

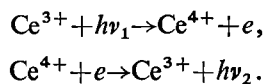
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Changes in resistivity of glass containing cerium to ionizing radiation after photothermal processing**

Cerium is a commonly used addition protecting the glass against the effect of ionizing radiation. The mechanisms of cerium operation as well as condition, which must be fulfilled to make cerium operate, are not quite explained. Usually it is believed that resistive action against the ionizing radiation in glass occurs due to oxidizing processes in glass. The experimental results presented in this paper suggest that an essential role in resistivity action against the oxidizing processes of cerium is played by structural elements to which cerium also belongs. These elements transfer the excitation energy and electrons. It seems that the energy scattering takes place most frequently in the form of luminescence of cerium Ce^{3+} .

1. Introduction

Ionizing radiation increasing the glass absorption in the visible spectrum range is an unwanted phenomenon, as it deteriorates the quality of optical instruments working under irradiative conditions. In order to protect the glass against the irradiation effects it is doped with cerium during melting. Resistive properties of cerium are by some authors [1-7], [12, 13] attributed to processes of oxidation and reduction of cerium ions



However, it seems that the structural properties are more significant than oxidizing and reducing processes. Special conditions must be fulfilled to make the cerium containing glass resistive to ionizing radiation. The resistivity to radiation is characteristic of glasses in which cerium concentration is $0.05 < x < 6\%$ [3]. Both above and below this concentration the protective action of cerium lowers. At respectively low concentrations cerium may even make the glass sensitive to ionizing action of radiation. Also the conditions of melting seem to be essential [6, 10] as well as the content of alkali ions in glass [7, 11]. In glasses containing cerium and melted under reducing conditions a smaller increase in light absorption caused by action of ionizing radiation on glass is observed than in glasses melted under oxidizing conditions [6]. Thus, the glasses melted under redu-

cing conditions are more resistive to ionizing radiation. The resistivity of glass increases also with the increasing content of alkali metal oxides [7, 11]. E. g., for the same amount of cerium (1%) the change in the amount of Na_2O from 5% to 20% causes a tenfold reduction in glass colouration due to exposition to γ -radiation. An opposite effect appears for the 0.1% cerium content. The absorption by cerium depends also on percentage contents Na_2O [11]. The conditions specified above influence the coordination polyhedron of glass, thus they are of structural character [10]. According to some authors [8, 9] the resistivity of glass undoped with resistive ions may be associated with its structure. There are strong analogies in the conditioning of resistive properties to radiation between glasses undoped and doped with cerium. In both cases the melting conditions (temperature, additions of reducing agents) decide about resistivity. In this paper we present the results of our investigations concerning the influence of X-ray and UV-radiation on the cerium ions in glass. The purpose of this work was to find whether and to what degree the mechanisms of electrons and holes trapping by cerium ions is essential in the balance of scattered energy originating from ionizing radiation as well as to explain the relations between the resistivity of glass doped with cerium and the structural conditions.

2. The experimental method

The subject of investigations were the optical glasses like: BK1, BK7, Bak 2, Bak 4 belonging to crown glasses, and resistive to ionizing action, due to cerium doping. All the glasses have been produced

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in Optical Works in Jelenia Góra (Poland). For examination we used glass plates polished on both sides of sizes $10 \times 20 \times 0.5$ mm. The changes in absorption caused by irradiation with an appropriate sort of ionizing radiation were measured within the UV and visible range, registered with the help of Specord UV VIS spectrophotometer. In the latter the difference between the optical density of irradiation and nonirradiated plates was measured as a function of wavenumbers, the changes of spectral luminescence being recorded in a photoelectric setup.

A series of measurements have been made for samples irradiated by UV, X-ray and γ -radiation, respectively. Independently, the measurements have been made for samples irradiated successively by UV and X-ray and γ -radiation as well as in their opposite sequence. For ultraviolet irradiation a HBO-200 mercury lamp was employed. This lamp has a very intensive line at 365 nm, having simultaneously no spectral components in the range below 300 nm. The samples of glass were irradiated for 30 min at temperature 100°C . For X-ray irradiation of glass a Roentgen lamp with tungsten anticathode was used which worked at 18 kV voltage and 20 mA current. The irradiation time was 30 min. The irradiation of samples with γ -radiation of 0.585 Mr dose has been realized in a cobalt bomb. The irradiation with X-ray and γ -radiation was done at the room temperature.

3. The results of experiments

In figs. 1 and 2 the spectral distributions of changes in optical density for BK 101 and BK 107 glasses are presented, which were evoked by irradiating the glasses with a HBO-200 lamp (100°C), with X-rays and γ -radiation at room temperatures. This irradiation resulted in an appearance of a broad absorption band with a maximum at $38 \times 10^3 \text{ cm}^{-1}$ for BK 101 glass and at $35 \times 10^3 \text{ cm}^{-1}$ for BK 107 glass. The differences in interaction with glass are visible also within the absorption band of Ce^{3+} .

A change in transmission of BK 101 plates measured with respect to the air after irradiating by γ -radiation (curve 3) and UV radiation (curve 2) is shown in fig. 3. When comparing the curves the basic differences between the effects of γ - and UV-radiations become visible. The possibility of imposing the transmission curve after the γ -irradiation to become identical with that after UV-irradiation has also been shown (curve 4). For this reason glass sample irradiated with γ -radiation was subjected to irradiation

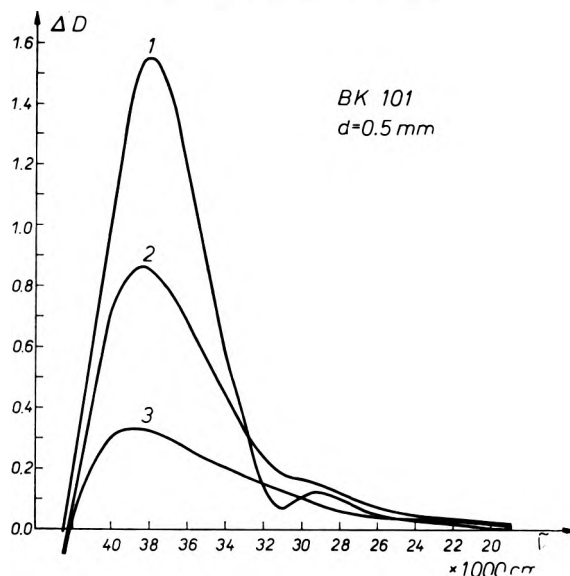


Fig. 1. Increase in optical density vs. the wavenumber after exposure to UV-, X-rays and γ -radiation, for BK 101 glass: 1 - UV (HBO-200), 2 - γ , 3 - X-ray

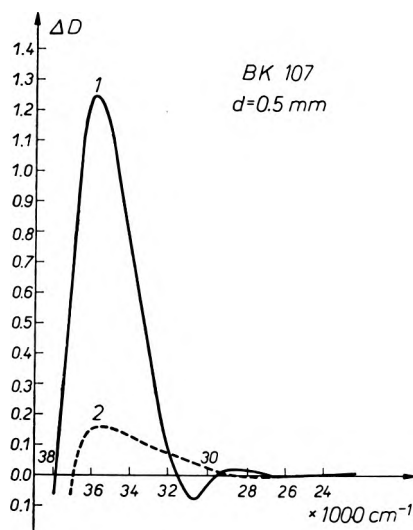


Fig. 2. Increase in optical density vs. the wavenumber after exposure to UV-, X-rays and γ -radiation, for BK 107 glass: 1 - UV (HBO-200), 2 - Rtg

from HBO-200 lamp. In this way the easily removable components have been eliminated, leaving typical changes similar to those induced by UV-radiation (365 nm) unaltered.

The next results shown in figs 4, 5, 6 present transmission of glass plates ($d = 0.5$ mm) vs. the wavenumber, obtained after exposure of BK 101, BK 107 and BK 104 glasses to γ -radiation and either, irradiated earlier by HBO-200 lamp (30 min) or not irradiated at all. These data concern the glasses BK 101, BK 107 and BK 104. In the visible range decrease in transmissivity is observed to be much higher for glasses

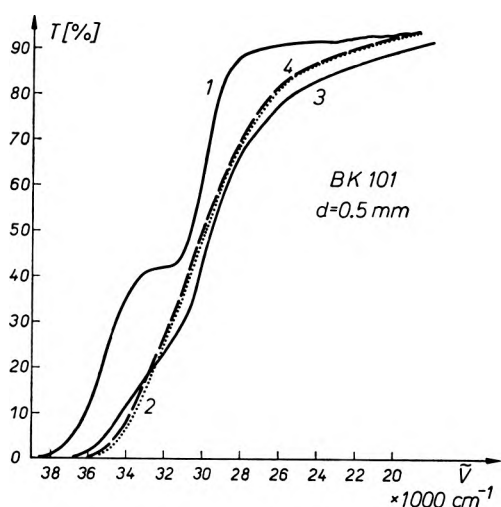


Fig. 3. Transmission vs. the wavenumber, for BK 101 glass at different ways of irradiation:

1 - non-irradiated, 2 - UV (HBO-200), 3 - γ , 4 - γ +UV (90 min)

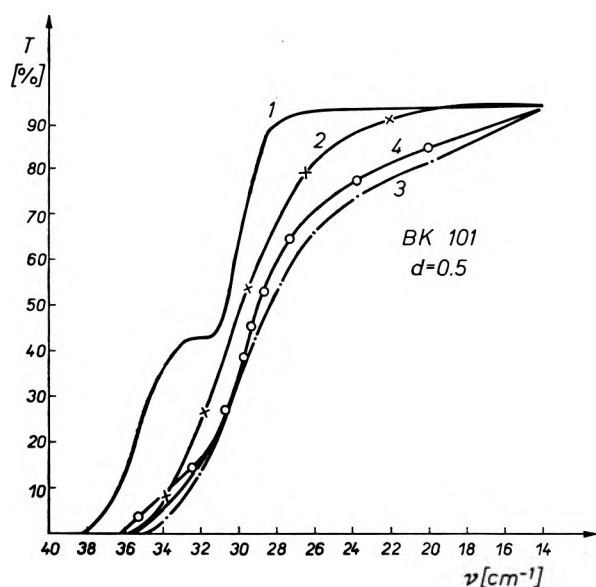


Fig. 4. Transmission vs. the wavenumber for different ways of irradiation:

1 - non-irradiated, 2 - UV, 3 - UV+ γ , 4 - γ

irradiated earlier by UV than that for nonirradiated samples. However, this is not a result of summing of the effects. It seems to be caused by the change of resistive properties due to oxidation from Ce^{3+} to Ce^{4+} . After irradiation by γ -rays no changes are observed in the absorption band of cerium (Ce^{3+}), thus the changes introduced earlier by ultraviolet radiation (HBO-200) are permanent. Under the influence of ionizing radiation no process of cerium reduction ($Ce^{4+} + e \rightarrow Ce^{3+}$) occurs either. In the general energy balance of the scattered energy introduced to glass by γ -rays the contribution of oxidizing-reducing processes for cerium is vanishingly small. The main part

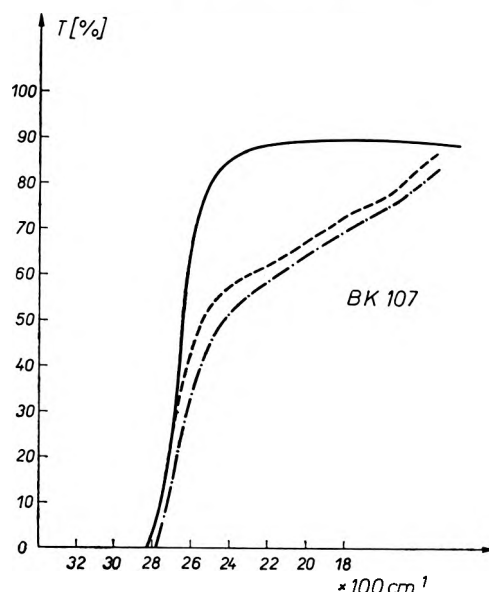


Fig. 5. Transmission vs. the wavenumber, for BK 107 glass before and after irradiation with γ -radiation:

- non-irradiated glass, - - - γ -irradiated, - · - · - UV+ γ

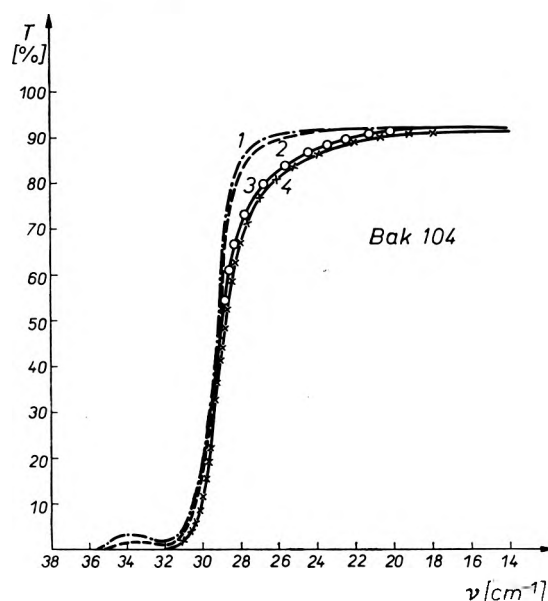


Fig. 6. Transmission vs. the wavenumber for Bak 104 glass at different ways of irradiation:

1 - non-irradiated, 2 - UV, 3 - γ , 4 - UV+ γ

of energy is scattered on structural elements which comprise cerium also. Hence, small changes in these elements result in changes in scattering strength of ionizing radiation.

Figs 7 and 8 present changes in optical transmission which result from irradiation of the BK 101 and BK 107 glass plates ($d = 0.5$ mm) both unexposed and exposed earlier to UV-irradiation (30 min). The X-rays do not cause any changes in the absorption band of cerium (Ce^{3+}), while in the visible re-

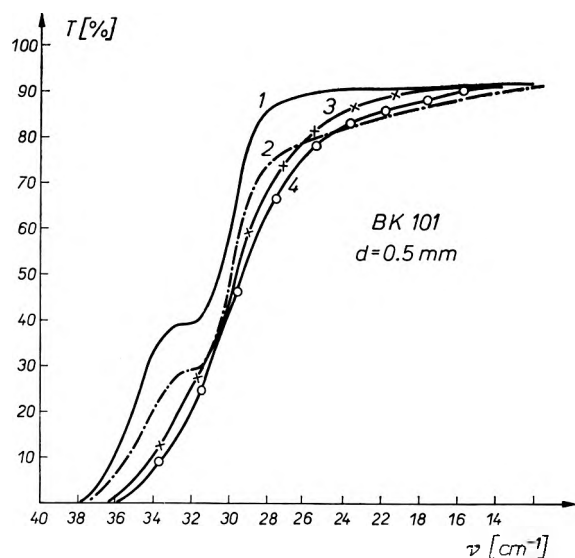


Fig. 7. Transmission vs. the wavenumber for BK 101 glass at different ways of X-ray irradiations:

1 - non-irradiated, 2 - X-ray, 3 - UV, 4 - UV+X-ray

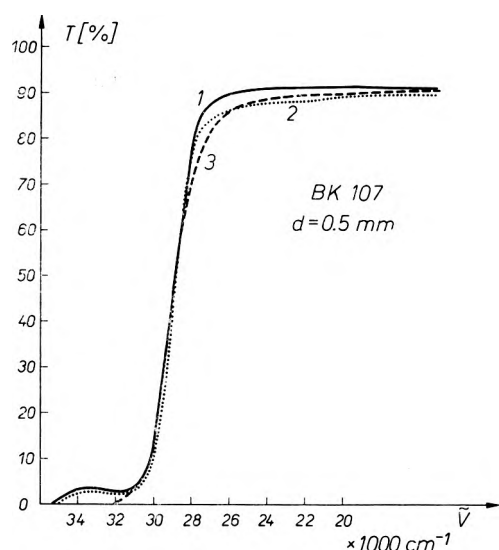


Fig. 8. Transmission vs. the wavenumber for BK 107 glass before and after irradiation with X-rays:

1 - non-irradiated, 2 - X-ray, 3 - UV+X-ray

gion the values of changes are greater for unexposed glass than for glass irradiated earlier with UV-radiation. This situation is opposite to that for samples irradiated with γ -radiation. The differences in changes of optical density, which occur due to exposure to γ - and X-ray radiation, within the visible spectrum over the region irradiated by UV and that nonirradiated, are connected with additional microchanges introduced affecting the state of cerium and its surrounding in different way.

The group of results from the measurements of Ce^{3+} luminescence in BK 101, BK 107 and BK 104

glasses is presented in figs. 9-11 concerning spectral luminescence distributions for nonirradiated glasses and those after irradiating with ultraviolet during 30 min. The greatest changes are observed in BK 101 glass where lighting of Ce^{3+} disappears practically completely. For other glasses the differences are smaller. The luminescence was excited by 365 nm line from the mercury lamp of low output via an

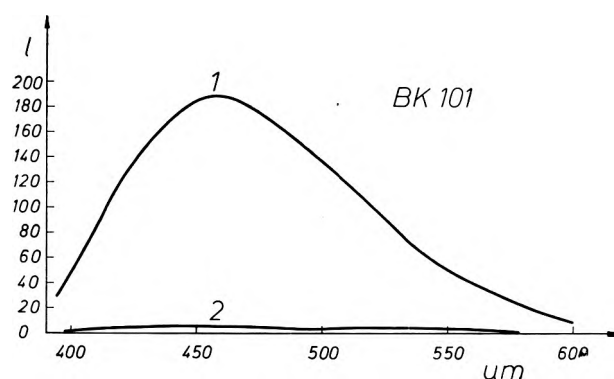


Fig. 9. Luminescence spectral distribution (in conventional units) for BK 101 glass before and after UV-irradiation:

1 - initial, 2 - after photothermal processing (HBO-200, $t = 100^\circ\text{C}$)

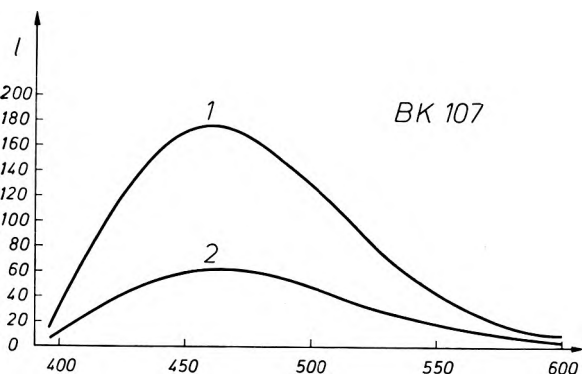


Fig. 10. Luminescence spectral distribution (in conventional units) for BK 107 glass before and after UV-irradiation:

1 - initial, 2 - after photothermal processing (HBO-200, $t = 100^\circ\text{C}$)

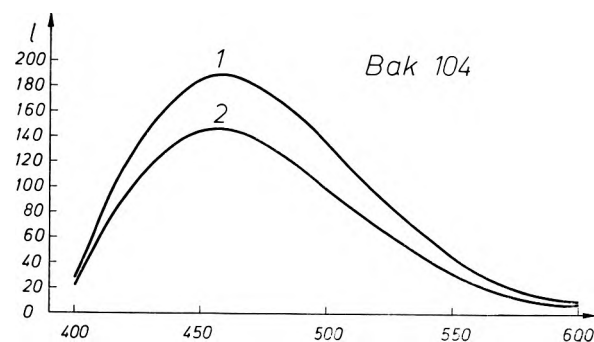


Fig. 11. Luminescence spectral distribution (in conventional units) for BK 104 glass before and after UV-irradiation:

1 - initial, 2 - after photothermal processing (HBO-200, $t = 100^\circ\text{C}$)

interference filter. In figs. 12 and 13 the spectral distributions of luminescence are presented for glass samples either unexposed or preexposed to UV-radiation and irradiated by γ -radiation. The differences in lighting introduced by UV as the result of oxidizing from Ce^{3+} to Ce^{4+} remain despite of γ -irradiation. Under the influence of X-ray radiation no changes of luminescence have been observed.

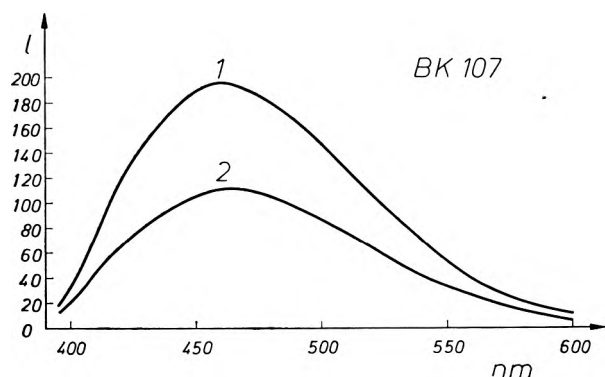


Fig. 12. Spectral distribution of luminescence (in conventional units) for Bak 104 glass after exposure to γ -radiation:
1 - γ -irradiated, 2 - UV+ γ -irradiated

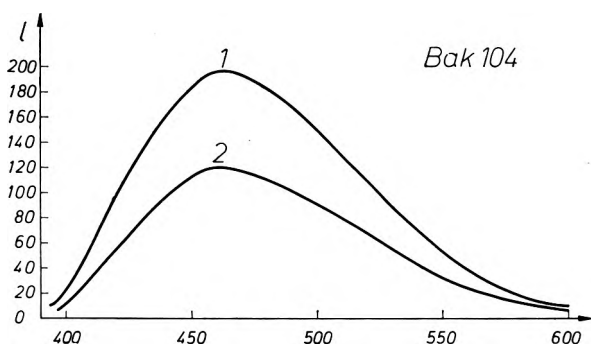


Fig. 13. Spectral distribution of luminescence (in conventional units) for Bak 104 glass after exposure to γ -radiation:
1 - γ -irradiated, 2 - UV+ γ -irradiated

4. Conclusions

There exists a common opinion that the protection of glass containing cerium against the results of ionizing irradiation may be reduced to oxidizing-reducing process ($Ce^{3+} \rightleftharpoons Ce^{4+}$). An exception to this opinion is the paper by Kriedl and Hensler [6], in which this role of cerium is questioned. The present paper goes much further both in methodology and the suggested solution. However, the conclusions should be restricted to the glasses under test.

By irradiating with ultraviolet (365 nm) we can relatively easily oxidize cerium to the four-valence state. These changes are permanent and easily obser-

vable due to differences in luminescence lighting and changes in absorption bands Ce^{3+} . On the other hand, the X-ray and γ -radiations either do not affect the absorption band in cerium or their effect is minimal. The fundamental differences between the results of irradiation by UV- and γ - (or X-ray) radiation consists in different influence on the absorption band of Ce^{3+} and differences in absorption within this visible range.

To build up a model of scattering mechanisms for energy introduced by ionizing radiation without destruction of the glass structure we shall refer to the concept of polymer structure of glass. This is the more justified that the effects observed under the influence of ionizing radiation in glass are similar to those observed in typical polymers. In polymers the radiative resistivity is connected first of all with the fact that the energy of excitation as well as the charges (electrons) absorbed in the place of polymer molecule may be transferred pretty far from the absorption point. An essential part in the energy scattering is played by aromatic and other compounds of delocalized π -electrons. The aromatic compounds, for instance, have low ionization potential and greater number of low-positioned excited states, which assures radiative resistivity. In systems, in which these compounds are presented, these levels are really the lowest ones on which the energy of excitation coming from the ionizing radiation is transferred. Excitation energy is transferred via resonance mechanisms [14]. In glasses containing cerium the resistivity to ionizing radiations occurs only within certain concentration range as well as at certain amount of alkali ions [11]. Thus, analogically to typical polymers, some cerium including structures should be created to assure both transfer of energy and its scattering. The energy from other atoms transferred by nonradiative transitions is scattered by cerium in the form of luminescence due to transition of electron from $5d$ to $4f$ level. This is in accordance with the data reported in the literature, from which it is known that the action of ionizing radiation is associated with very intensive luminescence of Ce^{3+} [1]. This explains the very small resistivity of glasses with great content of Ce^{4+} to the ionizing radiation. This is not the only role which is probably played by cerium. The ultraviolet by oxidizing Ce^{3+} to Ce^{4+} not only removes the scattering element from the structure but also due to photodegradation it changes in a fundamental way the conditions of energy transfer. That is why no reduction process is observed for Ce^{4+} under the influence of γ - and X-ray radiation.

Let us recall also the dependence of resistive

properties of cerium upon the reducing conditions of glass. The reducing-oxidizing conditions in the glass influence the coordination number of doping ions [10]. The increase in reduction degree lowers the coordination number facilitating the introduction of ions into glass structure. In other words, doping ions to which also cerium belongs are undergoing a process of polymerization. Hence, it follows that the structural groups with cerium, responsible for protection of the glass against the effect of ionizing radiation are also attributed to lower coordination degree of ions in glass. The lower coordination degree increases the effectivity of resistive action of cerium.

The presented idea according to the authors opinion explains the protection mechanism of the glass containing cerium against the ionizing reaction. This justifies the further investigations of this problem in both theoretical and experimental way.

Изменения в удельном сопротивлении стекла с содержанием церия ионизирующему излучению после фототермической обработки

Церий является распространенной присадкой, защищающей стекло от действия ионизирующего излучения. Механизм и условия, которые должны быть удовлетворены, чтобы возбудить действие церия, пока не вполне выяснены. Считают, как правило, что приобретение стойкости к действию ионизирующего излучения происходит в стекле благодаря окисляющим процессам церия. Опытные результаты, представленные в настоящей работе, показывают, однако, что существенную роль в придании стеклу

стойкости к названному излучению играют, так же как и в полимерах, структурные элементы, к которым относятся и церий. Они передают энергию активации и электроны. Кажется, что рассеяние энергии происходит чаще всего за посредством люминесценции церия 3^+ .

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