

## Decay kinetics of $Mn^{2+}$ ion luminescence in Mg, Zn, and Cd silicates and fluorides

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*Received May 11, 2004*

Kinetic properties of  $Mn^{2+}$  ions in Mg, Zn, Cd silicates and fluorides with red color luminescence have been studied. The luminescence decay time is increased when  $LaF_3$  or  $LiF$ ,  $CdF_2$ ,  $YF_3$  are introduced in the  $ZnF_2$  or  $MgF_2$  samples. The decay time and the kinetic curve shapes of the silicate phosphors are modified due to co-activation ( $MgF_2$ ,  $CaF_2$ ,  $BaF_2$  and  $SrF_2$ ). This is associated with the energy transfer through the conduction zone from the electron traps to the activator ion.

Исследованы кинетические свойства ионов  $Mn^{2+}$  в силикатах и фторидах Mg, Zn и Cd с люминесценцией красного цвета. Время затухания люминесценции увеличивается при введении  $LaF_3$  или  $LiF$ ,  $CdF_2$ ,  $YF_3$  в образцы  $ZnF_2$  или  $MgF_2$ . Формы кривых затухания силикатных кристаллофосфоров изменяются при соактивации ( $MgF_2$ ,  $CaF_2$ ,  $BaF_2$  и  $SrF_2$ ). Это связано с переносом энергии через зону проводимости от электронных ловушек к ионам активатора.

Luminophors of various emission colors activated with  $Mn^{2+}$  ion show moderate or long decay times (10 to 90 ms) up to the initial brightness decrease by a factor of  $e$  ( $\tau_e$ ). The emission color of that activator (the  ${}^4T_{1g}({}^4G) \rightarrow {}^6A_{1g}({}^6S)$  transition) depends on the symmetry and coordination number (c.n.) of ligands [1]. In this work, considered are crystal luminophors emitting in the orange-red region (570–640 nm) and having the c.n. 6. Among the fluoride luminophors with such parameters, it is  $MgF_2 \cdot ZnF_2 : Mn^{2+}$  ("Lotos") that is used industrially, while silicate and fluorosilicate crystal luminophors have a limited use [1–3]. The search for red emission crystal luminophors for such fields as radars, plasma PDP structures and electroluminescent plates and investigation of properties of such luminophors are actual. In [4, 5], we have described the spectral properties of luminophors on the basis of  $ZnF_2$ ,  $MgF_2$ ,  $KMgF_3$ ,  $Mg_2SiO_4$ ,  $2Mg_2SiO_4 \cdot MgF_2$ , and  $Mg_2SiO_4 \cdot MgF_2$ , and calculated the crystal field parameters

for those luminophors. The aim of this work is to study the luminescence decay kinetics of  $Mn^{2+}$  ions in red emission crystal luminophors in the presence of co-activators and the interrelation thereof with the structure and spectral properties at c.n. 6.

As co-activators, selected are fluorides of the I–III Groups elements capable of substitution for the matrix cations or of entering the lattice with electron trap formation. The main task is to improve the luminescence characteristics, in particular, to increase the afterglow duration. The co-activators were introduced into luminophors on the basis of  $ZnF_2$ ,  $MgF_2$ ,  $KMgF_3$ , and  $CdSiO_3$ . The  $Mn^{2+}$  ion luminescence decay parameters were also studied in binary compounds  $2Mg_2SiO_4 \cdot MgF_2$ , and  $Mg_2SiO_4 \cdot MgF_2$ . The  $Mn^{2+}$  ion afterglow kinetics is defined mainly by the relatively long lifetime of the excited  ${}^4T_{1g}({}^4G)$  level ( $10^{-2}$  to  $10^{-3}$  s). This is due to the fact that it is just the multiplicity-forbidden  $d-d$  transitions with the oscillator strength less than  $1 \cdot 10^{-6}$  that cor-

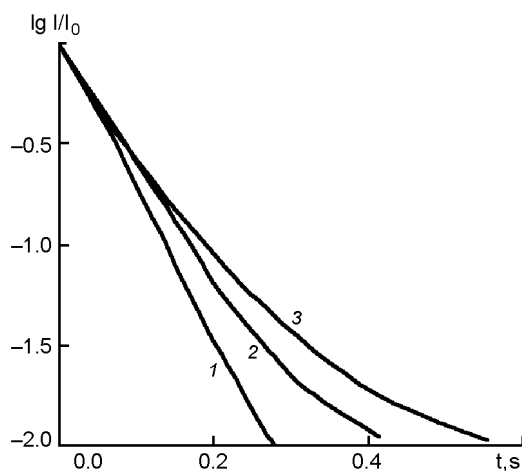


Fig. 1.  $\text{Mn}^{2+}$  luminescence in samples  $\text{ZnF}_2(\text{C})$  (1),  $\text{ZnF}_2(\text{LaF}_3)(\text{C})$  (2),  $\text{ZnF}_2(\text{LaF}_3)(\text{UV})$  (3). In all the figures: C, cathodic excitation; X, X-ray excitation; UV, ultra-violet excitation.

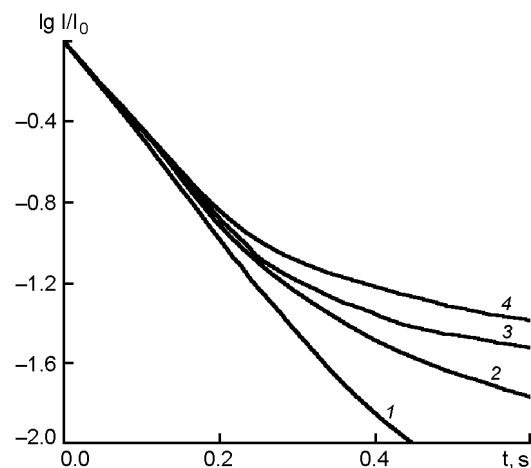


Fig. 2.  $\text{Mn}^{2+}$  luminescence decay in samples  $\text{MgF}_2$  (1) (UV),  $\text{MgF}_2(\text{C})$  (2),  $\text{MgF}_2(\text{CdF}_2)(\text{C})$  (3),  $\text{KMgF}_3(\text{C})$  (4).

respond to the  $\text{Mn}^{2+}$  ion absorption bands in the visible region. The exclusions are released in part in a crystal containing defects and local symmetry distortions. Nevertheless, the contribution to afterglow kinetics from the excited level lifetime is the limiting one. The structure defectness and the ability to store energy temporarily is another factor of importance that is of a particular significance when the vacuum ultraviolet (VUV), cathodic, and X-ray excitation sources are used. The presence of co-activators results in generation of additional traps that change substantially the decay curve shape [1, 2].

The  $\text{MgF}_2$  luminophors were prepared using the procedure described in [4]. Magnesium and co-activator carbonates were introduced into manganese fluoride solution in hydrofluoric acid at 80 to 90°C, and then the solution was evaporated. The initial blend was obtained also using solid phase technique, by blending the initial fluorides (analytical or chemical purity grade). The blend was washed, dried at 120–200°C and calcined with 1–2 %  $\text{NH}_4\text{F}$  additive at 900–1050°C for 1–2 hours. To synthesize silicate and fluorosilicate luminophors,  $\text{CdO}$ ,  $\text{MgCO}_3$ , and  $\text{SiO}_2$  (special purity of analytical purity grade) were used, the chromophore impurity concentrations were less than  $1 \cdot 10^{-3}$  mass. %. The activator was introduced by impregnating the samples with  $\text{Mn}(\text{CH}_3\text{COO})_2$  solution. The blend was triturated with ethanol, dried, and calcined in a tubular furnace at 1050–1200°C in air or in

reductive medium (closed carbon crucible with carbon) for 1–2 h.

The temperature schedules were selected according to the phase diagram and were 50 or 100°C lower than the melting points of corresponding compositions. The phase homogeneity of the luminophors was checked by XPA method using a DRON-3M unit ( $\text{Cu K}_\alpha$  emission, Ni filter). The cathodoluminescence properties were studied in a divisible electron-beam tube of IO 40.0035 or IO 40.0007 type provided with an extension for measuring the afterglow duration. For kinetic measurements under UV excitation, an AYG laser with neodymium was used ( $\lambda_{exc} = 266$  nm,  $t_{pulse} = 8$  to 15 ns) and an SDL-1 spectrometer. The X-ray luminescence (XRL) kinetics was studied using a home-made setup including an URS-55a apparatus.

$\text{ZnF}_2$  and  $\text{MgF}_2$  belong to rutile structure type, while  $\text{KMgF}_3$ , to perovskite one [6]. In all the three compounds,  $\text{Mn}^{2+}$  ions may substitute  $\text{Zn}^{2+}$  or  $\text{Mg}^{2+}$  ones close thereto in size and form centers with octahedral surrounding consisting of  $\text{F}^-$  ions. Among the fluoride luminophors, it is  $\text{ZnF}_2:\text{Mn}$  (Sample 2) that exhibits the highest brightness, however, its afterglow duration is relatively short for this luminophor class. Under prolonged action of high-energy excitations, broad absorption bands in the visible region appear in the samples. Those answer to manganese ions in the oxidation states exceeding 2+. The Samples 7–9 ( $\text{MgF}_2:\text{Mn}$ ) show a low brightness. To improve the luminescence characteristics, co-activators were introduced into the samples.

Among those, it is just  $\text{LaF}_3$  in  $\text{ZnF}_2$  (Samples 3 and 5) and  $\text{CdF}_2$ ,  $\text{YF}_3$ , and  $\text{LiF}$  in  $\text{MgF}_2$  (Samples 10–12) that provide the highest efficiency. Those favor formation of electron traps in the forbidden band and changes in the  $\text{Mn}^{2+}$  luminescence decay curve shape in the luminophors.

In Figs. 1 and 2, presented are some kinetic curves corresponding to various co-activators and excitation means. The decay curves in fluoride luminophors depend on several factors. Those are nearly exponential within a wide time interval only for pure  $\text{ZnF}_2$  and  $\text{MgF}_2$  under UV excitation (curves 1). In  $\text{KMgF}_3:\text{Mn}$ , there is a considerable hyperbolic component at the final emission stages (Table 1, Samples 14, 15). At energy values exceeding 3.8 or 4 eV, the spectra of the samples show the charge transfer bands. The excitation in those bands results in an effective ionization of the activator and in energy transfer to the traps through the conduction band. The afterglow duration is increased (Samples 10–13), in particular, at the final stages, and attain several seconds required to decrease the brightness down to 1 % of the initial one.

The  $\text{Mn}^{2+}$  luminescence decay curve shape in fluorosilicate and silicate crystal luminophors is nearer to the exponential one essentially for all the compositions (Fig. 3). The afterglow duration increase

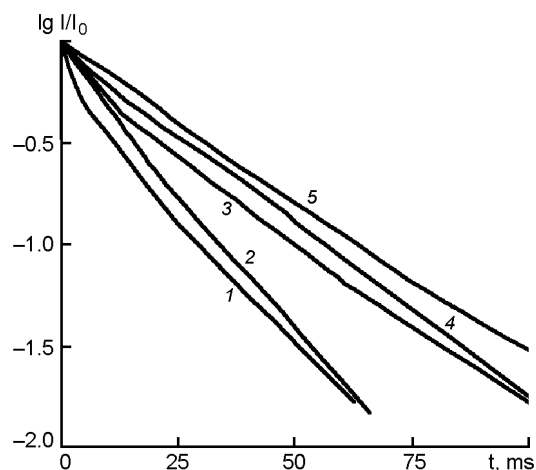


Fig. 3.  $\text{Mn}^{2+}$  luminescence decay in samples:  $\text{Mg}_2\text{SiO}_4$  (C) (1),  $2\text{Mg}_2\text{SiO}_4\cdot\text{MgF}_2$  (UV) (2),  $2\text{Mg}_2\text{SiO}_4\cdot\text{MgF}_2$  (C) (3),  $\text{Mg}_2\text{SiO}_4\cdot\text{MgF}_2$  (UV) (4),  $\text{CdSiO}_3$  (C) (5).

under cathodic and X-ray excitation (by 15 to 20 % as compared to the case of UV excitation) occurs more uniformly within the whole time range. It is associated also with the activation of the energy transfer processes through the conduction band involving the traps at the excitation energy exceeding 4 or 4.5 eV. The shortest afterglow is characteristic of  $\text{Mg}_2\text{SiO}_4:\text{Mn}^{2+}$  (curve 1). The same sample shows low emission brightness (Table 2, Sample 1). The

Table 1. Luminescence characteristics of Mg and Zn fluorides at optimum concentrations of the activator

No.	Matrix	Co-activator	Conc. % (mass)		Excitation	$\lambda$ , nm	I, a.u.	Afterglow, ms		
			Mn	Coactiv.				<i>e</i>	10 %	1 %, s
1	"Lotus"		1.2		C	590	100	75	210	0,44
2	$\text{ZnF}_2$		1.2		C	590	140	60	145	0.28
3	$\text{ZnF}_2$	$\text{LaF}_3$	1	0.5	C	590	128	73	175	0.42
4	$\text{ZnF}_2$	$\text{YF}_3$	1	1	C	595	120	55	140	0.30
5	$\text{ZnF}_2$	$\text{LaF}_3$	1	0.5	X	590	124	70	186	0.56
6	$\text{ZnF}_2$	$\text{YF}_3$	1	1	X	595	125	54	148	0.47
7	$\text{MgF}_2$		1.2		UV	595	56	95	214	0.44
8	$\text{MgF}_2$		1.2		C	595	58	98	230	0.49
9	$\text{MgF}_2$		1.2		X	595	61	102	246	0.79
10	$\text{MgF}_2$	$\text{CdF}_2$	1.2	2	C	595	93	100	235	1.20
11	$\text{MgF}_2$	$\text{YF}_3$	1.2	3	C	595	86	101	257	2.40
12	$\text{MgF}_2$	$\text{LiF}$	1.2	2	X	595	56	95	214	3.20
13	$\text{MgF}_2$	$\text{NaF}$	1.2	2	X	595	59	98	240	2.80
14	$\text{KMgF}_3$		1.2		UV	595	52	79	234	0.65
15	$\text{KMgF}_3$		1.2		X	595	58	98	254	3.40

Table 2. Luminescence characteristics of Mg and Cd silicates and fluorosilicates at optimum concentrations of the activator

No.	Matrix	Co-activator	Conc. % (mass)		Excitation	$\lambda$ , nm	I, a.u.	Afterglow, ms		
			Mn	Coactiv.				E	10 %	1 %
1	Mg <sub>2</sub> SiO <sub>4</sub>		0.4		C	640	28	9	28	86
2	2Mg <sub>2</sub> SiO <sub>4</sub> ·MgF <sub>2</sub>		0,4		UV	625	93	16	50	110
3	2Mg <sub>2</sub> SiO <sub>4</sub> ·MgF <sub>2</sub>		0.4		C	625	95	18	57	126
4	2Mg <sub>2</sub> SiO <sub>4</sub> ·MgF <sub>2</sub>		0.4		X	625	98	19	62	132
5	Mg <sub>2</sub> SiO <sub>4</sub> ·MgF <sub>2</sub>		0.6		UV	620	100	22	60	115
6	Mg <sub>2</sub> SiO <sub>4</sub> ·MgF <sub>2</sub>		0.6		C	620	100	25	65	136
7	Mg <sub>2</sub> SiO <sub>4</sub> ·MgF <sub>2</sub>		0.6		X	620	100	25	68	142
8	CdSiO <sub>3</sub>		0.6		UV	590	90	25	73	
9	CdSiO <sub>3</sub>	MgF <sub>2</sub>	0.6	2	UV	590	78	26	82	
10	CdSiO <sub>3</sub>	CaF <sub>2</sub>	0.6	2	UV	590	80	20	58	
11	CdSiO <sub>3</sub>	BaF <sub>2</sub>	0.6	4	UV	590	70	18	55	
12	CdSiO <sub>3</sub>	SrF <sub>2</sub>	0.6	4	UV	590	72	18	56	

presence of fluoride ions in the matrix structure makes it possible to improve substantially the luminescence characteristics of those luminophors (Samples 2–7). The decay curve shape is exponential within a wide time range (curves 3, 4). For CdSiO<sub>3</sub>:Mn<sup>2+</sup>, it is possible to increase the afterglow time by using MgF<sub>2</sub> as a co-activator (Table 2, Sample 9).

The luminophors based on magnesium fluorosilicates and cadmium silicates can be used in manufacturing of grid-free display screens. The most bright samples are of promise for PDP structures, since those are excited well and retain the stability both under UV rays and under higher energy excitations. The fluoride crystal luminophors

with longest decay times can be used in radar screens.

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## Кінетика затухання люмінесценції іонів Mn<sup>2+</sup> у силікатах і фторидах Mg, Zn і Cd

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Вивчено оптичні властивості іонів Mn<sup>2+</sup> у силікатах і фторидах Mg, Zn і Cd з люмінесценцією червоного кольору. Термін затухання люмінесценції зростає за умов введення LaF<sub>3</sub> або LiF, CdF<sub>2</sub>, YF<sub>3</sub> у зразки ZnF<sub>2</sub> або MgF<sub>2</sub>. Форми кривих затухання силікатних кристаллофосфорів змінюються за умов соактивації (MgF<sub>2</sub>, CaF<sub>2</sub>, BaF<sub>2</sub> і SrF<sub>2</sub>). Це пов'язано з перенесенням енергії через зону провідності від електронних пасток до іонів активатора.