THE PHOTOLUMINESCENCE OF Mn^{2+} IONS IN MAGNESIUM BROMIDE WITH SOME BIVALENT CATIONS IMPURITIES

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1. INTRODUCTION

Emission and excitation spectra of Mn^{2+} ions in $MgBr_2 6H_2O$ basis as well as the influence of additional impurity ions : Zn^{2+}, Cd^{2+} and Pb^{2+} on its photoluminescence properties have been investigated. The following phosphors of: type A — $MgBr_2$: Mn; type B — $MgBr_2$: Zn, Mn; type C — $MgBr_2$: Cd, Mn; type D — $MgBr_2$: Pb, Mn have been synthetized.

Polycrystalline samples were prepared by crystallization process from the corresponding aqueous solutions of salts: $MgBr_2 6H_2O$, $MnCl_2 4H_2O$, $ZnCl_2$, $CdCl_2 H_2O$ and $Pb(CH_3COO)_2 3H_2O$. The value and the concentration ratio were varied for each pair of impurity ions in order to obtain a variety of luminescence centers.

The emission and excitation spectra were observed with an Aminco-Bowman spectrophotofluorimeter at the room temperature (293 K) and at the liquid nitrogen temperature (77 K).

2. RESULTS

The emission spectrum of the phosphor of type A has one band only with maximum at 670 nm. The position of this band does not depend on concentration of Mn^{2+} ions that might vary in a wide range (optimum is at 30 at% approximatively), Fig. 1.1.

In the emission spectrum of the phosphor of type B the bands having maximum at 670 nm, 600 nm and 546 nm can eppear, depending on concentration of Mn^{2+} and Zn^{2+} ions. We investigated the samples having constatnt concentration of Mn^{2+} ions of 12 at% while the concentration of Zn^{2+} ions ranged from 0,1 to 40 at%. For concentrations of Zn^{2+} ions: up to 4 at% in the spectrum all the three mentioned bands are present; for concentrations within 4 — 14 at% the two bands, at 600 nm and at 546 nm are evident; for concentrations ranging from 14 to 40 at% only one band is present at 546 nm (Fig. 2) [1].

In the emission spectrum of the phosphor of type C during the crystallization process the samples emitting a band with maximum at 670 nm and another one having a maximum at 600 nm can be observed depending on the quantitative ratio of components in the $MgBr_2$ — $MnCl_2$ — $CdCl_2$ system. The emission at 600 nm characterizes the plycrystalline samples having the concentration of Mn^{2+} constant at 12 at% while the concentration of Cd^{2+} ions varied from 10 to 18 at% (Fig. 1., 2.).

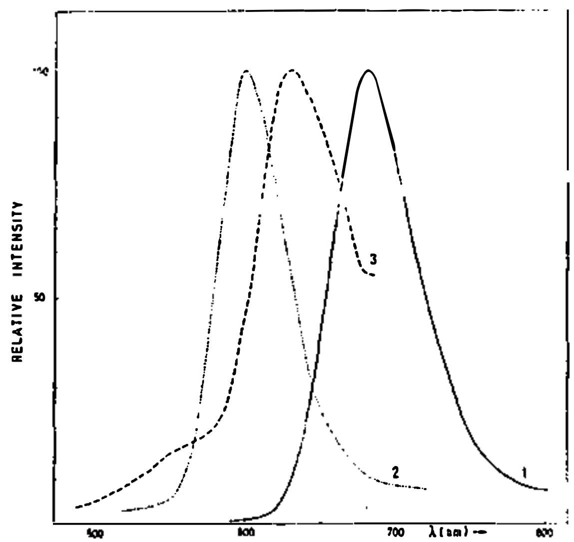

Fig. 1. Emission spectra of the phosphors A, C and D at 77 K. The concentration of impurity ions are: 1. 30 at% Mn^{2+} (A); 2. 12 at% Cd^{2+}, 12 at% Mn^{2+} (C); 3. 5 at% Pb^{2+} 1 at% Mn^{2+} (D).

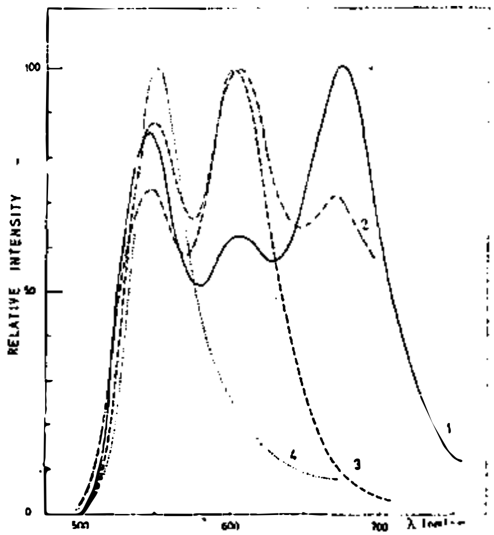

Fig. 2. Emission bands of the phosphor B at 77 K. Concentrations are: 12 at% Mn^{2+} and 1 at% Zn^{2+} (1) 2 at% Zn^{2+} (2); 12 at% Zn^{2+} (3); 16 at% Zn^{2+} (4).

In the emission spectrum of the phosphor of type D the bands that belong to transitions in Pb^{2+} and Mn^{2+} ions are present. With the Mn^{2+} ions the bands with maxima at 670 nm, 630 nm and 540 nm are associated. The appearance and intensity of them depends on the value and concentration ratio of Pb^{2+} and Mn^{2+} impurity ions. An intensive emission at 630 nm (Fig. 1., 3.) is characteristic for samples with concentrations of Mn^{2+} ions ranging from 2 to 15 at% and concentration of Pb^{2+} ions not less then the concentration of Mn^{2+} ions. At higher concentrations of Mn^{2+} ions a band at 670 nm appears as well, while at lower concentrations a weak emission in the green part of spectrum at 540 nm approximatively is evident.

The excitation spectrum for the 670 nm band is characteristic for Mn^{2+} ion in octahedral symmetry (Table 1.). The excitation spectra for emission bands at 600 nm and 546 nm are identical and characteristic for the Mn^{2+} ion in the tetrahedral symmetry (Fig. 3, 1). These spectra were interpreted by the Orgel's weak field matrix for quartet levels of d^5 configuration [3, 4]. The Racah parameters B and C together with the crystal field strenght 10 Dq were determined as well as the deviations of experimentaly obtained positions of excitation bands from expected ones (Table 1.). The excitation spectrum for the emission band at 630 nm is given on the Fig. 3.3. and for the band at 540 nm on the Fig. 3.2. for the phosphor of the type D.

Table 1. Experimental positions of bands in the excitation spectra of crystallophosphors A, B and C and their relative errors with respect to the expected values, obtained from the energy diagrams for the d^5 configuration

Mn^{2+} ion in octahedral coordination $B = 529\ cm^{-1}$, $C = 3468\ cm^{-1}$; $10\ Dq = 6500\ cm^{-1}$			Mn^{2+} ion in tetrahedral and quasi-tetrahedral coordination $B = 543\ cm^{-1}$, $C = 3460\ cm^{-1}$ $10\ Dq = 3600\ cm^{-1}$		
Energy levels	Experimental positions of bands in cm^{-1} (nm)	Relative errors in %	Energy levels	Experimental positions of bands in cm^{-1} (nm)	Relative errors in %
$^4T_{1g}(G)$	18800 (532)	1,5	$^4T_1(G)$	21190 (472)	0,6
$^4T_{2g}(G)$	21830 (458)	0,9	$^4T_2(G)$	21980 (455)	1,3
$^4E_g\,^4A_{1g}(G)$	23260 (430)	–	$^4E_1\,^4A_1(G)$	22730 (440)	–
$^4T_{2g}(D)$	26460 (378)	1,6	$^4T_2(D)$	25510 (392)	1,6
$^4E_g(D)$	27400 (365)	–	$^4E\,(D)$	26520 (377)	–
$^4T_{1g}(P)$	29590 (338)	8,0	$^4T_1(P)$	27250 (367)	8,3
$^4A_{2g}(F)$	35090 (285)	5,9	$^4A_2(F)$	34130 (293)	5,2
$^4T_{1g}(F)$	37310 (268)	1,5	$^4T_1(F)$	34480 (290)	5,2
$^4T_{2g}(F)$	38910 (257)	3,3	$^4T_2(F)$	35710 (280)	4,1

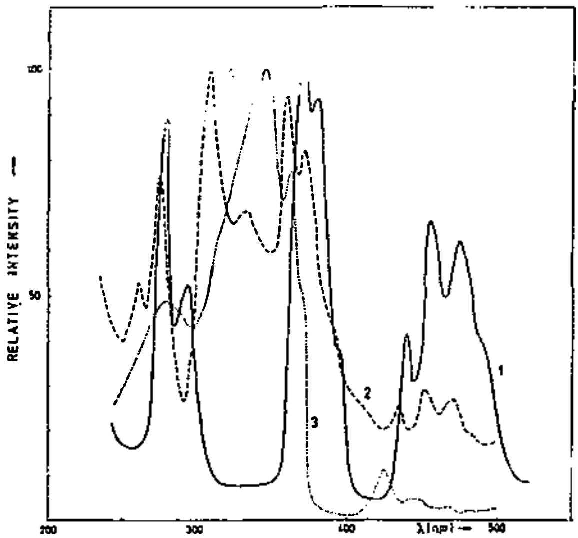

Fig. 3. Excitation spectra at 77 K for emission bands at: 546 nm and 600 nm of the phosphors B and C (1); 540 nm (2) and 630 nm (3) for the phosphor D.

3. DISCUSSION AND CONCLUSION

The synthetized phosphors of type A, B, C and D are solid solutions in which isomorphic Mg^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} ionic exchange and the formation of a variety of impurity aggregates may take place. The crystal structure of the basic lattice of $MgBr_2 6H_2O$ consists of two separate groups of $Mg(H_2O)_6Hal_2$, where six molecules of water octahedrally surround the Mg^{2+} ion, while the halogenide ions join the upper and lower side of this octahedron [2]. In the phosphor A the Mn^{2+} ion is in the octahedral coordination; this is the consequence of the isomorphic exchange with Mg^{2+} ion. In phosphors of type B, C and D, depending on type of impurity ions and their relative concentrations compared to Mn^{2+} ions, the Mn^{2+} ion can exist in the lattice $MgBr_2 6H_2O$ in octahedral $Mn(H_2O)_6^{2+}$ (emission at 670 nm), tetrahedral and quazitetrahedral coordination $MnHal_4^{2-}$ as well as in a complex with a simpler symmetry (emission bands at 600 nm, 546 nm and 630 nm). The emission at 600 nm is attributed to transitions between the lowest excited $^4T_1$ (^4G) and the ground $^6A_1$ (^6S) states of Mn^{2+} ion in tetrahedral, while the band at 546 nm in deformed tetrahedral (quasitetrahedral) coordination. The origin of the band at 630 nm is the same as of the band at 600 nm and can be associated with the presence of lead impurity [5]. In the $MgBr_2$: Pb, Mn system the emission band at 630 nm can be attributed to transitions between the lowest perturbed quartet and ground levels of Mn^{2+} ions while the origin of the band at 540 nm is the same as the origin of the 540 nm band in $MgBr_2$: Zn, Mn phosphors.

If we compare the excitation spectra for the emission bands of Mn^{2+} ions at 540 nm and 630 nm of the phosphor of type D with the excitation spectrum of the Mn^{2+} ion emission at 546 nm and 600 nm phosphors B and C (Fig. 3), it is obvious that the band at 310 nm for emission at 540 nm and the same shoulder like band for emission at 630 nm, do not belong to Mn^{2+} ions, are present in the spectra of the phosphor D. They are attributed to transitions in Pb^{2+} ions. This means that Pb^{2+} ions, present in the samples $MgBr_2$: Pb, Mn, play the role of sensitizer and that a mutual interaction exists between Pb^{2+} and Mn^{2+} ions, having the energy transfer as a result. As the transitions in the longer wave part of the spectrum of Mn^{2+}, with maxima ranging from 430 to 490 nm (Fig. 3, 2 and 2), are of low intensity, it can be concluded that quenching of a part of excitation energy of Mn^{2+} ions by migration of energy to Pb^{2+} ions occurs along with the emission relaxation.

REFERENCES

1. R. Mićić, B. Drašković, Phys. Stat. Sol. (b) 128, 489 (1985).
2. K. Andress, J. Gundermann, Z. Krist. 87a, 345 (1934).
3. J. Orgel, J. Chem. Phys. 23, 1822 (1955).
4. K. Bingham, S. Parke, Chem. Glasses 6, 224 (1965).
5. R. Mićić, B. Drašković, Žn. Prikl. Spek. 45, 1 (1986).