Luminescence method of examination of $3d$ level structure of Mn²⁺ ions in glasses

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It has been shown that in the glasses activacted with Mn²⁺ no absorption bands are noticed which would correspond to the transitions d–d because of the presence of the absorption band Mn³⁺ among others. It has been stated that the application of the luminescence excitation spectra allows to examine the structure of the sublevel $3d$ for Mn²⁺ ions. The method of the luminescence excitation separate offers a number of advantages: among others, it allows to spectra Mn²⁺ (4) and Mn²⁺ (6)* in a simple way.

1. Introduction

The manganese ions (Mn²⁺) of electron configuration $3d^5$ belong to the group of very efficient luminescence activators, therefore the problem of luminescence Mn²⁺ is widely discussed in papers [1–8].

The luminescence properties of Mn²⁺ activated glasses of different compositions are the subject of interest of many authors [1–5]. The luminescence of Mn²⁺ ions is solely connected with the transition of electrons from the excited level $^4T_{1g}[^4G]$ to the fundamental level $^6A_{1g}[^6S]$. The electrons transit from the other excited levels to the fundamental level $^4T_{1g}[^4G]$ without luminescence emission [9]. Since the position of the level $^4T_{1g}[^4G]$ depends on the coordination symmetry of the surrounding ligands (for oxide ion glass), then the spectral properties of luminescence is also conditioned by this symmetry. In general, it is assumed that Mn²⁺(4) gives green luminescence, while Mn²⁺(6) — the luminescence of red colour. In the presence of both Mn²⁺(6) and Mn²⁺(4) the resulting curve of the spectral distribution of luminescence will depend on the quantitative Mn²⁺(4)/Mn²⁺(6) ratio, which depends upon its glass composition, an essential part being played by the quantity and sort of Me₂O oxides.

Thus, by increasing the number of Mn²⁺ ions for the constant composition of basic glass we will increase the number of Mn²⁺ which cannot be imbedded in the glass structures in the tetrahedric surrounding [10].

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* Symbol ( ) means coordination number.

The examination of the structure of the level $3d$ for Mn^{2+} ions and the determination of crystallic field parameters B, C, Dq is based exclusively on the results of absorption measurements. The absorption bands as well as the corresponding wave numbers are sought for the electron transitions from level $^6A_{1g}[^6S]$ to the levels: $^4T_{1g}[^4G]$, $^4T_{2g}[^4G]$, $^4A_{1g}[^4G]$, $^4E_g[^4G]$, $^4T_{2g}[^4D]$, $^4E_g[^4D]$. The ions $Mn^{2+}(6)$ and $Mn^{2+}(4)$ show similar splitting of the levels depending on parameters Dq. They are presented in the diagram due to Tanaka and Sugano [6, 7] (fig. 1). Electron transitions
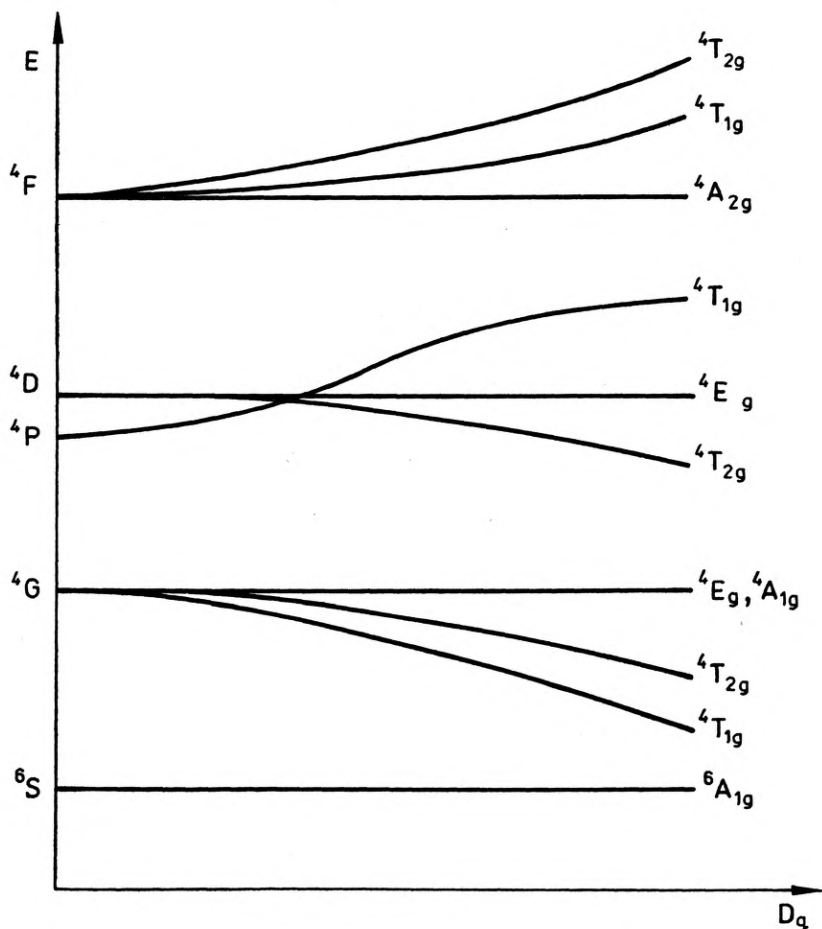

Fig. 1. The energy diagram for ions of electron configuration d^5 as a function of Dq parameter

for Mn^{2+} ions of coordinations 4 and 6 differ in intensity and shift in the respective light wavelengths. The absorption bands are of very low intensity due to the fact that these transitions (between the levels) belong to the for-

bidden ones. The dependence of the sublevel splitting upon the crystal field is different. If the sublevels $^4A_{1g}[^4G]$, $^4E_g[^4G]$, and $^4E_0[^4D]$ are independent of the field strength (up to $D_q/B \approx 3$) then the remaining levels are characterized by the directional coefficients and the respective band width depends on the value $dE/d(Dq)$. Thus, the energy of transition on the levels $^4T_{1g}^{\cdot}$ and $^4T_{2g}$ depends on the field strength. With the increase of the field strength the transition energy lowers, causing an absorption band shift toward the longer wavelength region. In a field octahedric symmetry the levels $^4E_g[^4G]$ and $^4A_{1g}[^4G]$ superimpose each other. A reduction of symmetry results in splitting the above levels [6, 7].

In the examinations of the d-d type transitions for Mn^{2+} the most difficult problem consist in finding the corresponding absorption bands. If the concentration of Mn^{2+} is low or if some other absorption bands appear simultaneously, for instance, those attributed to Mn^{3+}, the recovery of those bands is practically impossible. In this paper we shall show that in spite of the fact that the spectral examinations cannot be carried out by using the absorption method it is possible to determine the structure of $3d$ level for Mn^{2+} ions by applying the method of luminescence excitation spectra.

2. Measurement method

The optical glasses with an addition of Mn_2O_3 melted in the ironless ceramics were used for examinations. The content of Mn_2O_3 in the respective glasses is the following: 0.5% in FK5, 0.1% in BK7 and SK4. The glass samples were of the sizes $13 \times 14 \times 30$ mm and $0.5 \times 12 \times 20$ mm. The absorption measurements were performed on a Specord UV VIS spectrophotometer. The measurements of the spectral luminescence distributions were made in the setup consisting of HBO-50 spectral lamp, Hg Mon 436 and SIF 436 filters of C. Zeiss make, the UM-2 monochromator, the M12 FC 51 photomultiplier of spectral type, S20/SbKNaCs cathodes of the sensitivity range $320-760$ mm, and the G1-B1 plotter which, being coupled with a monochromator was able (beside drawing the graphs) to change the wavelength. The excited luminescence was recorded in the setup composed of a halogen lamp (100 W), deuter lamp, a SPM-2 monochromator with a quartz prism, a FK attachment, interference and glass filters, an M12 FC 51 photomultiplier and a G1–B1 plotter, which being again coupled with a monochromator changed the exciting wavelength.

The luminance temperature of the halogen lamp was 3200 K, its spectral distribution $I_0(\lambda)$ was the same as that of black body of the same temperature. In the near ultraviolet $I_0(\lambda)$ takes very low values, and with increasing light wavelength (in accordance with the Planck formula)

the intensity becomes respectively higher. The application of the steady geometric width of the monochromator slit, as it was in our case, results in some increase of the differences in the value of luminescence exciting light flux between the near ultraviolet and the visual range. To obtain the true distributions of the excitation spectra the indication of the plotter should be divided by $I_0(\lambda)\,\Delta\lambda$.

For examination of the excitation spectra of Mn^{2+} ions luminescence the deuter lamp was used. This allowed to broaden the excitation spectral range (starting with 200 nm) and to make it closer to the true spectra. In order to select the intervals of the luminescence spectra with the help of filters the generally used division was assumed, according to which the luminescence within the wavelength range of 500–600 nm comes from the Mn^{2+} ions in the tetrahedric complexes, while that within the 600–700 nm wavelength range is emitted by the Mn^{2+} ions in the octahedric complexes.
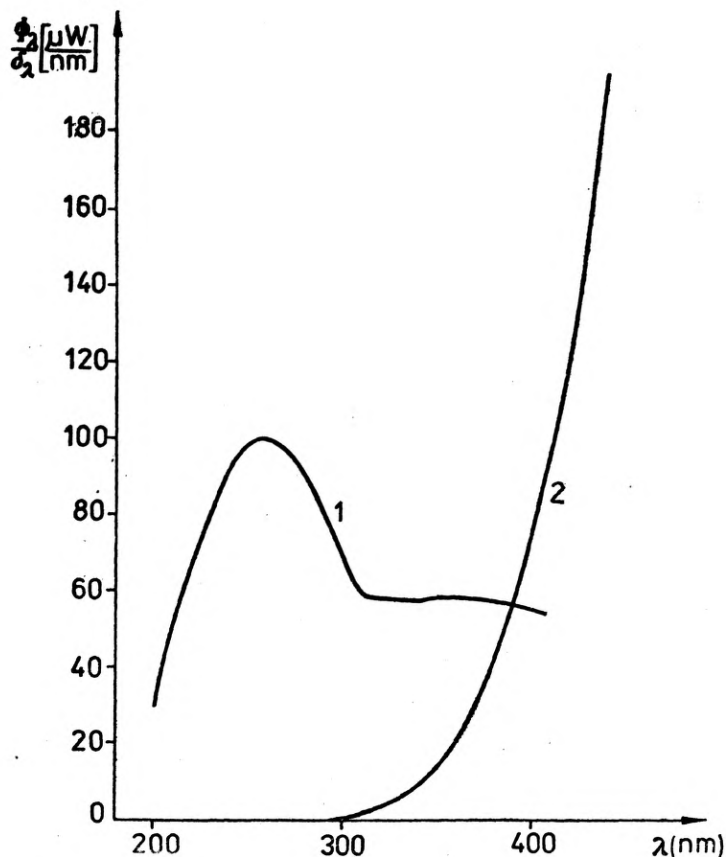

Fig. 2. The spectral distribution of exciting light beam from the deuter lamp (1) and halogen lamp (2), as related to the constant differences of the light wavelength

In the figure 2 the dependence between the light flux and the wavelength is shown for a deuter lamps (1) and a halogen lamp (2) measured with a vacuum VTh 5 thermoelement supplied with a quartz window. The results were referred to a constant light wavelength interval.

3. Results of examinations

The presentation of the results of examination will be started with showing the dependence of the optical density upon the wave-number for the samples 14 mm thick made of FK5 glass containing 0.5 % of Mn_2O_3 and of BK7 and SK glasses with 0.1 % content of Mn_2O_3. In the glasses FK5 and BK5 the wide absorption band of Mn^{3+} may be noted. In contrast to this, bands connected with the d-d transitions for Mn^{2+} ions are practically unnoticeable (fig. 3).
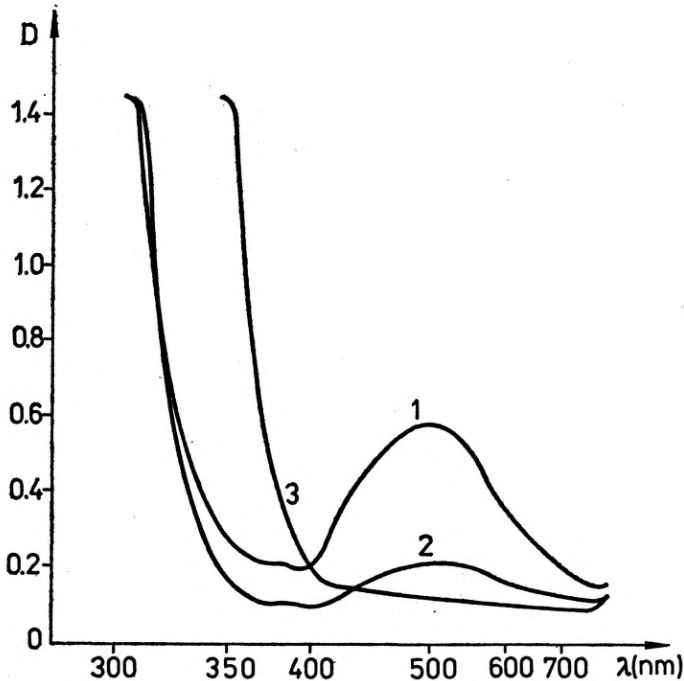

Fig. 3. Dependence of the optical density upon the wave number for glasses activated with manganese ($d = 14$ mm).
1 — FK5 (0.5%Mn_2O_3), 2 — BK7 (0.1%Mn_2O_3), 3 — SK4 (0.1%Mn_2O_3)

In the figure 4 the curves of luminescence spectral distribution are shown for the sample of FK5, BK7 and SK4 glasses activated by manganese ions. The spectral distribution of manganese luminescence indicate

approximately the proportions of those ions depending on the coordination. Thus the results obtained for the BK7 glass (curve 2) speaks for a decisive dominance of luminescence coming from the Mn^{2+} (4) ions. In the SK4 glass the quantities of Mn^{2+} (4) and Mn^{2+} (6) are comparable (curve 3), while in the FK5 glass the predominance of the component coming from Mn^{2+} (6) is very distinct (curve 1). For these glasses the intensity of luminance due to Mn^{2+} is different. The curves in fig. 4 are plotted for different ranges of the plotter sensitivity.

In the figures 5–7 the excitation spectra of luminescence are shown in the spectral range corresponding to the Mn^{2+} (4) and Mn^{2+} (6) bands. Above 600 nm wavelength the luminescence was separated by the edge filter ($\lambda > 600$ nm). From the longer wavelength side the spectral range was restricted by the limit of photometer sensitivity. On the other hand, the spectral range of Mn^{2+} (4) luminescence was separated by IF 550 interference filter of the half-width 5.0 nm — for excitation with a halogen lamp,
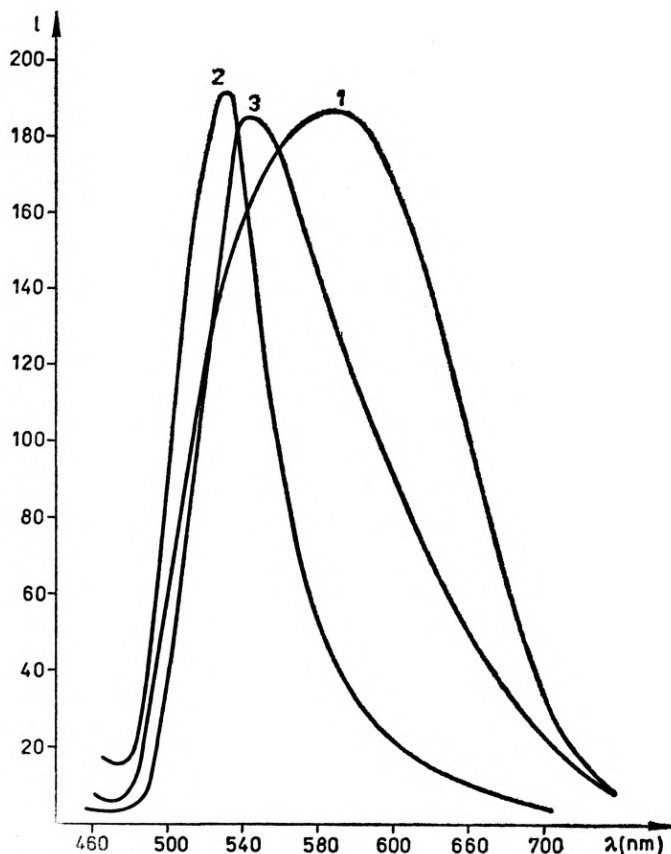

Fig. 4. The spectral distribution of luminescence in glasses activated with manganese
1 — FK5 (0.5% Mn_2O_3), 2 — BK7 (0.1% Mn_2O_3), 3 — SK4 (0.1% Mn_2O_3)

and by a glass filter (green VG, 2 mm) for the deuter lamp. The excitation spectra are registered in the graphs, which correspond to Mn^{2+} (4) luminescence (curves 1) and to the Mn^{2+} (6) luminescence (curves 2). The curves of excitation spectra induced by the deuter lamp (1a, 2a) as well as by the halogen lamp (1a, 2b) are presented for the fixed width of the monochromator slit. While the intensities of the excitation band for deuter lamp are closer the true ones, the intensities of the excitation bands induced by the halogen lamp (for which an increase of the light flux occurs with the increase of the light wavelength) are enhanced.

Many bands are observed in the excitation spectra of Mn^{2+} luminescence in the FK5 glass (fig. 5). A band with a maximum at 220 nm appears for
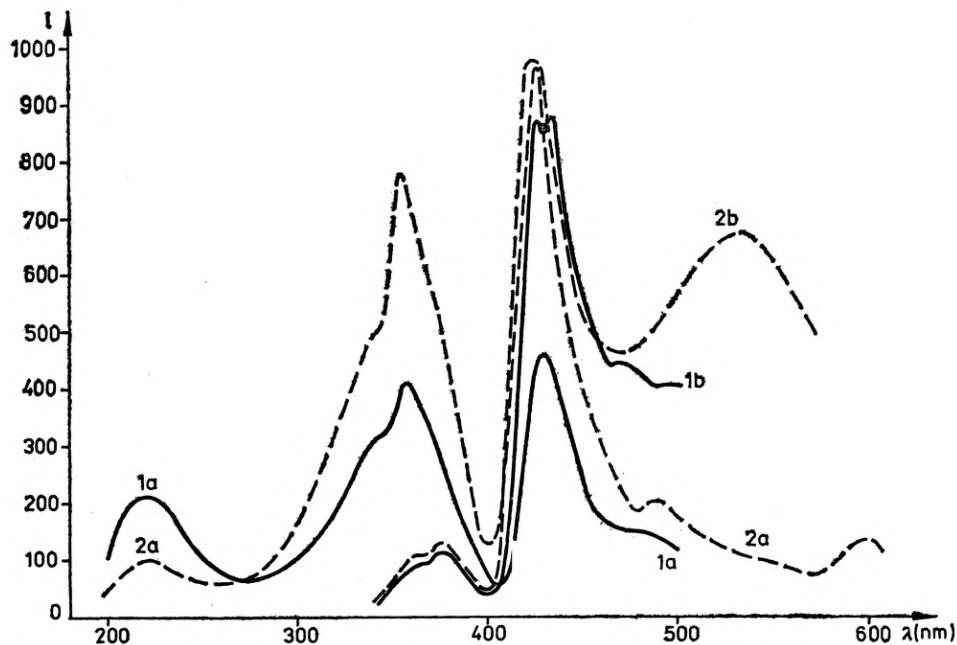

Fig. 5. The luminescence excitation spectra for Mn^{2+} ions embedded in FK5 glass under the influence of deuter lamp (a) and under the influence of halogen lamp (b)
1a — green glass filter (VG-9), 2a — edge filter (600 nm), 1b — interference filter (550 nm), 2b — edge filter (600 nm)

luminescence when measured at the presence of either a green filter or a red one. The intensity of this band is twice less for luminescence of Mn^{2+} (4) than that for luminescence of Mn^{2+} (6). There exist several bands within the interval 300–400 nm, the highest intensity being associated to the band with the maximum positioned between 350 and 360 nm (^4E_g [^4D]. Within this spectral region the intensity of the bands is definitely higher for luminescence due to Mn^{2+} (6). However, the highest intensity for this glass corresponds to the bands with maxima for the wavelength ranging

between 420 and 430 nm (^4E_g $^4A_{1g}$). It may be noted that these bands are splitted. The bands, corresponding to the transitions to the sublevels $^4T_{2g}$ and $^4T_{1g}$, are very low and wide. Only by increasing the light flux (halogen lamp) they may be made well visible. An increase of the light flux with the increase of the wavelength causes an apparent shift of these bands toward the longer wavelength.

In the BK7 glass the concentration of manganese ions is considerably lower (0.1%) and by the same means the ratio $Mn^{2+}(4)/Mn^{2+}(6)$ is different. Here, the greatest number of ions with four ligands occurs and therefore the band with maximum at 220 nm for $Mn^{2+}(4)$ has the highest intensity (fig. 6). On the other hand, the excitation spectrum for luminescence of $Mn^{2+}(6)$ within the interval 200–300 nm has two bands with maxima at 220 and 275 nm, but of lower intensity. Within the interval 300–400 nm two bands of maxima at 350–360 nm and 380 nm are visible and very low intensity is observed if compared to bands from the interval 200–300 nm. The bands ^4E_g $^4A_{1g}$ (420–440 nm) are also of less intensity but their splitting may be seen very well. The ratios of these bands are different for $Mn^{2+}(4)$ and $Mn^{2+}(6)$.

In the case of SK4 (fig. 7) glass the differences in the excitation spectra distribution are observed between 200–300 nm. Here, there exists one
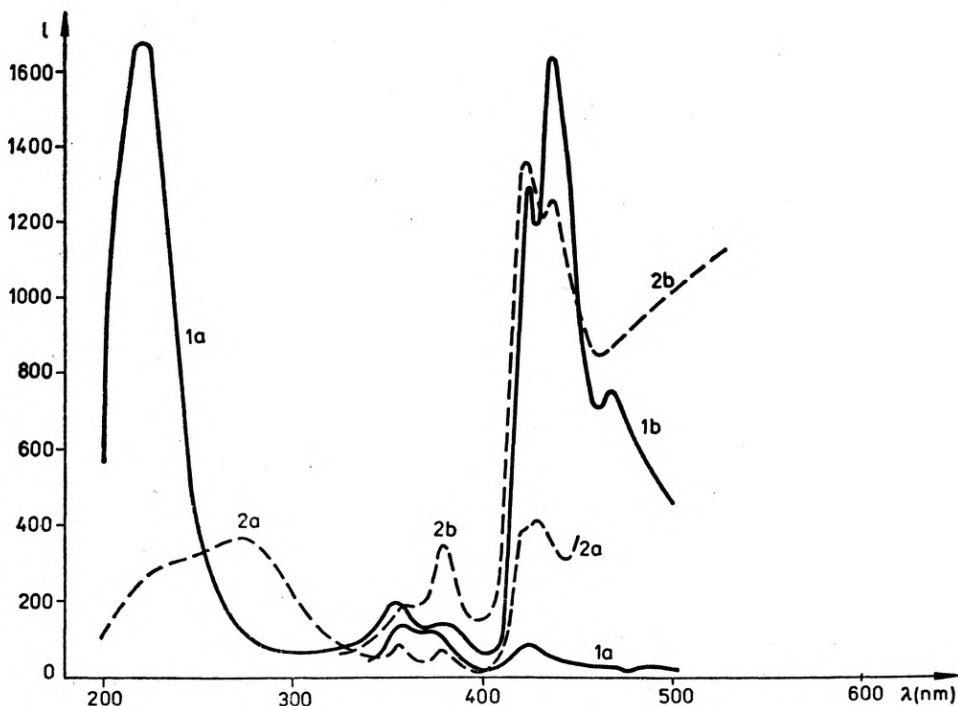

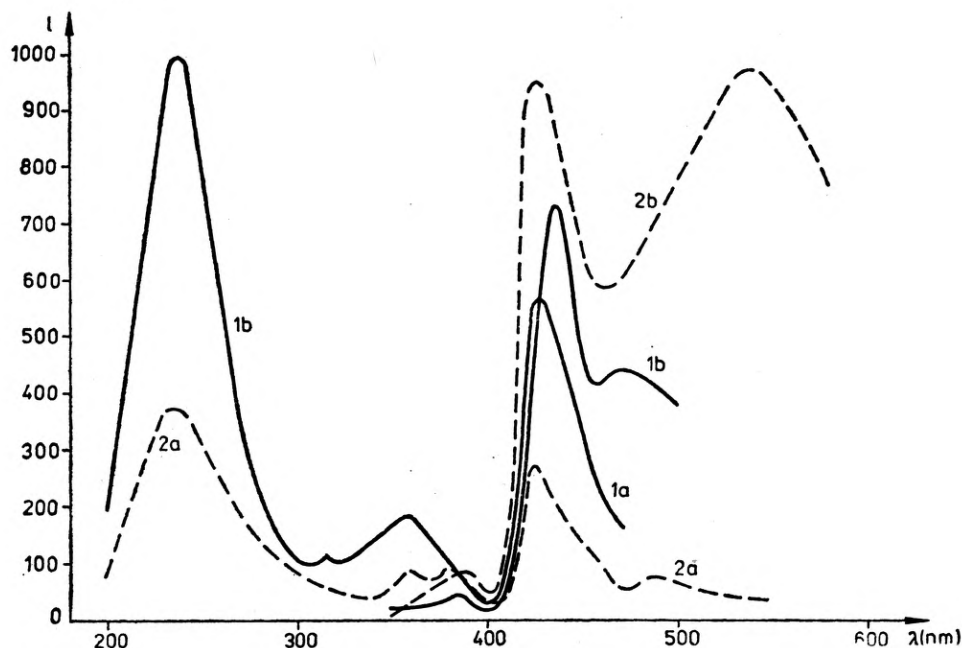Fig. 6. The same as in the fig. 5 but for BK7 glass

Fig. 7. The same as in the fig. 5 but for SK4 glass

wide band extended between 230 and 240 nm. In spite of this, the $^4E_g\,^4A_{1g}$ (420–440 nm) are splitted to a less degree. This is probably due to the excitation of Mn^{2+} in two coordinations.

4. Discussion of results

The luminescence method may be used to examine the structure of the $3d$ level in Mn^{2+} ions and determine the crystal field parameters in a much more perfect way than it is allowed by absorption measurements. The method discussed may be also applied to examine the samples for which the d-d transitions may not be controlled by absorption measurements.

The positions of the absorption bands of Mn^{2+} for the silicon glasses are known from the literature data. For instance, the band connected with the electron transition to the levels $^4E_g[^4G]$ and $^4A_{1g}[^4G]$ is associated with the wave numbers within the region 23500–23800 cm^1 [1], while the transition to the level $^4E_g[^4D]$ is associated with the wave numbers 28000 cm^{-1}. These results are absolutely consistent with those obtained from the excitation spectra luminescence. The exparimental data for the luminescence excitation spectra of Mn^{2+} (4) and Mn^{2+} (6) as well as the parameters of the crystal field are contained in table. In this table no excitation bands are reported which would be contained between 200 and

Table. Wave numbers for Mn^{2+} (6) and Mn^{2+} (4) and the parameters for the crystal field

Notations		FK5 [cm^{-1}]		BK7 [cm^{-1}]		SK4 [cm^{-1}]	
		Mn^{2+} (6)	Mn^{2+} (4)	Mn^{2+} (6)	Mn^{2+} (4)	Mn^{2+} (6)	Mn^{2+} (6)
$^4T_{1g}$	^4P	30300		29400			
^4E_g	^4D	28170	28410	28090	28250	27930	28200
$^4T_{2g}$	^4D	26400	27300	26300	27300	26400	27200
^4E_g	^4G	23700	23580	23700	23500	23700	23600
$^4A_{1g}$	^4G	23250	23000	23000	23000	23400	23000
$^4T_{2g}$	^4G	20400		20400		20400	
$^4T_{1g}$	^4G		21500		21500		20200
B		638	690	627	678	604	657
Dq		870	460	900	460	770	550

300 nm. The latter bands of very high intensities may be ascribed to conduction bands. The respective calculations have been carried out on the base of formulae from the books by BARTECKI [6] and BERSUKER [7].

The results obtained in this work are (within the measurement accuracy) consistent with the literature data. The measurement accuracy of the applied method may be improved by the respective changes in the measuring setup and by perfectioning the measurement technique.

The splitting of the ^4E_g and $^4A_{1g}$ bands indicate that there exist considerable deviations from the octahedrical symmetry. For instance, in the BK7 glass the difference between the wave numbers for $^4E_g[^4G]$ and $^4A_{1g}[^4G]$ bands is equal to 700 cm^{-1}. The method of the luminescence excitation spectra is the simplest so far as the separation of the components coming from Mn^{2+} (4) and Mn^{2+} (6) is concerned. Such a separation would not be possible with the help of absorption measurements.

References

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Люминесцентный метод исследования структуры уровня 3*d* ионов Mn^{+2} в стеклах

Показано, что в активированных стеклах Mn^{+2} полосы спектра поглощения, соответствующие переходам *d-d*, не обнаруживаются, между прочим — из-за наличия полосы спектра поглощения Mn^{+3}. Доказано, что применение в этом случае спектров возбуждения люминесценции позволяет успешно исследовать структуру подуровня 3*d* ионов Mn^{+2}. Метод спектров возбуждения люминесценции обладает рядом преимуществ, позволяя, между прочим, несложным образом разделять Mn^{+2} (4) и Mn^{+2} (6).