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Thermoluminescence of ZnF_2:Mn

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The thermoluminescence of undoped and Mn-doped ZnF_2 was investigated at the dopant concentration of 1.5 % mole Mn after γ - ray irradiation at room temperature. The glow curve from undoped ZnF_2 presents two peaks centered at 86°C and 273°C, while the ZnF_2:Mn presents two peaks located at higher temperatures (325°C and 365°C), whose height ratio is modified with dose. The dose responses and fading process were also examined. The radiative thermostimulated recombination was found to be of the second kinetic order based on the geometric factor calculation. The trap parameters were obtained as activation energy and frequency factor.

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1. Introduction

Thermoluminescence (TL) is emission of light that is observed, when irradiated materials are heated (glow curve). The emission arises from thermally activated recombination of trapped charges at luminescence centers. The temperature at which TL emission occurs reflects the energetic depth of the traps. The traps are characterized by certain parameters that include trap depth (E) and frequency factor (s).

The kinetics of the processes giving rise of TL glow peaks have been discussed in literature based on the models involving "first order" kinetics (i.e. on the assumption that mobile electrons thermally liberated from centers in which they have been trapped all recombine with positive holes at luminescence centers, giving rise to the emission of light) and "second order" kinetics (when the mobile electrons may either recombine at luminescence centers, as in the first order case, or may be retrapped in unchanged trapping centers) [1-5]. In the study of relatively deep trapping states for various solid state materials, a detailed analysis of TL glow curves is indispensable. In order to obtain E and s parameters, one needs to fit the glow curve data to above mentioned TL models.

The TL properties of pure and doped alkaline earth fluorides have been intensely investigated [6-16], but very few results have been published on the TL of fluorides from secondary subgroup of the periodic table [17-20].

In this paper the thermoluminescence properties of ZnF_2 doped with manganese are investigated.

2. Experimental

The samples of ZnF_2:Mn containing 1.5% mole Mn were prepared from reagent grade chemicals accordingly to the methods reported in the literature [21]. The activated zinc fluoride was sintered at 900°C for 2h and then it was cooled slowly to room temperature. Undoped samples of ZnF_2 were prepared for comparison**.** When the material ground to a size of 250 μm, a white powder was obtained.

TL measurements (integral luminescence) were carried out using a commercial LTM Fimel apparatus (Harshaw) at the heating rate of q = 5°C/sec.

The irradiation was performed with a ^{137}Cs GAMMATOR M-38-2 installation (USA) at a dose rate of 0.4 KGy/h.

3. Results and discussion

The TL glow curve of undoped ZnF_2, produced under the same preparation procedure as doped one, exhibits two well-defined glow peaks situated at 86°C and 275°C (fig.1). The 86°C TL peak occurs at temperature close to the room temperature and therefore is probably related to the shallow trap recombination. The 275°C TL peak was tentatively attributed to the recombination between the F-centers and holes centers.

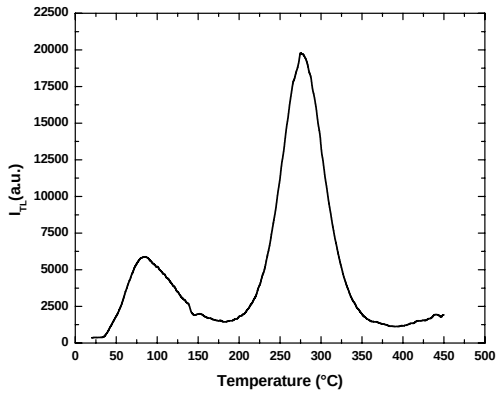

Fig. 1. TL glow curve of undoped ZnF_2 sample (65 Gy).

For the determination of the trap depth from experimental glow curve it was necessary to establish first the kinetic order of the thermostimulated recombination of the opposite charge carriers. For this purpose, the geometrical factor (μ_g) method has been used [22]. According to this method, the μ_g parameter can be obtained by the relation:

$$\mu_g = \frac{T_2 - T_m}{T_2 - T_1} \quad (1)$$

where: T_m – the temperature of maximum emission intensity; T_1 and T_2 – the temperatures for which the intensity reaches half of its maximum value at the ascending and descending part of the peak, respectively.

For the prominent peak in figure 1, T_1 = 521K, T_2 = 584K and T_m = 548K. In this way we obtained a value of μ_g = 0.57 which very close to 0.52 for the first peak, the typical values for the second order processes. The obtained values of the trap depth calculated by various methods are listed in table 1.

Table 1. The trap depth for undoped ZnF_2.

Method and references	E (eV)	
	first peak	second peak
Kelly – Laubitz [23]	0.36	1.20
Chen [24]	0.53	1.44
Lushchik [25]	0.44	1.43
Grossweiner modified by Chen [1]	0.74	1.52
Mean value	0.52	1.40

The frequency factor (s) based on second – order kinetics was calculated from the relation [25]:

$$s = q \cdot K \cdot u^2 \cdot e^{\frac{u}{E}} \quad (2)$$

where

$$u = \frac{E}{KT_m} \quad (3)$$

In the above equation K is Boltzmann constants, q is the rate of heating and T_m is glow peak temperature.

The following frequency factors were calculated: $s_1 = 1.83\times10^{13}$ s^{-1} for the first peak, and $s_2 = 6.07\times10^{8}$ s^{-1} for the second peak.

The glow curve of ZnF_2:Mn (1.5% mole Mn) is shown in figure 2. As can be seen the presence of Mn in the host crystal modifies the glow curve structure. It presents also two peaks which are located at 325°C and 365°C (shoulder), but the ratio of the two peak heights is modified with the increasing dose. The overlapped peaks were separated to single glow peaks by a thermal bleaching method [26].

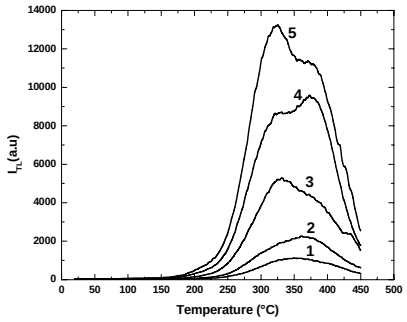

Fig. 2. Tl glow curves for ZnF_2:Mn (1.5% mole Mn) samples irradiated at different doses: (1) 2.2 Gy; (2) 8.8 Gy; (3) 17.6 Gy; (4) 32.5 Gy; (5) 65 Gy.

The apparent kinetics relative to the two peaks is also of second order (μ_g = 0.55 for the first peak and 0.52 for the second one). The activation energies corresponding to these glow peaks are shown in Table 2.

Table 2. The trap depth for ZnF_2:Mn (1.5 mole% Mn).

Method and references	E (eV)	
	first peak	second peak
Kelly – Laubitz [23]	0.72	1.26
Chen [24]	0.98	1.39
Lushchik [25]	0.87	1.54
Grossweiner modified by Chen [1]	1.19	1.28
Mean value	0.94	1.36

Using the mean values of trap depth in table 2, the following frequency factors were calculated: $s_1 = 5.62\text{x}10^8$ s^{-1} for the first peak; $s_2 = 1.22\text{x}10^8$ s^{-1} for the second peak was also determined.

A number of interesting studies are available on the effect of the environment of manganese ion in various inorganic systems. In Mn^{2+}-doped MgF_2 it was suggested that the dopants do not change the nature of the traps already existing in the host matrix giving only different luminescence efficiencies [27]. However, in the present case the Mn-doping the distribution of the traps is completely changed, i.e. new and more stable traps appear as was shown by the TL glow curves. It was observed that in gamma- irradiated Mn^{2+}-doped MgO samples the EPR (Electron Paramagnetic Resonance) signal associated to the Mn^{2+} ion is stable up to 100 kGy irradiation dose [28]. It shows that the Mn^{2+} ions do not trap holes, i.e. the mobile hole centers, either V_K centers or any secondary hole species, to produce stable hole centers. Therefore, it is very likely in Mn^{2+}-doped that Mn^{2+}-ion induces the formation of deeper levels of the energy distribution of the trapping centers.

For ZnF_2:Mn the relationship TL signal (first peak) – exposure dose is linear at small doses as can be seen from figure 3. Above this exposure dose, saturation effects become apparent for both peaks (Fig. 4). The linearity range suggests that the energy storage occurs in the close

vicinity of luminescence centre, within an "aggregate", where the recombination probabilities depend linearly on the concentration of radiation-induced defects, and the interaction of defects carrying opposite charge makes them to behave as one centre. However, at higher doses, above about 100 Gy damage effects can appear which reduce the TL signal of ZnF_2:Mn (Fig. 4).

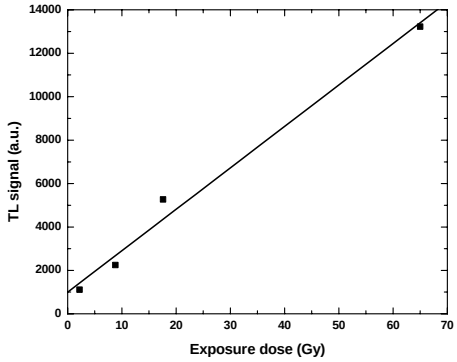

Fig. 3. TL signal as a function of exposure dose for ZnF_2:Mn (1.5% mole Mn).

In order to quantitatively describe and interpret the dose response, it is convenient to define the linearity index, f(D) [29, 30]:

$$f(D) = \frac{I(D)/D}{I(D_0)/D_0}$$

where I(D) is the TL signal measured after dose D, and D_0 represents a "low" reference dose, at which ZnF_2:Mn response is linear (65 Gy).

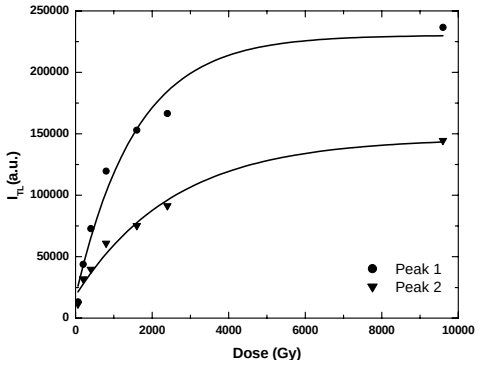

Fig. 4. Dose response of the TL peaks of ZnF_2:Mn (1.5 % mole Mn) exposed to γ rays

The linearity index f(D) as a function of dose is presented in figure 5. It is clear that the dose response of ZnF_2:Mn at doses starting around 100 Gy is purely sublinear.

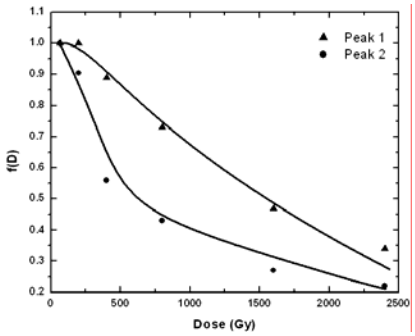

Fig. 5. Plot of linearity index of ZnF_2:Mn exposed to various γ - rays doses.

When the incident γ or X – radiation energy is in the region between 20 and 100 KeV, the photoelectric interaction is predominant and it depends on the third power of the atomic number; so in that region of energies there is an over – response in the case of materials having a high atomic number. ZnF_2:Mn (1.5 mole % Mn) has a very high effective atomic number Z_{eff} = 22.3 as it was calculated using Müller formula [31]. A suitable combination of metal filters is therefore necessary to make its response photon energy independent.

The fading characteristics at room temperature of the ZnF_2:Mn powder under gamma radiation effects was 1.2 % during the first 96 hours and it becomes negligible after this time. This small value is due to the deeper levels of the energy distribution of the trapping centers.

Permanent efforts have to be made to improve our understanding of the influence of various parameters on the characteristics of thermoluminescence systems.

4. Conclusions

The study on the thermoluminescence of ZnF_2:Mn pointed out the presence of two peaks on the high temperature range, which demonstrate the deep depth of the traps. The same assessment may be stated on the basis of activation energy estimation. The geometric factor values calculated for both doping states (with and without Mn) of the samples have demonstrated that the recombination process kinetics is of the second order. The mean values of activation energy are E_1 = 0.94 eV and E_2 = 1.36 eV for first and second peak, respectively. The corresponding frequency factors are $s_1 = 5.62\times10^8$ s^{-1} for the first peak, and $s_2 = 1.22\times10^8$ s^{-1} for the second peak. A straight line dependence of TL signal intensity on the exposure dose was obtained only on the low dose range up to about 100 Gy. The deviation from the linearity for the doses exceeding 1.5 kGy is attributed to the saturation effect. The sublinearity in the dependence of linearity factor on dose was obtained for a large dose range (up to 2.5 kGy).

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