DEPENDENCE ON CONCENTRATION AND TEMPERATURE
OF Mn^{2+} LUMINESCENCE IN ZINC METAPHOSPHATE GLASSES

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The spectral distribution of the luminescence of zinc metaphosphate glasses with 10^{-4} to 10^{-r} mole Mn^{2+} content was measured between 103 and 603 °K. The dependence of the spectral distribution on concentration and temperature as well as the behaviour of temperature quenching of the Mn^{2+} luminescence are very similar to those found in magnesium metaphosphate glasses. The formula $I/I_o = \left(1 + Ce^{-\frac{W}{kT}}\right)^{-1}$ was found to be suitable for the description of the temperature quenching only at temperatures exceeding room temperature. The calculated activation energies were between 0.12 and 0.22 eV for magnesium metaphosphate glasses, and between 0.18 and 0.26 eV for zinc metaphosphate glasses.

It has been shown by KORDES et al. [1, 2] that Zn-, Mg- and Be- phosphate glasses have special physical properties, different from those of other phosphate glasses, and this anomalous behaviour was explained by the circumstance that the structure of these glasses is similar to that of quartz and alkali silicate glasses. Only few systematical investigations concerning the luminescence of these glasses were made [3, 4, 5, 6]. In the case of manganese activated crystalline luminophores several authors tried also to find relationships between the very different luminescence properties of different luminophores and the structure of the host lattice [7—10]. Owing to the special structure of the Zn-, Mg- and Be- phosphate glasses and the great variety found in the luminescence properties of Mn^{2+}-activated crystalline phosphates, it seemed justified to examine the luminescence of the Mn^{2+} ion in these "anomalous" phosphate glasses. Earlier [11, 12] we dealth with the dependence on concentration and temperature of the luminescence of magnesium metaphosphate glasses activated with Mn^{2+}. The present paper describes our investigations on zinc metaphosphate glasses.

Experimental

As the apparatus and the methods of measurement described earlier [12] remained unchanged, only the conditions used in preparing the glasses and the properties of the latter will be described here.

The $Zn(PO_3)_2$ used as starting material was synthesized from ZnO and H_3PO_4 of analytical purity. The manganese content (10^{-4} to 10^{-1} mole) was introduced

in the form of manganous acetate. The charges were melted in covered biscuit ware crucibles exposed to the ambient atmosphere in an electric furnace at 1200° C. The duration of the clear melting as well as conditions of the annealing and further steps in the preparation of the samples were the same as described for magnesium metaphosphate glasses.

The zinc metaphosphate glasses obtained are less resistent to moisture than magnesium metaphosphate, therefore the samples were stored under kerosene, except for the time of examination. The samples were freed from kerosene by acetone before the measurements.

The results of chemical analysis showed that the losses due to the melting process did not cause changes higher than ±5% in the chemical composition.

The densities measured with pycnometric method are in good agreement with the results of KORDES et al. [1] and the concentration dependence is similar to that obtained for magnesium metaphosphate glasses [12].

Results and discussion

Emission spectra of glasses of 10^{-3} mole to 10^{-1} mole Mn^{2+} content measured at 103, 303 and 603 °K are shown in Fig. 1. The maximum of the emission spectra shifts with increasing manganese concentration towards longer wavelengths: the colour of the luminescence changes from greenish yellow to red. The extent of the changes is in good accordance with data found in literature [4, 5]. At low Mn^{2+} concentrations ($< 5 \cdot 10^{-2}$ mole Mn^{2+}), the green band, unusual in phosphate glasses, appears also in zinc metaphosphate glasses; it is best resolved at 103 °K. The green band is comparatively the strongest in glasses of $5 \cdot 10^{-4}$ and 10^{-4} mole Mn^{2+} concentration, it is, however, very difficult to measure exactly the spectral distribution of the emission because of the very low absolute intensities.

With increasing temperatures the green band becomes less pronounced, the intensity ratio between red and green bands decreases. It may be supposed that the temperature quenching of the green band is less than that of the red one. See e.g. [13]. Owing to the decrease of the intensity ratio and the shift of the red band towards shorter wavelengths, the green band is less pronounced at higher temperatures. The band-widths of the emission spectra increase with increasing temperature. It has to be remarked that the measurements at 603 °K, chiefly in the case of the lowest manganese concentrations, are less accurate than those measured at lower temperatures, because the intensity of luminescence at this temperature is very low.

The temperature dependence of the positions of the emission maxima in the case of different Mn^{2+} concentrations is shown in Fig. 2. The same dependence for Mn^{2+} activated magnesium metaphosphate glasses is to be seen in Fig. 3. At Mn^{2+} concentrations less than $5 \cdot 10^{-2}$ mole, the course of the curves is almost the same for both metaphosphate glasses. Though the value of $d\lambda/dT$ is not constant, the shift occurs in the same direction, namely the position of the emission maximum shifts towards shorter wavelengths with increasing temperatures. The curves can be divided into two parts of different slope, the bending point being around room temperature. In the case of Mn^{2+} concentrations higher than $5 \cdot 10^{-2}$ mole, the maxima of the red band shift towards the red from 103 °K up to a temperature depending on concentration, then the green shift usual at lower Mn^{2+} concentrations
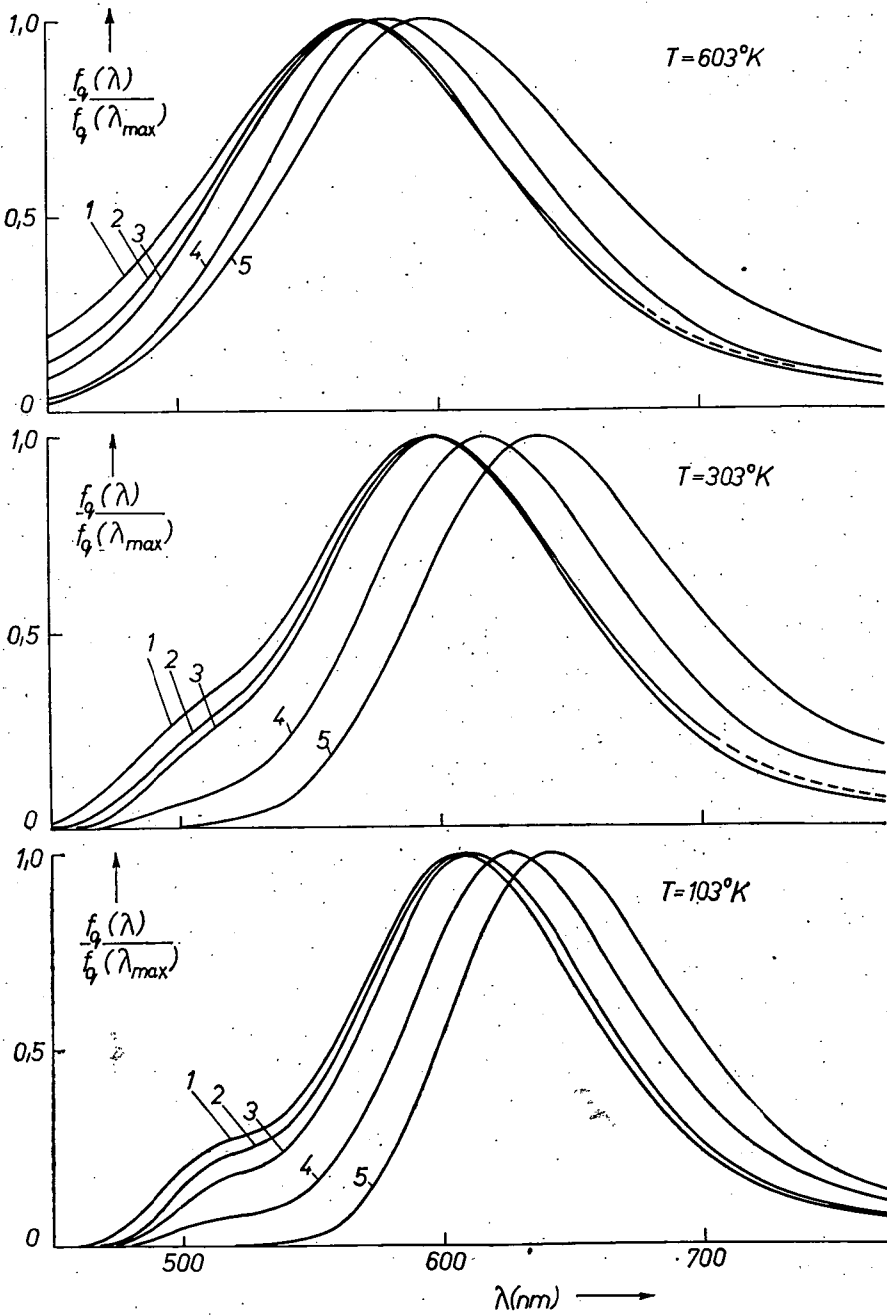
Fig. 1. Emission spectra of $ZnO.P_2O_5:10^{-3}$ mole Mn^{2+} (1); $5 \cdot 10^{-3}$ mole Mn^{2+} (2); 10^{-2} mole Mn^{2+} (3); $5 \cdot 10^{-2}$ mole Mn^{2+} (4); 10^{-1} mole Mn^{2+} (5) glasses. $\lambda_{exc.} = 410$ nm.
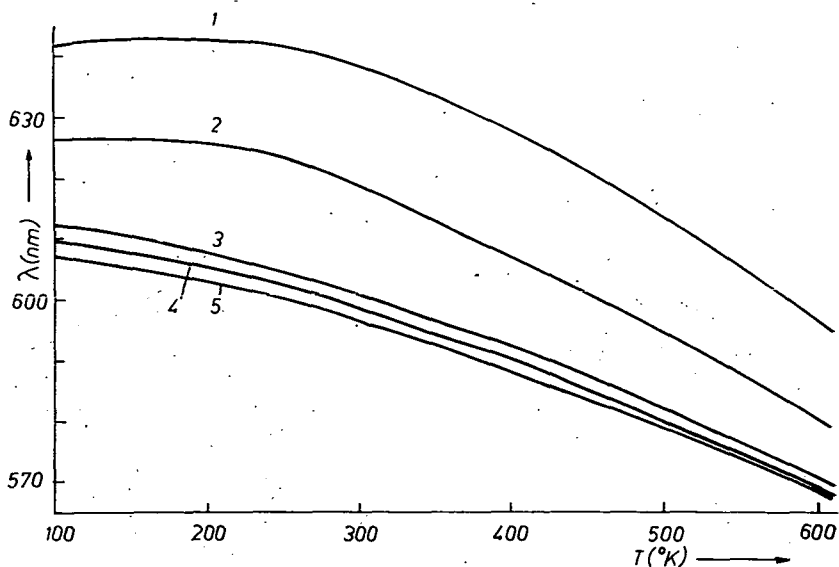
Fig. 2. Temperature dependence of the positions of the emission maxima of ZnO.P_2O_5:10^{-1} mole Mn^{2+} (1); $5 \cdot 10^{-2}$ mole Mn^{2+} (2); 10^{-2} mole Mn^{2+} (3); $5 \cdot 10^{-3}$ mole Mn^{2+} (4); 10^{-3} mole Mn^{2+} (5) glasses.
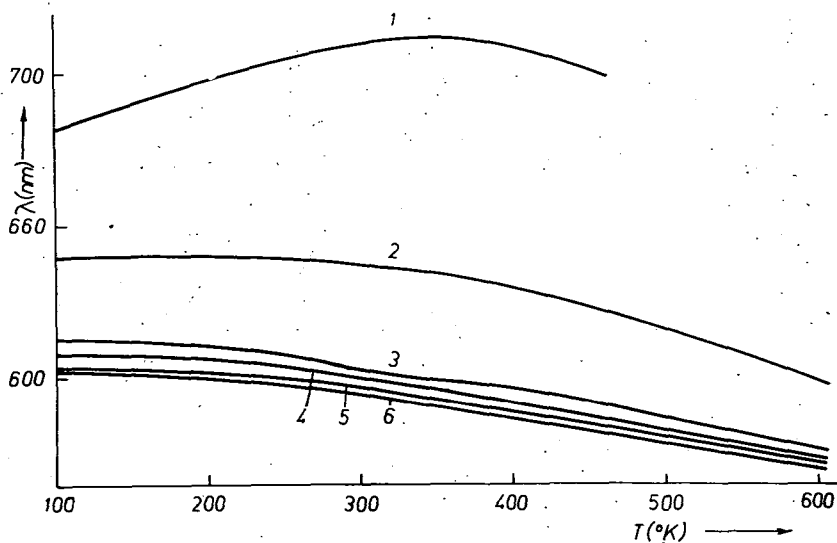

Fig. 3. Temperature dependence of the positions of the emission maxima of MgO.P_2O_5:$5 \cdot 10^{-1}$ mole Mn^{2+} (1); 10^{-1} mole Mn^{2+} (2); $5 \cdot 10^{-2}$ mole Mn^{2+} (3); 10^{-2} mole Mn^{2+} (4); $5 \cdot 10^{-3}$ mole Mn^{2+} (5); 10^{-3} mole Mn^{2+} (6) glasses.

is observed again, i.e. $d\lambda/dT$ changes its sign. It can be stated that the rate of the shift increases with increasing concentration and is substantially higher in the case of $5 \cdot 10^{-1}$ mole Mn^{2+} concentration than for other concentrations.

The formula given by PARKE [14] for the temperature shift of the spectral position of the luminescence maximum can be directly applied only in the case of glasses emitting in a single band, because the ligand field strength figuring in the formula is valid only for octahedral or for tetrahedral symmetry. In our glasses Mn^{2+} ions are probably found at most concentrations in environments of both kinds of symmetries, therefore Parker's formula cannot be used for interpreting our results.
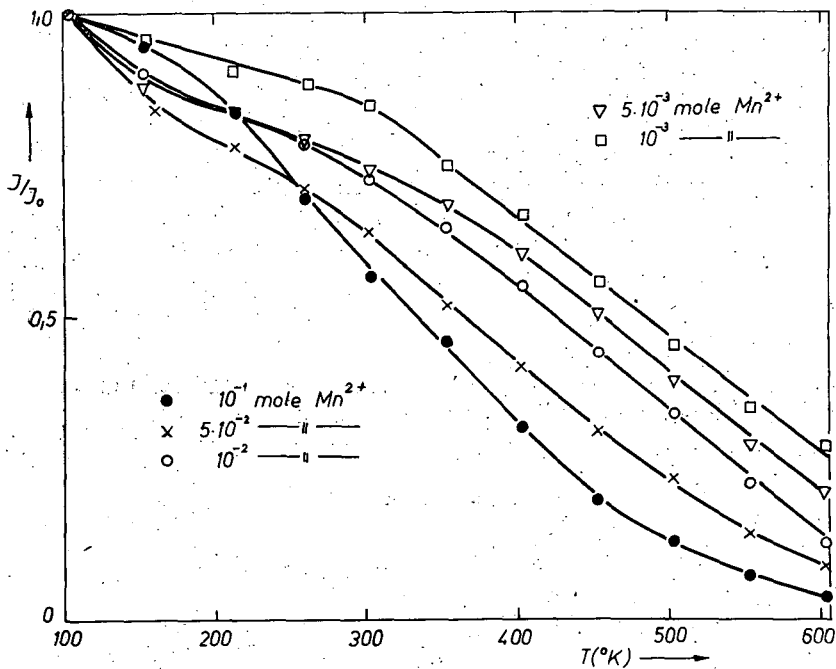

Fig. 4. Concentration dependence of the temperature quenching of $ZnO.P_2O_5$ glasses.

Temperature quenching curves of zinc metaphosphate glasses with different Mn^{2+} concentrations are presented in Fig. 4. At the lowest temperature measured the intensity of the emission did not reach its maximum value. The temperature quenching curves in the temperature range from $103\,°K$ to room temperature show a rather individual behaviour. It can be stated, however, that similarly to the magnesium metaphosphate glasses [12] the temperatures corresponding to half intensity decrease with increasing manganese content. The range of the individual behaviour mentioned is the same as that of the first part of the spectral shift curves (Figs. 2 and 3).

The formula

$$\frac{I}{I_o} = \left(1 + Ce^{-\frac{W}{kT}}\right)^{-1}$$

is often used for describing the temperature quenching of luminescence on the base of the configuration coordinate model [15, 16]. Here I_o denotes the maximum intensity of emission, I the emission measured at temperature T, W the activation energy, C is the so-called frequency factor, k Boltzman's constant. To determine the parameters W and C, $\log\dfrac{1 - I/I_o}{I/I_o}$ vs. $1000/T$ was plotted. W was obtained from the high temperature range of the quenching curve as the slope of the straight line calculated with the less square method. The calculated values of W were between 0.12 and 0.22 eV for magnesium metaphosphate glasses, and between 0.18 and 0.26 eV for zinc metaphosphate glasses. The values are in good agreement with those obtained by PARKE for silicate glasses [14].

It can be stated that the dependence of the spectral distribution on concentration and temperature as well as the temperature quenching of the Mn^{2+} luminescence in zinc metaphosphate glasses are very similar to those observed in magnesium metaphosphate glasses. Our results support the findings of KORDES concerning the structure of these glasses.

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ЗАВИСИМОСТЬ ЛЮМИНЕСЦЕНЦИИ ДВУХВАЛЕНТНОГО МАРГАНЦА В СТЕКЛАХ ИЗ МЕТАФОСФАТА ЦИНКА ОТ КОНЦЕНТРАЦИИ И ТЕМПЕРАТУРЫ

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Измерены спектры люминесценции стекол метафосфата цинка, содержащих $(10^{-4}-10^{-1})$ моль Mn^{2+}, в интервале температуры 103—603 °К. Оказалось, что концентрационная и температурная зависимость спектров и температурное тушение этих стекол весьма подобны с соответствующими характеристиками стекол метафосфата магния. Температурное тушение описывается формулой $I/I_o = (1 + Ce^{-W/kT})^{-1}$ только выше комнатной темтературы Рассчитанные энергии активации для магнийметафосфатных стекол имеют значения 0,12—0,22 eV, а для стекол из цинкметафосфата 0,18—0,26 eV.