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Thermal Shift of the Long-wavelength Absorption Edge in the Optical Glass

The paper contains a review of main mechanisms of absorption in the region of ultraviolet for the optical glasses and the estimation of the influence of thermal stimulation of oxidizing-reducing processes on the absorption band appearance. It happens that the contribution of this bands in the spectral range is very great. The changes of absorption are ascribed to the complex compounds of iron with other ions.

1. Introduction

In the last period of time the number of papers devoted to long-wave length absorption edge in the glass, as referred to the ultraviolet region has increased rapidly. The subject of interest is absorption connected with the glass structure, and due to content of ions of variable valency. At elevated temperatures the presence of such ions causes a shift in absorption edge toward the longer wavelengths. The works published so far in this field deal mainly with the two-component, such silicon-sodium and borium-sodium ones.

In these glasses various concentrations of multivalent iron starting with $10^{-4}\%$ [1–6] have been introduced. A shift in the absorption edge toward longer wavelengths, occuring at elevated temperature is due to the presence of Fe^{3+} ions and proportional to their concentration. Two regions of proportionality have been observed: one at the concentration below $5 \cdot 10^{-2}\%$, for which the Fe^{+3} ions appear as single events, and the second above $5 \cdot 10^{-2}\%$ at which iron appears in colloidal form. At constant iron concentration the differences in the absorption edge shift depend upon the glass composition [4].

In practice it is very difficult to obtain pure glass, hence the absorption edge effect is most usually influenced by a number of various phenomena.

A different absorption mechanism occurs, among other, in photothermic oxidation and reduction of transition metals and appearence of colour centres.

The analysis of long-wave length absorption edge is faced with difficulties, due to lack of respective theory for dielectrics in this spectral range [1]. Hence, all the works connected with absorption edge in the glass are based on the Urbach Law referred to the ion crystals [10, 11]. According to Urbach, the long-wavelength absorption edge is described by the formula

$$K(\nu) = K_0 \exp\left(-\frac{\sigma}{kT}(h\nu_0 h\nu)\right),$$

where $K(v)$ – coefficient of absorption for frequency v,

K_0, σ, v_0 – constants characterizing a given temperature – independent absorption band.

According to this formula the energy of transition within the region of low frequency spectrum consists of electron excitation energy and local energy caused by phonon i.e. the quantum transition occurs from the levels corresponding to the quasi-continuous oscillation spectrum of the crystal structure. On the other hand, the phonon states of thermal excitations at a given temperature are consistent with the Boltzman Law [1, 11].

The applicability of Urbach Law to the glasses examined has been determined. By verifying the dependence of ln K upon the frequency for $T = \text{const}$ a linear dependence was obtained only within a small frequency interval [1, 5, 6]. The dependence of the cut-off frequency $v_{\lim}$ upon the temperature is of a linear type [5]. However, the dependence of ln K on the temperature for $v = \text{const}$, which

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may be concluded from the formula (1), does not hold. Instead of relation of

$$\ln K = A_1 + B_1 \frac{1}{T}$$

type the relation $\ln K = A_2 + B_2 T$ was obtained.

The relation

$$\frac{d \ln K}{dv} = \frac{B}{T}$$

is not satisfied either.

The value of the derivative is practically independent of temperature. In the place of Urbach formula the following empirical formulae has proposed by Glebov and Tolstoj [5]:

$$K = K \exp\left(Av + \frac{T}{T_1}\right),$$

where: K, A and T are constant.

Another factor affecting the absorption edge in the glass is connected with the transition metals and most commonly with the iron ion. The existance of the broad absorption band of high absorption coefficient is attributed to the charge transition from the ligand to the central ion [1, 3, 6].

The third factor is the existence of colour centres which give absorption at the boundary region between the ultraviolet and visual spectrum. These centres are produced by the u.v. radiation excitation in the region of specific absorption edge of glass [6,7]. A correlation between the excitation spectrum of colour centres and the position of long-wavelength limit of specific absorption has been found [7].

The subject of this paper is to examine the long-wavelength absorption edge in the ultraviolet range of spectrum. Such a kind of examinations have not been performed for optical glasses yet. The variety of chemical composition of glasses examined by preserving the same order of iron content allows to determine the range of changes in the absorption limit.

2. Results of measurement

The measurements were made with a SPECORD U.V. VIS spectrophotometer supplied with an accessory device to the work at a higher temperature. The applied temperatures ranged from 20°C to 220°C. The samples were made of typical optical glasses produced in Jeleniogórskie Zakłady Optyczne (Poland). The measurements were performed for 25 types of glasses. The thickness of sample cubes amounted to 12–14 mm. The spectrophotometer allowed to measure the optical density up to $D = 1.4$. Thus, the spectra up to wave number 32,000 cm^{-1} could be measured. Although this limited considerably the spectral range it improved the observation of the doping absorption effects within the far ultraviolet region. The impurities in the optical glass are either introduced intentionally, or occur as imperfections of the materials used. The dopings materials may include the following elements: As, Sb, Ce, Fe, Mn, Mg, Cu, Ti, Ag and so on.

The typical results of measurements concerning the absorption edge shift under the influence of the temperature are presented in Fig. 1–4. The values of optical density (D) are given on the y-axis, the wave numbers ($\tilde{v}$) are being layed out on the x-axis. The families of curves have been analogically obtained for all the glass examined.

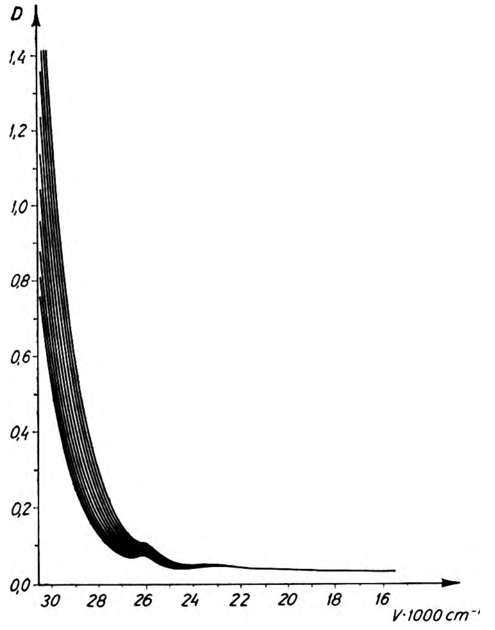

Fig. 1. The shift of absorption edge in the 2K 1 glass within the 20°C – 220°C temperature range

The measurements were performed in a 20 degree intervals. An increase of temperature caused a shift in the absorption curve toward the smaller wave numbers. The absorption wedge shift has different values. In the temperature range within 20–220°C for $D = 1.30$ the wave number (v_{lim}) shifted from 400 cm^{-1} to 1,700 cm^{-1}.

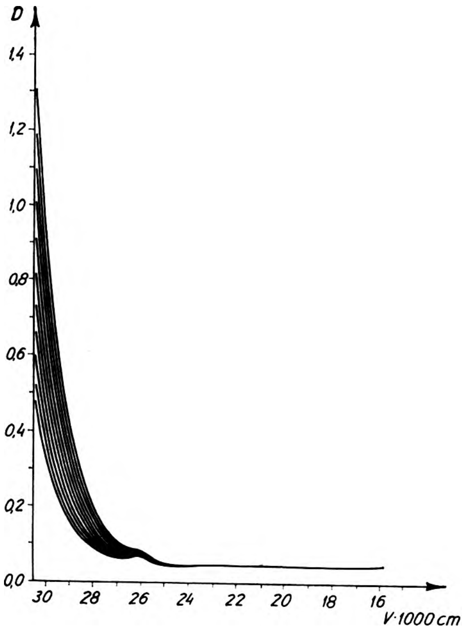

Fig. 2. The shift of absorption edge in the K3 glass within the 20°C – 220°C temperature range

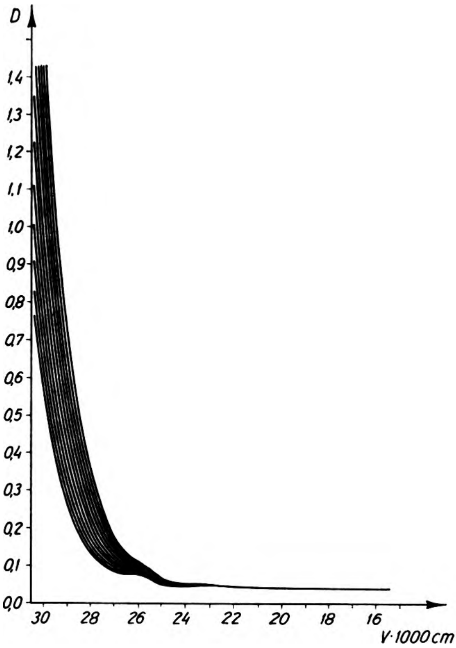

Fig. 3. The shift of the absorption edge in the Bak 2 within the 20°C – 220°C temperature range

The dependences $\ln D$ versus $\tilde{\nu}$ are presented in Fig. 5 for F.2 glass and three temperatures (20°C, 120°C and 220°C). The run shown in this figure is an example of a distinct deviation from the linearity. This type of deviation was characteristic of more then one half of the glasses examined, all the flints (BalF, LF and F) and a part of the barium crowns included. However, a part of the glass exhibits the runs similar to those presented in Fig. 6

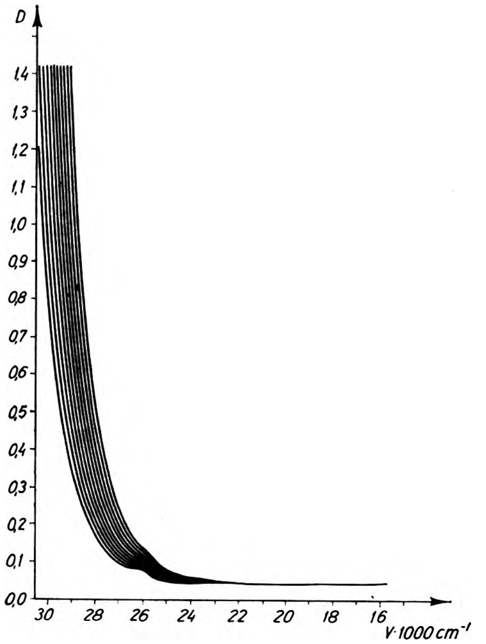

Fig. 4. The shift of the absorption edge in the F5 glass within the 20°C – 220°C temperature range

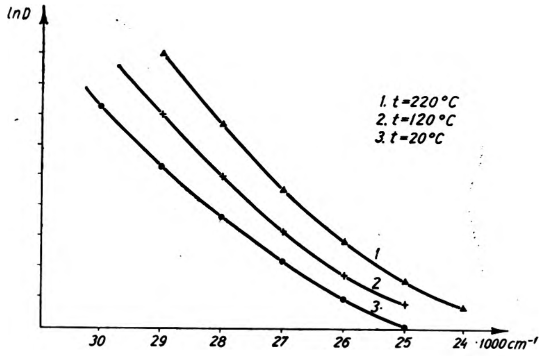

Fig. 5. The dependence of $\ln D$ upon $\tilde{\nu}$ for F2 glass at the temperatures 20°C, 120°C, 220°C

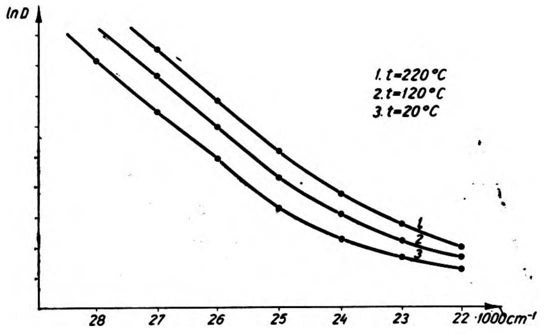

Fig. 6. The dependence of $\ln D$ upon $\tilde{\nu}$ for SF2 glass at the temperatures 20°C, 120°C and 220°C

for SF2 glass. In certain region of $\tilde{v}$ the curve $\ln D(\tilde{v})$ may be approximated by a straight line. This group includes haevy flints and some crowns (like K, 2K and PSK).

In Figs. 7 and 8 the curves $\ln\frac{D(230)}{D(20)}$ versus $\tilde{v}$ are shown for several examined curves differing dramatically in composition. The run

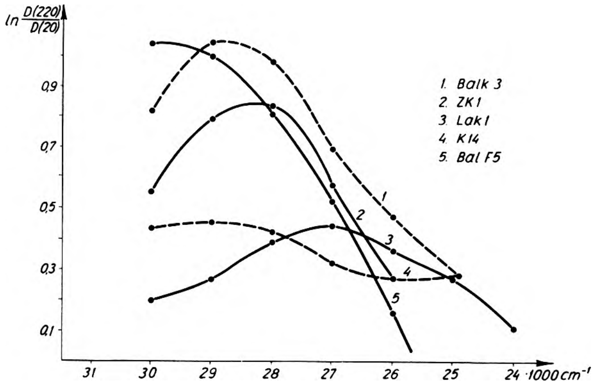

Fig. 7. The dependence of $\ln\frac{D(220°C)}{D(20°C)}$ upon $\tilde{v}$ for optical glasses

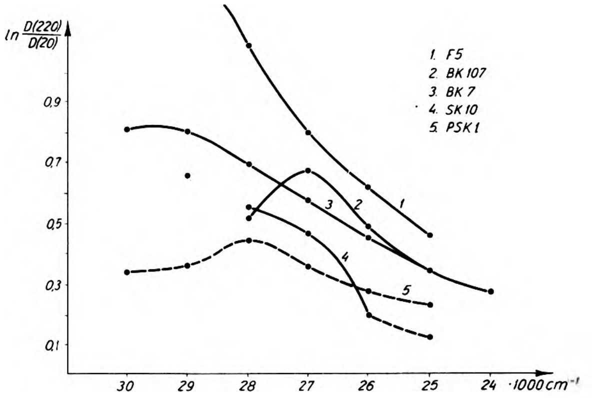

Fig. 8. The dependence of $\ln\frac{D(220°C)}{D(20°C)}$ upon $\tilde{v}$ for optical glasses

of curves allows to infer a superposition of two absorption mechanisms: that of the glass structure and of impurity absorption by dopening ions broad band spectrum of distinct maximum.

For some compositions the maximum of impurity absorption was positioned outside the measurement range. Many curves are characteristic of both the whole groups of glasses of similar chemical composition, as well as of species of ions of variable valency responsible for those bands. For instance the curves, for glasses of series 100 with an addition of cerium are similar to these for BK107 glass (Fig. 8). These glasses exhibit a large absorption band in the near ultraviolet with the maximum close to 320 nm generated by cerium. This curve is resultant of interaction between cerium and iron absorption bands. The runs of curves suggest that, analogically to similarly to the cerium glasses – the differences in the curve shapes are due not only to the basic compositions but also to the complex compounds of iron formed in these compositions.

A strong temperature dependence of

$$\frac{d\ln D}{dv}$$

Bak 4 is shown in Fig. 9. It appears that the

$$\frac{d\ln D}{dv}$$

value is also dependent on the position within the spectral range. If we look for it in the visual range where the left wing of the impurity band is positioned we always observe a decrement of

$$\frac{d\ln D}{dv}$$

with the increasing temperature (curve 1, Fig. 9).

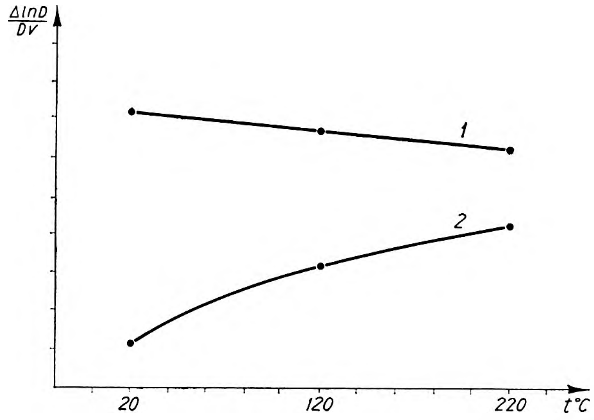

Fig. 9. The dependence of the derivative $\frac{d\ln D}{dv}$ upon the temperature for the Bak 4 glass

1 – in the left wing of the absorption band, 2 – in the right wing of the absorption band

If however, we look for it within the right wing of the absorption band an increase of

$$\frac{d\ln D}{dv}$$

with the increasing temperature is observe (curve 2, Fig. 9). In the region of maximum of the absorption band the derivative

$$\frac{d\ln D}{dv}$$

does not depend on temperature.

In Fig. 11 the dependences ln D on temperature are shown for constant values of $\tilde{v}$. The value ln D rises linearly with the increase of temperature.

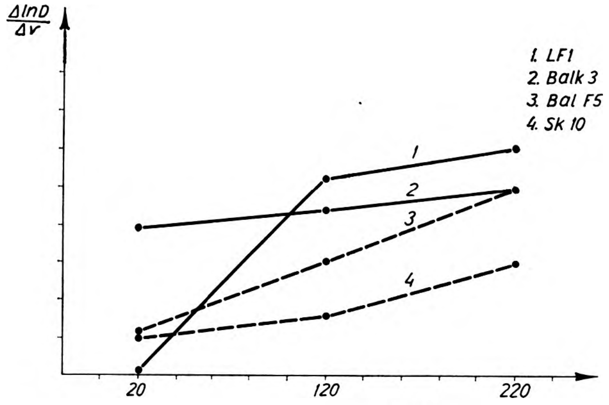

Fig. 10. The dependence of $\ln\frac{d\ln D}{dv}$ in the right wing of the absorption band for several glasses

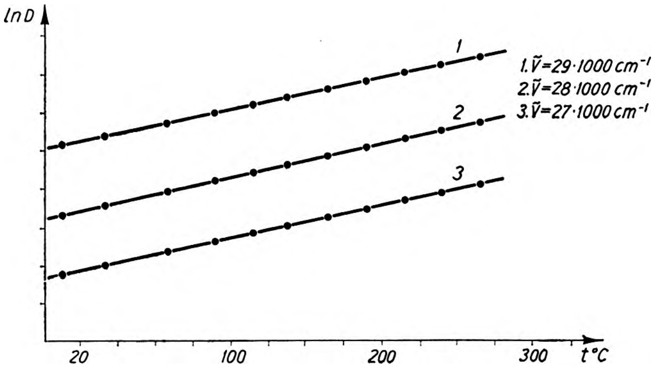

Fig. 11. The dependence of ln D upon t for $\tilde{v}$ = const for PSK 1 glass

Similar relations are observed for all the examined glasses. The slope of these straight lines alway increases with the increasing $\tilde{v}$. In Fig. 12 the changes of $\tilde{v}_{\rm lim}$ due to the temperature changes are shown for different values of D in the F 102 glass. The dependences of $\tilde{v}_{\rm lim}$ on temperature are linear. The slope of the straight lines depends on the value of D. The results for the measurements for BK7 glass are presented in Fig. 13 and show the influence of illumination with the HBO-200 lamp on the $D = D(\tilde{v})$ dependence type. Oxidation-reduction processes of the ions of variable valency in the glass evoked by the illumination with the ultraviolet radiation result in some permanent changes in the optical density observed occuring both the near ultraviolet and visual ranges of spectrum.

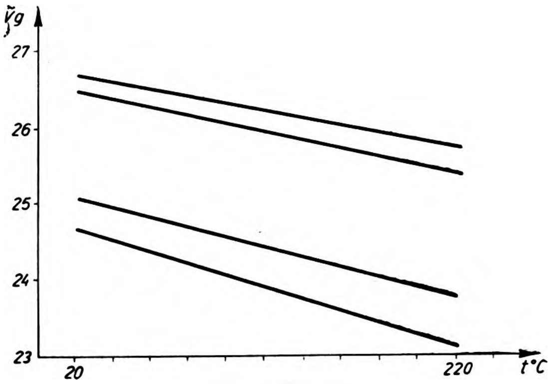

Fig. 12. The dependence of $\tilde{v}_{\rm lim}$ upon the temperaturs at D = const (1.30, 1.00, 0.30, 0.20) for the F102 glase

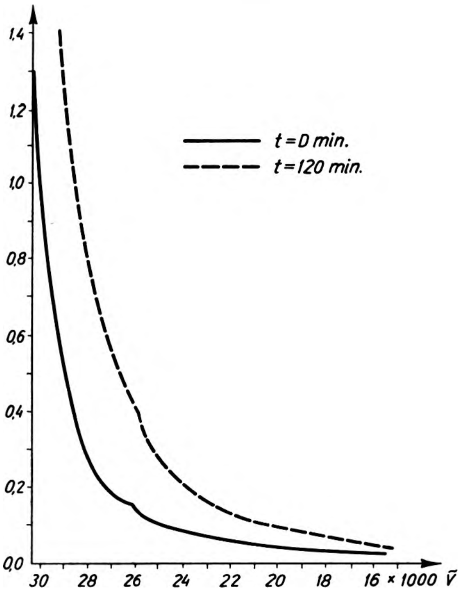

Fig. 13. The permanent changes in the optical density of BK7 glass after two-hour irradiation with the HBO-200 lamp

3. Conclusions

As far as a formal discription of the shifting effect of the absorption edge shift is conserned the present work provides some new materials.

1. The exponential curve decribes the phenomenon of limiting absorption to a certain extent and for some kinds of glasses only.

2. The derivative

$$\frac{d\ln D}{dv}$$

depends on temperature, and its changes versus the wave number describe the absorption band of electron transition for doping metal ions.

Although many problems are not yet solved nevertheless it is known that the oxidation-reduction processes play an important part in the light absorption. This effect should be even more distinct when applying higher light intensities. When considering the reduction-oxidation processes two procedures may be assumed:

1. The changes in ion polarization, in other words, occurrence of the secondary polarization connected with the charge shift.
2. The changes in the absorption band for ions due to changes in oxidation degree and changes in the structure of coordination compounds.

The iron make chromofor complexes of (Me-O-Fe) type, where Me may be replaced by Si, Pb, Ti, Ce, Ag etc. The transition of electron into iron is associated with a change in the Me-O bounding strength. The transition energy of electron depends on the degree of polarization of the Me-O band in the iron complex. For instance the iron-titanium complexes may be very efficient [13]. In presence of titanium an increase of absorption may occur within the u.v. region of interest and the absorption edge can be shifted toward the longer wavelengths.

The reduction-oxidition changes are accompanied by the respective changes in the absorption bands. The changes of this type may be evoked in the glass by applying ultraviolet radiation. E.g. the change in the absorption (see Fig. 13) due to illumination of glass with the ultraviolet radiation from the HBO-200 lamp. The irradiated glass contains impurities which, when oxidized, generate the absorption bands in the visual spectrum.

Термическое перемещение предела длинноволнового поглощения в оптических стеклах

В работе дается обзор главных механизмов поглощения в длиноволновой ультрафиолетовой области для оптических стекол и приводятся результаты влияния термического стимулирования окислительно-восстановительных процессов на образование восстановительных полос. Оказывается, что доля этих полос в данной спектральной области, очень большая. Изменения в поглощении связываются с наличием комплексных соединений с различными ионами.

References

[1] Nemilov S.V., Zilin A. A., Z. Prikl. Spektr. Vol. 20, No. 2, p. 268, 1974.

[2] Nemilov S. V., Zilin A. A., Izv. ANSSSR Neorg. Mat. Vol. 10, No. 3, p. 513, 1974.

[3] Nemilov S. V., Zilin A. A., Izv. ANSSSR Neorg. Mat. Vol. 11, No. 3, p. 525, 1975.

[4] Zilin A. A., Fizika i chimija stekla, Vol. 1, No. 5, p. 463, 1975.

[5] Glebov L. B., Tolstoj M. N., Fizika i chimija stekla, Vol. 1, No. 5, p. 239, 1975.

[6] Glebov L. B., Popova L. B., Tolstoj M. N., Optiko-Mech. Prom. No. 4, p. 38, 1975.

[7] Glebov L. B., Tolstoj M. N., Kvant. Elektr. No. 1, p. 119, 1974.

[8] Klimashina E. V., Tchistoserdov V. G., Fizika i chimija stekla, Vol. 1, No. 2, p. 162, 1975.

[9] Burzyński J. M., Izv. ANSSSR Neorg. Mat. Vol. 8, No. 9. p. 1684, 1972.

[10] Mahr H., Phys. Reviev, Vol. 132, No. 5, p. 1880, 1963.

[11] Davidov A. S., *Teorija molekularnykh elecitonov*, Moskva 1968, lzd. "Nauka".

[12] Glebov L. B., Lunter S. G., Popova L. B., Tolstoj M. N. Fizika i chimija stekla, Vol. 1, No. 1, p. 87, 1975.

[13] Varsal B. G., Jusim L. M., Kniazer G. B., Izv. ANSSSR Neorg. Mat. Vol. 9, No. 12, p. 2202, 1973.

Received, April 27, 1976