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Impurity centers in LiF:Cu⁺ single crystals

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Abstract. The single crystals LiF with copper impurity were grown by Czochralski method. The concentrations of Cu in the crystals were 0,0004-0,002%. In order to determine a copper valence impurity, measurements of the ESR, emission, excitation and absorption spectra were performed. We found emission peak at 410 nm and excitation peak at 250 nm. In agreement with reference, these peaks point to presence of Cu⁺ in our samples. The mechanisms of capture and recombination providing process of thermoluminescence were recognized.

1. Introduction

A lithium fluoride is known as a thermoluminescence (TL) phosphor for the ionizing radiation dosimetry. The tissue-equivalence of lithium fluoride is the main advantage for thermoluminescent detectors on a LiF matrix. In additional, detectors based on lithium fluoride crystals are characterized by chemical inertness and weak sensitivity to ultra-violet and infra-red radiation. High sensitivity of a dosimeter is required for an individual radiation control which allows to measure doses from 0,01 mGy and provides a long preservation of the dosimetric information.

The LiF:Mg,Ti (TLD -100) single crystal detector technology have been made in our Institute [1]. However, detectors based on LiF:Mg,Cu,P [in short LiF(MCP)] become more popular in last time. Advantages of LiF(MCP) include high sensitivity comparing to LiF:Mg,Ti, almost flat photon energy response, low fading rate and linear dose response. The sensitivity of LiF(MCP) is approximately 20 times higher than the one of TLD-100 [2]. The main imperfection of LiF(MCP) dosimeter is sensitivity loss after pre-irradiation annealing of this materials at 240°C for 10 min (standard annealing). Chen and Stoebe [3] found that the Cu⁺ to Cu²⁺ conversion apparently caused a loss of the TL sensitivity of LiF(MCP) phosphors. Thus, the presence of Cu in the +1 state is apparently essential for the high TL sensitivity of LiF(MCP) phosphors. Also an essential disadvantage is a high background signal which limits measurement of small doses. The commercial LiF(MCP) are hot-pressed chips instead of a single crystal. As a result LiF(MCP) has a high level of the chemiluminescence.

A TL mechanism in LiF(MCP) is currently not well understood, and a reason to choose this specific set of impurities (Mg, Cu, P) is not clear. We have studied color centers and TL mechanisms in LiF:Mg,Ti system [4]. It has been shown that thermoluminescence process occurs through an intermediate stage and it leads to sensitivity loss of detectors. It is our opinion that such intermediate process can be excluded by direct recombination mechanism with using ions of monovalent copper. It

is expect that single crystals of LiF with monovalent copper impurity will be a new matrix for efficient tissue-equivalent detector LiF:Mg,Cu. It is supposed that light yield of the detector will be larger by a two order of magnitude than existent thermoluminescence detectors. A greater light yield is assumed to be due to direct recombination mechanism corresponded to monovalent copper ions.

Growth of LiF:Cu⁺ single crystal is difficult. Cu⁺ ions must replace the regular Li⁺ ions in crystalline lattice without charge compensators. Authors of paper [5] assumed that the LiF could not be doped with Cu⁺ impurity because of the ionic radius of Cu⁺ (0,96 Å) was much larger than the ionic radius of Li⁺ (0,68 Å). Therefore, the LiF crystal could be doped only with Cu²⁺ impurity which have smaller ionic radius (0,72 Å). Moreover, copper is instability in monovalent state. Copper monovalent ions actively reduce to metal (Cu⁰) or oxidize to divalent state. The instability of monovalent copper is due to from the reaction $2\text{CuF} \leftrightarrow \text{CuF}_2 + \text{Cu}$. To implement the left part of the reaction (monovalent copper) the temperature above 600°C is requested.

This article discusses problems of growth single crystal LiF:Cu⁺ and influence of the copper impurity on a luminescence process.

2. Experimental details

We synthesized the series of mixtures by solid state reactions before crystal growth to stabilize monovalent copper in lithium fluoride. Cu-doped LiF and Cu, Li-doped LiF mixtures were prepared by mixing LiF, CuCl, CuF₂·H₂O and Li₂CO₃ in various proportion. Doped LiF mixtures were prepared by addition 1-5% by weight of copper (CuCl and CuF₂·H₂O) and lithium (Li₂CO₃). The samples were ground to a fine powder in agate mortar and heated to 750°C for 15 h in air atmosphere. The phase purity of the compound was ascertained by X-ray diffraction studies. X-ray diffraction pattern confirmed a formation of a single-phase compound.

The ESR technique used for determination of copper valence in mixtures. The measurements were carried out on RE-1360 ESR spectrometer.

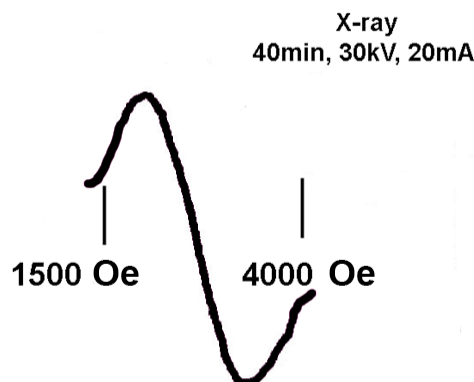


Figure 1. ESR spectrum of X-ray-irradiated LiF with CuCl mixture doping

Monovalent copper is not detected by ESR method, but Cu⁺ transforms to Cu²⁺ after X-ray irradiation. ESR spectrum of X-ray-irradiated LiF with CuCl mixture doping recorded at room temperature showed a broad unstructured signal in the region of 1500-4000 Oe (fig. 1). In paper [6] ESR spectra of LiF:Mg,Cu,P is considered. Authors of [7] also found a strong and wide signal attributed to bivalent copper impurity. Therefore, ESR spectra were recorded in the second derivative mode, where ESR spectral features could be better resolved. Thus the mixture LiF with CuCl doping was used as ligature in growth procedure.

Cu-doped LiF crystals have been grown by Czochralski method. Resistive nichrome heater and metal elements of thermal screens were used to avoid reduction of monovalent copper. The sintered powder was charged in a platinum crucible. Crystallization was made in argon and air atmosphere. The melting point of LiF is at about 870°C. The rate of single crystal growth was at about 5 mm/hour. The structure of crystals like NaCl and cuts is generally in $\langle 100 \rangle$ plane and least often $\langle 110 \rangle$ plane.

Chemical composition of mixtures and crystals were determined by atomic absorption spectrometry method. Copper content in crystals was 0,0004-0,002%.

Emission and excitation spectra were taken by exciting the samples with light from L2D2 lamp passed through a VMR-2 (600/mm) monochromator. The fluorescence was focused into MDR-2 (1200/mm) monochromator. The detector was a photomodule Hamamatsu H6780-04. ESR measurements were carried out on RE-1360 ESR spectrometer. All measurements have been made at room temperature.

3. Results and discussions

The Cu^+ ion have $3d^{10}$ filled shell in the ground state and $3d^94s$ and $3d^94p$ excited states. The absorption spectra of Cu^+ ions are well known for a number of alkali halide crystals ($\text{NaCl}:\text{Cu}^+$ [11], $\text{NaF}:\text{Cu}^+$ [5], $\text{LiCl}:\text{Cu}^+$ [8] and others). The cubic field of crystal split the d^9 hole state into e_g and t_{2g} states. According to the investigation the absorption band of Cu^+ ion is expected to consist of two bands corresponding with $^1A_{1g} \rightarrow ^1E_g$ and $^1A_{1g} \rightarrow ^1T_{2g}$ transitions [5]. The fundamental absorption edge of LiF crystal is well into deep VUF region (14.5 eV or 85.5 nm) allowing to observe the $3d^{10} \rightarrow 3d^94s$ absorption which occur near 250 nm in most alkali halides [8]. According to the authors of paper [6] it is expected the Cu^+ emission at 340 – 400 nm in LiF, with the Cu^{2+} emission assuming at near 460 nm [9].

Figure 2 shows emission spectra of LiF crystal with Cu impurity, excited at $\lambda_{\text{exc}} = 200$ nm and $\lambda_{\text{exc}} = 222$ nm. The maximum of emission spectra shifted from 410 nm to 435 nm at $\lambda_{\text{exc}} = 222$ nm. Figure 3 illustrates the excitation spectra of LiF crystal doped with copper impurity observed in emission band at $\lambda_{\text{em}} = 450$ nm. The peaks at 190 nm, 220 nm and weak peak at 250 nm observed in excitation spectrum after Cu doping of LiF crystal. Two bands at about 220 nm and 250 nm observed in absorption spectra in LiF with Cu impurity (fig. 4 solid line). After X-ray irradiation these bands disappeared and the wide band at 260 nm was observed (fig. 4 dot line).

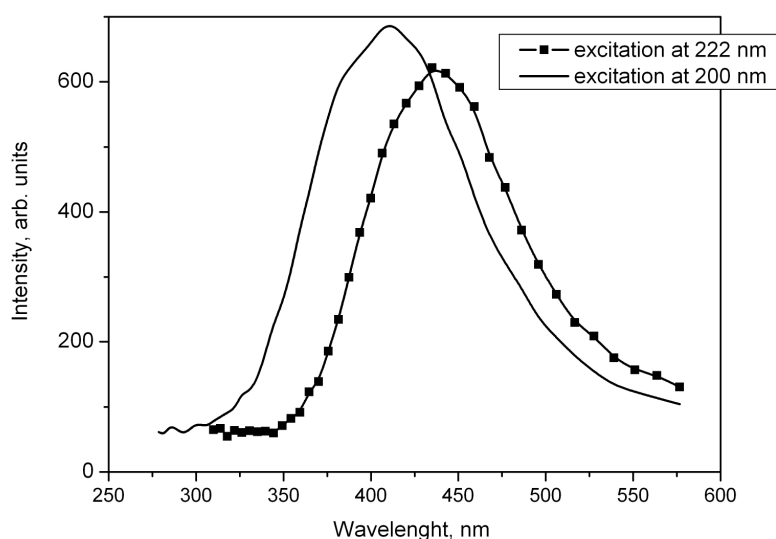
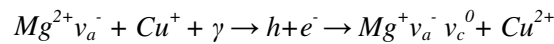


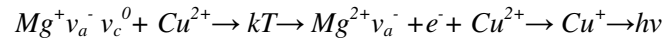
Figure 2. Emission spectra of LiF crystal with Cu impurity ($\lambda_{\text{exc}} = 200$ nm and $\lambda_{\text{exc}} = 222$ nm).

E. Radzhabov pointed in [10] that absorption of metal-oxygen centers was in the region 180-230 nm and emission in the 400-450 nm region. So, we assumed that the excitation and absorption bands at 220 nm are due to copper-oxygen centers. In absorption spectrum a band at 250 nm was found. In the excitation spectra this band is also observed, but its intensity is very weak. The band at 250 nm could be corresponded to Cu^+ centers [8]. Intensities of 220 nm and 250 nm absorption bands are similar. But in excitation spectra the band at 250 nm is dramatically weaker than the 220 nm band. A low concentration of copper and possible non-radiative transitions from Cu^+ to oxygen centers are the causes of weak intensity of the 250 nm band in excitation spectra. After X-ray irradiation Cu^+ centers transform to Cu^{2+} centers and F-centers appear. The absorption band at 260 nm corresponds to F-centers (fig. 4 dot line) [12].

Single crystals of LiF with monovalent copper impurity may be a new matrix for efficient tissue-equivalent detector LiF:Mg,Cu. Cation vacancies v_a^- formed as charge compensators of Mg^{2+} ions, which replaced Li^+ ions. $\text{Mg}^{2+}v_a^-$ clusters are capture centers and Cu^+ ions are recombination centers. Free electrons and holes are caused by irradiation. The electron are capturing by magnesium center creating $\text{Mg}^+v_a^-v_c^0$. The holes are settling on copper center creating Cu^{2+} .



Electrons from magnesium centers direct transfer to Cu^{2+} and radiatively recombined with holes after hating.



Direct transitions from capture centers to recombination centers can cause increasing of the thermoluminescence phosphor efficiency.

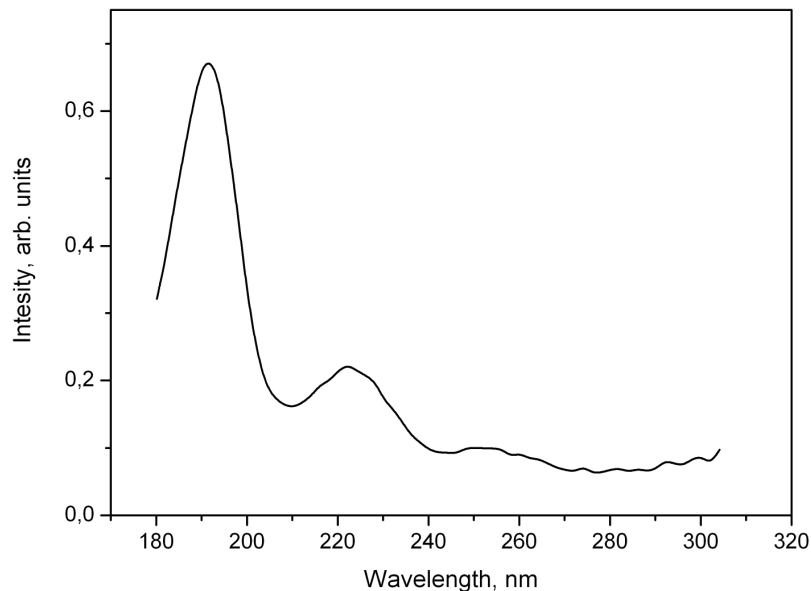


Figure 3. Excitation spectra measured for LiF crystal with copper impurity ($\lambda_{em} = 450$ nm).

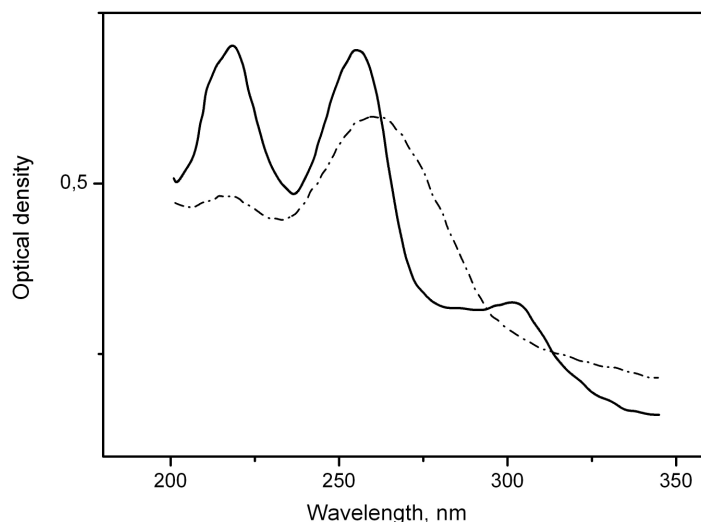


Figure 4. Absorption spectra in LiF with Cu impurity before (solid line) and after (dot line) x-ray irradiation.

4. Summary

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 copper percentage in crystals was 0,0004-0,002%. The absorption and excitation peaks at 250 nm in our LiF crystals doped copper are attributed with Cu^+ impurities. The monovalent copper is detected in the grown crystals by excitation band at 250 nm. Unfortunately, presence of oxygen impurity in the crystals reduces luminosity of Cu^+ centers.

Acknowledgments

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