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Interaction of low energy radiation on quartz glass below 6 eV
Part I. Thermoluminescence in quartz glasses excited by light of 200–800 nm wavelength interval *

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The paper presents the results of examination of thermoluminescence effects in quartz glasses melted from the natural materials. The thermoluminescence effects were excited within the spectral range (200–400 nm) as well as in the visible range at the room temperatures, using mercury, deuter and other lamps. Good results were obtained after irradiation with the sun light. The effectiveness of glass irradiation when using the monochromatic light of different wavelengths was examined. The highest effects were obtained after irradiation with the mercury lines of 436 nm wavelength. No absorption changes, i.e., no colour centres, were stated in the quartz glasses irradiated within the said spectral ranges.

1. Introduction

An increasing interest in properties of all kinds of the crystalline and glassy quartz is manifested in a relatively large number of papers on thermoluminescence in those materials [1–10], evoked, however, by high energy radiation. The purpose of this work is to present the analogical effects due to low energy radiation, as they are capable to indicate different kinds of glass impurities.

In the quartz glasses produced of natural materials there exists some impurities such as: Al, Na, Li, Ge etc. [1]. In these glasses also some technological impurities (technological "additions") such as H_2, Cl_2, O_2, H_2O, HCl, and so on tend to occur (mainly in synthetic glasses) [1], [15], [16]. The structure of silica glasses is partly defected. These defects are compensated by the above mentioned impurities. When concentration of impurities is high, part of them remain unbounded, and they decide about the quality of quartz glass, especially about its optical properties. They also determine real structure of the lattice defects as well as the physico-chemical properties of glass. The real defects are electrically neutral. The situation becomes radically different after the glass is subject to high energy radiation, e.g., to γ-radiation. Then a system of positive and negative centers is formed, where

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electrons constitute the negative centres. The γ-radiation drives out the electrons from the oxygen orbitals and breaks the bonds, giving rise to the relaxation and occurrence of new states. Among the above mentioned "additions", which participate in these states, H and H_2 play the most important role. The absorption properties are connected with the presence of positive and negative centres, hence the latter are called also the colour centres. Their concentrations are not always mutually proportional. For instance, the quantities of centres E' and centres on nonbridged oxygen atoms as well as their resistivities to the temperature may be different [15].

The effects of high energy radiation are complex being dependent on the presence of all the "additions" [1]. The colour centres may be partly liquidated with the help of light and totally by applying the thermal processing. In the last case the emission of energy takes the form of luminescence. The maximal temperature of luminescence defines thermal energy of ionization of both electron and hole centres [6], [11]. It is commonly believed that the thermoluminescence is completely attributed to the colour centres and is a part of the recombination process of the above state [1], [4]. The thermoluminescence is a single effect, i.e., it cannot be repeated once more unless the sample is subject again to a high energy radiation. For the natural quartz crystals, thermoluminescence is an indication that the radioactive materials are present in the vicinity [2], [5], [6]. When heating up the samples, one observes a change of luminescence intensity, while the thermoluminescence is characterized by a system of bands appropriate of the given material, and strictly speaking of the impurities occurring in it. The bands emitted in the temperature ranging within 330–400 K, 450–500 K and 520–550 K are attributed to OH group, E' centre and sodium, and other alkalies at the presence of $[AlO_4]^0$, respectively, [12]. The higher thermoluminescence intensity is observed in the quartz glasses melted under the reducing conditions [2], [3]. There are some publications indicating that there is the lack of complete identity of the positions of both thermoluminescence maxima and colour centre fading maxima [13] as well as that in the presence of Al_2O_3 or other elements of the III group the respective intensities are not mutually proportional [1]. Beside the γ-radiation the X-ray radiation is exploited most commonly [1]. Some trials with the UV irradiation in vacuo were made independently [14]. In the available literature there are no works which would deal with the quartz glass irradiation by using the radiation of even lower energy in order to examine the due thermoluminescence. In this work we present the first part of the results of investigation, in which the 200–400 nm UV radiation and visible light were used.

2. Method of examination

The quartz glass samples coming from different producers and made of natural materials (quartz crystals) were prepared for examinations. These samples belong to the quartz glasses of either the first group with natural impurities and low water content or to the second group where glass has a higher water content. They differed both in the kind and quantity of "additions", the dominant imperfections being Al and Na. The main object of investigations was the glass produced by the Polish firm in Ożarów from the Brazilian quartz. The examinations included also the glasses produced by Heraeus firm (Heralux WG) and those produced by French firm Quartz et Silice. These glasses contain smaller quantity of impurities, the proportions of which are different from that in Polish glasses, mentioned above. In one case the Vitreosil produced by Thermal Syndicate Ltd. was exploited. Its thermoluminescence curve was similar to that of quartz glass from Ożarów. The samples of quartz glass were exploited many times according to following sequence of processing: irradiation – annealing – irradiation, and so on. For thermal processing a linear furnace of annealing rate 13.5 K/min was built and installed in front of a photomultiplier. In front of latter, in turn, both heat filter and colour (Hg Mon 436) filter of 420–480 nm transmission were placed. The changes in luminescence intensity were recorded on a plotter. The furnace after cooling was repeatedly heated up in order to record its shining at elevated temperatures.

Since the purpose of the work was to examine the conditions under which the thermoluminescence effect appears, the lamps used for irradiation were of different spectral ranges. In particular, we have applied a mercury Q400 lamp with all its spectral lines within the UV and visible regions, and a mercury HBO–200 lamp emitting 365 nm line together with all lines within the visible spectrum range, and a deuter lamp of continuous spectrum in the 200–400 nm range, as well as the sun light. Irradiation with monochromatic light was realized with a high pressure (500 W) mercury lamp and a SPM2 monochromator equipped with a quartz spectral prism. For the comparative measurements the samples were subject to a single irradiation with either X-rays (20 mA, 40 kV) or with γ-rays of 20.7×10^{18} eV/g dose.

3. Results of examinations

For the sake of comparison the thermoluminescence curves for glasses having been irradiated by using a high energy (γ- and X-rays) radiation are presented in Figs. 1 and 2, and the curves obtained after irradiating the glass with UV and visible radiation – in Figs. 3–5. The curves 1, 2 and 3 in Figs. 1 and 2 refer to the quartz glass from Ożarów, to the glasses from Quartz et Silice firm, and to glasses from Heraeus firm, respectively. The curves showing the luminescence intensity distribution vs temperature are affected by both the presence and the quantity of impurities of various kind. The luminescence curve vs temperature in Fig. 3 is shown for the case when the Q400 mercury lamp emitting all the lines in UV and the visual range is used for irradiation. The curve 1 referring to the Vitreosil glass produced by Thermal Syndicate Ltd. is similar to that produced in Ożarów. The curve 2 is characteristic of quartz glasses produced by Quartz et Silice, while the

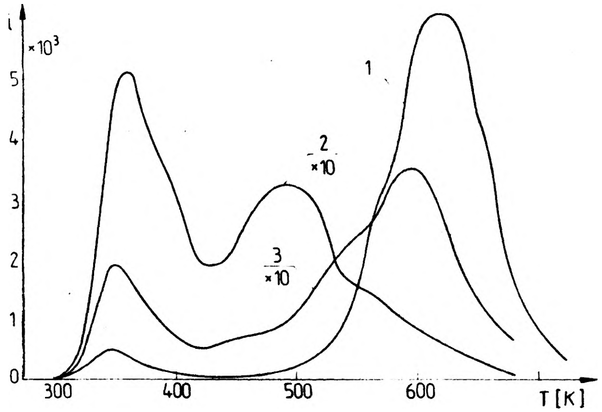

Fig. 1. Thermoluminescence in quartz glass after γ-irradiation: 1 — quartz glass produced by Polish firm from Ożarów, 2 — quartz glass produced by French firm Quartz et Silice, 3 — quartz glass produced by German firm Heraeus

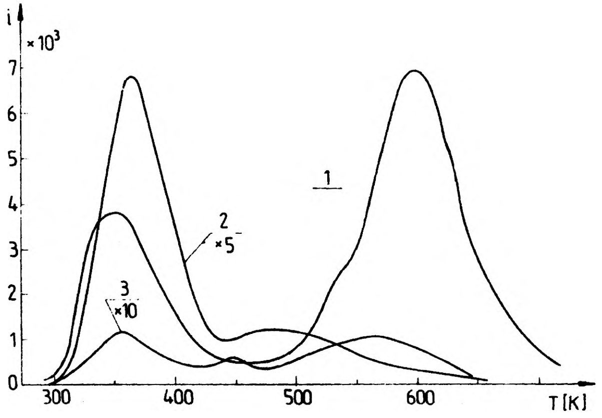

Fig. 2. Thermoluminescence in quartz glass after X-ray irradiation: 1, 2 and 3 — as in Fig. 1

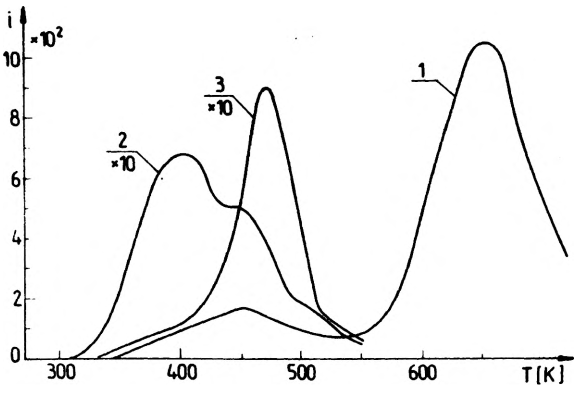

Fig. 3. Thermoluminescence in quartz glass after irradiated with mercury lamp Q400 (1 h): 1 — quartz glass produced by English firm Thermal Syndicate Ltd., 2 — quartz glass produced by French firm Quartz et Silice, 3 — quartz glass produced by German firm Heraeus

curve 3 refers to glass produced by Heraeus. These curves differ from the curves shown in Figs. 1 and 2.

Several thermoluminescence curves for glasses irradiated with lamps of different spectral ranges are shown in Fig. 4. As the irradiation objects the glass samples from Ożarów were used. The curve 1 shows the results of irradiation with Q400

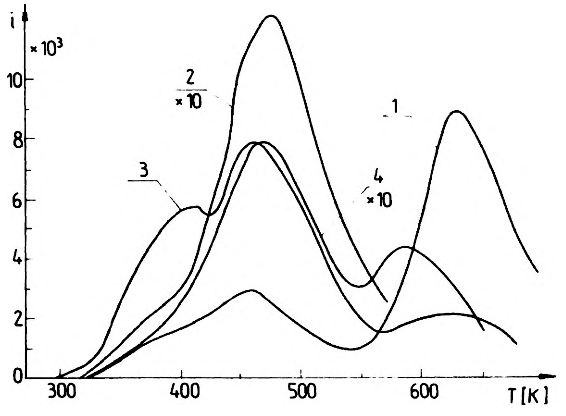

Fig. 4. Thermoluminescence in quartz glass produced by Polish firm in Ożarów irradiated with: 1 – mercury lamp Q400, 2 – mercury lamp HBO–200, 3 – deuter lamp, 4 – sun light

mercury lamp, curve 2 corresponds to irradiation with HBO–200 lamp emitting, beside the 365 nm line, some other lines in visible range, curve 3 corresponds to irradiation with deuter lamp of a continuous spectrum within the 200–400 nm range. The curve 4 shows the thermoluminescence distribution after irradiation of glass with the sun light. The obtained curves differ significantly from one another which means that there exists the thermoluminescence due to particular dopings and is in some way interrelated with the spectral ranges of interaction. Figure 5 shows the examples of luminescence distribution versus temperature after irradiation of glass plates from Ożarów with monochromatic light of different wavelengths. The source of light was the high power (500 W) mercury lamp, the particular light wavelength being selected by means of SPM2 monochromator supplied with a quartz prism. Curves 1, 2 and 3 show the thermoluminescences after irradiation with 546 nm, 436 nm, 365 nm, and 265 nm monochromatic light, respectively. The thermoluminescence curves for the wavelength of 313 nm and 303 nm, for which one obtains very low thermoluminescence effects, as well as shifts toward the higher temperatures are not presented in this paper. Thus, there exists a high selectivity while sensitizing the thermoluminescence.

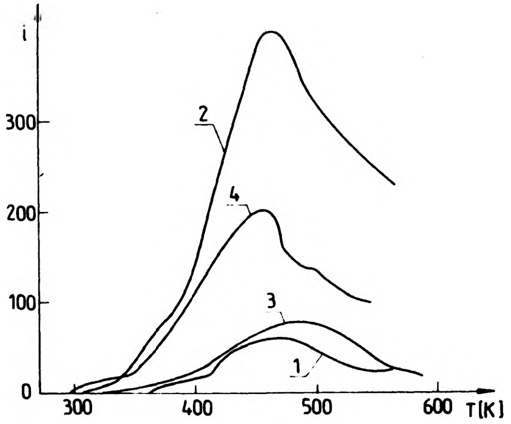

Fig. 5. Thermoluminescence in quartz glass made by Polish firm in Ożarów when irradiated by monochromatic light: 1 – $\lambda = 546$ nm, 2 – $\lambda = 436$ nm, 3 – $\lambda = 365$ nm, 4 – λ – 265 nm

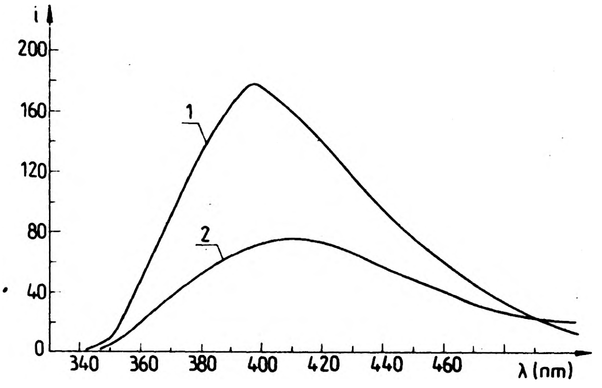

Fig. 6. Spectral distribution of the thermoluminescence in quartz glasses produced by Polish firm in Ożarów: 1 – after γ-irradiation (500 K), 2 – after irradiation with the Q400 mercury lamp (550 K)

Figure 6 includes the spectral distributions of thermoluminescence after γ-irradiation, at the temperatures of 600 K and 650 K, (curve 1), and irradiation by means of Q400 lamp (curve 2), respectively. An example of relative changes in transmittivity of quartz glass from Ożarów after γ-irradiation (curve 1) and X-ray irradiation (curve 2) is also presented (Fig. 7). An analogical relative distribution

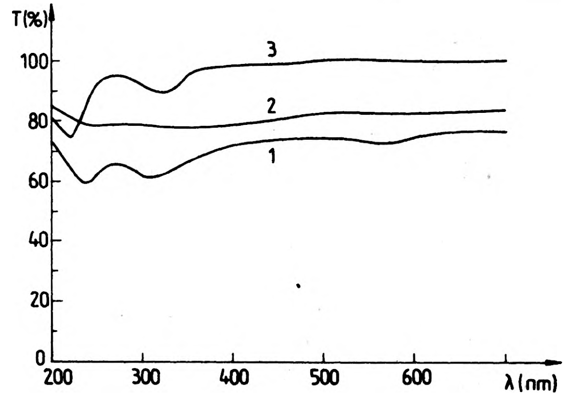

Fig. 7. Relative transmittivity after quartz plate irradiation: 1 – quartz glass from the Polish firm in Ożarów after γ-radiation, 2 – quartz glass from the Polish firm in Ożarów after X-ray irradiation, 3 – quartz glass from the German firm Heraeus after γ-radiation

after γ-irradiation for Heraeus glasses (Heralux WG) is shown by curve 3. The measurements were performed on a Specord UV VIS spectrometer. In this case no changes were noticed after either UV irradiation or visible radiation. This information is important because of the fact that so far thermoluminescence effects have been attributed to absorption and vice versa.

4. Conclusions

We restrict ourselves to formulate some important conclusions following from the results obtained. A more detailed discussion will be given in the next part of this work. The most important observation is the lack of any changes in absorption after UV irradiation, which means that, contrary to results obtained, the thermoluminescence centres are not associated with the appearance of colour centres, as it would follow from the standard method of transmission measurement. Therefore, it may be expected that a proper model of thermoluminescence mechanism in the quartz glass may be developed based on the low energy interaction.

In the up to now examinations of quartz glasses the light was used only in the processes including recombination of colour centres. In our case the colour centers were not affected. Before the irradiation was started each sample was subject to the thermal processing during which the centres of electron-hole type were removed. The type of irradiation applied in this work affects both the defects compensated by the technological "additions" and these impurities of quartz glass which are in unbounded states. This effect is similar to the photosensitive processes. Low energy radiation and the appropriate choice of spectrum allow selective treatment of the particular "additions" in the quartz glass. This gives the proper basis to the development of the method of detection of imperfections in glass and for the knowledge about the processes occurring between them.

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Низкоэнергетическое воздействие на кварцевое стеклю ниже 6 эВ. Часть I. Исследования условий термовысвечивания в кварцевом стелкле, возбужденным светом 200–800 нм

Представлены результаты исследования эффектов термовысвечивания в кварцевых стеклах, варенных из природных материалов. Эффекты термовысвечивания возбуждались в области спектра 200–400 нм, а также в пределах видимого света в комнатной температуре. Для этого применены ртутные дуговые лампы, дейтериевые лампы и т. д. Хорошие результаты получены при облучении солнечным светом. Обследована эффективность облучения стекол при использовании монохроматического света разной длины. Самые хорошие эффекты получены при излучении эмиссионной линей длиной в 436 нм. Не обнаружены абсорбционные изменения, т. е. не обнаружены центры окраски в кварцевых стеклах, при излучении в вышеупомянутых областях спектра.