Growth of solid solutions with colquiriite structure
LiCa$_{0.2}$Sr$_{0.8}$AlF$_6$: Ce$^{3+}$

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Abstract. Aim of this work were experiments on growing new materials based on fluoride crystals with the colquiriite structure LiSr$_{0.8}$Ca$_{0.2}$F$_6$, as well as the study of their phase composition. It is shown that for a series of crystals LiSr$_{0.8}$Ca$_{0.2}$F$_6$ distribution of reflections observed corresponds to the colquiriite structure, and the dependence of the lattice constant in the transition from LiCaAlF$_6$ crystal to LiSrAlF$_6$ crystal is linear. Also it found that absorption coefficient in mixed samples is much larger than in not mixed.

1. Introduction
Rare-earth doped LiCaAlF$_6$ (LiCAF) and LiSrAlF$_6$ (LiSAF) crystals has been investigated for various optical and scintillation applications. Especially, Ce doped LiCAF and LiSAF crystals have been gathering attentions as a novel neutron scintillator material with a good sensitivity to thermal neutron and fast decay time [1,2,3]. The advantages of these compounds over oxide crystals - the melting point is significantly lower (810°C) and the band gap is much wider (11 eV). Significant inhomogeneous broadening of the vibrational laser transitions of these ions causes a broad amplification band which gives ability to wavelength tuning and ultrashort pulses generation [4, 5].

Ce$^{3+}$ activators in Ce:LiCAF are supposed to substitute sites occupied by Ca$^{2+}$, which has an ionic radius similar to that of Ce$^{3+}$ (1Å and 1,03 Å respectively) [1]. However, it is difficult to increase the Ce$^{3+}$ concentration in Ce:LiCAF crystals because of the difference between the valences of Ce$^{3+}$ and Ca$^{2+}$ ions, which can give rise to defects nearby to preserve the electroneutrality of the crystal. Consequently, the segregation coefficient of Ce$^{3+}$ ions in Ce:LiCAF crystals is quite small [4]. It is known, that varying the chemical structure of the compound, namely a set of crystal lattice cations, one can improve the optical quality by increasing the isomorphic capacity of solid solution [6].

The aim of this work are experiments on growing new materials based on mixed fluoride crystals with the colquiriite structure LiSr$_{0.8}$Ca$_{0.2}$F$_6$ (LiSCAF) as well as the study of their phase composition.

2. Conditions, characteristics and growing complexity of the materials.
A special role in the successful use of fluorides plays chemical purity of crystalline samples: removing traces of oxygen and hydroxyl groups in the crystals concomitant reduction of impurities - the rare earth ions and ions of the iron group. Furthermore, the final performance of the solid-state laser crystal material is affected strongly by its optical quality and the number of defects of crystal structure which in turn is influenced by especially the crystal growth and subsequent machining. In particular, one of the main problems arising from the operation of materials under intense UV radiation is the degradation of their optical properties.
As a method of crystal growth the Bridgman-Stockbarger was selected, where crystals are grown in closed crucibles. This maintains the chemical composition of the melt and allows to produce crystal samples with various activator ions even for the case of extremely low segregation coefficients of demanded impurities, which takes place for investigated Ce$^{3+}$:LiCAF crystals.

The melting point of the crystals comprise 810 °C [7]. These systems are multicomponent, and, as indicated above, are characterized by an extremely low segregation coefficient of Ce$^{3+}$ ions which are active ions of the gain medium. Therefore, it is critical to arrange a sufficient temperature gradient in the crystallization zone during growth of these crystals [8]. The temperature gradient is determined by the geometry of the following elements: conductor current, heater, heat shields and crucible.

Complexity of growing is in the fact that aluminum is volatile, therefore: it is not allowed to overheat the melt, since the components include the aluminum fluoride, which is a compound with a high saturated vapor pressure and does not exist in a liquid state, so overheating of the melt will lead to depletion of this component. Also, when the temperature is set taking the value with an excess (about 20°C) to ensure melting of the substance.

![Figure 1. Crucible (a) and the heater (b) of the growth chamber. Crucible consists of: 1) lid, 2) container for teflon, 3) container for charge, 4) the pin in which put the seeding crystal. b) body of resistive heater construction: 5) place for shield, 6) heater, 7) variable thickness to form a gradient field, 8) mounting place for coupling to the current conductor.](image)

Crucible also participates in the formation of a temperature gradient. The wall thickness of the crucible should be minimal (in order 2-3mm) to distort the temperature field as little as possible.

Series of crystals Ce$^{3+}$:LiCAF: and Ce$^{3+}$:LiSCAF with 1 at. % content of CeF$_3$ in the initial charge were grown with Bridgman-Stockbarger method. A fine powder samples were prepared for investigation by X-Ray diffractometry from the synthesized material. Also samples for optical spectroscopy were prepared from the synthesized boules. Polished plane-parallel windows were made along the boule of Ce:LiCAF crystal. For the Ce:LiSCAF crystal plane-parallel plates with polished windows were prepared. The optical c-axis was kept in the plane of polished windows. Length of the optical path in crystals Ce:LiCAF and Ce:LiSCAF was 8 mm and 2 mm respectively.
3. Diffractometry results

Phase composition of crystallized material was investigated by means of X-ray diffractometry technique. The correspondent reflections distributions are shown at Fig. 2.

![X-ray diffraction patterns](image)

**Figure 2.** X-ray diffraction patterns of the samples: LiSCAF:Ce$^{3+}$ experimental data and LiCAF and LiSAF from the works [9, 10]: a) experimental data, b) comparison data, c) table data.

The diffraction pattern obtained for Ce$^{3+}$:LiSCAF corresponds to colquiriite structure. From comparison to LiCAF and LiSAF data [9, 10] it is seen that Ce$^{3+}$:LiSCAF reflections are lying between LICAF and LISAF data as it was expected due to shift of lattice constant.

We have also obtained the diffraction lattice constant dependence on the concentration ratio of mixed and unmixed samples (Figure 3).
Figure 2. Dependence of the lattice constants $a$ and $c$ of crystallized Ce$^{3+}$:LiSCAF material on the SrF$_2$ content.

We see that lattice constants for Ce$^{3+}$:LiSCAF lie on the straight lines between LICAF and LISAF and this means that our crystal is monocrystalline and has the only phase according to Vegard’s rule.

4. Absorption spectra results

At Fig. 4 the absorption bands corresponding to lowest 4f-5d transition of Ce$^{3+}$ ion in are presented. In the absorption spectrum we see a small blue shift of the band. But we remind you that this is a superposition of a number of spectrum bands corresponding to different nonequivalent impurity centers of Ce$^{3+}$ [11]. An important result is that the absorption coefficient of the mixed sample about 5 times larger than the absorption coefficient of not mixed sample (Figure 4).

Figure 3. Absorption bands of Ce$^{3+}$:LiCAF and Ce$^{3+}$:LiSCAF in different polarizations.
5. Conclusion
Solid solutions with chemical formula LiSr$_{0.8}$Ca$_{0.2}$F$_6$ doped with Ce$^{3+}$ ions were grown. It is shown that for a series of crystals LiSr$_{0.8}$Ca$_{0.2}$F$_6$, distribution of X-ray diffraction reflections observed corresponds to the colquirite structure, and the dependence of the lattice constant in the transition from LiCaAlF$_6$ crystal to LiSrAlF$_6$ crystal is linear. These facts indicate that the synthesized crystals are single-phase crystals. Also it was found that absorption coefficient in mixed samples is much larger than in not mixed and this speaks for higher distribution coefficient of Ce$^{3+}$ ions in mixed crystals.

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