DEPENDENCE ON EXCITING WAVELENGTH OF EMISSION SPECTRA OF Mn^{2+} ACTIVATED MAGNESIUM METAPHOSPHATE GLASSES

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The dependence on exciting wavelength of emission spectra of Mn^{2+} activated magnesium metaphosphate glasses was measured using a phosphoroscope and lock-in amplifier for four different activator concentrations at room temperature and at 100 °K. The emission spectra are very different for different exciting wavelengths. This finding seems to support the microheterogeneous structure of these glasses.

In the last years RZHEVSKII *et al.* used succesfully luminescence methods for investigating the structure of various phosphate glasses, among others insoluble magnesium metaphosphate glasses.

They mixed powders of Dy^{3+} activated glasses with different decay times and slightly different emission spectra in a given volume ratio, then measured the emission spectra and decay times of the mixtures. They were able to calculate the emission spectra and decay times of the components using a formula [1]. Later they applied the method to different Dy^{3+} activated phosphate glasses, measuring the decay times at different wavelengths of the emission spectra with a special phosphoroscope [2, 3]. On the base of the different decay times they stated the existence of two luminescence centres and calculated the spectra and decay times of both centres.

The possibility of the existence of different kinds of centres is supported by the circumstance that in most phosphate glasses the decay process of Mn^{2+} is reported to be non-exponential [4].

However, if different luminescence centres exist in the glass, then their excitabilities are expected to be different, too. This gave the idea to investigate more thoroughly the influence exerted on the emission spectra by excitation with different wavelengths.

This paper deals with the dependence on exciting wavelength of the emission spectra of Mn^{2+} activated magnesium metaphosphate glasses studied earlier [5].

Experimental

The steps of preparing the samples and their physico-chemical properties are described in detail in an earlier paper [5].

For the measurement of the emission spectra the exciting monochromator of our home-built spectrofluorimeter was substituted by a glass prism monochromator and the apparatus was completed by a PARKER phosphoroscope [6]. The chopping frequency was 400 c/s. The signal of the multiplier was amplified by a Unipan selective nanovoltmeter type 227, rectified by a Unipan homodyne rectifier voltmeter type 202B, than recorded. The changes in intensity of the luminescence emission amounted to almost three orders of magnitude within each series of measurements. The exciting light flux was measured with a rhodamine B quantum counter [7]. This phosphoroscope arrangement was chosen in order to exclude the difficulties caused by the exciting light in measuring the weak luminescence of the samples. It was possible to apply this method and chopping frequency, because in these glasses the decay time of the manganese luminescence is of the order $\tau \approx 10^{-2}$ s [4].

Results and discussion

It was found experimentally that with the same exciting wavelength, the emission spectra measured in the "in phase" and "out of phase" position of the phosphoroscope are the same. Because of the scattering of the exciting light in the "in phase" position, the identity of the spectra could be demonstrated exactly only for excitation wavelengths pertaining to the ascending branch of the emission spectra (generally up to 520 nm).

The emission spectra of glasses containing 10^{-3}, 5.10^{-3}, 5.10^{-2} and 10^{-1} mole manganese were measured for wavelengths from 405 to 600 nm, at room temperature and at 100 °K. Between 400 and 440 nm the measurements were performed in steps of 5 nm, from 440 to 600 nm in steps of 10 nm. It was found that, for the same manganese concentration and increasing exciting wavelengths, the emission spectra shifted towards longer waves.

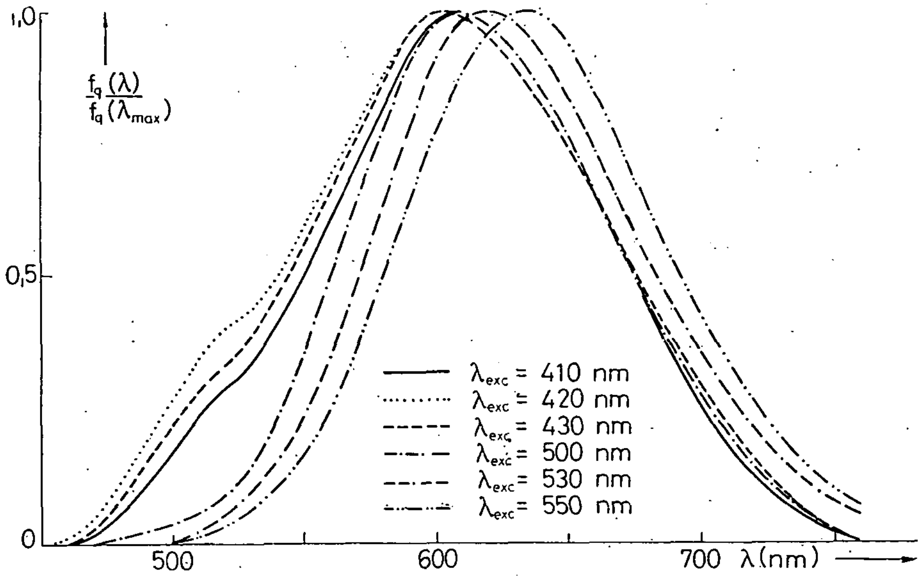

Fig. 1

Fig. 1 and 2 show the emission spectra of glasses containing 5.10^{-2} mole Mn^{2+} measured with different exciting wavelengths at room temperature and 100 °K respectively. For the sake of clearness, some of the measured spectra are not plotted in the figures. It can be seen that with exciting wavelengths generally used for these glasses (405—420 nm), the location of the red band remains essentially unchanged.

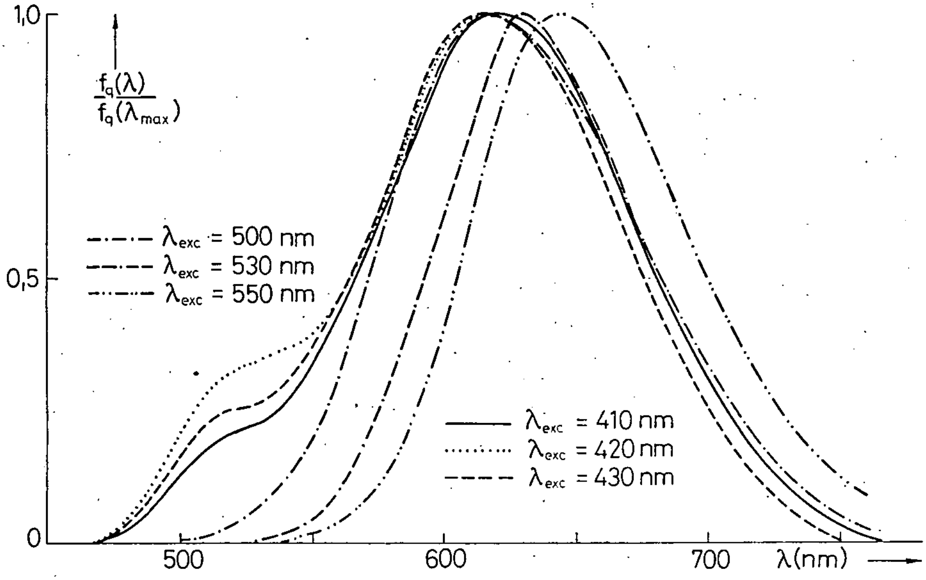

Fig. 2

The dependence on exciting wavelength of the green band is more interesting. By increasing the exciting wavelength, up to 420—425 nm, the relative intensity of the green band gradually increases; with higher exciting wavelengths it decreases again and practically disappears for about 490 nm. Dramatical changes in the red emission can be observed from 470 nm exciting wavelengths on. It seems remarkable that, with increasing activator concentration, the shift of the red band gradually decreases and the spectra converge to a "limiting" emission spectrum independent of concentration. Comparing Figs. 1 and 2, it can be seen that the above statements are valid for both temperatures, with the only difference that at 100 °K the emission spectra are more red for all exciting wavelengths than those measured at room temperature, and consequently a shift of about 20 nm can be observed also in the position of the maximum of the "limiting" spectrum. This is true for all concentrations.

The results of our measurements proved unequivocally that the influence of the exciting wavelength on the quantum distribution of the emission spectra is highly important; therefore the excitation spectra of these glasses are to be measured with special care. It is evident that the excitation spectra determined by monitoring only one wavelength or waveband of the emission spectrum are only approximatively valid for the whole range of excitation [8, 9].

The quantitative interpretation of the dependence on exciting wavelength seems to be complicated, though it appears reasonable to explain the shift of the emission spectra by supposing the existence of manganese centres of different absorptivity at different places of the glass.

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ЗАВИСИМОСТЬ СПЕКТРОВ ИЗЛУЧЕНИЯ МАГНИЙ-МЕТАФОСФАТНЫХ СТЕКОЛ, АКТИВИРОВАННЫХ Mn^{2+}, ОТ ДЛИНЫ ВОЛНЫ ВОЗБУЖДАЮЩЕГО СВЕТА

Л. Селлеши, Т. Сереньи, К. Санка

С помощью фосфороскопа и синхронного усилителя исследованы спектры люминесценции двухвалентного марганца в магний-метафосфатных стеклах для 4-х концентраций активатора при комнатной температуре и 100 °К при разных длинах волн возбуждающего света. Спекры излученя существенно отличаются друг от друга. Эти результаты, повидимому, подтверждают микрогетерогенное строение этих стекол.