EXCITATION SPECTRA AND CONCENTRATION-DEPENDENT LUMINESCENCE OF Mn^{2+} IN METAPHOSPHATE GLASSES

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Emission and excitation spectra of Mn^{2+}-activated magnesium metaphosphate glasses were investigated using two base glasses at different Mn^{2+} concentrations. The spectral position of the peaks of the normalized excitations spectra is independent of concentration, while the relative height of the different excitation bands is concentration-dependent. In the case of low Mn^{2+} concentrations a green band appears in the emission spectra consisting generally of a single broad red band. The peaks of emission are shifted from 595 nm to 677 nm with increasing manganese concentration. Our results show that the explanation given by TURNER and TURNER for the concentration dependence of Mn^{2+} luminescence in silicate glasses seems to be applicable also for phosphate glasses.

In the last years several authors [1, 2, 3, 4, 5, 6] dealt with the luminescence of Mn^{2+}-activated glasses studying also the question of the validity of the classical LINWOOD-WEYL model. LINWOOD *and* WEYL [7, 8] stated that in silicate glasses the Mn^{2+} is of tetrahedral coordination and emits green fluorescence, whereas in phosphate glasses it is of octahedral coordination, the fluorescence being dominatly red. According to their investigations on concentration quenching, this effect occurred at significantly lower manganese concentrations in silicate glasses than in phosphate glasses. They consider these results as supporting the tetrahedral or octahedral symmetry of the Mn^{2+} coordination in the respective glasses. KREIDL [9] obtained analogous results. The first quantitative investigations on absorption and fluorescence of manganese activated glasses were made by BINGHAM and PARKE [1]. Their results, supported by calculations based on the ligand-field theory, confirmed the suggestion of LINWOOD and WEYL concerning the position of Mn^{2+} in the glass. They already noticed the shifting of the emission peak with increasing manganese concentration irrespective of the composition of the base glass without giving however, quantitative data. According to WILKE's observations on metaphosphate glasses [10], the colour of luminescence becomes more and more red with increasing manganese concentration. LUNTER and KARAPETJAN [2] found a shift of the emission maxima from 16155 cm^{-1} to 13650 cm^{-1} by increasing the MnO_2 concentrations from 0.05 wt% to 50 wt% in $ZnO.P_2O_5$ glasses. TURNER and TURNER [5] investigated in detail the concentration dependence of the luminescence in manganese activated silicate glasses. They found significant spectral changes and suggested exchange coupled groupings as explanation, which may also explain the changes in colour found by other authors in borate and phosphate glasses.

Therefore it seemed justified to investigate the concentration dependence of the luminescence of manganese activated magnesium metaphosphate glasses. In the present paper the dependence of luminescence emission on exciting wavelength glass composition, and activator concentration is dealt with. Instead of the poorly resolved absorption spectra excitation spectra were measured.

Experimental

To prepare our samples, according to the method described by WILKE, MgO and $(NH_4)H_2PO_4$ was thoroughly mixed and thermolysed until ammonia was totally expelled. The charges were melted in alumina crucibles in an electric furnace at temperatures from 1200 to 1300°C for 12 and 16 hours, respectively, depending on the $MgO:PO_3$ ratio. The melted glass was poured in steel moulds preheated to 500°C and subjected to annealing for 16 hours. The measurements were performed on samples polished on both sides. The manganese concentration of the samples was determined colorimetrically.

A home-built spectrophotometer consisting of light sources XBO 500 W or HBO 200 W, quartz prism and glass prism monochromators SPM 2, a multiplier EMI 9558 AQ and a Zeiss recorder G1B1, and a digital Voltmeter EMG 1361 and a printer was used.

In measuring the excitation spectra, the exciting light was divided into two parts by a quartz plate placed behind the exit slit of the quartz prism monochromator. One of these beams was focused on the sample, the luminescence light of which was observed through suitable filters and a light pipe using a multiplier RCA 1P21. The other beam was focused on a 2 mm quartz cuvette filled with alcoholic fluorescein solution. After passing a crossed filter, the fluorescence light fell on a multiplier Zeiss M10FS25. The photocurrents were detected with the aid of recorders G1B1.

The quantum yield of fluorescein being independent from the exciting wavelength up to the long wave absorption maximum, the excitation spectrum was calculated with the formula

$$Exc(\lambda) = \frac{I_s(\lambda)}{I_{fl}(\lambda)}\left(T_c(\lambda) - T_{fl}(\lambda)\right),$$

where I_s and I_{fl} are photocurrents proportional to the quantum emission of the sample and of the fluorescein, T_{fl} and T_c the transmission of the cuvettes filled with fluorescein solution and with the solvent, respectively, compared with that of air.

Results and discussion

Before measuring the excitation spectra, it has been examined whether the emission spectrum for a given glass composition and Mn^{2+} concentration depends on the exciting wavelength. According to our measurements, in case of excitation with the 366, 406 and 436 nm line-groups of a mercury lamp the relative quantum distribution of the red band of the emission spectra is independent from the exciting wavelength. Therefore in measuring the excitation spectra, only one pair of filters was used for eliminating the exciting light.

In Fig. 1 excitation spectra of glasses of composition $MgO:PO_3 = 1:3$ are shown. The reference numbers 1, 2, 3, 4 of the curves normalized at 409 nm denote manganese concentration of 0.1, 1.6, 3.8 and 7.7 wt% respectively. The band width of excitability increases with increasing concentration, the spectral position of the bands remaining the same, while the intensity of the band with maximum at 346 nm increases significantly as compared with that of the 409 nm maximum, the secondary maxima becoming more and more pronounced at the same time.

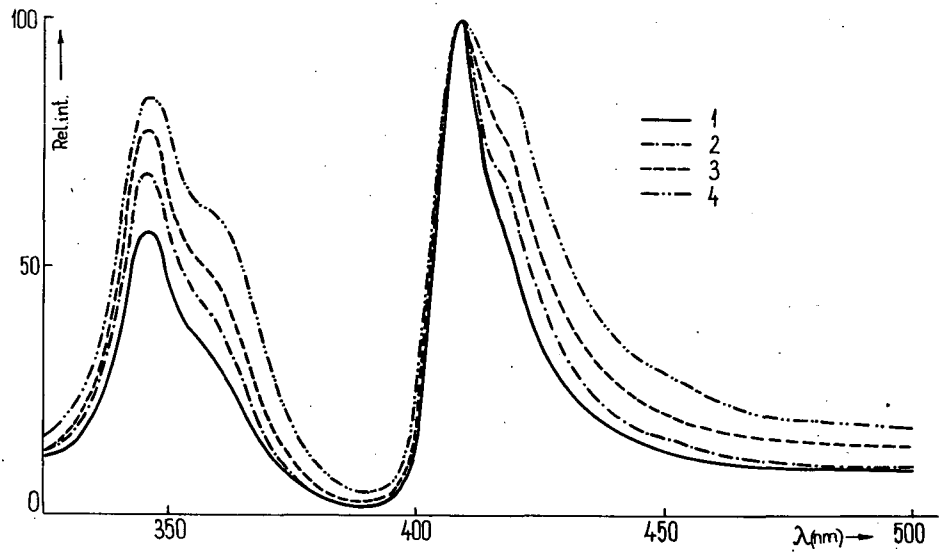

Fig. 1. Concentration-dependence of the excitation spectra

In the literature, the emission of the Mn^{2+} activated phosphate glasses has been characterized chiefly by the visual emission colour which was found to change from yellow to red, depending on concentration and composition. According to LUNTER and KARAPETJAN [2, 3] the changes in colour of the emission of phosphate glasses are due to the shift of the single red band towards longer waves. The visual emission colour of our samples was found to change from light yellow to deep red. At low concentrations a green band appears in the spectrum near 518 nm (see curves 1, 2, 3 in Fig 2 and 3), with improved resolution at the temperatures of liquid air. Our apparatus was calibrated to obtain correct luminescence quantum spectra. The green band becomes weaker with increasing concentration (it is not observable at concentrations higher than 3 wt%), the long wave band being shifted towards red at the same time. For the green band, such a shift of the spectral position could not be observed for the concentration range investigated. Our results seem rather surprising, because for phosphate glasses the green band is not predicted by the Linwood—Weyl model.

A change in the composition of our base glass from 1:3 to 1:2 did not cause any essential changes in the concentration dependence of the Mn^{2+} luminescence (see Figures 2 and 3, respectively). Emission spectra of glasses with Mn^{2+} concentration

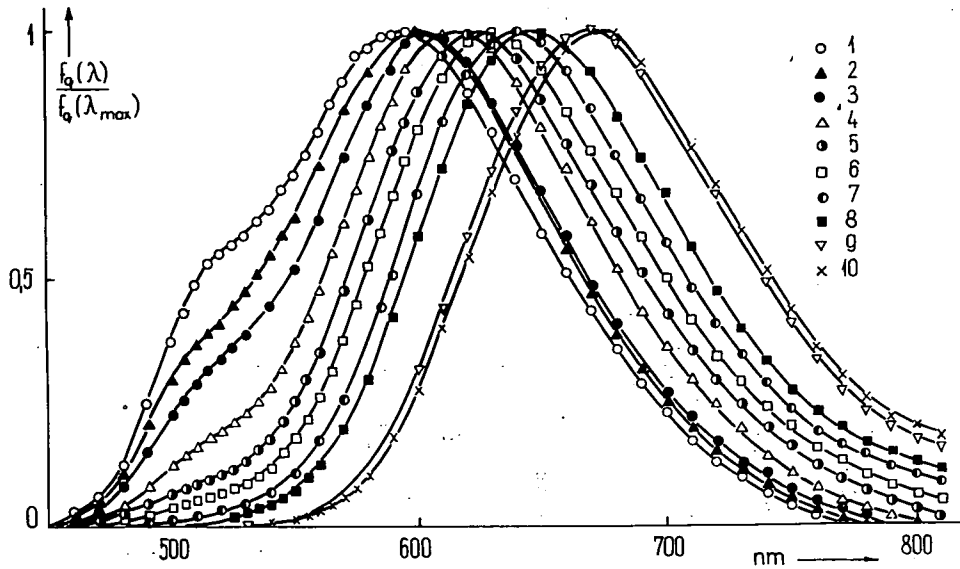

Fig. 2. Room temperature fluorescence spectra of $MgO.3PO_3$:0.07 wt% Mn (1); 0.47 wt% Mn (2); 0.79 wt% Mn (3); 1.60 wt% Mn (4); 2.31 wt% Mn (5); 3.09 wt% Mn (6); 3.80 wt% Mn (7); 4.22 wt% Mn (8); 6.29 wt% Mn (9); 7.70 wt% Mn (10). λ_{exc} 410 nm.

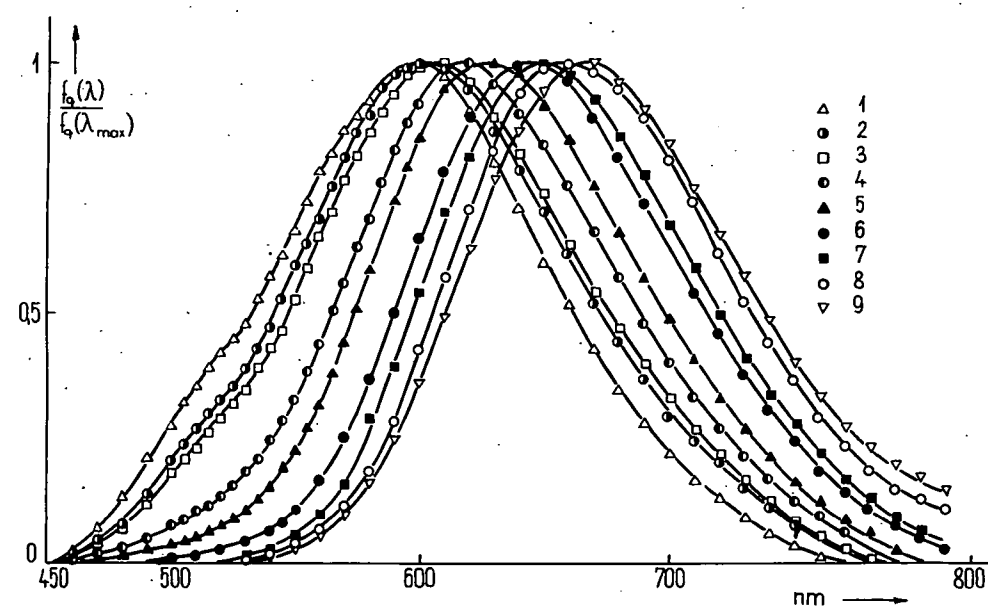

Fig. 3. Room temperature fluorescence spectra of $MgO.2PO_3$:0.10 wt% Mn (1); 0.56 wt% Mn (2) 0.67 wt% Mn (3); 1.94 wt% Mn (4); 3.13 wt% Mn (5); 4.12 wt% Mn (6); 5.03 wt% Mn (7); 6.20 wt% Mn (8); 8.16 wt% Mn (9). λ_{exc} 410 nm.

lower than 0.1 wt% could not be determined because of the very low luminescence intensity. It is remarkable that, with increasing temperatures, the spectra are shifted towards the green spectral region. Detailed observations concerning the temperature dependence of luminescence are to be published later.

A plausible interpretation of the observed shift of the emission spectra can be found in the supposition, suggested by TURNER and TURNER [5], that by changing the distance between the Mn^{2+} ions in specific position able to emit, new emitting centres responsible for the red luminescence are produced.

The formation of such centres should implie changes in the absorption spectrum. However, because of the very low absorptivity of the samples, such changes could not be found in the case of Mn^{2+} either by [1] or by [5]. The existence of such new centres seems to be supported by our observations on excitation spectra.

Measurements and calculations concerning interactions between Mn^{2+} ions are in course in order to find a model describing the luminescence of Mn^{2+} activated glasses.

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ЗАВИСИМОСТЬ СПЕКТРЫ ЛЮМИНЕСЦЕНЦИИ И ВОЗБУЖДЕНИЯ СТЕКОЛ ИЗ МЕТАФОСФАТА МАГНИИ ОТ КОНЦЕНТРАЦИИ Mn^{2+}

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Исследовались спектры излучения и возбуждения стекол из метафосфата магнии активированных с различными концентрациями Mn^{2+}. Место максимумов нормированных спектров возбуждения не зависит от концентрации марганца, а относительная интенсивность полос возбуждения показывает концентрационную зависимость. При маленьких концентрациях Mn^{2+} кроме красной полосы излучения появляется и полоса в зеленой области спектра. Максимумы спектров излучения при увеличении концентрации марганца смешается от 595 нм до 677 нм. Наши результаты позволяют применять объяснение Турнера концентрационной зависимости данного для объяснения люминесценции стекол из силикатов.