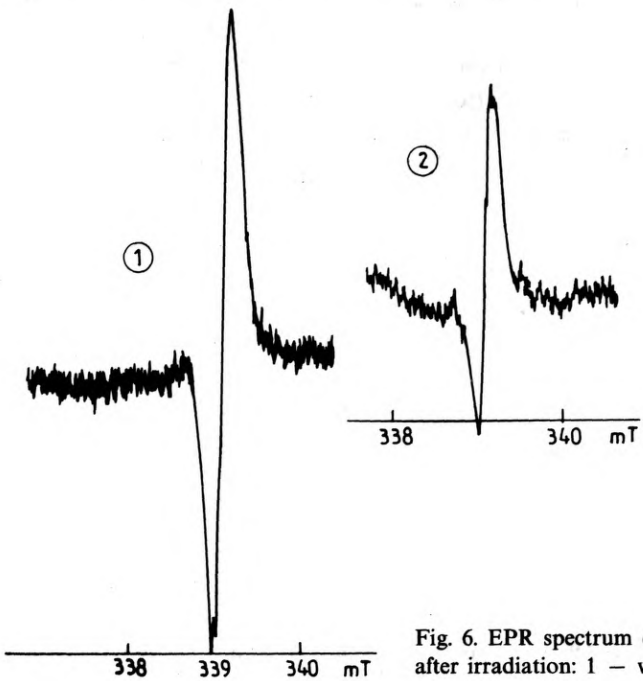

Fig. 6. EPR spectrum of quartz glass of Red Telequartz type after irradiation: 1 – with Hg lamp, 2 – with halogen lamp

The examinations of the changes of absorption in the same samples of glass after irradiation with the same lamps were also performed. The measurements of the irradiated plate with reference to the nonirradiated one were carried out. A Specord UV VIS spectrophotometer was used for the measurements. Similarly as before, this time no changes of absorption were observed, which could be attributed to the irradiation coming from the used lamps. This is inconsistent with the concept that the thermoluminescence is due to the process of recombination of colour centres.

3. Discussion of the results

We shall discuss some problems which remain within the field of interest of the author and which will be subject of the further eaxminations. First, we offer an explanation of the mechanism of the process which takes place in the quartz glass after its irradiation. Referring to what was already said in the Introduction the statement that there exists a state of equilibrium between the own defects of the SiO_2 lattice and the gas dopings in the atomic or other forms should not evoke any objections. Our experiments allow us to draw an even more general conclusion.

The changes introduced in any component defect of the quartz glass result in

changes in the whole system including the changes in the own defects. Therefore, to produce the own defects we need not apply the nuclear radiation. If suffices that we produce the changes in the gaseous dopings which result in automatic changes in the whole system. Thus, the centres E' are produced by using only visual light of energy < 3 eV and not, as it was the case up to now, energy from the 17–33 eV interval [3]. This allows also to explain the formerly obscure effects.

Which kind of effects are dominant here? The ionization is less probable due to high energy needed (ionization of H – 13.595 eV, H_2 – 15.422 eV, Na – 5.138 eV, etc.) even if we take account of the fact that in the condensed phase the ionization potential is lower than in the gaseous phase by the energy of polarization. It should be assumed that the main processes are those of absorption of the light and dissociation into free radicals. The latter are characterized by a high chemical reactance. They need only slight activation energy. Their main feature is the ability of attacking the neighbouring particles: atoms, ions, and so on.

The description of the defects in glass is both difficult and controversial. With the development of the knowledge about the defects in the solid state physics some concepts like colour centres, for instance, have been carried over into the glass science. Similar transfers from physics of semiconductors were made. Therefore, we speak about recombination and trapping centres and the like. There are some authors who consequently build up the knowledge about the defects in glass in the mentioned way [7]. In contrast to that, in this work the chemical description is dominating. The author believes that the knowledge about the properties of the oxidizing-reducing defects is more adequate here for the description of quartz glass reality than the mentioned concepts of the solid-state physics. In our case the energetic spectra of thermoluminescence are not attributed to the depth of traps and holes but inform rather about the activation energy of the respective chemical reactions. Thereby, the thermoluminescence is not a recombination process for colour centres. If after light irradiation E' remains in glass at room temperature, it is not because of it being trapped but because of the lack of a partner to realize the recombination processes and other chemical reactions.

What kind of information is provided by thermoluminescence in glass? The most important points are:

i) the glass is doped,
ii) no oxygen deficit occurs,
iii) the glass morphology is nonstechiometric.

The more dopings and the higher the glass reductivity degree, the stronger the thermoluminescence intensity. The doping concentration may be determined by plotting the gauging curve between the above relations for the quartz glass. As it is well known, the temperature-dependent spectrum reflects the doping composition. From the works on thermoluminescence in quartz irradiated with the nuclear radiation the band at 370 K is connected with hydrogen (H, H_2, OH). The band at 450 K with the centre E', and the band at 520 K is attributed to $(AlO_4)^0$, while the bands at 515 K, and 550 K are associated with alkalium [8]. This requires some further investigations.

References

[1] GREAVES G. N., J. Non-Cryst. Solids **32** (1979), 295–311.
[2] LEKO V. K., MAZURIN O. V., *Svoistva kvarcevogo stekla*, (in Russian), [Ed.] Nauka, Leningrad 1985.
[3] ZAKIS Yu., SILIN A. R., TRUKHIN A. N., Fiz. Khim. Stekla **2** (1976), 481–488, (in Russian).
[4] GĘBALA S., Opt. Appl. **16** (1986), 201.
[5] BREKHOVSKIKH S. M., VIKTOROVA Yu. N., LANDA L. M., *Radiacionnye Efekty v Steklakh* (in Russian), [Ed.] Energoizdat, Moskva 1982.
[6] TAYLOR C. P., *Resonance Effects in Glasses. Glass I: Introduction with Electromagnetic Radiation*, Academic Press, 1977.
[7] ZAKIS Yu. R., *Defekty v Stekloobraznom Sostoianii Veshchestva*, (in Russian), [Ed.] Zinatne, Riga 1984.
[8] JANI M. G., HALLIBURTON L. E., KOHNKE E. E., J. Appl. Phys. **54** (1983), 6321–6328.

Received December 18, 1986

Низкоэнергетическое воздействие на кварцевое стекло (E < 6 eV). Часть II. Модель механизма происходящих процессов

Это вторая из серии работ на тему низкоэнергетического воздействия на кварцевое стекло. В ней представлены термолюминесценционные эффекты после световой экспозиции из источников разных спектров в кварцевом стекле, вареных в электрической печи из бразилийского кварца типа „Бахия" и „красный Телекварц". Представлены также термостимулированные электрические эффекты и спектр EPR в этих же стеклах после похожих световых экспозиций. Сделаны выводы: 1. Между всеми собственными дефектами и примесями в стекле существует состояние химического равновесия. 2. Введение изменений в любой составной части системы ведёт к изменениям во всей системе. 3. Вводя изменения в самих примесях автоматически получаем изменения во всей системе. Представлен пример изготовления центра E' посредством световой экспозиции видимым светом. Это обосновывает все дефекты, связанные с облучением стекла. Представлены и другие выводы, вытекающие из настоящей работы.