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Growth of $LiY_{1-x}Lu_xF_4$ crystals under CF_4 atmosphere

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Abstract

Crystals of $LiY_{1-x}Lu_xF_4$ (x=50, 75, 100 mol%) doped with neodymium were successfully grown by the Czochralski technique, under CF_4 atmosphere. The lattice parameters, calculated from X-ray diffraction data, showed a linear relationship with the molar composition, in accordance with the Vegard law for ideal solid solutions.

Keywords: Rare earth compounds; Crystal growth

1. Introduction

Lithium and rare earth fluorides with general formula $LiREF_4$ or RELF (RE=Y, rare earth), have been studied in the last 30 years mainly due to their applications as laser active media, when doped with rare earth ions. Among them, special attention has been focused on YLF crystals doped with ions emitting in the near infrared as neodymium (Nd), holmium (Ho), erbium (Er), thulium (Tm) and ytterbium (Yb).

YLF crystals, in particular, are the most successful host for Nd ions. They are used as Q-switching medium power oscillator because they require a smaller number of stages to reach the same output power when compared to Nd:YAG. Other advantage is their use in diode pumped lasers, since the neodymium fluorescence lifetime in YLF is twice the value in Nd:YAG, resulting in the storage of two times more energy for the same input power. Some applications of Nd:YLF lasers are in the following areas: material processing, environment monitoring with light detection and ranging (LIDAR) technique, fusion by inertial confinement, medicine, dentistry and scientific research where high power densities are necessary.

New Nd laser hosts presenting the same YLF properties but with broader emission bandwidth and the possibility to accept high Nd concentration without losses to the optical quality, is a goal to produce more efficient lasers. These were the main reasons to propose the development of $LiY_{1-x}Lu_xF_4$ crystals. In the beginning of this work, the assumption was that the substitution of a certain quantity of Y ions by an ion with smaller ionic radium could enhance the site volume near this ion. It was expected that by diffusion Nd ions could prefer these sites and would be incorporated in higher concentrations than in YLF. However, this did not occur. The main effect of Lu codoping was the decrease of the lattice parameters, resulting in a broadening of the Nd emission band.

Fluorides react strongly with oxygen and moisture. When these impurities are present during the growth process there is the formation of oxygen complexes in the crystals. The optical properties of the crystals are greatly influenced by the presence of these complexes, as they are responsible for scattering centers that cause losses in the laser media. When oxygen or moisture are present, they are usually accompanied by other oxygen complexes, such as, O^{2-}+ vacancy, domains with fluorine–hydroxyl substitutions ($RE[OH]_3$), $Me(OH)_2$ (M=Mg, Mn or Ti) complexes, or HCO^- molecules [1]. Oxygen-related impurities can be easily detected due to their characteristic infrared (IR) absorption spectra. The use of a reactive atmosphere, such as, HF or CF_4 prevents the degradation of the material [2,3].

$LiY_{1-x}Lu_xF_4$ (x=9, 31, 47.3 and 100 mol%) crystals were studied in a previous paper [4], but only small crystals were obtained by the Czochralski method, when argon atmosphere was utilized during the growth process.

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In this work, this study was extended to higher Lu concentrations (x=50, 75 e 100 mol%) and the utilization of a reactive atmosphere of CF_4 resulted in crystals free of oxygen-related complexes.

2. Experimental

Commercial starting materials of YF_3, NdF_3 (Rare Metallic, 99.99% or 99.999%), LuF_3 (AC Materials, 99.999%) and LiF (Optron, 99.9%) were added in a platinum crucible, heated in vacuum (10^{-4} Torr) up to 500 °C, then melted in CF_4 (99.9999%) atmosphere just before the growth process.

Single crystals were grown by the Czochralski technique under the same atmosphere, with automatic diameter control. The crystal-pulling rates were 0.5–1 mm/h for ⟨100⟩-oriented boules, with 8–15 rev./min rotation rates. Four $LiY_{1-x-y}Lu_xNd_yF_4$ crystals were grown with concentrations in the melt of x=50, 75 and 100 mol% and y=0 or 2.7 mol%. The crystals henceforth will be designated always by their nominal concentrations.

Powder X-ray diffraction (XRD) measurements for the lattice parameter determinations were carried out on a Bruker AXS diffractometer, model D8 Advance, operated at 40 kV and 30 mA in the 2θ range of 18–66°. Two samples were obtained from the beginning and from the end of the crystal to measure the composition variation over the length of the boule. The rare-earth compositions were determined using a scanning electron microscope (SEM) model XL30 from Philips with an energy-dispersive spectrometer model eDXAUTO from EDAX.

Bandwidth measurements were performed at room temperature, from the emission spectra at 1047 nm, which were obtained using a 4 W GaAlAs diode laser (SDL2382P1) for the pumping excitation at 792 nm.

3. Results

The four grown crystals did not present scattering centers when inspected with a He–Ne laser (Fig. 1). The LLF:Nd crystal suffered a sudden change in diameter at the end of the upper cone, causing the appearance of a cloud formed by planes of submicroscopic defects, which disappeared after the diameter became constant.

The segregation coefficients were determined from EDS measurements, considering the mean value of 10 measurements to each sample. Their values were determined using the ratio between the normal solidification equation to each sample:

$$k = 1 + \log\,(C_{S1}/C_{S2})\,(\log 1 - g_1/1 - g_2)^{-1} \tag{1}$$

The results are presented in Table 1.

For lutetium and yttrium, the segregation coefficients were very close to one, and for neodymium, it decreases slightly when the lutetium concentration increased, but it is greater than a value cited in the literature as 0.2 [5]. The lattice parameters were determined from the X-ray diffraction data, using the least square method [6] (Table 2). The

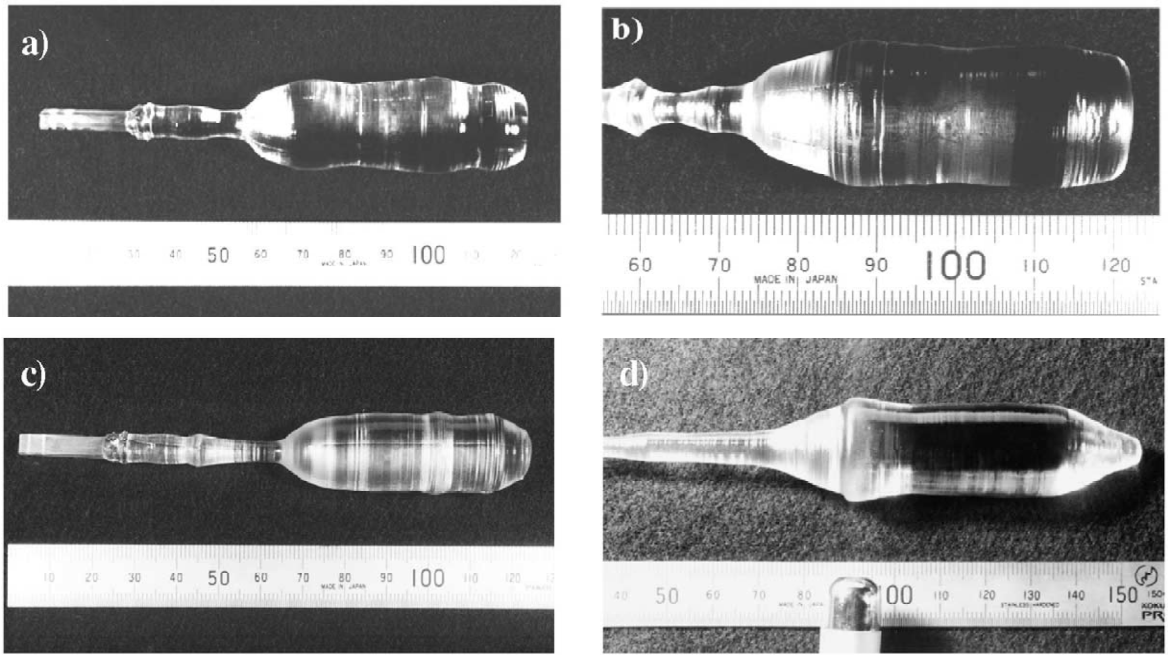

Fig. 1. $LiY_{1-x-y}Lu_xNd_yF_4$ crystals grown in CF_4 atmosphere: (a) $LiLuF_4$ (m=100 g); (b) $LiY_{0.5}Lu_{0.473}Nd_{0.027}F_4$ (m=87 g); (c) $LiY_{0.25}Lu_{0.723}Nd_{0.027}F_4$ (m=81 g); and (d) $LiLu_{0.973}Nd_{0.027}F_4$ (m=125 g).

Table 1
Rare-earth segregation coefficients determined for the $LiY_xLu_{1-x-y}Nd_yF_4$ crystals

Crystal	$LiLu_{0.973}Nd_{0.027}F_4$		$LiY_{0.25}Lu_{0.723}Nd_{0.027}F_4$			$LiY_{0.5}Lu_{0.473}Nd_{0.027}F_4$		
	Lu	Nd	Y	Lu	Nd	Y	Lu	Nd
k	1.01 (1)	0.31 (6)	1.03 (1)	1.00 (1)	0.34 (6)	1.00 (1)	1.01 (1)	0.36 (6)

Table 2
Lattice parameters and densities determined for the grown crystals

Sample	Lattice parameter (Å)	Density (g/cm^3)
$LiY_{0.99}Nd_{0.01}F_4$ [4]	$a=5.168$ (1) $c=10.741$ (2)	3.991 (2)
$LiY_{0.936}Lu_{0.053}Nd_{0.011}F_4$ [4]	$a=5.170$ (1) $c=10.733$ (2)	4.098 (2)
$LiY_{0.700}Lu_{0.288}Nd_{0.012}F_4$ [4]	$a=5.156$ (1) $c=10.694$ (4)	4.609 (4)
$LiY_{0.568}Lu_{0.420}Nd_{0.012}F_4$ [4]	$a=5.150$ (1) $c=10.659$ (3)	4.902 (3)
$LiY_{0.52}Lu_{0.470}Nd_{0.01}F_4$	$a=5.151$ (2) $c=10.660$ (5)	4.902 (3)
$LiY_{0.26}Lu_{0.73}Nd_{0.01}F_4$	$a=5.139$ (1) $c=10.592$ (3)	5.578 (3)
$LiLuF_4$	$a=5.130$ (1) $c=10.550$ (3)	6.169 (4)

values obtained for the crystals grown in a previous paper have been reported for comparison [4]. The lattice parameters decrease linearly with Lu concentration in the sample, which is in accordance with the Law of Vegard [7] for ideal solid solutions (Fig. 2).

The absorption spectra of the crystals in the vacuum ultraviolet (VUV) and in the infrared (IR) were obtained to verify the transparency limit and possible contamination related to oxygen impurity. In the VUV, the LLF crystal presents a transparence limit around 130 nm (9.56 eV) (Fig. 3). YLF and LiF spectra are presented for comparison. The absorption limit is dislocated to 180 nm (6.91 eV) in the doped crystals due to intense neodymium absorption bands related to the 4f–5d transitions [8].

In the infrared, the crystals presented no absorption bands due to oxygen complexes as OH^- and $Me(OH)_2$ (Me = divalent transition metals), which absorb in the range of 3700–3500 cm^{-1} and are a simple way to detect the crystal contamination with moisture (Fig. 4). Nd bands were observed in the ranges of 4000–3800 cm^{-1} and 2300–1800 cm^{-1} and the CO_2 gas residual band around 2345 cm^{-1}. The LLF crystal presented two very small bands at 2920 and 2850 cm^{-1} that are attributed to HCO^- complexes and probably resulting from the reaction between the OH^- and the carbon present in the material [1]. The formation mechanism of these complexes is not well

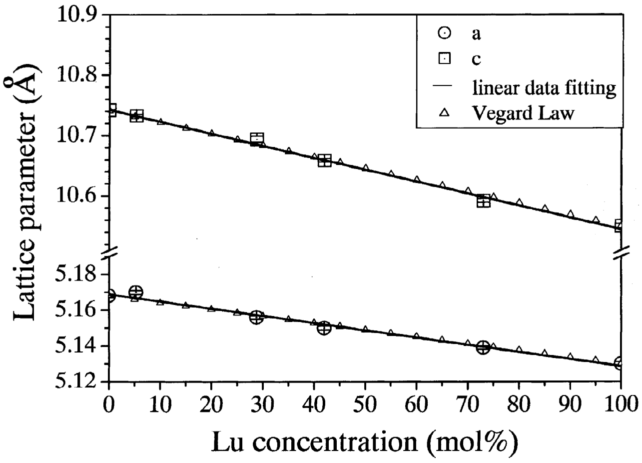

Fig. 2. Lattice parameter dependence with Lu concentration.

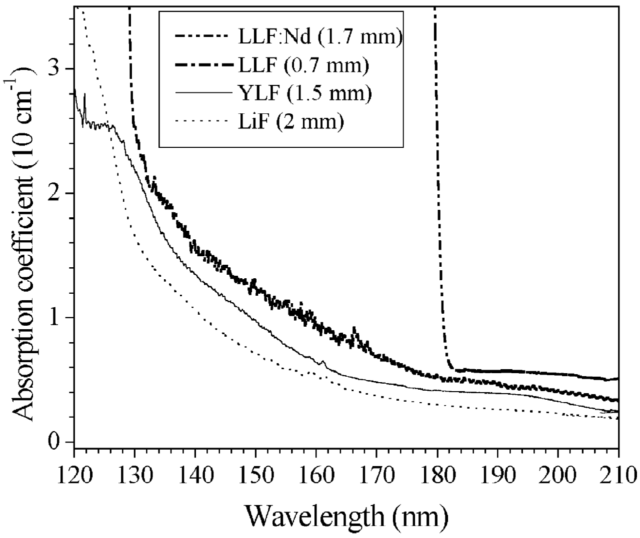

Fig. 3. VUV absorption bands of LLF:Nd, LLF, YLF and LiF crystals.

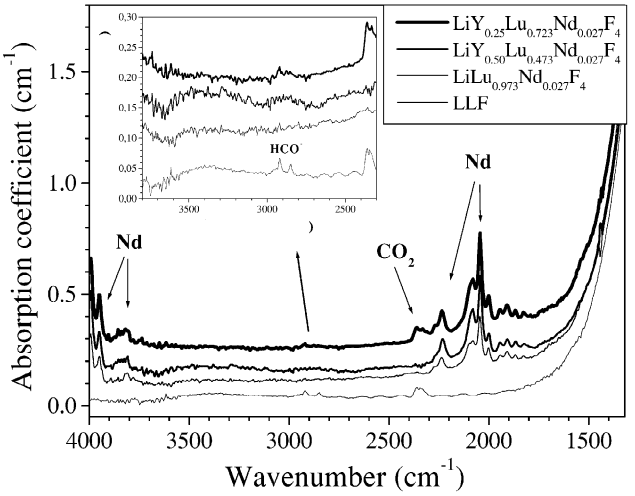

Fig. 4. Absorption bands of the grown crystals in the infrared.

Table 3
Nd emission bandwidth at 1.047 nm

Sample	Nd emission bandwidth (nm)
$LiY_{0.99}Nd_{0.01}F_4$ [4]	1.447 (145)
$LiY_{0.936}Lu_{0.053}Nd_{0.011}F_4$ [4]	1.586 (159)
$LiY_{0.700}Lu_{0.288}Nd_{0.012}F_4$ [4]	1.725 (172)
$LiY_{0.568}Lu_{0.420}Nd_{0.012}F_4$ [4]	1.790 (179)
$LiY_{0.52}Lu_{0.470}Nd_{0.01}F_4$	1.803 (180)
$LiY_{0.26}Lu_{0.73}Nd_{0.01}F_4$	1.845 (195)
$LiLuF_4$:Nd	1.825 (182)

understood and other carbon complexes also absorb in the same wavelengths. The same transitions appear in the literature related to the CH_3 and are due to the reaction with organic reagents, as in alcohol adsorption in oxides [9,10] and during the crystallization of inorganic compounds in biological materials [11]. Therefore, it is difficult to eliminate the possibility of contamination with organic reagents during the cutting and polishing of the samples.

The most significant spectroscopic result was obtained by the measurement of the emission bandwidth for the $LiY_{0.26}Lu_{0.73}Nd_{0.01}$ crystal, which completed the spectroscopic characterization for this family of solid solutions. In Ref. [4], it was observed that for Lu concentration around 45 mol% the emission bandwidth has the same value of the emission bandwidth of the Nd in LLF. This is an advantage considering that the cost of lutetium compounds is very high. In this work, it was demonstrated that above 45 mol% of Lu, the emission bandwidth saturates value around 1.82 nm (Table 3).

Laser modelocking operation of the $LiY_{0.568}Lu_{0.420}Nd_{0.012}$ (LuYLF) crystal grown in argon atmosphere resulted in pulses with 4.5 ps, and presented better laser performance in respect to intracavity losses [12]. New laser tests utilizing the new solid solutions obtained in this work are in progress.

4. Conclusions

It was demonstrated that it is possible to grow very pure rare-earth fluoride crystals from commercial fluoride powders using a CF_4 reactive atmosphere. Referring to the system $LiF–LuF_3–YF_3$, it was demonstrated also that $LiY_{1-x}Lu_xF_4$ crystals form ideal solid solutions in the entire range of Lu substitution. It was confirmed that the interaction of the neodymium ions with the lattice increases with the Lu concentration but reaches a maximum when 45 mol% of the ions are substituted. Given the very high cost of lutetium oxide, it is a big financial advantage if crystals with the same bandwidth as pure LLF:Nd can be grown with much less lutetium concentration.

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