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Analysis by the Rietveld Method of Pure and Doped $LiSrAlF_6$ and $LiCaAlF_6$ Crystals at Different Temperatures

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In the last decade hexafluoroaluminates with general formula $LiM'M''F_6$ (M'=Sr, Ca; M''= Al, Ga) were identified as potential laser crystals. In special, Cr^{3+}-doped $LiSrAlF_6$ (LiSAF) have attracted considerable attention as near-infrared laser gain material [1] and Ce^{4+}-doped $LiCaAlF_6$ (LiCAF) as an important candidate for tunable all-solid-state-laser in the UV region [2].

One of the main problems in the growth and laser application of these colquiriite-type crystals is their anisotropic thermal properties. Thermal gradients can easily result in crack of the crystals. LiSAF, for example, when heated exhibits thermal expansion along a axis and thermal contraction along c axis. In this work, the Rietveld method was employed in the study of the behavior of the hexagonal a and c cell parameters of pure and doped LiSAF and LiCAF crystals as a function of temperature. The objective was to compare the changes in the lattice of pure and doped crystals.

LiSAF, LiCAF, Cr:LiCAF, Cr:LiSAF, Ce:Na:LiCAF and Ce:Na:LiSAF crystals were grown by Czochralski method under reactive atmosphere. A slab of each crystal was powdered for x-ray measurements. The study was performed with x-ray powder patterns measured under vacuum, at room temperature and from 100 to 600°C, in steps of 100°C. The patterns were analyzed by the program DBWS-9807a [3] which makes the refinement of the structural parameters using the Rietveld method. The variations of the parameters with the temperature were fitted to third-order polynomials. The parameters behave in a way which is compatible to the thermal properties of the compounds. The measured lattice parameters of Cr:LiCAF are larger than those of pure and Ce:Na-doped crystals, which showed very similar values. The same was not observed for LiSAF host. The measured lattice parameters of Ce:Na:LiSAF are larger than the observed values of pure and Cr-doped LiSAF.

References:

[1] Payne, S.A.; Chase, L.L.; Smith, L.K.; Kway, W.L.; Newkirk, H.W. "Laser performance of $LiSrAlF_6:Cr^{3+}$", J. Appl. Phys. 66, 1051 (1989).

[2] Liu, Z.; Izumida, S.; Ohtake, H.; Sarukura, N.; Shimamura, K.; Mujilatu, N.; Baldochi, S. L.; Fukuda, T. "High pulse-energy, all-solid-state, ultraviolet laser oscillator using large Czochralski-grown Ce:LiCAF crystal" Jpn. J. Appl. Phys., 37, L1318 (1998).

[3] Young, R.A.; Larson, A.C.; Paiva-Santos, C.O. User's guide to program DBWS-9807a for Rietveld analysis of x-ray and neutron powder diffraction patterns. School of Physics, Georgia Institute of Technology. Atlanta, (1999).

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Phase Diagram of the System $LiF-GdF_3-YF_3$

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$LiGdF_4$ crystals have an important application as laser active media when doped with rare earth ions[1]. The $LiF-GdF_3$ phase diagram presents two invariant points: a eutectic at 25 mol% GdF_3 and 698 °C, and a peritectic at 34 mol% GdF_3 and 750 °C. GLF is the unique intermediary compound. In a previous paper [2] it was investigated the codoping of GLF crystals with yttrium, and good quality crystals could be obtained using the peritectic composition of the system $LiF-GdF_3$ as starting composition.

In this work the phase diagrams of the system LiF- $Gd_{(1-x)}Y_xF_3$ (x= 0.5 e 0,75) have been constructed using differential thermal analysis. The measurements were performed with samples weighing around 50 mg placed in open platinum crucibles, under a flux of purified helium, with a heating rate of 10 °C/min. The phase diagrams were determined up to compositions of 40 mol% LiF: 60 mol% $Gd_{(1-x)}Y_xF_3$.

To determine the phases present in the phase diagrams, some samples were melted under a flux of hydrogen fluoride gas and cooled at rates of 10-20 °C. One of the samples was observed using a scanning electron microscope with an energy-dispersive spectrometer. The other sample was pulverized to be analyzed by powder X-ray diffraction. Lattice parameters of the identified phases were calculated using a least square refinement.

In the phase diagram of the system LiF $-Gd_{0.5}Y_{0.5}F_3$ the addition of 50 mol% of YF_3 shifted the peritectic composition to 57,5 mol% LiF: 42,5 mol% TRF_3, at 800 °C and maintained the eutectic composition unaltered. In the system LiF$-Gd_{0.25}Y_{0.75}F_3$ the eutectic composition is at 22,5 mol% $Gd_{0.25}Y_{0.75}F_3$ and the peritectic reaction occurs very near the stoichiometric composition at 818 °C.

To determine the yttrium concentration that makes the system congruent, the mixture compositions were fixed at 50 mol% LiF: 50 mol% $Gd_{(1-x)}Y_xF_3$ and the rare earth concentration (x) were changed from 0.5 up to 1. This composition was determined to be 50 mol% LiF: 50 mol% $Gd_{0.3}Y_{0.7}F_3$ at 815°C. Thus, the gadolinium is totally soluble in the YLF lattice to concentrations smaller than 30 mol%. With these data a ternary phase diagram of the system $LiF-GdF_3-YF_3$ is proposed.

References:

[1] X.X. Zhang, A.B. Villaverde, M. Bass, and B.H.T. Chai, J. Applied Phys.74 (2) (1993) 790-796.

[2] I.M. Ranieri, K. Shimamura, K. Nakano, T. Fujita, L.C. Courrol, S.P. Morato, T. Fukuda, J. Crystal Growth 217 (1-2) (2000) 145-150.

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