FOURTH INTERNATIONAL CONFERENCE ON LUMINESCENCE DOSIMETRY
Krakow – Poland August 1974

Recombination Luminescence and Dosimetry Properties of LiF-Si and LiF-Mg,Eu Crystals

I.A.Parfianovich, B.D.Lobanov, L.P.Smolskaya,
A.I.Nepomnyashchikh, L.M.Georgievskaya, A.G.Shneider

Irkutsk State University, Irkutsk, USSR

In this paper X-ray luminescence, thermostimulated luminescence and dosimetry properties of LiF single crystals doped with the chemical combinations of silicium, magnesium and europium have been investigated. The role of silicium has been investigated in the recombination luminescence of LiF crystals because of silicium being one of the main uncontrolled impurities in lithium fluoride. The connection is found between the luminescence and silicate lithium phase formation in LiF:Si. In crystals doped with europium there form two types of luminescence centers responsible for emission bands at 500 nm and 640 nm. In LiF:Mg,Eu crystals the europium ions as a coactivator decrease the low temperature glow peak (110°C) and increase the high temperature glow peak (210°C). The operation mecanism of Eu-coactivator in LiF-Mg,Eu crystals is suggested.

1. Introduction

The experimental investigation of Lithium fluoride is considerably stimulated by its wide use in ionizing radiation dosimetry: personal, clinical, radiological and radiobiological. The advantage of LiF as compared to the other known dosimetric luminophors is marked mainly by the fact that the accumulated light sum is linear to the ionizing radiation dose on a large scale. Another important fact is that a bleached light sum is proportional to the biological equivalent of the ionizing radiation dose.

Inspite of the numerous investigations [1-15], neither nature of colour centers and luminescence centers nor luminescence mechanism was identified in most cases. Even experimental results and their interpretation by different authors do not always agree, sometimes contradicting [7-12].

Because the physical process is not clear ahd the nature of colour centers and trapping centers is not quite known dosimetric parametries of lithium fluoride are not optimal.

This paper deals with the investigations of X-ray luminescence (XL), thermoluminescence (TL) and some dosimetric characteristics of single crystals of LiF-Si and LiF-Mg,Eu carried out to find out the nature of luminescence centers and trapping centers as well as the action of the coactivator mechanism in LiF-Mg,Eu crystals.

2. Experimental

The studied crystals of LiF were grown by Stockbarger method in graphite crucible in inert atmosphere from the stapting material "chemical pure". The dopant was added in form of chemical combinations of Li_2SiF_6, Li_2SiO_3, SiO_2, MgF_2, MgO and EuF_3. Measurments were taken on plates of 10x7x1 mm^3 splitted from the single monocrystals. In case of the powders compressed tablets of the same size were used.

XL and TL spectra studies were made with the help of DMR-4 double monochromator and ФЭУ-79 and ФЭУ-39a photomultiplier. The luminescence spectra were corrected for monochromator dispersion and photomultiplier spectrum sensitivity. Optical absorption measurements were taken on a "Specord" and UR-20 recording spectrophotometres.

An X-ray apparatus УРС- 55a with Mo-target tube operated at 10 mA and 50 kV was used as an X-ray saurse. The sample temperature was measured with a copper-constantan thermo - couple and a galvanometer M-95. The glow curves were recording with linear heating rates 15°C/min.

3. Recombination Luminescence of LiF:Si Crystals.

It is known that LiF recombination luminescence spectra depends on the nature of dopants [2, 16-18]. As it has been stated before [19] dark blue luminescence intensity of LiF rises with the increase of Si concentration. A supposition has been made that the luminescence centers responsible for this emission are related to the presence of Si in LiF.

Certain authors [2,17] suppose that dark blue luminescence in LiF crystals takes place due to oxygen. XL spectra measurementes of LiF crystals doped with Li_2O shows that at room temperature in these samples an emission band at 425 nm predominated (Fig.1, curve 1). In LiF crystals doped with silicium the emission band is slightly shifted to the shorter wave length region of the spectrum and peaked at 415 nm (Fig.1, curves 2 and 3). Thus, both oxygen and silicium dopants intensify dark blue luminescence in LiF crystals.

In crystals $LiF:Li_2SiF_6$ over 0,5 wt.% or $LiF:SiO_2$ besides dark blue emission, luminescence bands peaked at 480 nm and 560 nm appear (Fig.1, curve 3 and 8). The comparison of XL spectra of Li_2SiO_3, Li_2SiF_6 and SiO_2 (Fig.1, curves 5, 4 and 7) with XL spectra of LiF crystals doped with here mentioned chemical combinations (Fig.1, curves 6, 3 and 8) showed that dark blue emission of LiF:Si crystals is close tothe the emission of Li_2SiO_3 as well as Li_2SiF_6, while the luminescence band at 560 nm is close to the emission of SiO_2.

It is interesting to note that the hydrolysis of Li_2SiF_6

$$Li_2SiF_6 + 2 H_2O \rightarrow SiO_2 + 2 LiF + 4 HF$$

causes a band at 560 nm characteristic of SiO_2 classified "chemical pure" and "extra pure". Heated Li_2CO_3 and SiO_2 form a complicated mixture of ortho- and meta-silicate of lithium that gives a dark blue band of luminescence.

Several bands of emission in X-ray luminescence of LiF:Si accounts for the facts that an activator reforms in the process of crystal growth. So according to Alexandrov and Andreyev [20] lithium silicate forms during the lithium fluoride growth as a result of interaction between SiO_2 and LiOH. This makes clear the fact that the dark blue emission will intensify when LiF is doped with SiO_2 as well as emission at 560 nm intensifies when LiF is doped Li_2SiF_6. The likeness in XL spectra of silicium chemical combinations anf LiF:Si crystals allows to make a supposition that silicium forms an activator phase in the single crystals. The following experiments prove it:

1.Studies of laser beam scattering (λ = 632 nm) in LiF:Si discovered quality relation between the scattering intensity and X-ray luminescence: the less the scattering the less XL intensity. A long heating (4 hour, 800°C) of the samples of LiF:Li_2SiF_6 3 wt.% and fast cooling to room temperature decreases considerably both XL and scattering intensities.

2. X-ray microspectroscopy analysis carried out on a MS-46 microanalyser of "Cameca" firm showed that in LiF:Li_2SiF_6 crystals impurities of 1 - 5 micron size are present the principal elements of them are ions of silicium.

LiF:Si crystals TL studies allowed to register a number of peakes. At small concentrations of the dopant the peak in the region of 140°C predominantes. The spectra of LiF:Si crystals TL are close to the emission spectra of lithium silicates.

LiF:Si crystals dosimetric characteristics studies showed that detectors on LiF:Si have good responce but lose approximately 18% of information a month and have a rather small top level for dose detection.

4. X-ray Luminescence and Termoluminescence in LiF-Mg and LiF-Mg,Eu Crystals

Emission bands in the region of 300 - 400 nm appear in LiF crystals doped with MgF_2 in XL spectra at room temperature, because the emission band at 425 nm. Dark blue emission band at 425 nm predomonates at TL of this crystals.

In LiF crystals doped with EuF_3 emission bands predominate at 500 nm and 640 nm both in XL and TL. Intensity ratio of two bands changes considerably in the process of X-ray radiation and in thermal treatment of the samples. This allows to make a conclusion that these bands are related to different Eu centers.

It's known [21] , that the dosimetric properties of LiF:Mg crystals improve response rises and fading decreases when a coactivator is premixed. But the coactivator mechanism is not clear. To study the Eu coactivator mechanism TL in crystals of LiF:Mg and LiF:Mg,Eu are investigated at over room temperatures. The experimental results are as follows.

Glow curves of LiF:MgO crystals have an intensive peak at 110°C and a low peak at 210°C (Fig.2, curve 1). For LiF:MgF_2 crystals a reverse ratio of the peak intensities are registered (Fig.2, curve 2). When the growing LiF:MgF_2 and LiF:MgO single crystals from the melt adding CdF_2 into the melt, oxigen concentration gets low [22] and the TL peak at 110°C lowers considerably while the TL peak at 210°C rises[23].

In IR-absorbtion spectra of LiF:MgO crystals an absorbtion band is registered at 3575 cm^{-1} which is 24 dependent on the complex ($Mg^{2+}OH^-v_c^-$) where v_c^- is a cation vacancy. It has turned out that in LiF:MgF_2 samples this absorbtion band has a much weaker intensity or it's absent, if CdF_2 has been added into the melt. On the basis of the studied correlation between the TL peak at 110°C and IR absorbtion band at 3575 cm^{-1} the conclusion was made that the complex of ($Mg^{2+}OH^-v_c^-$) is the trapping center responsible for the 110°C peak. According to the authors 7,8 Mg-trapping centers free of oxygen are perhaps responsible for the peak at 210°C.

Europium as a coactivator to LiF:MgF_2 lowers considerably the TL peak at 110°C while the intensity peak at 210°C grows as compared to LiF:Mg subjected to the same dose of radiation (Fig.2, curve 2). The low temperature peak of LiF:Mg,Eu of TL decreases most probably due to reduction of the concentration of ($Mg^{2+}OH^-v_c^-$) complexes because in IR absorbtion spectra, contrary to LiF:Mg crystals, absorbtion bands connected with hydroxylic group do not occur.

The 210°C dosimetric peak intensity rise may be explaned both by the emission centers concentration growth after the europium has been added and concentration growth of magnesium free of oxygen trapping centers responsible for this peak. The following experimental dates account for it:

1. Besides the dark blue luminescence emission bands peaked at 500 nm and 640 nm related to Eu ions are observed in TL

spectra of LiF:Mg,Eu crystals.

2. Absorbtion bands intensity peaked at 310 nm is considerably higher in LiF:Mg,Eu crystals than in LiF:Mg crystals though the radiation dose is equal and the concentration of Mg is the same. As it was stated [7] it depends on the free of oxygen magnesium centers.

The observed phenomena may probably be explained by the fact that europium ions bind oxygen ions to compensate an extra positive charge. Such centers are found for example in NaF:Eu crystals [25]. Thus, the essence of the action of the Eu-coactivator mechanism in LiF:Mg,Eu crystals is: 1) Emission centers consentration increases; 2) Free of oxygen magnesium trapping centers concentration rises because Eu-ions bind oxygen ions.

The LiF:Mg,Eu crystals have a higher TL output than LiF:Mg crystal: 1.8×10^{10} and 1.63×10^{10} quantum per gramm rad respectively.(The detector TL output was measured with the help of permanent action lightcomponents). Besides, while dosimetric information losses for the LiF:Mg crystal amounted 5 % a month, for the LiF:Mg,Eu crystal it was not registered.

Acknowleggments

The authors express their sincere gratitude to L.Zavyalova, who carried out X-ray microspectroscopic analysis.

REFERENCES

1. D.W.Zimmerman, I.R Cameron, Health Phys. 12, 525 (1966).
2. K.K.Shvarts, Ya.G.Kristapson, D.Yu.Lusis, A.V.Podin, Radiat. Fisika 5, 179, Riga (1967).
3. R.M.Grant, I.R.Cameron, J.Appl.Phys. 37, 3791 (1966).
4. A.V.Podin, Izv. Acad. Nauk Latv. SSR, Ser. Fiz. i Techn. Nauk, 3 125, (1967).
5. D.Yu.Lusis, Izv. Acad. Nauk Latv. SSR, Ser. Fiz. i Techn. Nauk 3, 120 (1967).
6. M.M.Shuhnovich, A.N.Gubenko, Radiat. Fizika 4, 125, Riga (1966).
7. E.W.Claffy, Phys.Stat.Sol. 22, 71 (1967).
8. C.L.Klick, E.W.Claffy, S.L.Gorbics, F.H.Attise, I.H. Shulman, I.G.Allard, J.Appl.Phys. 38, 3887 (1967).
9. T.V.Nakajima, J.Appl.Phys. 39, 4811 (1968).
10. M.R.Mayhugh, R.W.Christy, N.M.Jonson, J.Appl.Phys. 41, 2968 (1970).
11. A.N.Panova, V.V.Uglanova, T.A.Charnina, Sb. Monokristaly i technica 3, 78, Harkov (1970).
12. L.D.Miller, R.H.Bube, J.Appl.Phys. 41, 3687 (1970).
13. I.S.Dryden, B.Shuter, J.Phys.D: Appl.Phys. 6, 123 (1973).
14. T.Nakajima, J.Phys.D: Appl.Phys. 3, 300(1970).
15. A.M.Harris, I.H.Jackson, J.Phys.D: Appl. Phys. 3, 624, (1970).
16. E.Tiede, Ber.Deutsch.Chem. Ges. 72, 611 (1939).
17. A.M.Belyaev, Z.B.Perekalina, V.N.Varfolomeyeva, A.N. Panova, G.F.Dobrzansky, Crystallographiya 5, 757 (1960).
18. E.P.Alekseeva, Fisika shchelochnogaloidnikh Kristallov, p. 211, Riga (1962).
19. B.D.Lobanov, L.P.Smolskaya, A.J.Nepomnyashchikh, L.M. Georgievskaya, Izv. Akad. Nauk SSSR, Ser. Fiz. 6, 1312 (1974).
20. B.P.Aleksundrov, G.A.Andreyev, Fizika TverdogoTela 3, 2831 (1961).
21. M.Frank, W.Stolz, FestkÖrperdosimetrie ionisierender strahlung, Dresden (1969).
22. I.V.Stepanov, P.P.Feofilov, Sb. Rost Kristallov, v.1, "Nauka" M. (1957).
23. A.I.Nepomnyashchikh, I.L.Lapidis, A.A.Bobr-Sergeyev, N.E. Antipina, Izv. Akad. Nauk SSSR, Ser. Fiz. 6, 1315 (1974).
24. T.G.Stoebe, Bull. Amer. Phys. Soc. 11, 886 (1966).
25. G.D.Potapenko, B.F.Pisarenko, Optika i Spektr. 34, 800 (1973).

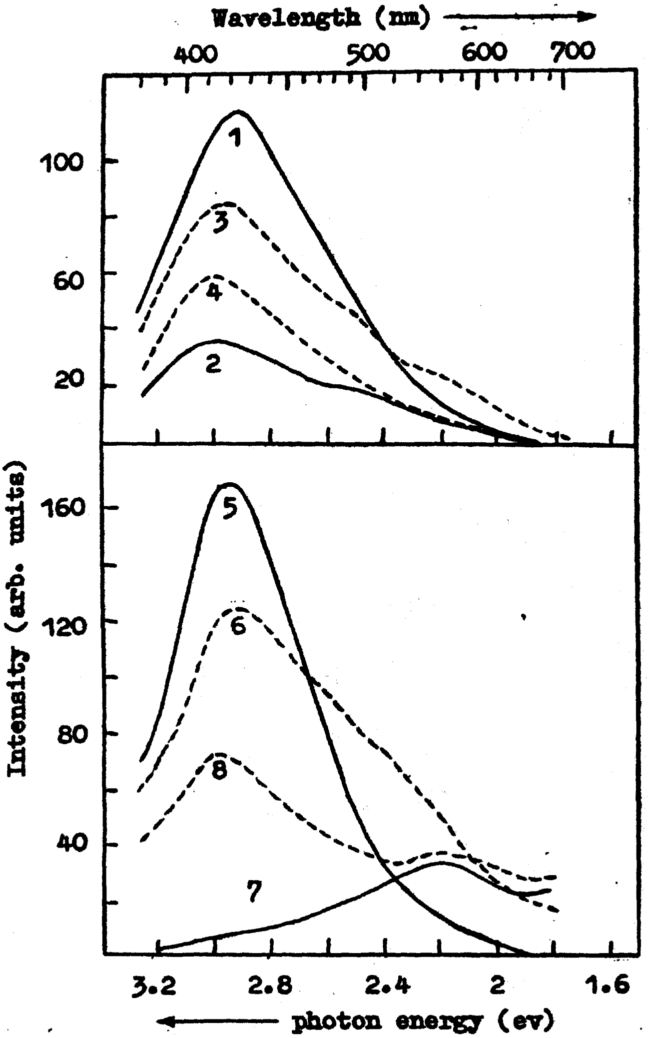

Fig.1. X-ray luminescence spectra at room temperature: 1 - of crystal LiF, doped with 0.1 wt.% Li_2O; 2 - of crystal LiF, doped with 0.1 wt.% Li_2SiF_6; 3 - of crystal LiF, doped with 3 wt.% Li_2SiF_6; 4 - of powder Li_2SiF_6; 5 - of powder Li_2SiO_3; 6 - of crystal LiF, doped with 0.3 wt.% Li_2SiO_3; 7 - of powder SiO_2 ; 8 - of crystal LiF with 0.1 wt.% SiO_2. The ordinates for curves 4,6,7 and 8 are increased four times.

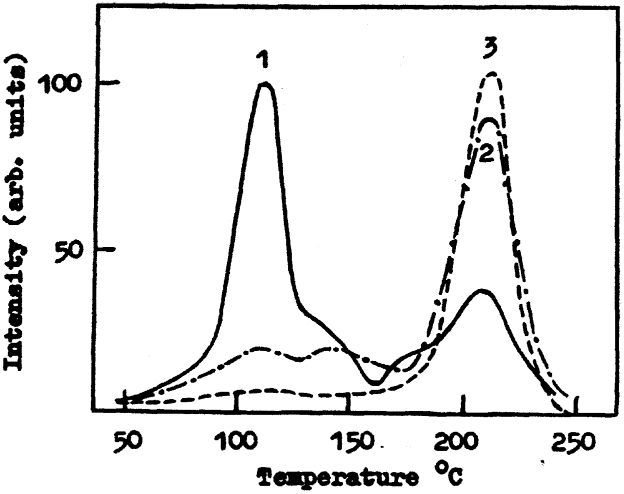

Fig.2. Glow curves of crystals: 1 - LiF-MgO; 2 - LiF-MgF_2; 3 - LiF-Mg,Eu.