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EXAFS STUDIES OF $LiYF_4$–$LiREF_4$ SOLID SOLUTIONS

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In this work we are investigating dopant environments in $LiYF_4$–$LiREF_4$ (RE = rare-earth cations) solid solutions, via EXAFS. The main aims are to identify the local environmental symmetry and the average lattice distortion as a function of the concentration and the type of the RE ion. $LiY_{1-x}RE_xF_4$ (RE = Gd or Lu) ($0 < x < 1$) single crystals were grown by the Czochralski technique under argon or CF_4 atmosphere, crystal-pulling rates were 0.6–1 mm/h for <100>-oriented boules, with 8–25 rpm rotation rates. Most of the crystals were also codoped with 2.7 mol% of neodymium in the melt. EXAFS measurements were performed in transmission and fluorescence modes in the synchrotron XAS line of the LNLS, Campinas, Brazil, in and above the L_{III} absorption edges of the RE ions. The samples were prepared as powder films, for the transmission mode measurements, and as powder or single crystals for fluorescence mode measurements. The WINXAS program was used for data reduction and fitting, and the FEFF6 package was used for the simulations of the spectra. The EXAFS oscillation curves were obtained by standard procedure.

Keywords: $LiYF_4$; EXAFS; Rare-earth dopants

1. INTRODUCTION

$LiYF_4$:Nd (YLF:Nd) crystals are widely used for diode-pumped solid-state lasers [1, 2]. For such systems it is necessary to produce crystals with high optical quality to support high-density pumping power. The $LiLuF_4$ (LuLF) crystal is the host isostructural to YLF that has the broader bandwidth for neodymium [3]. Although the LuLF has a congruent melting behaviour and presents good optical quality, there are drawbacks like the high cost of the lutetium compounds and the small segregation coefficient for neodymium. It was recently shown by Ranieri *et al.* [4] that the solid solution YLF-LuLF doped with Nd is a promising hosts since it preserves the same optical properties as LuLF but with an increase in the amount of Nd that can be dissolved in the matrix, and with a lower cost.

It is well accepted that rare earth ions in YLF-type structure will take the place of the trivalent ion and no charge compensation will be required. Most of the optical properties of these systems and, in particular, the laser action of the systems depend on the local symmetry.

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Possible deformation of the host lattice will certainly induce changes in that properties. These effects can be even more critical in mixed systems like YLF-LuLF, where different trivalent sites are available. EXAFS technique was used in the present work to gain precise information of the local structure around the dopant, to know the site occupied by the dopant in the mixed systems and the distance and nature of the co-ordinating atoms.

2. EXPERIMENTAL

Single crystals were grown by the Czochralski technique under a purified argon atmosphere. The crystal-pulling rate was 1 mm/h for [1 0 0] or [0 0 1]-oriented boules, and 20–25 rpm rotation rates, YLF seeds were used for the codoped crystals. $LiY_{(1-x-y)}Lu_xNd_yF_4$ crystals with $x = 9$, 31, 47.3 and 100 mol% and $y = 0$ to 2.7 mol% were grown. Nevertheless, it was found that the actual concentration of the Nd is about 1 mol% in all samples. Small crystals

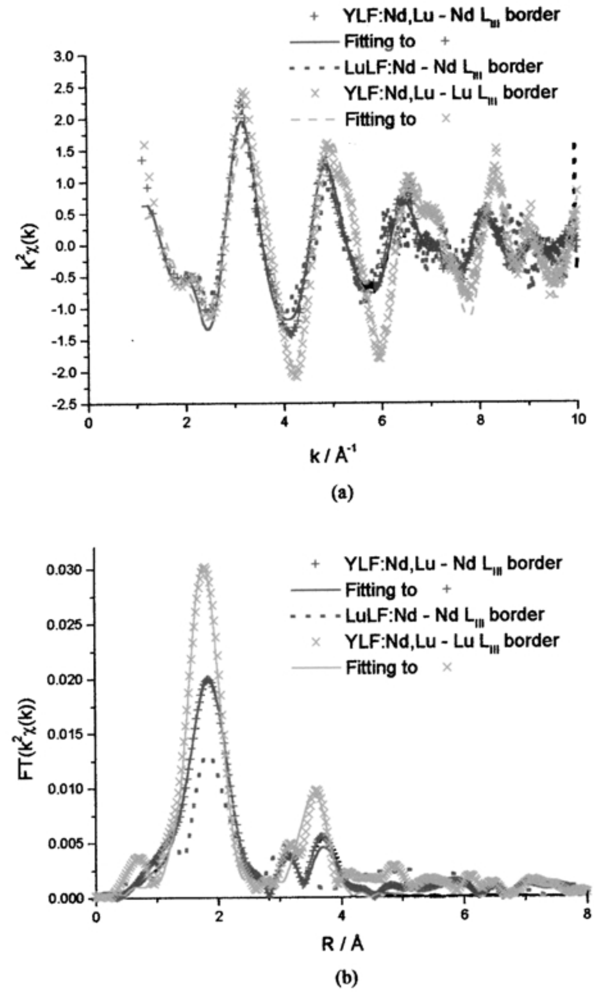

FIGURE 1 EXAFS oscillations (a) and the Fourier transform (b) of the oscillations for the YLF samples doped with 1 mol% Nd and 4 mol% of Lu and for the LuLF samples doped with 1 mol% of Nd.

of good optical quality weighing around 50 g were obtained, except for the LuLF where only a 10 g crystal was obtained. The crystal with 50 mol% Lu was more fragile, presenting some fractures on handling.

The XAS experiments were performed on and above the L_{III} absorption edge of the Y, Nd and Lu ions in fluorescence and transmission mode at room temperature. A number of spectra were recorded for each system and they were averaged to enhance the signal-to-noise ratio. The results were analyzed using the WinXAS and FEFF8 packages following standard procedures.

3. RESULTS AND DISCUSSIONS

Figure 1 displays the EXAFS oscilations and the corresponding Fourrier transform for the YLF samples doped with Nd and Lu and LuLF samples doped with Nd. Simulations were carried out using the FEFF8 code. A selected subset of the FEFF paths were chosen to fit the experimental oscillations. The resulting simulated curves were also plotted.

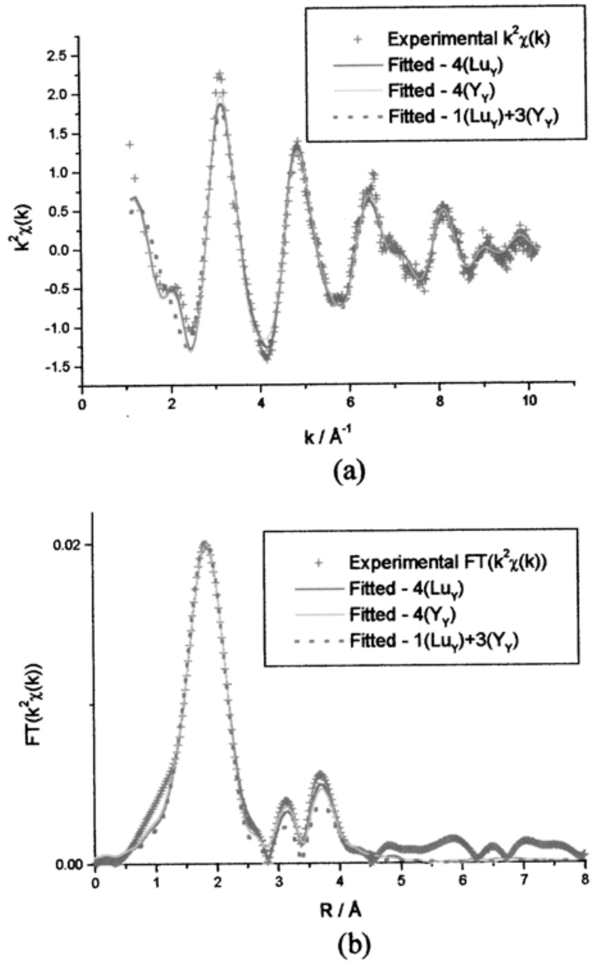

FIGURE 2 FEFF simulations and fittings to the EXAFS oscillations for the YLF:4 mol%Lu, 1 mol%Nd samples. (a) Exafs oscillations. (b) Fourier transforms of the EXAFS oscillations. Different combinations of Y and Lu were used in the first Y shell of the YLF structure. The corresponding radial distribution functions were also shown.

TABLE I First Two Coordination Shells Surrounding the Nd Ions in the YLF:Nd and YLF:Lu,Nd Samples Obtained from the Fitting Procedure Described in Figure 2. The Values in Brackets are the Values Obtained from the Lattice Structure of the YLF Matrix.

System	*Ions*	*N*	$R/\text{Å}$	σ^2
YLF:Nd	Y-F	4	2.4121 (2.244)	0.02
	Y-F	4	2.809 (2.297)	0.04
YLF:Nd,Lu ($4Lu_Y$)	Y-F	4	2.327 (2.244)	0.03
	Y-F	4	2.347 (2.297)	0.01
YLF:Nd,Lu ($4Y_Y$)	Y-F	4	2.282 (2.244)	0.01
	Y-F	4	2.352 (2.297)	0.04
YLF:Nd,Lu ($3Y_Y$-$1Lu_Y$)	Y-F	4	2.307 (2.244)	0.02
	Y-F	4	2.370 (2.297)	0.01

For the codoped YLF:4 mol%Lu, 1 mol%Nd system measured on and above the Nd L_{III} border, different configurations of Y and Lu were considered for the FEFF simulations and fittings. In YLF, the first Y neighbouring shell is composed of 4 symmetrically equivalent positions at 3.7252 Å [5] and the occupancy of those positions were varied form 4Y to 4Lu. The result of that can be shown in Figure 2. The best agreement was obtained for the model where all 4 neighbouring Y sites to the central Nd are occupied by Lu ions, giving the smallest χ^2_{red} and the smallest residual after the fitting.

The parameters obtained in the fitting routine are shown in Table I together with the values calculated from the lattice structure of each system.

The following conclusions can be drawn from the results:

- The first neighbouring F shells in all systems are very similar, indicating that Nd enters in the Y site in YLF and in the Lu site in the LuLF system, keeping a typical coordination number and distances.
- In the YLF systems, the lattice around the Nd ions are expanded, increasing the distance from the Nd^{3+} to the neighbouring ions. This result is expected since the Nd ionic radius is greater than the Y^{3+} one.
- In the YLF codoped system, there is a tendency for forming clusters where the Nd site is surrounded by 4 Lu in the neighbouring Y sites. This could explain why the actual concentration of Nd in the samples is around 1 mol%, about 4 times smaller than the Lu actual concentration in the same sample.

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