Luminescence of F_2-centers in MgF_2 Crystals During Electron Beam Pulse

S.S Vilchinskaya, V.I. Korepanov.

Tomsk Polytechnical University, Lenina 30, Tomsk, 634050, Russia, (83822) 418914, Fax: (83822) 419831, E-mail: svetvil@tpu.ru

Spectral and kinetic characteristics of pulse cathodoluminescence (PCL) of $F_2(C_{2h})$- color centers in MgF_2 crystal when excited nanosecond electron pulses in temperature range 30 – 300 K have been studied. Spectrometer with the parameters: spectral measurement region 200–1200 nm; time resolution – 7 nanoseconds; temperature range of measurements – 12.5–700 K; the duration of the nanosecond electron beam current pulse (NEB) – 2–10 nanoseconds; the electron beam current density – 0,1–1000 A/cm^2; the maximum electron energy – 400 keV.

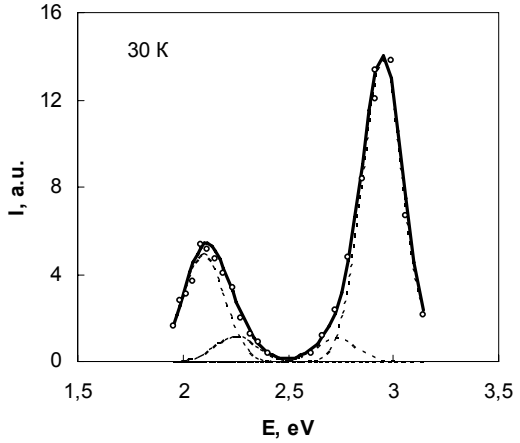

Fig. 1. The amplitude PCL spectrum of MgF_2 crystal at 30 K

At low temperatures luminescence bands of F_2 -centers contain only nanosecond decay components with the duration τ < 20 ns. The amplitude spectrum of cathodoluminescence pulse (PCL) of MgF_2 crystal at 30 K, i.e. the spectrum measured at peak intensity (in 10 nanoseconds after the termination of the NEB pulse) is presented in Fig. 1 and consists of four Gaussians. The luminescence bands 2.95 and 2.73 eV are in F_2 (C_{2h})-centers [1], and 2.1, 2.25 eV are in F_2 (C_1)-centers. Two bands of F_2 (C_1)-centers have been considered for the first time.

The volume of parameters of PCL decay kinetics of F_2 -centers in MgF_2 change at temperature above 150 K, slower decay components occur . In the region of 1.78–2.48 eV occur the most evident changes. PCL spectra at 300 K, the amplitude and the measured after 100 nanoseconds ones, are presented in Fig. 2 (curves 1 and 3 respectively). The slow luminescence component spectrum (curve 3) consists of 2.95 eV and 2.25 eV bands. The maximum and the half width of the 2.25 eV band of both components coincide. This fact as well as the reduction of the light sum of the slow component of 2.25 eV band at temperatures of $F_2(C_1)$-centers annealing testifies its belongings to $F_2(C_1)$-centers. For the same reasons the slow luminescence decay component in 2.95 eV band belongs to $F_2(C_{2h})$-centers.

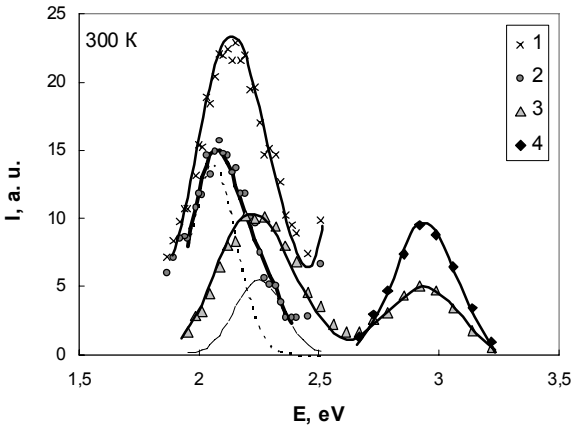

Fig. 2. PCL spectra of MgF_2 crystal at 300 K. 1 – amplitude spectrum; 3 – measured after 100 nanoseconds; 2 – difference of spectra 1 and 3 (nanosecond component); 4 – amplitude spectrum is reduced by a factor of 60 times. Dotted curves – the result of spectrum 2 decomposition

Thus, at room temperature the 2.25 eV luminescence band of $F_2(C_1)$-centers being excited by electron pulse consists of the fast, τ <20 nanoseconds, and slow, τ = 500 nanosecond components, with the intensity ratio 1:2, and the 2.1 eV band contains only nanosecond luminescence decay component. At low temperatures both of the luminescence bands of these centers contain only nanosecond decay components. It refers also to $F_2(C_{2h})$-centers luminescence, which at 300 K consists of the fast (τ <20 nanoseconds) and slow (τ = 1.0 ms) luminescence decay components with the intensity ratio 100:1, and at 30 K only the fast one.

In contrast to CPL the photo stimulated luminescence spectrum contains only nanosecond luminescence decay components at all the temperatures in the range of 30–300 K.

The temperature dependence of luminescence intensity 2.95 eV ($F_2(C_{2h})$ -centers) at the maximum in the range of 30–300 K are presented in Fig. 3. A number of specific features was found on this curve. The first one is the luminescence intensity of $F_2(C_{2h})$ -centers at temperatures above 60 K increases by the

order. The amplitude intensity volume depends on the number of NEB pulses made in the time range 1–2 min at small range of temperatures 50–70 K. The intensity is the maximum after the first pulse (curve 1) and reduces after the excitation by the subsequent pulses (curves 2, 3) with the saturation up to the certain level (Fig.3).

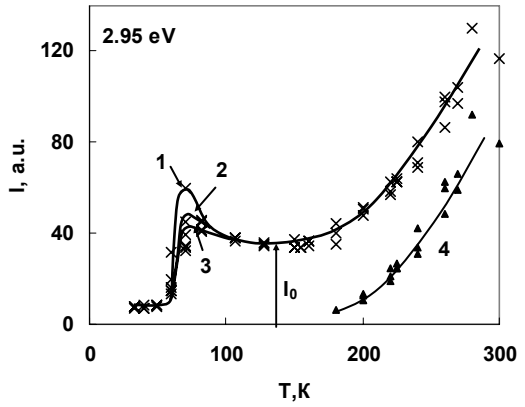

Fig. 3. The temperature dependence of the PCL of $F_2(C_{2h})$ -centers intensity. 1, 2, 3 – according to the results of the first, second and third NBE pulses, respectively. 4 – difference I-I_0

As there is the delocalization of self-trapped exciton's nuclei (STE) with H-centers at 60 K the increase of luminescence intensity of $F_2(C_{2h}$)-centers in this temperature range should be connected with these particles. Since at low temperatures the number of H-centers made during electron pulse is much less, than no STE and besides none of the hopping diffusion at 60 K efficiency of the F-centers generation was observed the mechanism of $F_2(C_{2h})$-centers excitation by means of mobile electron excitation is the most evident.

The STE movement occurs as a result of their delocalization at 60 K by hopping diffusion. Therefore, the diffusion mechanism of STE interaction with F_2-centers at 60 K occurs at T>60 and the luminescence kinetics of F_2 –centers should have a long luminescence stage. However the glow kinetics of $F_2(C_{2h})$-centers is constant at temperature 30–50 K. It means that the center excitation mechanism in this temperature interval is also constant but the number of excitation particles found in the zone of interaction with the F_2-centers during the electron pulsing changes. It means that the excitation process can be carried out by the mobile electron excitation up to their localization. This electron excitation can be localized in the units of the lattice at T < 60 K. This is the reason why most of them fail to reach the luminescence centers. The run up to self – trapping of the particles increases and the probability of their trapping in the zone of interaction with color centers increases. Luminescence intensity reduction at fixed temperature in the interval 50–70 K after each of NEB pulses as compared to the previous is supposed to be connected with interaction of H-centers with $F_2(C_{2h})$-centers which come to be mobile at these temperatures. The other feature of PCL temperature dependence of $F_2(C_{2h})$-centers is that the luminescence intensity increases again by a factor of ~ 2 – 3 with crystal temperature increasing from 150 to 300 K. In this temperature interval the slow luminescence decay component occurs in luminescence decay kinetics and it grows while temperature increases (τ = 1 ms at 300 K). This component's contribution to the light sum grows when temperature increases and makes 50 % at 300 K (the intensity contribution being 1%).

The ΔI increase at temperatures above 150 K is presented by curve 4 in Fig.3, obtained as a result of the difference I – I_0, where I_0 – PCL intensity in the linear region at 120–150 K. Since after the luminescence duration remains constant the ΔI is proportional to the light sum $S = I \cdot \tau_{имп}$.

The results obtained suggest that ΔI correlates with the temperature dependence of $F_2(C_{2h})$-centers destruction efficiency. The activation energy calculated from the relation/dependence ln $\Delta I = f(1/T)$ at linear region 150–350 K equal to 0.12 eV and coincide with stimulated destruction activation energy value of $F_2(C_{2h})$-centers. Hence, the PCL intensity increase at temperature above 150 K can be connected with the formation processes of the divided pairs of Frenkel defects. The $F_2(C_{2h})$-centers luminescence at high temperatures can be excited by H-centers rather effectively. The measured temperature dependences of the decay constant τ, intensity I, the light sum $S = I \cdot \tau$ for the slow component of the luminescence band decay are presented in Fig.4.

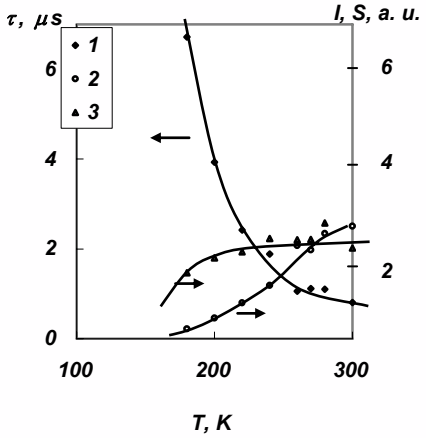

Fig. 4. Temperature dependences τ (1), I (2), S (3) of slow luminescence decay component in 2.95 eV band in MgF_2 crystal

Temperature dependences of the decay constant τ, intensity I, and the light sum S for 2.25 eV band are presented in Fig.5. From the results obtained it follows that the intensity of slow luminescence decay component in 2.25 eV band at T > 150 K grows , the decay time con-

stant of this luminescence decreases, and the light sum $S = I\tau$ increases, remains constant at $T > 200$ K, and decreases in annealing temperature range of $F_2(C_1)$- centers (350 K). In the range of 150–350 K the dependence $\tau = f(T)$ of slow luminescence decay components in 2.25 eV band and 2.95 eV band is described by Arrenius law $1/\tau = \nu_0 \exp(-E_a/\kappa T)$, with activation energies equal to $E_a = 0.11$ eV for 2.25 eV band and $E_a = 0.087$ eV for 2.95 eV band.

PCL results from recombination processes, therefore luminescence decay kinetics can be limited by reactions of charge carriers recombination or internal transitions in the center of a luminescence after its excitation. The first case corresponds to bimolecular mechanism. Therefore, despite the fact that luminescence decay kinetics can be of the first order, i. e. described by the $I = I_0 \cdot \exp(-t/\tau)$ exponent, the amplitude value of luminescence intensity I_0 should be proportional to a square of exciting pulses intensity (energy of electron beam per pulse), and τ – inversary proportional to the intensity of exciting pulses.

The second variant corresponds to the luminescence decay kinetics of the first order which is always described by the exponent when τ does not depend on excitation intensity , and I_0 linearly depends on excitation density. Our study of decay kinetics and luminescence intensity dependence on excitation density has shown that luminescence decay kinetics does not vary at excitation by NEB pulses which differ in their energies in 10 times per pulse. Thus, luminescence decay kinetics by slow PCL components of F_2-centers is defined by processes within centers.

The experimental results obtained indicate that the dependences S(T), I(T) and τ(T) of slow luminescence decay components of $F_2(C_1)$- and $F_2(C_{2h})$ - centers differ in values of luminescence decay kinetics parameters, activation energies of reduction process τ, absolute values I and S. However, the dependences at $T > 150$ K are similar, therefore the origin of the luminescence of both centers at pulse electron excitation is supposed to be the same. As there are no slow components at photo stimulated luminescence, then only some specific features of this kind of luminescence centers excitation can cause their occurrence in PCL.

Temperature dependence of the light sum of this luminescence component does not correlate with temperature dependences of F, H-pairs generation and decay efficiency of super equilibrium F_2-centers by H-centers. Therefore, the occurrence of a slow component is supposed to be caused by electron-hole recombination processes. PCL saturation is, apparently, determined by the limits of amount of particles – participants of the recombination process.

The slow luminescence component duration is great enough ($\tau = 0.5–1.0 \cdot 10^{-6}$ c) and is determined by transitions, hence, the luminescence center appears to be in a relaxed excited state after pulse electron excitation, the transition from which is prohibited by rules of selection. Triplet states are just this kind of states in F_2 -centers. Radiation can occur as a result of recombination radiation conversion $T \rightarrow S_0$, or by transition in the excited singlet (S_1) state and the subsequent irradiating transition in a basic (S_0) state ($T \rightarrow S_1 \rightarrow S_0$). The first variant is realized due to partial removal of a ban, for example, because of the spin-orbital that causes high excited singlet state to be added to the triplet level. The second variant requires to overcome the thermal barrier corresponding to power gap between the singlet (S_1) and triplet (T) states of a molecule.

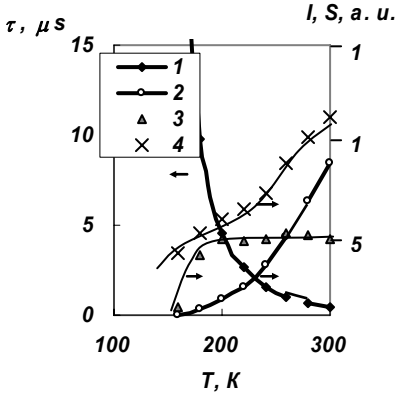

Fig. 5. Temperature dependences τ(1), I(2), S(3) of slow luminescence decay components in 2.25 eV band in MgF_2 crystal. 4 – total intensity of fast and slow decay components

Luminescence spectra of fast and slow PCL components of F_2-centers coincide. The light sum of 2.25 eV band is constant (there is no suppression of luminescence) at temperature 200–300 K. After the termination of nanosecond electron beam excitation, the triplet level becomes populated, temperature dependence $\tau_{\text{triplet 1}}$ is described by Arrenius law. These facts allow us to conclude that the second variant ($T \rightarrow S_1 \rightarrow S_0$) of radiation transition is realized in MgF_2 and it is possible to make the following expression for the probability of transition from triplet state:

$$1/\tau_{\text{triplet}} = 1/\tau_R + 1/\tau_{T \rightarrow S1} = 1/\tau_R + \nu_0 \cdot \exp(-E_a/\kappa T),$$

where, τ_R – radiation life time of F_2-center in a triplet state, that defines/determines the probability of $T \rightarrow S_0$ conversion; $1/\tau_{T \rightarrow S1}$ – the probability of $T \rightarrow S_2$ conversion. Thus, calculated from temperature dependences τ values E_a (0.08 eV and 0.11 eV) are equal to difference of T and S_1 levels for F_2 (C_1)- and F_2 (C_{2h})-centers respectively. As calculations and experimental results [2] show, the energy gap between singlet and triplet states of F_2-centers in ionic crystals lays within the limits of 0.06–0.57 eV (in KCl from the experiment – 0.06 eV). That is, the volumes of the energy gap between singlet and triplet states determined for F_2 (C_1) – and F_2 (C_{2h})-centers in MgF_2 keep within this range.

Thus, the study of the results of PCL of the irradiated MgF_2 crystals suggests that two equal mechanisms of color center luminescence excitation caused by their interaction with primary defects in this material after NEB are realized: by electron excitation and by H-centers. Electron excitation participates in luminescence/glow excitation at all the temperatures in the range 30–300 K. The efficiency of this process at low temperature is determined by the run up to the localization of electron excitation, and at high temperatures it is defined by the thermal stability of the center. It was found that at T >150 K $F_2(C_{2h})$ – and F_2 (C_1) - centers are excited while electron excitation is being trapped in a triplet state. To the greatest degree it is characteristic of F_2 (C_1)-centers. The H-centers participate in excitation only of nanosecond luminescence components at high temperatures (T > 170 K) when the generation efficiency of spatially divided components of Frenkel defect pairs is high.

Ionizing irradiation generates a great amount of electrons and holes in wide apertured materials which can make run at significant distances before thermaliziation and subsequent localization in regular units and the subsequent localization of a lattice or in the defect region. Therefore the most widespread mechanism of luminescence center excitation in ionic crystals after electron excitation is the recombination of charge carriers that can occur as a result of subsequent trapping of zone holes and electrons by the center or their recombination in the region near the defect. On the basis of these facts it is possible to assume that the formation of F_2 (C_1)- and F_2 (C_{2h})- centers in singlet and triplet states in MgF_2 can take place when zone holes and electrons are being subsequently trapped by the center as well. The reactions describing this process, by analogy with those for LiF [3], can be written as follows:

$$e^- + p + F_2 \rightarrow F_2^+ + e^- \rightarrow F_2(S) \rightarrow F_2(S_0) + h\nu(F_2).$$
$$e^- + p + F_2 \rightarrow F_2^+ + e^- \rightarrow F_2(T) \rightarrow F_2(S_0) + h\nu(F_2).$$

However, no accumulation of excited color center was found in MgF_2. Therefore to explain the existence of this kind of processes and the absence of charged defects accumulation processes is possible only if to assume that long electron localization or (and) holes in defects, including F_2-centers does not occur.

References

[1] Facey O.E., Sibley W.A., Phys. Rev B.-1970. V. 2, 4. – P. 1111–1116.
[2] Stownham A.M. Theory of defects in solids. – M.: the World, 1978, T.1.-569c.; T.2. – 357 c.
[3] Lisitsyna L.A., Isv. High schools. Phisics. – 1996. T. 39, 11. C. 57–75.