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A. NEPOMNYASHCHIKH, A. SHALAEV, N. BOBINA, R. SHENDRIK, A. PAKLIN, A. MYASNIKOVA

GROWTH AND OPTICAL CHARACTERIZATION OF COPPER-DOPED LITHIUM FLUORIDE SINGLE CRYSTALS[1]

The paper discusses the results of optical and spectroscopic studies of lithium fluoride crystals doped with copper ions. The influence of copper impurities on thermoluminescent (TL) processes and the effect of magnesium concentration on the radiation sensitivity of LiF:Mg,Cu crystals are studied.

Keywords: *lithium fluoride, impurities, Czochralski method, luminescence, thermoluminescent dosimeter.*

1. Introduction

Lithium fluoride is widely used in solid state dosimetry because of similar effective atomic number (8.14) with biological tissue (7.42). This allows the bioequivalence of the radiation dose to evaluate. In addition, LiF crystals have a complex of properties that correspond well to the needs of many areas of dosimetry [1].

LiF:Mg,Cu,P (briefly LiF(MCP)) detectors have the highest sensitivity compared to other thermoluminescent dosimeters based on lithium fluoride [2]. A serious problem for practical applications of LiF(MCP) detectors is to reduce the TL sensitivity of the dosimeters after heating to a temperature of 240 °C. Such loss of phosphor sensitivity happens due to Cu^+ transition to Cu^{2+} state [3]. We assume that the presence of copper in the monovalent state will increase the sensitivity of phosphor. LiF(MCP) is available commercially in the form of hot-pressed chips and because of that have a high level chemiluminescence signal, limiting the measurement of small doses. Single crystal detectors free these drawbacks.

Detectors LiF:Mg,Ti (DTG-4) are most widely used in dosimetry. The thermoluminescence processes in LiF:Mg,Ti phosphors occur through intermediate stages, as a result the detector TL sensitivity is significantly reduced [4]. The activation by monovalent copper ions is believed to eliminate the intermediate stages due to the direct transitions during recombination. Hence, lithium fluoride single crystals with Cu^+ impurity can be used as matrix for efficient tissue-equivalent LiF:Mg,Cu detector. The TL sensitivity of this detector is expected higher than of existing models.

But the growth of $LiF:Cu^+$ single crystals is difficult because of a copper unstability in monovalent state. Copper monovalent ions actively reduce to metal or oxidized to two-valence state. We managed to grow crystals of lithium fluoride doped with copper in the monovalent state.

Results of optical properties of LiF:Mg,Cu single crystals are considered in this paper.

2. Experimental

Lithium fluoride crystals with Cu impurity were grown by the Czochralski method. Resistive nichrome heater and metal elements of thermal screens were used to avoid monovalent copper reduction. We synthesized the mixture for growth by method of solid state reaction at temperature 750 °C. CuCl was used as source of copper for crystal doping [5].

The sintered powder was charged in a platinum crucible. Crystallization was performed in argon atmosphere. The melting point of LiF is about temperature 870 °C. A rate of single crystal growth was about 5–8 mm/hour. Crystal structure likes NaCl and cuts generally in <100> plane and least often in <110> plane.

Chemical composition of mixtures and crystals were determined by atomic absorption spectrometry method. The cupper percentage in crystals was 0,0004–0,002 %. Such concentration of copper is enough for efficient thermoluminescence process [6].

Magnesium concentration in our samples was 0,05–0,2 %.

Excitation and emission spectra were obtained with a Perkin-Elmer LS55 luminescence spectrometer. The absorption spectra were measured in the visible and ultraviolet regions (200–500 nm) with a Perkin-Elmer Lamda 950UV/Vis/NIR Spectrophotometer. TL measurements were carried out with the thermoluminescent reader “STEND”. The TL reader had been designed at Irkutsk State University. All measurements were performed at room temperature.

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3. Results and discussion

Figure 1 shows photoluminescence, excitation and absorption spectra of LiF:Cu. Absorption spectrum is shown in Fig. 1, curve *3*. A wide plateau at 250–320 nm and following increasing optical density are found in the spectra.

Excitation in the 275 nm in the plateau region yields wide emission band shifted to short wavelength region. This band is detected at 360 nm. In excitation spectrum of this luminescence intense band at 200 nm is also observed, in addition to that a band at 275 nm is seen. Emission band at 360 nm under 275 nm excitation is not registered in pure LiF and appears only in the copper doped crystals. Authors of [6] also observed luminescence band in the same region and attributed these to emission of Cu^+ centers.

The glow curves of our samples LiF:Mg,Cu are shown in Fig. 2. The glow curves have been created as result of consequent linear heating up to 300 °C. The TL sensitivity of phosphor rises with increasing heating number and remains stable after several readouts (Fig. 2). The TL sensitivity of the similar phosphors [8] depends not only of concentration cooper and magnesium impurities, but depends of relative correlation of quantitative content. The authors [8] found that the TL sensitivity of samples with 0,2 % Mg concentration decreases as compared to samples with 0,1 % Mg. Such diminution is observed for LiF:Mg,Cu,P with 0,05 % Cu. However, if the thermoluminophor contains 0,005 % Cu, then opposite dependence is exhibited. In this case the TL sensitivity of samples with 0,2 % Mg increases as compared to samples with 0,1 % Mg. Also, the shape of glow curves is changes. Such dependence of TL sensitivity from relative Mg and Cu concentrations is typical for LiF:Mg,Cu,P phosphor. Another dependence is observed in our samples (Fig. 3). The single crystals LiF:Mg,Cu have been grown with different concentration of Mg (0,2 and 0,005 %). The concentration of cooper makes up 0,001 % in our samples. According to reference [8], the sensitivity of phosphors must rise with Mg concentration increases.

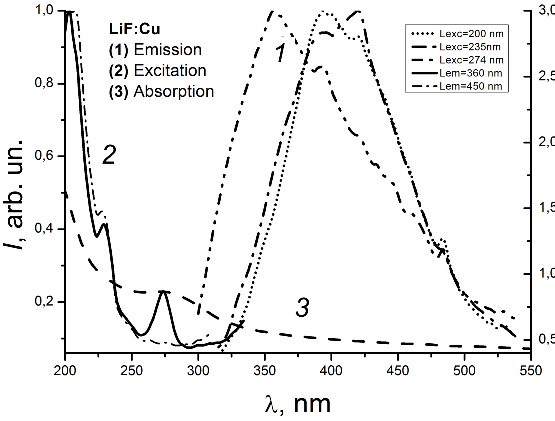

Fig. 1. Emission (*1*), exitation (*2*) and absorption (*3*) spectra of LiF crystal with Cu impurity.

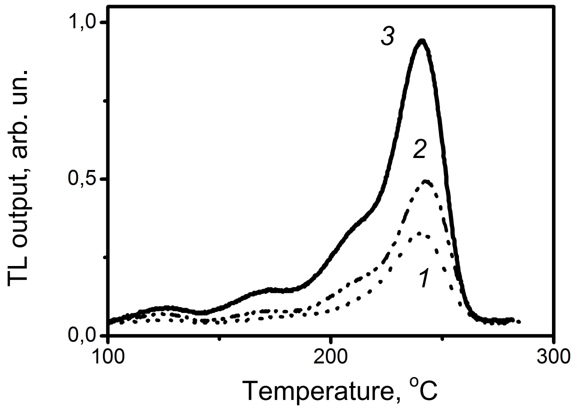

Fig. 2. The glow curves of LiF:Mg,Cu during consequent linear heating up to 300 °C; 1-st readout (*1*), 2-nd readout (*2*), 3-d readout (*3*).

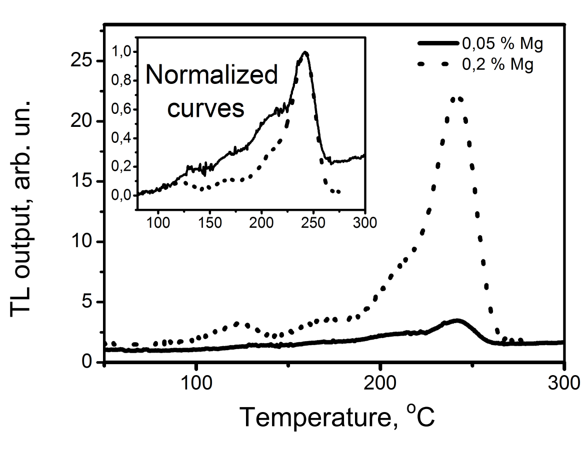

Fig. 3. The comparison of main peak intensity for LiF:Mg,Cu with different contents of Mg (0,2 and 0,05 %).

But the sensitivity LiF:Mg,Cu with 0,05 % Mg content considerably is reduced as compared with samples doped 0,2 % Mg. The glow curves structure is not changed, but relation of peak intensity varies. This is seen in Fig. 3 with normalization curves. The samples with 0,05 % Mg have been researched during several consequent heating. The TL sensitivity of LiF:Mg,Cu with 0,05 % Mg increases during consequent heating as also TL sensitivity of LiF:Mg,Cu with 0,2 % Mg. The LiF:Mg,Cu single crystals were annealing at 400 °C during 10 min. The sensitivity of the sample after annealing treatment increases and become equal in magnitude of sensitivity after consecutive heating up to 300 °C.

The LiF:Mg,Cu sensitivity is nearly equal DTG-4 sensitivity (DTG-4 is well known as single-crystal thermoluminescent detector). But it is less than LiF:Mg,Cu,P sensitivity in 15–20 time. This is because, the third impurity is absent in our phosphor. A lot of publications have been appearing to study influence third impurity (P, Si, Na) on TL process, but with a limited success. However, it is established fact, that the doping of third impurity significantly improves TL sensitivity of LiF:Mg,Cu.

The P, Si, Na, Ti can be by third impurity, at reference [4]. In what follows, we intends to increase sensitivity of the phosphor by doping by third impurity and by choice of corresponding annealing treatment.

4. Conclusion

Single crystal of LiF doped with monovalent copper impurity promises a new matrix for efficient tissue-equivalent detector LiF:Mg,Cu. The copper is instability in monovalent state. Copper monovalent ions actively reduce to metal or oxidize to two-valent state. Cu-doped LiF crystals have been grown by Czochralski method used specially made mixture. Chemical composition of mixtures and crystals were determined by atomic absorption spectrometry method. The cupper percentage in crystals was 0,0004–0,002 %.

Emission peak at 400 nm and excitation peak at 275 nm in our LiF crystals doped copper are attributable to Cu+ impurities. The monovalent copper is detected in the grown crystals by excitation band at 275 nm.

The TL sensitivity of phosphor rises with increasing heating number and remains stable after several readouts. Perhaps a thermal mode selection to improve the TL capability of phosphors. Also, doping of third impurity (such as P, Si, Na, Ti) significantly improves thermoluminescence properties of LiF:Mg,Cu.

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*Vinogradov Institute of Geochemistry SB RAS, Irkutsk, Russia
**Irkutsk State University, Faculty of Physics, Irkutsk, Russia
E-mail: alshal@igc.irk.ru

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Nepomnyashchikh Alexander Iosifovich, doctor physics and mathematics science, professor, assistant director of science;
Shalaev Alexey Aleksandrovich, candidate of physics and mathematics science, scientific associate;
Bobina Natalia Sergeevna, engineer;
Shendrik Roman Yurievich, candidate physics and mathematics science, scientific associate;
Paklin Alexey Sergeevich, engineer;
Myasnikova Alexandra Sergeevna, candidate physics and mathematics science, senior staff scientist.