Optical and Luminescence Properties of Single Crystals of LiF:Cu and LiF:Mg, Cu

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Abstract—Results from spectral studies of the optical and luminescent properties of single crystals of lithium fluoride grown using the Czochralski technique and doped with ions of copper and magnesium, are presented. The effect of heat treatment regimes and the dependence of the concentration of magnesium impurities on the sensitivity of crystals of LiF:Mg, Cu to ionizing radiation are discussed.

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INTRODUCTION

Detectors based on lithium fluoride are now widely used in the field of individual thermoluminescence dosimetry (TLD). Compared to other compositions, these detectors best satisfy all of the requirements for dose monitoring and are also tissue-equivalent [1]. Four types of detectors have so far received widespread commercial distribution: powder, tableted, polycrystalline, and monocrystalline.

It is well known that any thermoluminophor for TLD contains two active ingredients: recombination centers and centers of electron capture (the presence of electrons is determined by the introduced impurity). To meet practical requirements, impurities introduced into a luminophor must ensure:

—stable centers of capture and luminescence whose physical properties depend little on other defects (vacancies, dislocations) and different temporary impacts (e.g., heating, cooling, climatic conditions, mechanical shocks);

—the high-temperature position of the main dosimetric peak of thermally stimulated luminescence (TSL); i.e., trapping centers of considerable depth are required to ensure the long-term preservation of dosimetric information, but not at the temperatures of intracenter quenching and below the thermal emissions of the heating element;

—the simplest form of the thermoluminescence curve;

—the high intensity of the main dosimetric peak, for which the effective establishing of centers of electron capture is necessary to ensure high yields of recombination luminescence.

These requirements dictate the choice of the needed activator.

Of all thermoluminescent dosimeters based on lithium fluoride known to date, the ones most sensitive are detectors made of LiF:Mg, Cu, P [2]. Such detectors are polycrystalline compressed tablets and thus have high levels of chemiluminescence signals. This limits their use in measuring small doses. Another great practical drawback is the loss of sensitivity of detectors made of LiF:Mg, Cu, P after heating to 240°C (the standard flashing mode). This limits the number of cycles of thermoluminescence and reduces the reusability of these detectors. Some authors [3] associate the reduction in the sensitivity of LiF:Mg, Cu, P after heating to 240°C with copper's transition from the monovalent to the divalent state. The number of recombination centers is then reduced, along with detector sensitivity. However, the ultimate model for describing the energy processes that occur in LiF:Mg, Cu, P has yet to be devised.

Monocrystalline detectors have none of the drawbacks inherent to powdered and tableted samples: they produce low background signals, collect light from the volume of the detector more completely, and interact poorly with the environment. In developing single crystal detectors, however, the disadvantages inherent to them must be considered. First, there is the difficulty of growing monocrystalline luminophores with homogeneous thermoluminescent properties over the volume of a single crystal. In addition, the growing of single crystals is not possible with a number of the effective activators used in powdered and tableted detectors, as impurity ions are not incorporated into the crystal lattice properly. The possibility of powdered and tableted samples being activated by virtually any impurities thus allows the synthesis of thermoluminescent detectors with high light yields, to which single-crystal detectors (e.g., LiF:Mg, Ti) are inferior in sensitivity.

The aim of this work was to create a single-crystal thermoluminescent detector of ionizing radiation
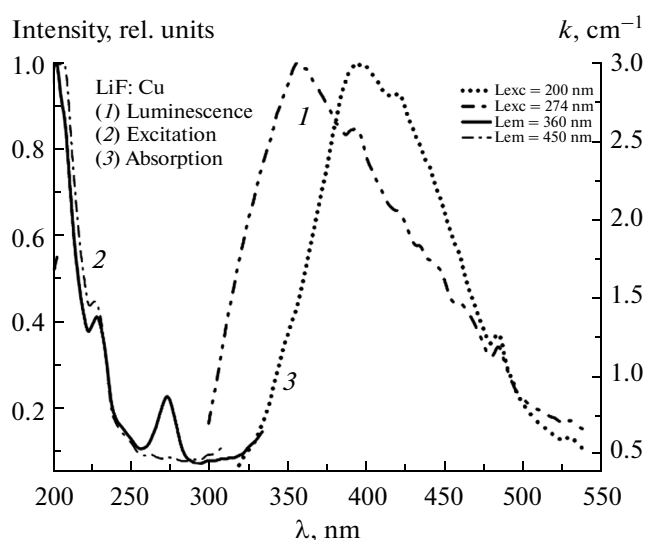
Fig. 1. Spectra of the luminescence and excitation of LiF:Cu crystals.

based on lithium fluoride with the impurities most effective for TLD.

One of the most common single crystal detectors in the world today is the TLD-100 model (LiF:Mg, Ti). In this luminophor, however, thermoluminescence passes through intermediate stages, reducing the sensitivity of such detectors [4]. We assume that due to direct recombination transitions, the activation of the crystals by cuprous ions will allow us to avoid these intermediate stages and increase the sensitivity of the thermoluminophores.

Unfortunately, there are practically no works on the optical spectroscopy of monovalent copper in the crystals of LiF today, although extensive studies of the structure and properties of this ion in other crystalline matrices (NaCl, LiCl, NaF) have been conducted [5–7]. This is because monovalent copper ions are either reduced to active metal or oxidized to the divalent state. Such instability of Cu ions in the monovalent state makes it harder to obtain crystals of LiF:Cu^+.

In [8], we sought the best options for batch preparation and selecting the conditions for growing crystals of lithium fluoride activated by monovalent copper impurities. As a result, we obtained crystals of LiF:Cu^+ and LiF:Cu, Mg. Growing crystals of LiF:Cu, Mg was the next stage in this work, after which spectral measurements of the LiF:Cu crystals convinced us that our growth conditions favored the emergence of copper in the cuprous state. This work is devoted to studying the effect copper and magnesium impurities have on the thermoluminescent properties of lithium fluoride.

EXPERIMENTAL

Single crystals of lithium fluoride were grown by the Czochralski method. Activation by copper impuri-

ties was accomplished using a specially prepared charge that contained copper chloride [8]. According to atomic absorption analysis of the samples, the copper content ranged from 0.0004 to 0.002%. As was shown in [9], such copper concentrations are sufficient for the efficient proceeding of luminescent processes in the widely used LiF: Mg, Cu, P thermoluminophores. MgF_2 was used as our magnesium activator. The concentration of magnesium in our samples varied in the range of 0.05−0.2%.

Excitation and emission spectra were obtained using a PerkinElmer LS55 fluorescent spectrofluorimeter; the absorbance of the samples was measured in the visible and ultraviolet range (200−500 nm) on a PerkinElmer Lambda 950UV/Vis/NIR spectrophotometer. The excitation, emission, and absorption spectra were recorded at room temperature.

Thermoluminescence measurements were made on the STEND laboratory setup developed at Irkutsk State University. This setup allows us to implement different profiles of heating for the heat treatment and flashing of samples.

A Sr^{60}−Y^{60} source of β-radiation was used to irradiate the samples. They were irradiated with a test dose of 0.3 Gy, and then flashed. Flashing was done at linear heating rate of 4°C/s up to 300°C. A series of consecutive flashings was performed for each sample to study changes in the sensitivity of luminophores after heating to 300°C.

Our results were processed using facility at Center for Common Use of Scientific Equipment and Devices, Irkutsk Scientific Center, Siberian Branch of the Russian Academy of Sciences.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of photoluminescense and excitation for a single crystal of LiF:Cu. In the absorption spectrum, a broad band in the region of 250−320 nm is observed with a subsequent increase in absorbance at shorter wavelengths.

A broad band in the region of 400 nm is observed in the photoluminescence spectrum at excitation of 200 nm (Fig. 1, curve *1*), which, possibly, caused by uncontrolled oxygen impurities [10]. This luminescence is observed in the non-activated crystals of lithium fluoride.

The excitation at 275 nm band (in the broad absorption band) shifts the emission band to shorter wavelengths—360 nm.

In the excitation spectrum peaks around 200 nm, 230 nm and 275 nm can be distinguished in the flashing band at 360 nm; this agrees well with the absorption spectrum. Bands at 230 nm and 275 nm appear in this excitation spectrum upon the activation of lithium fluoride by copper impurities. It is known from the literature [10] that the absorption of metal−oxygen centers is located in the region of 180−230 nm, and their
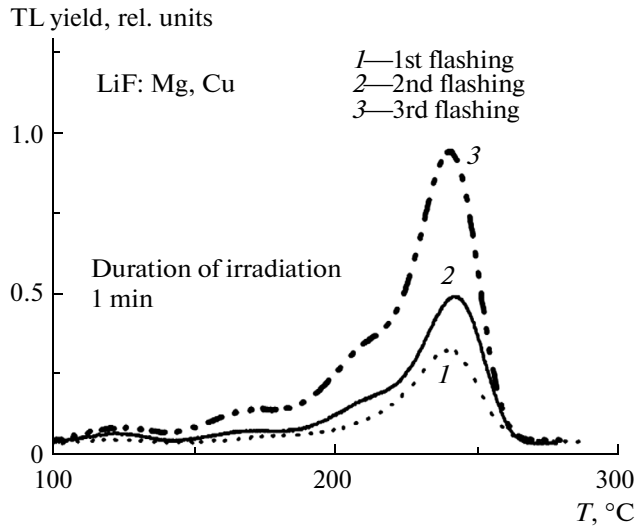
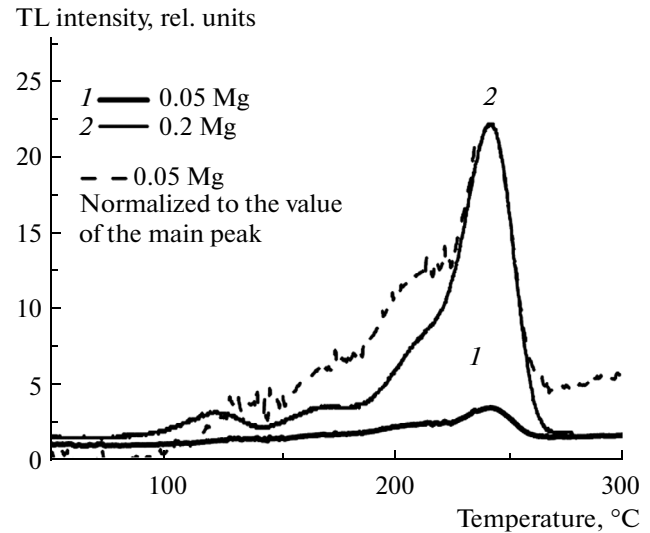**Fig. 2.** Glow curves obtained for LiF:Mg, Cu (Mg 0.2%) crystals via consecutive heating up to 300°C.

Fig. 3. Glow curves of LiF:Mg, Cu crystals with different concentrations of magnesium.

luminescence is observed in the region of 400–450 nm. The excitation band at 230 nm could thus be due to copper–oxygen centers.

The emission band at 360 nm in the photoluminescence spectrum upon the excitation with light of 275 nm appears only after the activation of lithium fluoride crystals by copper impurities. The author of [9] observed such a band in the same area and explained it as a result of the emergence of Cu^+ centers.

After analyzing the spectral data of the optical spectra, we may assume that our methods of batch preparation and growth conditions allow us to activate crystals of lithium fluoride with copper impurities in the monovalent state.

We also investigated the thermoluminescent properties of our crystals of LiF:Cu and LiF:Mg, Cu.

The glow curve of a single LiF:Cu crystal is a peak at 180°C, which is in good agreement with the literature data [11, 12]. The sensitivity of the LiF: Cu crystal remained unchanged during consecutive flashings.

The glow curves of single LiF:Mg, Cu crystals are shown in Fig. 2. It was found that after activating crystals of LiF:Cu with magnesium ions, thermoluminophore sensitivity increased along with the number of flashings and reached a constant value after 3–4 cycles of heating up to 300°C. It was also noted during thermoluminescent measurements that no loss of sensitivity is observed in crystals of LiF:Mg, Cu after heating to 240°C, as happens with LiF:Mg, Cu, P.

According to the literature [13], the sensitivity of phosphores and the shape of the curve are influenced not only by the quantitative content of impurities of copper and magnesium, but also by their mutual relationship. We grew crystals with magnesium contents of 0.2 and 0.05%. The sensitivity of LiF:Mg, Cu with a content of Mg 0.05% was considerably lower than that of the samples activated with 0.2% magnesium (Fig. 3). The form of the curve did not change upon altering the quantitative content of magnesium impurities (Fig. 3), but the ratio of the peaks did change (see the normalized glow curves in Fig. 3). The samples of LiF:Mg, Cu with 0.05% Mg were also tested for reproducibility in several flashings. Like LiF:Mg, Cu with 0.2% Mg, they showed increased sensitivity in consecutive flashings. It was found that annealing our crystals of LiF:Mg, C at 400°C for 10 minutes affected the yield of thermoluminescence. It was established that such heat treatment increased their sensitivity up to that of samples after three or four successive heatings to 300°C. The sensitivity of the samples remained stable after such temperature training.

Evaluation of the sensitivity of our LiF: Mg, Cu crystals showed that the intensity of the main peak of glow curve was comparable to those of the well-known LiF:Mg, Ti (DTG-4) single crystal detectors.

As was indicated above, heat treatments affect the sensitivity of LiF:Mg, Cu to ionizing radiation. By arranging suitable thermal treatment, we can thus obtain detectors with higher efficiencies.

CONCLUSIONS

We investigated the optical and luminescent properties of crystals of lithium fluoride grown using the Czochralski technique with impurities of copper and magnesium.

The luminescence band at 360 nm and the excitation band at 275 nm for LiF crystals with copper impurities corresponds to Cu^+, as is confirmed by the literature data. We may therefore assume that our methods of batch preparation and growth conditions allowed us

to activate the crystals of lithium fluoride using impurities of copper in the monovalent state.

The thermoluminescent properties of the resulting LiF:Cu and LiF:Mg, Cu crystals were studied. It was established that the sensitivity of the LiF:Cu samples did not change upon heating and remained constant during subsequent flashings. For crystals of LiF:Mg, Cu, however, an increase in sensitivity was observed after several linear heatings up to 300°C. There was thus no loss of sensitivity after heating to 240°C, as happens with LiF:Mg, Cu, P.

The dependence of the concentration and the mutual ratio of impurities of Mg and Cu on the sensitivity of the LiF:Mg, Cu crystals of was determined. It was established experimentally that at certain concentrations of Cu, the sensitivity of thermoluminophores declines significantly along with the content of Mg.

The light yield of our LiF:Mg, Cu crystals' thermoluminescence was comparable to those of the well-known LiF:Mg, Ti (DTG-4) monocrystalline detectors in the intensity of the thermoluminescence curve's main peak. Based on our findings, we may conclude that heat treatment (annealing at 400°C for 10 minutes or linear heating up to 300°C) does not result in lower sensitivity, as happens with conventional LiF:Mg, Cu, P powders. On the contrary, there was actually an increase in sensitivity. We should thus bear in mind that the temperature training of thermoluminophores is required to achieve stability and good reproducibility. We may therefore conclude that by choosing the optimum modes of heat treatment and considering the acceptable ratios of the concentrations of magnesium and copper impurities, we can increase the thermoluminescent efficiency of LiF:Mg, Cu crystals.

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