

Communiqué

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On Photothermal Reduction of Luminescence of Cerium in Crown Glasses

Crown glasses containing cerium have been subjected to photothermal ageing. The resulting oxidation of cerium from III-valent to IV-valent state is accompanied by a respective reduction of luminescence.

1. Introduction

In order the glass be protected against the influence of the ionizing radiation it is usually doped with cerium. The reduction and oxidation processes, in which cerium is involved, protect the glass against colour centres, occurring due to electron trapping in the defects of the structure. On the other hand, the introduction of a great number of Cr^{3+} ions [1-7] gives the luminescence of glass, which in case of optical glasses is a negative property.

The purpose of the work is to examine the influence of the photothermal oxidation of Cr^{3+} to Cr^{4+} in order to reduce the luminescence connected with the Cr^{3+} content.

2. The measuring stand

The glasses under test were optical glasses of BK 107, Bak 102, and Bak 104 types, produced by Jeleniogórskie Zakłady Optyczne (Optical Works) in Jelenia Góra, Poland. These glasses contained cerium and arsenic in accordance with their receipt, but the presence of iron ($20 \cdot 10^{-3} \%$) was stated additionally by chemical analysis.

The measuring system for examination of photothermal ageing processes is shown in Fig. 1.

To excite the luminescence a mercury HBO-50 lamp was used. The exciting light passed through a UG. 1 filter ($d = 1.5$ mm, $\lambda_{\text{max}} = 365$ nm, the half-width 55 nm). A SPM-2 monochromator with a quartz prism was used

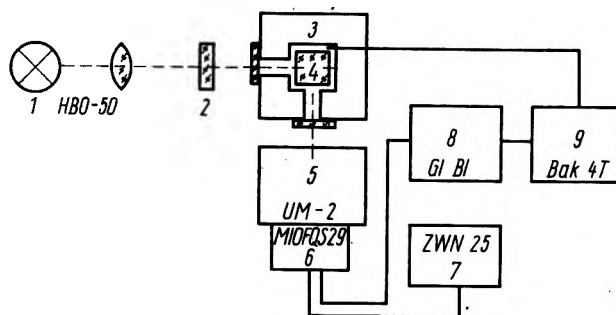


Fig. 1. A block diagram of the measuring system: 1 - light source, 2 - UG1 filter, 3 - furnace, 4 - glass sample, 5 - UMI-2 monochromator, 6 - M10FQ523 photomultiplier, 7 - ZWN-2,5 supply, 8 - G1B1 compensator, 9 - XY BAK 4I recorder

instead of the UG-1 filter, when the spectrum of radiation exciting the luminescence was to be used.

3. The results of measurements

The excitation and luminescence emission spectra are presented in Figs 2 and 3. In Fig. 2 changes in luminescence intensity at

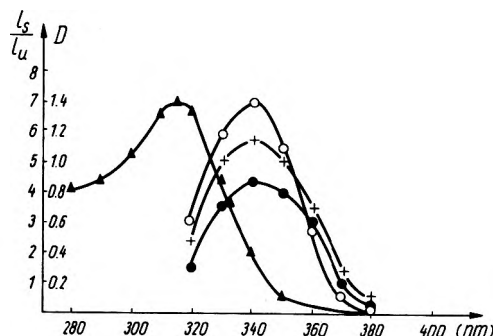


Fig. 2. An excitation spectrum of luminescence ($\lambda = 440$ nm) and an absorption spectrum for BK 107 glass, as referred to BK-7 glass (curve 4)

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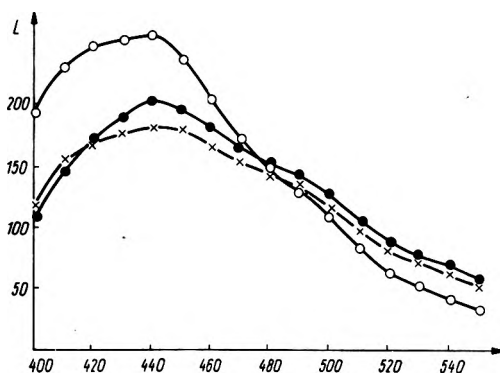


Fig. 3. The luminescence intensity ($\lambda = 365$ nm) vs. the wavelength

$\lambda = 440$ nm is presented as a function of the exciting light wavelength. These curves, corresponding to real spectra of luminescence exciting radiation, were calculated with respect to the luminescence intensity of the uranyl glass. The spectral distribution of luminescence in uranyl glass within the wavelength interval 300–400 nm images the spectral distribution of the exciting lamp. The y -axis is scaled with the ratio of the luminescence of the examined glass to the luminescence of uranyl glass, while the wavelength of the luminescence exciting radiation is presented on the x -axis.

In the same graph a curve which represents the dependence of the optical density upon the wavelength for a BK 107 glass plate as referred to a BK 7 plate is shown, additionally.

A distinct maximum is observed at about 315 nm. The maximum of excited luminescence and that of absorption are shifted with respect to each other. This effect was observed already by KARAPETJAN [2], who explained it by spectral dependence of the quantum efficiency for Cr^{3+} . The said shift of maxima can be explained also by superposition of two absorption bands: the cerium band and a wing of the spectrum having a maximum in the far ultraviolet.

In Fig. 3 typical spectral distributions of luminescence are shown for excitation with a $\lambda = 365$ nm mercury line.

In Figs 4 and 5 some examples of changes in luminescence as functions of temperature are shown for double treating and cooling. In the case of 30 min heating the luminescence drops rapidly, while at a 30 min cooling it slowly increases. In this case the sample does not return to the original state. By repeating this procedure the differences increase. Since a part of the sample was subjected to the photothermal interaction and the remaining part was treated only by thermal ageing the

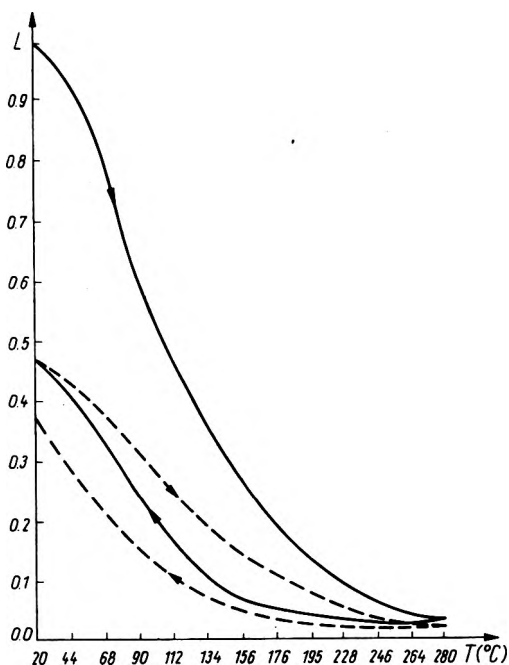


Fig. 4. Luminescence in BAK 102 glass vs. temperature

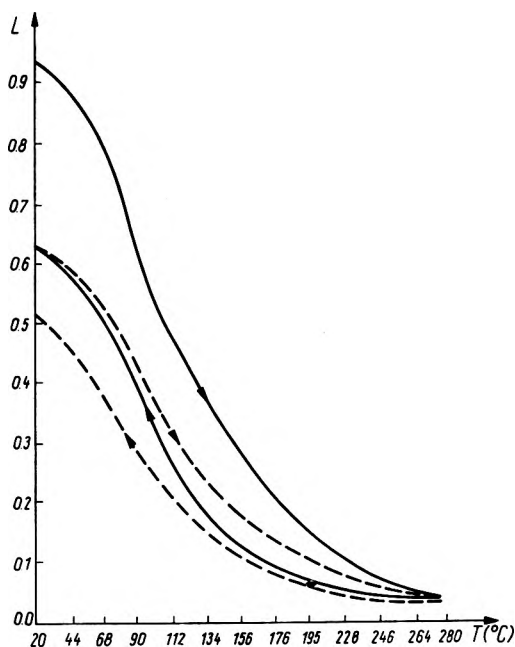


Fig. 5. Luminescence in BAK 107 glass vs. temperature

differences in luminescence of the respective parts could be observed and measured. The rate of temperature changes appeared to be not the same within all temperature intervals.

A dependence of luminescence (at $\lambda = 440$ nm) on the time of exposure to ultraviolet light at temperature 200 °C is shown in Fig. 6. The particular samples were illuminated under the same conditions, but the exposure times were different. The values of luminescence ratio after the photothermal treatments of the same sample (curve 1) were plotted

on the y-axis. In the same graph the experimental data obtained for the same samples after 6 months period are also given (curve 2).

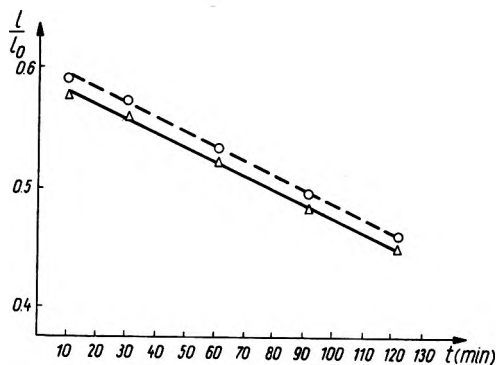


Fig. 6. The luminescence intensity vs. the exposure time at 200 °C

The samples were kept in the darkness at the room temperature.

In Fig. 7 a dependence of the light emission from the BK-107 glass at the room temperature upon the exposure time is shown. The

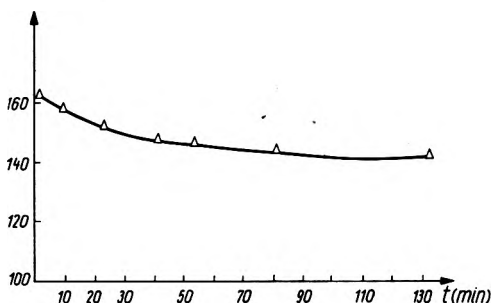


Fig. 7. The luminescence intensity vs. the exposure time at the room temperature, for BK 107 glass

changes in luminescence are very small when compared to the changes at higher temperature.

In Fig. 8 the dependence of the transmission of a thin BK-107 glass plate ($d = 0.5$ mm) upon the wave number is presented. On the curve 1, showing results of measurements for the non-exposed glass, the absorption band belonging to Cr^{3+} may be observed. After a 1 h exposure of the sample to ultraviolet at 100 °C (curve 2) the following changes have been observed:

1. In the far ultraviolet there is an absorption band, its wing occupying the spectral range below 310 nm reduces the transmittivity to zero.
2. An increment in transmittivity is observed in the right hand side wing of the absorption band of cerium.

A decrement of transmittivity is, however, observed in the long wavelength part of ultraviolet as well as in the visible region. The

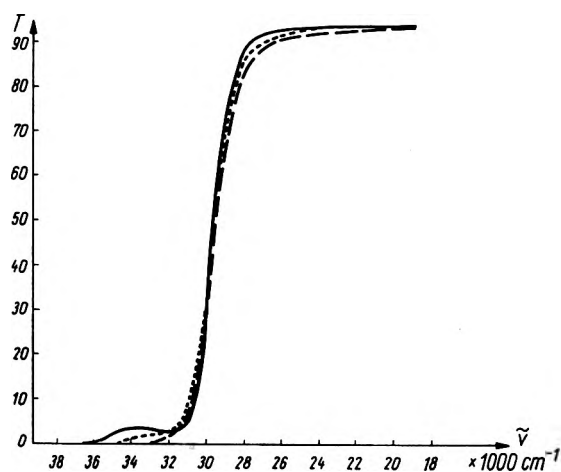


Fig. 8. Transmittivity of BK 107 glass plates ($d = 0.5$ mm) as a function of wavenumber 1 — the original transmittivity, 2 — transmittivity after irradiation, 3 — transmittivity after irradiation and annealing

distribution of transmittivity at the same glass plate, which occurs after 2h heating at 450 °C, is shown in the curve 3. An increase in transmittivity is observed within the whole spectral range.

In Fig. 9 transmittivity ratio of irradiated and non-irradiated blocks is shown within the near infrared spectral range. The measurements

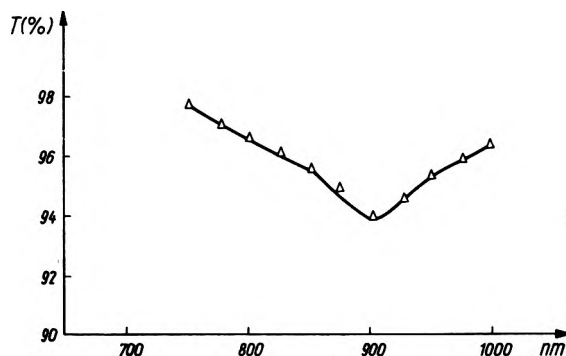


Fig. 9. Transmittivity ratio of radiated to non-irradiated parts of a BK107 glass cube as a function of the wavelength

were performed at the presence of interference Zeiss filter, an M3FD 13 photomultiplier being used as a detector. A distinct band which is observed may be attributed to the Fe^{2+} band.

4. Conclusion

The most probable explanation of the effects observed is that the process of cerium oxidation from III-valent to IV-valent state occurs simultaneously with the reduction of some doped ions, of Fe^{3+} among others. We observe a decreased intensity of the absorption band Fe^{2+} in the infrared region (Fig. 9). On the other hand, a band in the long wavelength range of ultraviolet, which is observed as a shift of

absorption edge toward the long wavelength direction in the thicker glass blocks, seems to be a wing of the absorption band, whose maximum lies below 300 nm. This wing is deformed by the Cr^{3+} band. The effect observed after the glass is irradiated results from superposition of two effects: a decrease in cerium band intensity and an increase in intensity band, which should be attributed to electron transitions connected with a transport of charge in the chemical bonds [9].

References

- [1] APPEN A. A., *Khimiya stekla*, Izd. Chimija 1974.
- [2] KARAPETJAN G. O., *Izv. AN SSSR s. fiz.*, Vol. 23, No. 11, p. 1382, 1959.

- [3] KARAPETJAN G. O., *Optika i Spekr.* Vol. 3, p. 641, 1957.
- [4] KARAPETJAN G. O., VARGIN V. V., *Glastechn. Berichte* 1959, Nov., p. 443.
- [5] JAHN W., *Schott Glasforschung* 20, p. 304.
- [6] BURZYNSKIJ J. M., PECHNEVA O. B., *Izv. AN SSSR Neorg. Mat.*, Vol. 8, No. 9, p. 1687, 1973.
- [7] SYRYCKAJA Z. M., VLASOVA M. A., *Izv. AN SSSR Neorg. Mat.*, Vol. 7, No. 9, p. 1701, 1972.
- [8] ADLI BISHAY, *J. Non-Cryst. Solids.* 3 (1970) 54, 114.
- [9] GLEBOV L. B., LUNTER S. G., POPOVA L. B., TOLSTOJ M. N., *Fizyka i chimiya stekla* Vol. 1, No. 1, p. 87, 1975.

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