TEMPERATURE DEPENDENCE OF THE LUMINESCENCE OF MAGNESIUM METAPHOSPHATE GLASSES ACTIVATED WITH Mn²⁺

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The intensity and spectral distribution of the fluorescence of magnesium metaphosphate glasses containing divalent manganese were measured over the temperature range 103 to 603 °K and in a wide range of concentration. With increasing Mn²⁺ concentration the quenching temperature shifts towards lower temperatures. By increasing the temperature at low Mn²⁺ concentrations the red : green ratio decreases and the spectra move to shorter wavelengths. The temperature dependence of the spectral distribution of the glasses with more than 10^{-1} mole Mn²⁺ content shows an anomalous behavior.

The colour of the luminescence emission of Mn²⁺ ions changes from deep red to bright green depending on the host material and the way of preparation. Most authors try to correlate the colour of the luminescence of Mn²⁺ activated glasses with the nature (symmetry) of the environment of the ions, and to use the changes in colour of the emission as an indicator of structural changes in the base glass [1—5].

The structure of binary phosphate glasses was thoroughly investigated by KORDES et al. [6, 7]. They found that in metaphosphate glasses with certain alkaline earth metal oxides (MgO, ZnO, BeO) all alkaline earth metal ions are fourfold co-ordinated in the ideal case, and the structure and some other physical properties (dilatation, hardness, u.v. transmission) of these glasses are also similar to those of fused silica. Though WILKE [8], as well as LUNTER et al. [4, 5] had studied the concentration dependence of Mn²⁺ luminescence in magnesium and zinc metaphosphate glasses, GORBATCHEVA and KABAKOVA [9] were the first to explain the results with this anomalous glass structure. The observations of GORBATCHEVA and KABAKOVA are well supported by our investigations on the concentration dependence of the luminescence of manganese activated magnesium phosphate glasses, performed in a wider concentration range [10].

Quantitative data concerning the temperature dependence of the emission of glasses containing Mn²⁺ were first given by PARKE [11]. He found that the emission bands were shifted towards longer wavelengths by cooling. The temperature coefficient of fluorescence transition of energy E was given by

$$dE/dT = -5\beta\Delta(dE/d\Delta)$$

where β is the linear coefficient of expansion, Δ the ligand field strength and $dE/d\Delta$ the slope on the energy level diagram. In evaluating these results it has to be taken into account, that his method, generally used in measuring the temperature dependence of the emission intensity, neglects the changes in spectral distribution.

As the temperature dependence of the luminescence of Mn^{2+} activated magnesium, zinc and beryllium metaphosphate glasses has not been investigated before, it seemed justified to extend our investigations on magnesium metaphosphate glasses also in this direction.

Experimental

H_3PO_4 and MgO of analytical purity was used to prepare the samples according to BERAK [12]. The composition of the glass containing no activator was $Mg(PO_3)_2$. 10^{-4} to $5 \cdot 10^{-1}$ mole manganese was introduced in the form of manganous acetate. After drying, the charges were melted in covered biscuit ware crucibles in an electric furnace at 1300 °C. The clear melting was continued for 3 hours. The melt was poured into stainless steel moulds of 16 mm diameter and subjected to 16 hours annealing from 450 °C to room temperature. Samples of 15—20 mm length were cut from the glass bars and polished on both ends with diamond paste using kerosene as lubricant. The glass samples prepared with this "wet" method were almost free from bubbles and under microscope proved to be free from crystallization and phase separation. They were not hygroscopic and showed no changes after several months standing in free air.

The results of chemical analysis showed that the original composition underwent no changes exceeding 5% by losses during the melting process.

The densities of the glasses were measured with pycnometric methods and are listed in Table I.

Table I

Mn content in moles	$5 \cdot 10^{-4}$	10^{-3}	$5 \cdot 10^{-3}$	10^{-2}	$5 \cdot 10^{-2}$	10^{-1}	$5 \cdot 10^{-1}$
Density in g/cm³	2.4176	2.4320	2.4340	2.4363	2.4501	2.4887	2.8237

A home-built spectrophotometer consisting of a xenon lamp XBO 450, quartz prism and glass prism monochromators SPM 2, multipliers EMI 9558 AQ and Zeiss M 10 FS 25 with Zeiss recorders G 1B 1 was used. The EMI 9558 AQ was held at a constant temperature of −28 °C. A well-defined part of the exciting light was directed through a quantum counter to the Zeiss multiplier and the current of the latter, proportional to the exciting intensity, was recorded. This made possible to refer the emission spectra to the same exciting intensity. Our apparatus was calibrated to obtain correct luminescence quantum spectra.

The temperature dependence of emission was measured with different sample holders according to the temperature range. Between 103 and 303 °K a liquid nitrogen cooled glass dewar with quartz window and glass-to-metal junction was used. The sample was placed in a brass block containing also the heating elements. To

prevent precipitation of moisture, the system was evacuated to 10^{-2} torr. From 303 to 603 °K the brass block containing the samples was placed in an electric furnace. The temperature was held at the desired value by an electronic temperature controller. The error of temperature measurement and control was ± 2 °K maximum.

Results and discussion

On the base of measurements both of the spectral distribution and of the temperature dependence of the intensity of emission the glasses are of two different types depending on the Mn^{2+} content.

Emission spectra measured at 103 °K are shown in Fig. 1. By comparing these with spectra measured at room temperature, it can be stated that the green band
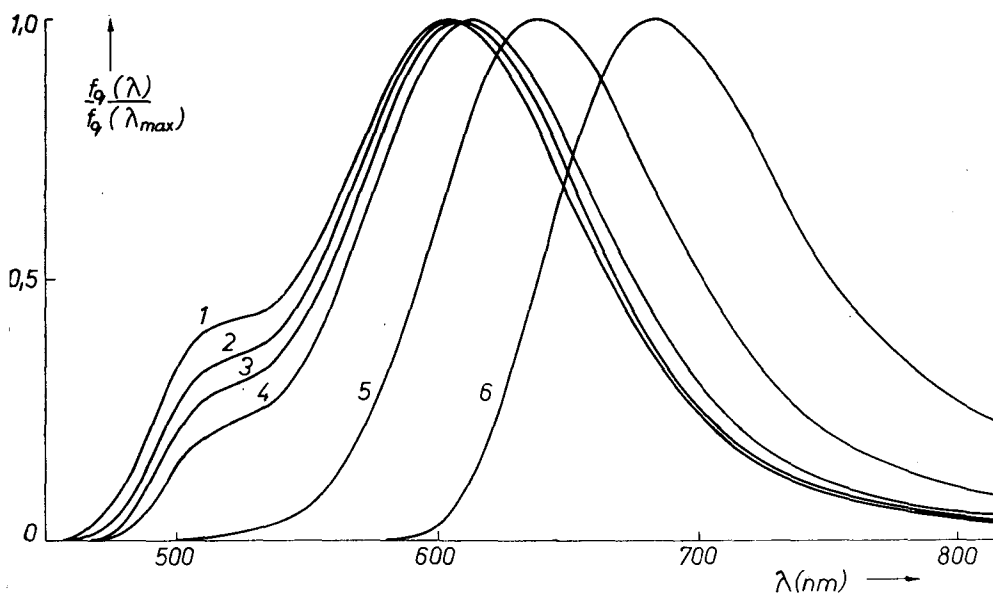

Fig. 1. Low temperature emission spectra of MgO·P$_2$O$_5$:10^{-3} mole Mn^{2+} (1); 5·10^{-3} mole Mn^{2+} (2); 10^{-2} mole Mn^{2+} (3); 5·10^{-2} mole Mn^{2+} (4); 10^{-1} mole Mn^{2+} (5); 5·10^{-1} mole Mn^{2+} (6) glasses. $\lambda_{exc}=410$ nm

in the emission spectra of glasses containing 10^{-3} to $5 \cdot 10^{-2}$ mole manganese became more pronounced, its position remaining essentially unchanged, while the longwave band shifted towards the red. The single red band of the glass with the highest ($5 \cdot 10^{-1}$ mole) manganese concentration shifted towards shorter waves. By increasing the temperature from 103 to 603 °K in the concentration range 10^{-3} to $5 \cdot 10^{-2}$ mole Mn^{2+}, the position of the maximum of the red band shifts continuously towards the green. Fig. 2 shows the emission spectra of the sample containing $5 \cdot 10^{-3}$ mole Mn^{2+} measured at different temperatures. The emission maxima of

the glasses with more than 10^{-1} mole Mn^{2+} content showed a long-wave shift from 103 °K to room temperature, while at higher temperatures a short-wave shift was found.

The temperature dependence of the intensity of the fluorescence is presented in Fig. 3 for six different Mn^{2+} concentrations. With increasing Mn^{2+} concentra-
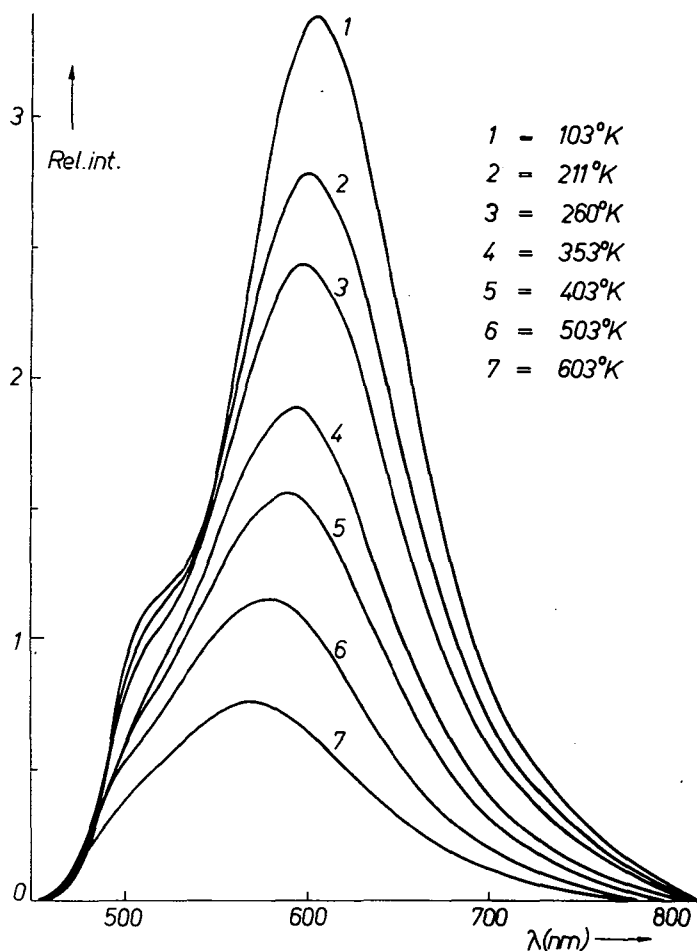

Fig. 2.

tion the quenching temperature (defined as the temperature at which the fluorescence has reached half its maximum intensity) shifts towards lower temperatures. The quenching rate in the concentration range 10^{-3} to $5 \cdot 10^{-2}$ mole Mn^{2+} is essentially lower than in the case of higher concentrations.

The concentration dependence of the luminescence at low activator concentration may be explained by the LINWOOD—WEYL model [2] supposing that the environ-

ment of the manganese ions is partly of tetrahedral and partly of octahedral symmetry. In this case the ions of tetrahedral symmetry would emit the green band and the octahedral ions the red one. Due to the rearrangement caused by the increase in Mn^{2+} concentration only the sites of octahedral symmetry would persist and thus the green band would gradually disappear. This process lasts up to about $5 \cdot 10^{-2}$ mole
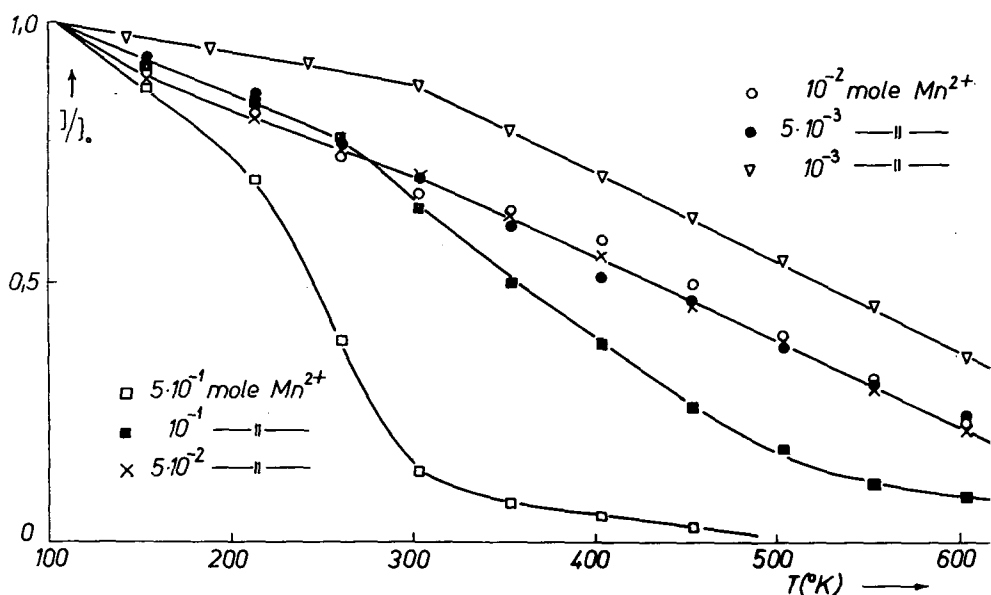

Fig. 3. Concentration dependence of the temperature quenching of $MgO \cdot P_2O_5$ glasses

Mn^{2+} content. At higher concentrations the distance between neighbouring manganese ions would decrease and new luminescence centres (so-called clusters) would form.

Another possible explanation would be, according to KROEGER [13], that several different bands may originate in one centre. The character of the fluorescence emission would depend on the properties of the levels responsible for the bands. Increasing concentration would increase the transition probabilities of the red band(s) and above a certain concentration range—the limits of which cannot be given exactly on the base of the present measurements—this effect would be increased by formation of Mn^{2+} pairs and clusters, resulting in the red shift of the persisting red band.

As to the temperature dependence of the spectral distribution, the change in the red:green ratio occurring at low concentrations may be interpreted by supposed differences in the temperature quenching of both kinds of centres [1]. In the case of higher concentrations the green shift could be explained with the LINWOOD—WEYL model only with the aid of additional suppositions.

Using the other picture [13], the spectral changes observed at low Mn^{2+} concentrations may be explained as follows: The thermal excitation would result in a relative increase in intensity of the green band with increasing temperature. Of course, radiationless de-excitation would compete both with the green and red transi-

tions, its probability increasing with increasing temperature. This picture may be valid up to highest concentrations, namely thermal excitation would enhance transitions of shorter wavelengths also in this case.

The shift observed in glasses of $5 \cdot 10^{-1}$ mole Mn^{2+} content cannot be easily explained by any of the above pictures.

Here we have to do with a luminescent system of a new structure, differing also in other physical properties from the former ones.

The decision of the problem, as to which picture would be more suitable for describing of the observations, may be expected from further measurements of decay time and other parameters.

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References

[1] *Weyl, W. A.:* "Coloured Glasses", The Society of Glass Technology, Sheffield, England, 1951.
[2] *Linwood, S. H., W. A. Weyl:* J. Opt. Soc. Am. **32**, 443 (1942).
[3] *Bingham, K. S., S. Parke:* Phys. Chem. Glasses **6**, 224 (1965).
[4] *Лунтер, С. Г., Г. О. Карапетян, Н. М. Бокин, Д. М. Юдин:* ФТТ, **9**, 2875 (1967).
[5] *Лунтер, С. Г., Г. О. Карапетян, Д. М. Юдин:* Изв. Сиб. отд. АН СССР сер. хим. н., **9**, 46 (1967).
[6] *Kordes, E., W. Vogel, R. Feterowsky:* Z. Electrochem. **57**, 282 (1953).
[7] *Kordes, E., J. Navarrete:* Glastechn. Ber. **46**, 113 (1973).
[8] *Wilke, K. Th.:* Z. Phys. Chem. (Leipzig) **219**, 153 (1962).
[9] *Горбачева, Н. А., А. И. Кабакова:* ЖПС **6**, 478 (1967).
[10] *Szöllősy, L., T. Szörényi:* Acta Phys. et Chem. **17**, 135 (1971).
[11] *Parke, S.:* J. Phys. Chem. Solids **32**, 669 (1971).
[12] *Berak, J.:* Roczn. Chem. **32**, 17 (1958).
[13] *Kroeger, F. A., P. Zalm:* J. Electrochem. Soc. **98**, 177 (1951).

ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ ЛЮМИНЕСЦЕНЦИИ МАГНИЙНО-МЕТАФОСФАТНЫХ СТЕКОЛ АКТИВИРОВАННЫХ Mn^{2+}

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В работе исследованы в интервале температуры (103—603)°К интенсивность и спектральное распределение флуоресценции магнийно-метафосфатных стекол, содержащих разные количества ионов Mn^{2+}. Температура тушения при увеличении концентрации Mn^{2+} смещается к более низким температурам. При малых концентрациях Mn^{2+} с увеличением температуры уменьшается отношение красная полоса: зеленая полоса, и спектры смещаются к коротким длинам волн. Температурная зависимость спектров показывает аномалию для стекол содержащих Mn^{2+} выше 10^{-1} моль.