

capture by corresponding traps, its recombination and capture of hole by luminescence centre (creation of recombination centre), respectively; n_1, n_2, n_r, n_e, n_h are concentrations of electrons captured by corresponding traps, recombination centres, free electrons and holes, respectively; N_1, N_2, N_r are total concentrations of corresponding traps and luminescence centres, respectively.

Solution of this set of equations is time dependence of concentrations of corresponding centres. Usually in the case of gamma irradiation the crystal is considered as one great track permanently excited by radiation with intensity I_{ex} during time t . This situation can be described by the set of equations (1–5) with term $I_{ex} \cdot t$ added in the equations (4) and (5) to simulate permanent excitation.

The simplest case is excluding of the traps (2) from the recombination process. Then dose dependence of the filled traps (1) will be linear with saturation. Dependence for TL will be the same. Intensity of photoluminescence (PL) will be proportional to concentration of luminescence centres $N_r - n_r$ and will decrease with increase of the recombination centres concentration. Intensity of XL will be determined by relation of probabilities of recombination and trapping and will increase with increase of concentration of filled traps and centres of recombination. $I_{XL} = I_{ex} \cdot A_r n_r / (A_r n_r + A_2(N_2 - n_2))$. These dependences are shown in the Figure 2 in schematic form.

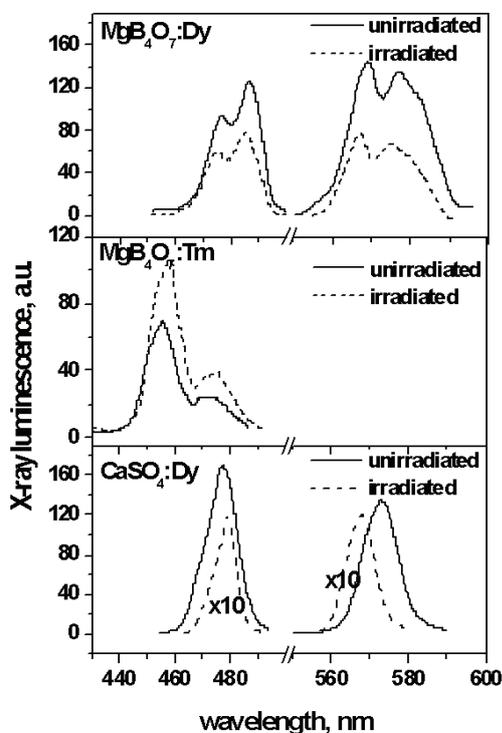


Fig. 2. X-Ray luminescence spectra of the samples

2. Experimental

The borate samples were prepared in our laboratory, $MgB_4O_7:Dy$ (TLD-580) and $LiF:Mg,Ti$ (TLD-400) were produced in Stavropol and $CaSO_4:Dy$ in Tartu. $LiF:Mg,Cu,P$ (GR-200) was commercial product.

Spectra of X-ray excited luminescence were measured with the MDR-2 monochromator. The spectra were not corrected on spectral sensitivity of the unit. Preliminary irradiation was carried out with X-rays (35kV, 20mA). Irradiation dose was about 10^4 Gy.

3. X-Ray spectra of the samples

The XL spectra (Fig. 2) are very close to TL spectra for the phosphors doped with the same rare earth (RE) ions [2].

Their shape is not changed sufficiently after irradiation, except the long wave band of $CaSO_4:Dy$. As for intensity, it decreases sufficiently (about 10 times) after irradiation for $CaSO_4:Dy$, more slightly (about 2 times) decreases for $MgB_4O_7:Dy$ and increases (about 2 times) for $MgB_4O_7:Tm$.

4. Discussion

Because of short spin lattice relaxation times, ESR signals of Dy^{3+} were not observable at room temperature, but we have enough information about its transformations, based on investigations of optical spectra split under crystal field [3]. Luminescence in visible region for Dy^{3+} ion is connected with transitions between Stark splitting components of electron levels $^4F_{9/2} - ^6H_{15/2}$ (480nm, 20000 cm^{-1}) and $^4F_{9/2} - ^6H_{13/2}$ (575 nm, 17800 cm^{-1}). For Tm^{3+} (470 nm for free ion) it is transition $^1G_4 - ^3H_6$.

In visible region unirradiated phosphors are colorless because of weak oscillator strength of f-f transitions. Intraconfiguration transition of such type are forbidden as intercombination ($\Delta S \neq 0$) and by selection rule for parity. Both the exclusions are violated by weak admixture of foreign wave functions. Notice that these mechanisms do not influence practically on positions of energetic levels but strongly effect on probabilities of transitions between them.

Transition f-d,s are situated in VUV region at wave-lengths shorter 180 nm [4] (width of forbidden gap in $CaSO_4:Dy$ is 8.2 eV), and were unavailable in present investigation. Dy^{3+} is known to transform to Dy^{2+} under intensive gamma irradiation. This transformation is accompanied by appearance of absorption in visible region and luminescence in IR region. Fig. 3 shows such absorption for $CaSO_4:Dy$ [5]. As a first approximation the absorption spectrum of irradiated $CaSO_4:Dy$ corresponds to absorption of Dy^{2+} connected with transitions 4f-5d,6s (bands 21000 and 7000 cm^{-1}) by general view and value of optical density. Naturally, the $CaSO_4:Dy$ spectrum is more blurred due to polycrystalline structure of the samples and more low symmetry of surrounding. Similarity between the details of the absorption curves obtained after different doses of irradiation are evidence of the

fact that these features are real structural elements of the spectra and can be connected with f-f transitions in Dy^{2+} ion from $^3\text{M}_{10}$ and $^5\text{S}_2$ to $^5\text{I}_{5,6,7,8}$ states (these transitions occupy spectral between Stark splitting components of electron levels $^4\text{F}_{9/2} - ^6\text{H}_{15/2}$ (480nm, 20000 cm^{-1}) and $^4\text{F}_{9/2} - ^6\text{H}_{13/2}$ (575 nm, 17800 cm^{-1}). For Tm^{3+} (470 nm for free ion) it is transition $^1\text{G}_4 - ^3\text{H}_6$. In visible region unirradiated phosphors are colorless

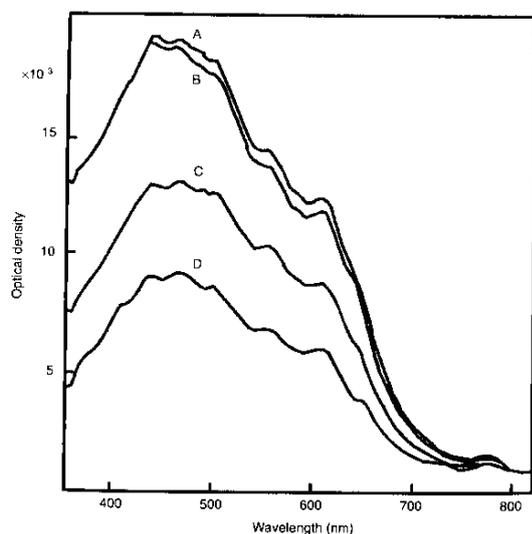


Fig. 3. Optical absorption of $\text{CaSO}_4:\text{Dy}$ irradiated with doses from 103 (D) up to 105 (A) rad

because of weak oscillator strength of f-f transitions. Intraconfiguration transition of such type are forbidden as intercombination ($\Delta S \neq 0$) and by selection rule for parity. Both the exclusions are violated by weak admixture of foreign wave functions. Notice that these mechanisms do not influence practically on positions of energetic levels but strongly effect on probabilities of transitions between them.

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Dy^{2+} ion from $^3\text{M}_{10}$ and $^5\text{S}_2$ to $^5\text{I}_{5,6,7,8}$ states (these transitions occupy spectral region between 400 and 900 nm), perturbed by crystal field. At doses more 10^5 rad saturation of the absorption connected with complete transformation of Dy^{3+} in Dy^{2+} is observed.

Nature of electron traps in all samples activated by RE is beyond question. As for hole traps, we could not find in the literature available any evidences on presence of common accepted model, even for $\text{CaSO}_4:\text{Dy}$, not to mention about $\text{MgB}_4\text{O}_7:\text{Dy}$.

Comparison of Dy^{3+} spectra in $\text{CaSO}_4:\text{Dy}$ and $\text{MgB}_4\text{O}_7:\text{Dy}$ shows that for MgB_4O_7 in energetic spectrum of Dy^{3+} the level $^4\text{F}_{9/2}$ is split, and for $\text{CaSO}_4:\text{Dy}$ it is level $^6\text{H}_{13/2}$.

Before discussing the influence of the samples structure on the spectra we have to stay on features of borate and sulphate structures. If to examine consequence of tetrahedral anionic complexes SO_4^{2-} , PO_4^{3-} , SiO_4^{4-} , BO_4^{5-} we should highlight such features as increase of the size and charge and decrease of internal bonds strengths (from 1.5 for SO_4^{2-} down to 0.75 for BO_4^{5-}) and corresponding decrease of rigidity of the structure. In particular, boron ion in borates can be not only in tetrahedral surrounding, but in trigonal too. In this case more freedom in ways of compensation of extra charge is possible.

In the case of recombination kinetics for thermoluminophors intensity of XL has to increase during the time of irradiation because of decrease of competition from filled traps and corresponding increase of holes captured by activator centers and created centers of recombination. Decrease of XL during the irradiation evidences about creation of local electron-hole complexes, which are excluded from recombination kinetics and appear in TL only. For the set of samples investigated we have both types of kinetics.

In the case of "normal" kinetics we see in XL spectra of irradiated samples the same centers but effected to influence of crystal field slightly changed because of presence in some distances of sufficient number of filled traps (electron and hole). In another case in the XL spectra of irradiated samples we see the centers which can not create complex because of their "abnormality" i.e. wrong way of local compensation. These centers were in the spectra from the very beginning but became visible only after excluding much more numerous "normal" centers. For such thermoluminophor dose dependence has to be linear with saturation because of reaching the limit of activator (saturation of dose dependence for $\text{CaSO}_4:\text{Dy}$ at 10^4 Gy corresponds to saturation of activator absorption). Many models of centers are discussed for $\text{CaSO}_4:\text{Dy}$. But, taking into account that after annealing up to 400 C only SO_3^- ESR signal remains, the model of $\text{Dy}^{3+}\text{V}_{\text{Ca}}\text{SO}_3^-$ center can be proposed. Double charged cation vacancy compensate two positive charges.

During irradiation Dy^{3+} consequently captures electron and it recombines with a hole, generating

luminescence. In opposite case free hole moving along anion rows meet double negative charged cation vacancy and localize near creating SO_4^- centre. One of positive charges becomes decompensate. But only Dy^{3+} can capture free electron because it moves along cation positions. After that the centre becomes compensated again but now it does not contain such great local charges as in previous case, so it is not so attractive for free carriers and can return to initial state only by thermally stimulated process. Different peaks of TL can be produced by this process depending on configuration of initial center or by including in the process other centers, such as O_2^{3-} (also indicated by ESR). Addition of Na^+ as compensator of valency leads to stabilization of this center, and to quenching of TL. In the case of $\text{MgB}_4\text{O}_7:\text{Dy}$ addition of Na^+ (or Li^+) as co-activator leads to increase of the TL output.

Investigation of XL sensitivity dependence for $\text{LiF}:\text{Mg,Cu,P}$ (GR-200) on X-ray irradiation does not show significant changes up to dose close to saturation

of TL output. Now we do not know how to explain such behavior.

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