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CONDENSED-MATTER SPECTROSCOPY

Impurity Cu$^+$ Centers in LiF Single Crystals

A. I. Nepomnyashchikh[a], **A. A. Shalaev**[a], **A. K. Subanakov**[b], **A. S. Paklin**[a], **N. S. Bobina**[a], **A. S. Myasnikova**[a], **and R. Yu. Shendrik**[a]

[a] *Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia*
[b] *Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Sciences, Ulan-Ude, 670047 Russia*
e-mail: alshal@igc.irk.ru

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Abstract—LiF single crystals with copper impurity (0.0004–0.002%) have been grown by the Czochralski method and investigated. The luminescence, excitation, and optical absorption spectra have been recorded. The luminescence spectrum contains a band at 450 nm upon 250-nm excitation. This band is attributed to Cu$^+$ centers in the samples grown. The mechanisms of capture and recombination during thermoluminescence are considered.10.1134/S0030400X11090189

INTRODUCTION

Currently, lithium fluoride thermophosphors for dosimetry are widely used all over the world. The interest of the researchers, practitioners, and developers of these materials is due to their advantages, which include tissue-equivalence, selective sensitivity to neutrons and fission products, small size, long-term data storage, and the absence of a dose effect up to 10^{11} rad. Emphasis should be made on their wide measurement range and high sensitivity compared to ionizing-radiation detectors based on other principles.

A technology of single-crystal LiF:Mg,Ti detectors (DTG-4) was developed at the Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences [1]; these devices correspond to the standard TLD-100 detectors in all parameters. However, detectors based on LiF:Mg,Cu,P (LiF(MCP)) have become more and more popular, since they have all of the advantages of TLD-100, but are characterized by a higher (by a factor of 20) sensitivity and a wider linearity region (up to 10 Gy). The energy response of these detectors, as well as that of TLD-100, is independent of the energy of absorbed photons, and the information loss during storage is close to zero [2]. The main drawback, which hinders the practical application of LiF(MCP)-based dosimeters, is the loss of sensitivity after annealing at 240°C for 10 min (standard annealing regime). There are data in the literature that explain this sensitivity loss in LiF(MCP) phosphors by the transition of Cu$^+$ ions to the Cu^{2+} state [3]. Based on this, it was suggested that the presence of monovalent copper is necessary to provide a high thermoluminescence (TL) sensitivity of LiF(MCP). Another drawback is the high level of background signal, which limits low-dose measurements. The reason is that the commercial LiF(MCP) detectors are pressed pellets with a high level of chemiluminescence. Single-crystal detectors are free of this drawback.

The thermoluminescence processes in LiF:Mg,Ti phosphors occur through intermediate stages, as a result of which the detector sensitivity is significantly reduced [4]. The activation by monovalent copper ions is believed to eliminate the intermediate stages due to the direct transitions upon recombination. Hence, lithium fluoride single crystals with Cu$^+$ impurity can be used as matrices for efficient tissue-equivalent LiF:Mg,Cu detectors, with a light yield that exceeds that of the existing samples.

The growth of LiF:Cu$^+$ single crystals is hindered because copper ions are unstable in the monovalent state and are either readily reduced to the metallic state (Cu^0) or oxidized to the divalent state. Cu$^+$ ions can be substituted for Li$^+$ ions in the lattice without incorporating charge-compensating impurities. However, this substitution is also hindered because the ionic radius of Cu$^+$ (0.96 Å) greatly exceeds that of Li$^+$ (0.68 Å) [5], whereas divalent copper ions have a smaller ionic radius (0.72 Å), which facilitates their incorporation.

In this paper, we report results on growing LiF:Cu$^+$ single crystals and studying their optical properties.

EXPERIMENTAL

The following conditions must be provided to grow lithium fluoride single crystals activated by monovalent copper ions: (i) the presence of copper in the monovalent state in the lithium fluoride melt (T_m = 843°C), (ii) the interaction of monovalent copper with lithium fluoride in the melt, and (iii) the formation of a solid solution of lithium fluoride with monovalent copper rather than copper fluoride CuF_2.

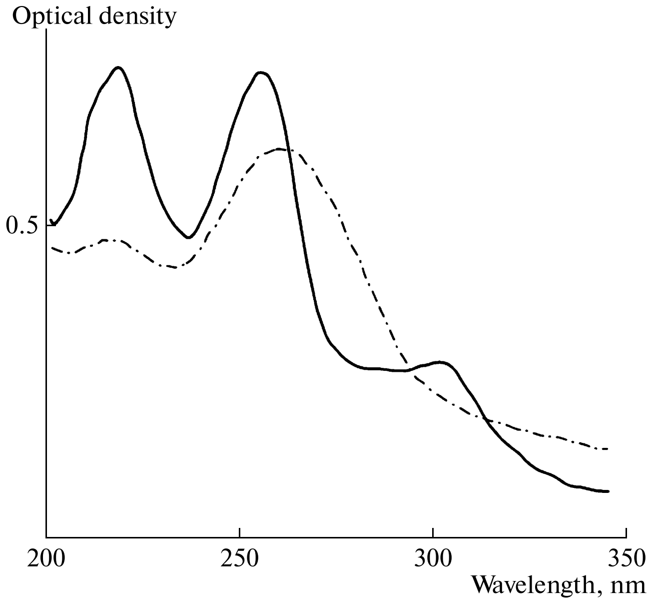

Fig. 1. Absorption spectra of LiF with Cu impurity recorded (solid line) before and (dot-dashed line) after X-ray irradiation.

The charge for growing LiF:Cu^+ single crystals can be prepared in the following ways:

(i) Preliminary sintering by solid-phase synthesis of monovalent copper in the form of chloride with lithium fluoride and the use of this raw material as a charge for growing LiF:Cu^+ single crystals.

(ii) Crystallization of LiF:Cu^+ in an inert atmosphere (argon), as a result of which metallic copper precipitates on the vessel bottom. The following reaction may occur: $2CuCl \rightarrow Cu + CuCl_2$.

(iii) Crystallization of LiF:Cu^+ in an oxidative atmosphere (fluorine), as a result of which a green film is formed on the vessel bottom and edges. The possible reactions are as follows:

$$(CF_2 - CF_2)_n\text{-} \rightarrow C_2F_4 \rightarrow 2C + 2F_2,$$

$$CuCl + F_2 \rightarrow CuF_2 + (1/2)Cl_2.$$

The above requirements can easily be satisfied if the problem of obtaining or synthesizing CuF is solved. However, an analysis of handbooks and other data in the literature casts doubt on the possibility of obtaining CuF because of its instability.

To stabilize monovalent copper in lithium fluoride, we synthesized a series of mixtures by solid-phase synthesis. These mixtures were prepared by adding 1–5% copper (CuCl and $CuF_2 \cdot H_2O$) and lithium in the form of Li_2CO_3 to LiF. The samples obtained were powders, which were heated in a muffle furnace to 750°C for 15 h in air.

The copper valence in the initial raw material was determined from ESR measurements on an RE-1360 ESR spectrometer.

LiF crystals with Cu impurity were grown by the Czochralski method. A powder synthesized was placed in a platinum crucible and heated to the melting temperature. Crystallization was performed from the melt in argon at a rate of 5–8 mm/h. To avoid copper reduction during growth, we used a resistive nichrome heater. The chemical composition of the charge and crystals was determined by atomic-absorption spectroscopy. The results of the analysis showed that the copper content in different crystals ranged from 0.0004 to 0.002%.

We investigated the luminescence and excitation spectra of the single crystals grown. Lminescence spectra were recorded using an MDR-2 monochromator (1200 lines/mm), a Hamamatsu H6780-04 photomultiplier, and an L2D2 lamp. All measurements were performed at room temperature. The samples were irradiated with a BKhV-12 X-ray tube with a palladium anode (35 kV, 10 mA) for 40 min.

RESULTS AND DISCUSSION

The Cu^+ ion has a filled $3d^{10}$ shell in the ground state and is characterized by excited $3d^94s$ and $3d^94p$ states. The absorption spectra of Cu^+ ions have been studied well for a series of alkali-earth crystals (NaF:Cu^+ [5], NaCl:Cu^+[6], LiCl:Cu^+ [7], etc.). The cubic crystal field splits $3d^94p$ into even e_g and t_{2g} states. The absorption spectra of Cu^+ ions suggested the occurrence of two bands, which involve the ${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions [5, 8]. The fundamental absorption edge of LiF crystals is in the deep vacuum ultraviolet region (14.5 eV or 85.5 nm), which allows one to observe the $3d^{10} \rightarrow 3d^94s$ absorption, which occurs at about 250 nm in most alkali-halide crystals [7].

Figure 1 shows the absorption spectrum of the LiF:Cu single crystals before and after X-ray irradiation. One can see that the intensity of the 220- and 250-nm bands decreases after the irradiation. Thus, we can relate these bands to the presence of monovalent copper, which passes to the divalent state after the irradiation.

Figure 2 presents the luminescence spectrum of the crystal upon excitation in the bands with λ_{exc} = 200 and 250 nm. It can be seen that the excitation in the 200-nm band results in a wide band peaking at 410 nm, whereas upon 250-nm excitation this band is red-shifted (peaks at 450 nm). The excitation spectrum of the LiF:Cu crystal in the 450-nm luminescence band is shown in Fig. 3. This spectrum contains pronounced peaks at 190 and 220 nm and a weak peak at 250 nm; this pattern is in good agreement with the absorption spectrum.

The 220- and 250-nm bands arise in the spectra of LiF crystals doped with copper impurity (Fig. 3). It is known [9] that the absorption of metal–oxygen cen-

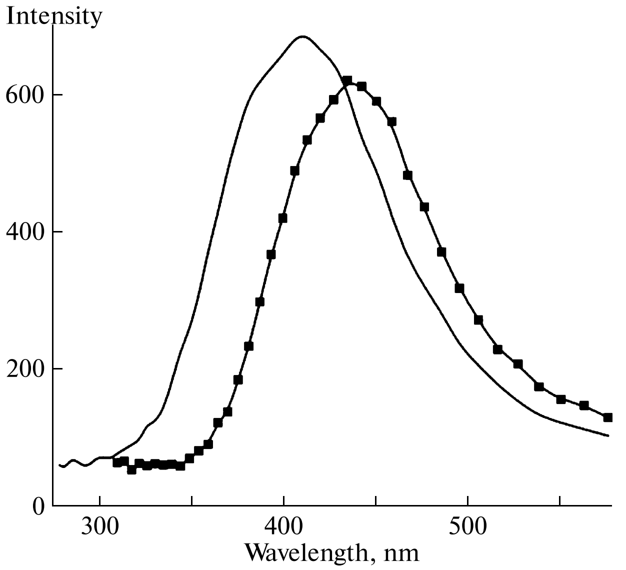

Fig. 2. Luminescence spectra of LiF crystal with Cu impurity, λ_{exc} = (solid line) 200 and (squares) 250 nm.

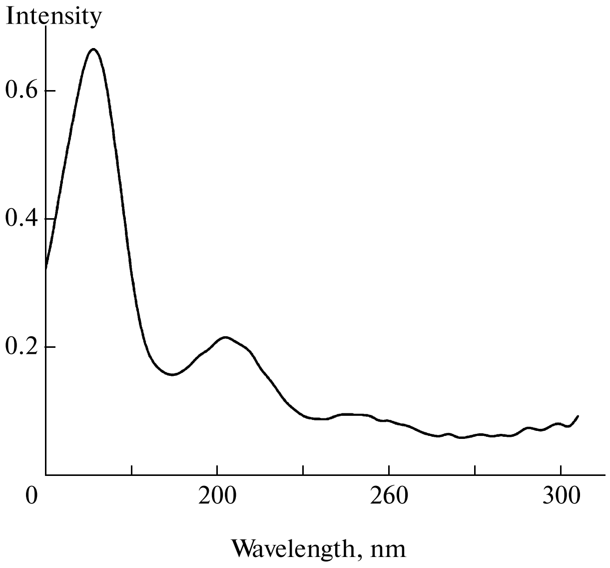

Fig. 3. Excitation spectrum of LiF with Cu impurity (λ_{em} = 450 nm).

ters is in the range of 180–230 nm, and their luminescence is observed in the range of 400–450 nm. Thus, the excitation and absorption bands at 220 nm can be due to the copper–oxygen centers. The absorption spectrum demonstrates a rather strong band at 250 nm. The excitation spectra also contain this band, but its intensity is very low. This absorption can be assigned to Cu^+ centers [7]. The 250- and 220-nm absorption bands have the same intensity. However, in the excitation spectra, the 250-nm band is much weaker than the 220-nm band. The low intensity of the 250-band in the excitation spectrum is likely due to the low copper concentration and possible nonradiative transitions between copper and oxygen centers. After irradiation, Cu^+ centers pass to the Cu^{2+} state to form *F* centers. The absorption peak at a wavelength of 260 nm is due to the absorption in *F* centers (Fig. 1, dot-dashed line) [10].

LiF single crystals with monovalent copper can serve a new matrix for efficient tissue-equivalent LiF:Mg,Cu detectors. The replacement of Li^+ ions with Mg^{2+} in the lattice leads to the formation of charge-compensating cationic vacancies v_a^-. Some types of clusters are formed based on $\mathrm{Mg}^{2+} - \mathrm{v}_a^-$ pairs, which act as capture centers and are responsible for the TL peaks observed. Cu^+ ions are recombination centers. An electron captured by a magnesium cluster forms an $\mathrm{Mg}^+\mathrm{v}_a^-\mathrm{v}_c^0$ center, while a hole captured by a copper center forms a Cu^{2+} ion:

$$\mathrm{Mg}^{2+}\mathrm{v}_a^- + \mathrm{Cu}^+ + \gamma \to h + e^- \to \mathrm{Mg}^+ + \mathrm{v}_a^-\mathrm{v}_c^0 + \mathrm{Cu}^{2+}.$$

The electrons from magnesium centers pass to Cu^{2+} ions to radiatively recombine with holes upon crystal heating:

$$\mathrm{Mg}^+\mathrm{v}_a^-\mathrm{v}_c^0 + \mathrm{Cu}^{2+} \to kT$$

$$\to \mathrm{Mg}^{2+}\mathrm{v}_a^- + e^- + \mathrm{Cu}^{2+} \to \mathrm{Cu}^+ \to h\nu.$$

The direct transitions from the capture centers to the recombination centers may increase the efficiency of the phosphor thermoluminescence.

CONCLUSIONS

LiF single crystals with monovalent copper ions are a kind of new matrix for efficient tissue-equivalent LiF:Mg,Cu detectors. Copper ions are unstable in the monovalent state because they are readily reduced to the metallic state or oxidized to the divalent state. LiF single crystals with copper impurity were grown by the Czochralski method from a charge, specially prepared by solid-phase synthesis. The chemical composition of the charge and crystals was determined by atomic-absorption spectroscopy. The copper content in the samples was in the range of 0.0004–0.002%.

The 450-nm luminescence band and 250-nm excitation band in the spectra of LiF crystals with copper impurity are due to Cu^+ ions; this assignment is confirmed by the data in the literature. The oxygen impurity present in the crystals grown reduces the luminescence of Cu^+ centers.

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