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Growth of un-doped and Nd-doped $LiGd_{1-x}Y_xF_4$ single crystals

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Introduction

$LiGdF_4$ (GLF) is isostructural to $LiYF_4$ (YLF), which has the inverse scheelite structure, space group $I4_{1/a}$, with lattice parameters of 5.219 Å ($a = b$) and 10.97 Å (c). The site symmetry for the lanthanide ion is S_4, which makes these crystals suitable as a laser host material. GLF crystals are promising for doping with rare earth ions with ionic radius greater than that of yttrium, but crystals with good optical quality have not yet been reported. The growth of GLF crystals is difficult because of a strongly incongruent melting behavior. The LiF-GdF_3 phase diagram presents two invariant points: an eutectic at 25 mol% GdF_3 and 627°C, and a peritectic at 34 mol% GdF_3 and 727°C. The GLF is the unique intermediary compound [1].

In this work, crystals of $LiGd_{1-x}Y_xF_4$ doped with neodymium were grown by the Czochralski technique using either argon or a CF_4 reactive atmosphere to obtain crystals with better optical quality. The influence of these atmospheres on the crystal quality, as well as the influence of the yttrium concentration in the $LiGdF_4$ crystals was investigated.

Experimental

The raw materials were prepared in two ways: 1) GdF_3, NdF_3, and YF_3 were prepared from pure oxide powders by hydrofluorination at high temperature in HF atmosphere. The LiF - GdF_3 mixtures, with or without YF_3, were synthesized in the same atmosphere with a composition of 1.94 LiF:GdF_3. LiF powder was zone-refined before it was added to the GdF_3. 2) GdF_3, YF_3, NdF_3 and LiF pure commercial powders were added in the crucible and melted in CF_4 atmosphere prior the growth run.

Single crystals were grown by the Czochralski technique under high purity argon or CF_4 atmosphere. The crystal-pulling rates were 0.6-0.8 mm/h for <100>-oriented boules, with 8-10 rpm rotation rates. The crystal diameter was controlled either visually or with an automatic diameter control. $LiGd_{1-x-y}Y_xNd_yF_4$ crystals with concentrations in the melt of x = 0 and 30 mol% and y = 0 and 2 mol% were grown in argon atmosphere. $LiGd_{1-x-y}Y_xNd_yF_4$ crystals with concentrations in the melt of x = 0, 30 and 50 mol% and y = 1 and 2.7 mol% were grown in CF_4 atmosphere.

The rare earth concentrations were obtained by electron probe microanalysis (EPMA). Powder X-ray diffraction (XRD) measurements were carried out in the 2θ range of 15-80° for the lattice parameter determinations

Results and discussion

Crystals grown in argon atmosphere, with raw materials prepared in HF atmosphere, were very difficult to obtain. The melt surface presented a carbon scum that was impossible to eliminate during the hydrofluorination process, making the seeding process sometimes impossible. The carbon came from the oxide synthesis also if the purity was four nines. The crystals possessed good quality only for small diameters. Cones of macro bubbles and planes of micro bubbles located parallel to the growth axis appeared when the diameter increased. Finally, the stoichiometry changed causing a segregation of one of the phases and the crystal became opaque.

Crystals grown in a CF_4 atmosphere, with the compounds in the fluoride form, were obtained easily. The better chemical quality and the reactive atmosphere were responsible for this improvement (Fig. 1). Nevertheless, the un-doped and the 30 mol% yttrium-doped crystals presented bubbles, as can be seen in Fig.2 a. On increasing the amount of yttrium to 50 mol%, was obtained a crystal of good quality with fine planes of micro bubbles in the cone that disappeared when the diameter became constant (Fig 2 b).

As the solidified fraction in all grown crystals was not greater than ten percent, the rare earth segregation coefficients were obtained from the mean value of the concentrations in the crystals. For gadolinium and yttrium, the segregation coefficient was very close to one, and for neodymium, it was 0.4. The segregation coefficient for neodymium is half of the one value reported in the literature (2). There is a possibility that the value of 0.8 has been incorrectly evaluated.

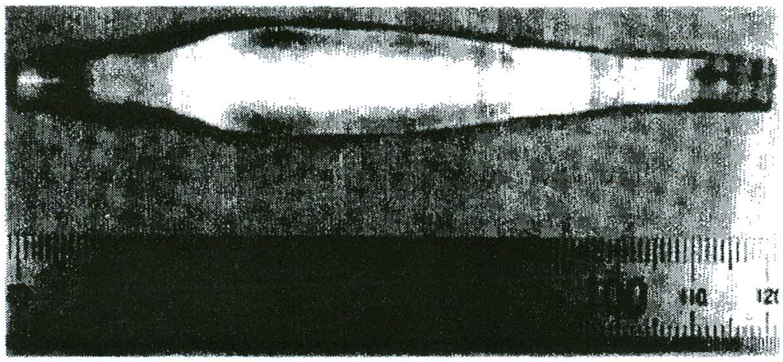

Fig. 1 - Crystals of $LiGdF_4$ doped with 50 mol% yttrium and 1 mol% neodymium;

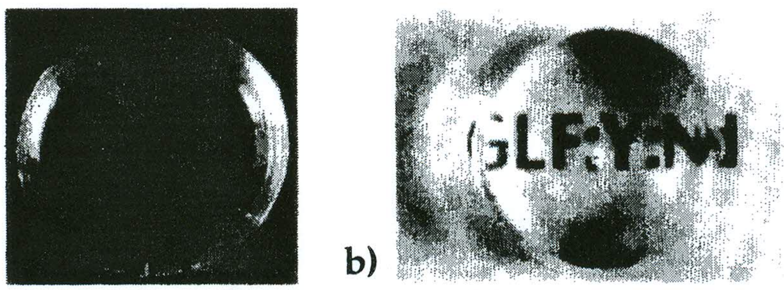

Fig. 2 - Crystals of doped $LiGdF_4$: a) 30 mol% yttrium and 0.35 mol% neodymium; b) 50 mol% yttrium and 1 mol% neodymium;

The lattice parameters obtained by XRD are presented in Table 1. As expected, the lattice parameters decreased for the crystals doped with 30 mol% of yttrium. Further measurements of the 50 mol% yttrium doped GLF, as well as the variation in the melting temperature related to the addition of yttrium in the GLF crystal melt (to be monitored by differential thermal analysis), are presently in progress.

Table 1.- The values obtained for the lattice parameters.

SAMPLE	Lattice constant (Å)	
$LiGdF_4$	a=5.214(1)	c=10.967 (3)
$LiGd_{0.70}Y_{0.30}Nd_{0.004}$	a=5.208 (3)	c=10.939 (15)
$LiYF_4$	a=5.167 (1)	c=10.730 (1)

The preliminary spectroscopic studies showed that there were no significant changes in the emission cross sections at 1,047 nm and 1,053 nm, nor in the level lifetimes for the crystals doped with 30 mol% yttrium.

In summary, it has shown that it is possible to grow GLF crystals with good optical quality by co-doping with yttrium. It was demonstrated that it is possible to grow crystals of $LiGd_{(1-x-y)}Y_xNd_yF_4$ with Y concentrations up to 50 mol %, and that the GLF can form solid solution with yttrium.

References

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2) A. Pham, J. Lefaucheur, G. Lutts, B. Chai and J. Nicholls, OSA Proceed. on Advanced Sol. Stat. Lasers, **15** (1993) 178.