

## Growth and evaluation of lanthanoids orthoniobates single crystals processed by a miniature pedestal growth technique

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Optimized conditions for the growth of lanthanoids orthoniobates ( $\text{LnNbO}_4$ , Ln = lanthanide elements) single crystal minirods by a floating zone technique were investigated. Adequate atmospheres and pulling to feeding speed ratios to grow these materials were determined. Emphasis is given to the study of  $\text{LaNbO}_4$  because of their more favorable growth conditions and crystalline quality. This material can be efficiently doped with rare earth elements such as erbium. It grows with high crystallinity and its preferential growth direction is  $[1\ 1\ 0]$ . A preliminary evaluation of optical properties of  $\text{Er}^{3+}$ -doped  $\text{LaNbO}_4$  single crystal under the Judd-Ofelt formalism indicates spectral parameters  $\Omega_t$  close and even larger than for  $\text{Er}^{3+}$  ions in  $\text{YVO}_4$ .

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### 1 Introduction

$\text{LnNbO}_4$  compounds (Ln = La, Ce, Pr, Nd, Sm, Eu, Dy, Ho and Er) are peculiar minerals that crystallize in the fergusonite structure [1, 2, 3, 4]. They exhibit remarkable paramagnetic properties ( $\text{NdNbO}_4$ ,  $\text{GdNbO}_4$  and  $\text{HoNbO}_4$ , mainly) and a characteristic ferroelasticity (pseudoelasticity or rubber-like behavior) attributed to domain walls formed during phase transitions [1, 5, 6, 7, 8]. Compounds containing La, Gd and Lu, show efficient intrinsic deep-blue emission.  $\text{LuNbO}_4$  exhibits blue luminescence (maximum emission at 405 nm) under ultraviolet excitation (at 260 nm) [9] comparable to that of  $\text{YNbO}_4$  at the same experimental conditions. Recently, attention to  $\text{LaNbO}_4$  was renewed because of its large negative compressibility in at least one direction. This property makes  $\text{LaNbO}_4$  attractive for potential applications in high pressure environments as those found in optical line systems installed in oceans [10]. Although all these applications are known, the research and study of  $\text{LnNbO}_4$  compounds have been scarce due to the large difficulty found to grow them as single crystals through traditional techniques that demand a crucible due to their aggressive melts reactivity and high melting points. For instance,  $\text{NdNbO}_4$ ,  $\text{GdNbO}_4$  and  $\text{HoNbO}_4$  bulk crystal growth by Czochralski method [5] at temperature above 2300 °C was reported at the beginning of the last decade, while the first growths of  $\text{LaNbO}_4$  and  $\text{NdNbO}_4$  crystals by the same method and similar conditions were reported about three decades ago [6]. Other  $\text{LnNbO}_4$  crystals investigated in past years were prepared by flux growth methods [11, 12, 13, 14]. The scarce research on the growth of these materials by a containerless method motivated us to investigate the feasibility and convenience of a floating zone technique against already used growth methods.

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## 2 Experimental

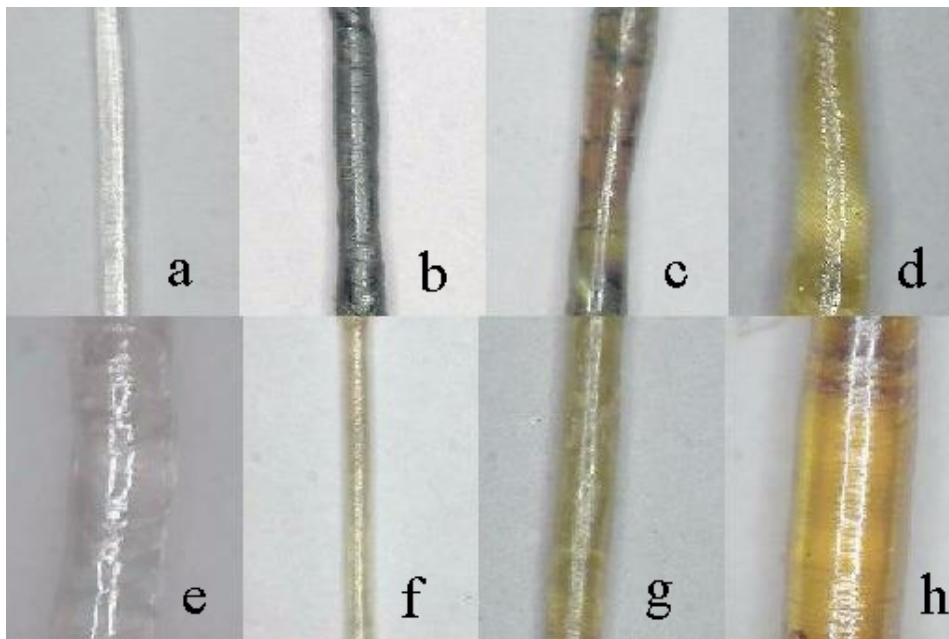
We used 99.9% purity  $\text{Ln}_2\text{O}_3$  (from Merck, Reacton and Johnson Matthey) and 99.99% purity  $\text{Nb}_2\text{O}_5$  (from Puratronic) powders as the starting materials. Except for Ce and Pr, all starting reagents were weighed in the 1:1 molar ratio of  $\text{Ln}_2\text{O}_3:\text{Nb}_2\text{O}_5$ . For Ce and Pr compounds, a  $2\text{Ln}_2\text{O}_3:\text{Nb}_2\text{O}_5$  molar ratio was used. The weighed powders were thoroughly dry mixed for 2 h and then combined with an organic binder (polyvinyl alcohol, PVA,  $10 \text{ g ml}^{-1} \text{ H}_2\text{O}$ ) and next thermally treated at  $1300 \text{ }^\circ\text{C}$  for 18 h. The crystals were obtained using a miniature pedestal growth technique known as laser-heated pedestal growth (LHPG) that is described elsewhere [15, 16].

Two thermally treated polycrystalline ceramic rods were employed as source and pulling rods in each experiment. A 125 W focused  $\text{CO}_2$  laser beam ( $\lambda = 10.6 \text{ } \mu\text{m}$ ) was used as the heat source. The source rod feeding and crystal pulling rates were in the ranges  $0.5 - 0.7 \text{ mm min}^{-1}$  and  $0.3 - 0.5 \text{ mm min}^{-1}$ , respectively. Seeding and preferential orientation was induced by shortening the width of the melt and then enlarging up to the desired crystal diameter. The crystal-to-source rod diameter reduction ratio was in the range  $0.7 - 0.8$  and not any source or seed rod rotation was used. The atmosphere in the growth chamber was air at pressure 0.1 MPa in all experiments except for  $\text{ErNbO}_4$ , which was grown in isostatic 0.1 MPa  $\text{N}_2/\text{H}_2$  atmosphere (95/5 volume ratio). Undoped 0.5 at.% and 2.0 at.%  $\text{Nd}^{3+}$ - and  $\text{Er}^{3+}$ -doped  $\text{EuNbO}_4$ ,  $\text{LaNbO}_4$ ,  $\text{YNbO}_4$  and  $\text{DyNbO}_4$  were grown under these conditions.

## 3 Results

The observation of the molten region and the diameter control were particularly difficult in the crystal growth experiments of all studied compounds. In each experiment was noted elevated brilliance and considerable heat irradiation from the melting region.

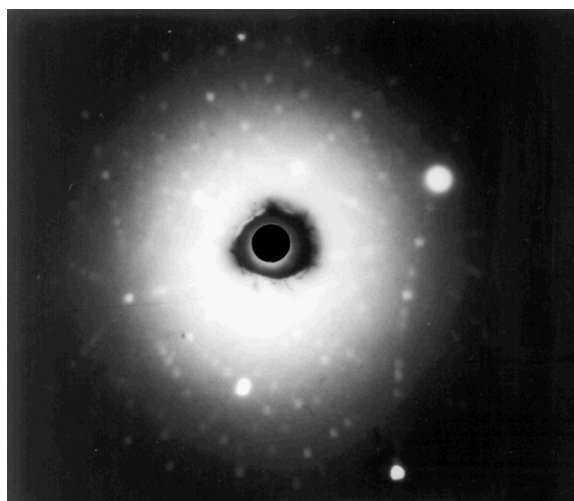
Fig. 1 shows as-grown crystals observed under the optical microscope. The samples are ordered from left to right and from top to bottom in such a way that the atomic weight of the rare-earth element increases in these directions.



**Fig. 1** Appearance of as-grown  $\text{LnNbO}_4$  minirods crystals prepared by LHPG. (a)  $\text{LaNbO}_4$ , (b)  $\text{CeNbO}_4$ , (c)  $\text{PrNbO}_4$ , (d)  $\text{SmNbO}_4$ , (e)  $\text{EuNbO}_4$ , (f)  $\text{DyNbO}_4$ , (g)  $\text{HoNbO}_4$ , (h)  $\text{ErNbO}_4$ . The diameter of each crystal scales approximately 0.8 mm.

It is noted a large dependence of the crystal coloration on the molecular weight of the compound. While heavier compounds give transparent crystals with yellowish coloration, the lighter compounds grow opaque with black or reddish colors. The origin of the different coloration is attributed to the coexistence of multiple Ln and Nb valence states, as well as to the presence of less than expected oxygen in the crystal lattice. It was evidenced absence of cracks or inclusions in most samples, mainly in those transparent and clear like LaNbO<sub>4</sub>. Only PrNbO<sub>4</sub> shows serious problems of inhomogeneous phase formation and tendency to present helicoidal cracks. The formation of inhomogeneous phases is a common problem found in the growth from a melt at high temperature of the crystals involving rare earth elements [17]. Formation and propagation of cracks is attributed to larger than permitted maximum acceptable axial thermal gradient near the melt – crystal interface, as it has been noted in other materials grown by the LHPG technique [18]. Among all grown crystals, undoped and Er<sup>3+</sup>-doped LaNbO<sub>4</sub> exhibit the more attractive features for investigating optical properties.

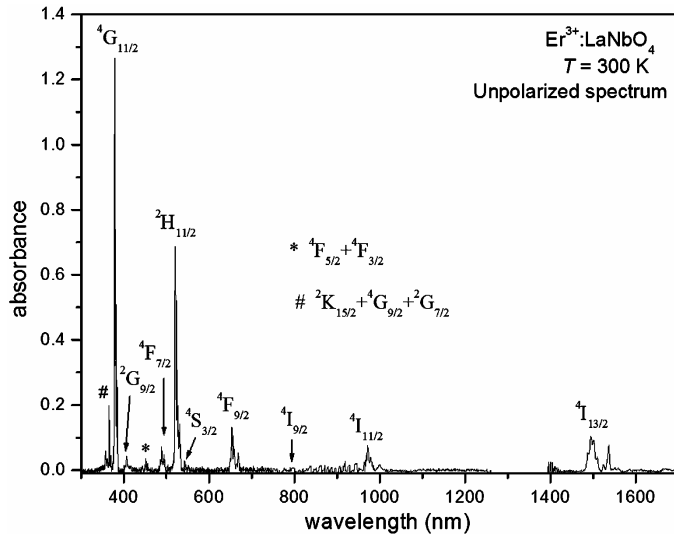
Fig. 2 shows a back reflection mode X-ray Laue diffraction pattern obtained from a LaNbO<sub>4</sub> as-grown single crystal indicating [1 1 0] as the crystal growth axis direction of the studied sample with crystal symmetry related to the high temperature fergusonite phase (tetragonal lattice,  $a = b = 5.458 \text{ \AA}$ ,  $c = 11.799 \text{ \AA}$ , space group I4<sub>1</sub>/a) that freezes above 520 °C [19]. The formation of this phase is attributed to the extraordinarily high thermal gradient at the solidification interface that can be as high as 1000 °C cm<sup>-1</sup> when the LHPG technique is used [20].



**Fig. 2** Back reflection X-ray Laue diffraction pattern of LaNbO<sub>4</sub> single crystal minirod showing [1 1 0] orientation of the crystal growth axis.

We noted that Er<sup>3+</sup>-doped LaNbO<sub>4</sub> single crystal exposed to an argon ion laser ( $\lambda = 514 \text{ nm}$ ) responds with unusual luminescence. The 300 K unpolarized optical absorption spectrum shown in Fig. 3 was obtained by passing light perpendicularly to the crystal growth axis of an Er<sup>3+</sup>-doped LaNbO<sub>4</sub> single crystal. A typical set of Er<sup>3+</sup>-related absorption bands was found and they are indicated with their respective labels in the spectral range 300-1700 nm. This spectrum was used to calculate spectral parameters in the framework of the Judd-Ofelt theory.

Measured and calculated line strengths  $S_m$  and  $S_c$ , respectively, were determined and fitted to those of the theoretical model to establish the values of the spectral parameters  $\Omega_t$  ( $t = 1, 2, 3$ ) [21, 22, 23]. Because there is conflicting information about structural data for LaNbO<sub>4</sub>, and this is needed for the calculations of spectral parameters, we performed several fittings and compared them to establish possible differences in the results of the fitting procedure. Table 1 summarizes the obtained data. The average values of each spectral parameter are  $\Omega_2 = 19.3 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 5.94 \times 10^{-20} \text{ cm}^2$  and  $\Omega_6 = 1.57 \times 10^{-20} \text{ cm}^2$ , which are respectively about 1.5, 2.5 and 0.9 times those of highly Er<sup>3+</sup>-doped YVO<sub>4</sub> [24]. The elevated values of  $\Omega_t$  in Er<sup>3+</sup>-doped LaNbO<sub>4</sub> are expected because of the large absorption coefficients of the crystal at about 380 nm and 520 nm compared to those of most Er<sup>3+</sup>-doped oxide hosts and glasses [24]. An interesting feature in Er<sup>3+</sup>-doped LaNbO<sub>4</sub> fitted spectral parameters is that  $\Omega_6 < \Omega_4 < \Omega_2$  like in Er<sup>3+</sup>-doped YVO<sub>4</sub>. This could be profitable to replace or to complement Er<sup>3+</sup>-doped YVO<sub>4</sub> in applications related to strong emission at about 1500 nm.



**Fig. 3** Unpolarized 300 K absorption spectrum of 2.0 at.%  $\text{Er}^{3+}$ -doped  $\text{LaNbO}_4$  single crystal.

**Table 1** Summary of experimental and reported data used to calculate spectral parameters using the Judd-Ofelt analysis.

dopant density = $1.36 \times 10^{20}$ ions $\text{cm}^{-3}$ , refractive index = 2.25, crystal thickness = 0.065 cm				
${}^a V_{\text{u.c.}} = 0.3150 \text{ nm}^3$ , ${}^b V_{\text{u.c.}} = 0.3325 \text{ nm}^3$ , ${}^c V_{\text{u.c.}} = 0.3359 \text{ nm}^3$				
${}^4 I_{15/2} \rightarrow J'$	Average wavelength (nm)	$S_m$ ( $10^{-20} \text{ cm}^2$ )	$S_g$ ( $10^{-20} \text{ cm}^2$ )	$ S_m - S_g $ ( $10^{-20} \text{ cm}^2$ )
${}^4 I_{13/2}$	1500.5	${}^a 3.37, {}^b 3.19, {}^c 3.22$	${}^a 3.42, {}^b 3.24, {}^c 3.27$	${}^a 0.05, {}^b 0.05, {}^c 0.05$
${}^4 I_{11/2}$	972.8	${}^a 1.94, {}^b 1.84, {}^c 1.86$	${}^a 1.22, {}^b 1.16, {}^c 1.17$	${}^a 0.72, {}^b 0.68, {}^c 0.69$
${}^4 F_{9/2}$	656.7	${}^a 3.70, {}^b 3.51, {}^c 3.54$	${}^a 3.98, {}^b 3.77, {}^c 3.81$	${}^a 0.28, {}^b 0.26, {}^c 0.27$
${}^2 H_{11/2}, {}^4 S_{3/2}$	522	${}^a 15.8, {}^b 15.0, {}^c 15.1$	${}^a 17.7, {}^b 16.8, {}^c 17.0$	${}^a 1.90, {}^b 1.80, {}^c 1.99$
${}^4 F_{7/2}$	487.9	${}^a 1.87, {}^b 1.77, {}^c 1.79$	${}^a 1.91, {}^b 1.81, {}^c 1.83$	${}^a 0.04, {}^b 0.04, {}^c 0.04$
${}^4 F_{5/2}, {}^4 F_{3/2}$	451	${}^a 0.45, {}^b 0.43, {}^c 0.43$	${}^a 0.56, {}^b 0.54, {}^c 0.54$	${}^a 0.11, {}^b 0.11, {}^c 0.11$
${}^2 G_{9/2}$	406.9	${}^a 1.36, {}^b 1.29, {}^c 1.30$	${}^a 0.47, {}^b 0.44, {}^c 0.44$	${}^a 0.89, {}^b 0.85, {}^c 0.86$
${}^4 G_{11/2}$	378.5	${}^a 22.9, {}^b 21.6, {}^c 21.8$	${}^a 21.2, {}^b 20.1, {}^c 20.3$	${}^a 1.52, {}^b 1.50, {}^c 1.50$
${}^2 K_{15/2}, {}^4 G_{9/2}, {}^2 G_{7/2}$	365.0	${}^a 3.25, {}^b 3.08, {}^c 3.11$	${}^a 2.60, {}^b 2.46, {}^c 2.49$	${}^a 0.65, {}^b 0.62, {}^c 0.62$
${}^a \text{rms} = 1.14 \times 10^{-20} \text{ cm}^2$ , $\Omega_2 = 20.0 \times 10^{-20} \text{ cm}^2$ , $\Omega_4 = 6.15 \times 10^{-20} \text{ cm}^2$ , $\Omega_6 = 1.62 \times 10^{-20} \text{ cm}^2$				
${}^b \text{rms} = 1.08 \times 10^{-20} \text{ cm}^2$ , $\Omega_2 = 18.9 \times 10^{-20} \text{ cm}^2$ , $\Omega_4 = 5.81 \times 10^{-20} \text{ cm}^2$ , $\Omega_6 = 1.53 \times 10^{-20} \text{ cm}^2$				
${}^c \text{rms} = 1.09 \times 10^{-20} \text{ cm}^2$ , $\Omega_2 = 19.1 \times 10^{-20} \text{ cm}^2$ , $\Omega_4 = 5.87 \times 10^{-20} \text{ cm}^2$ , $\Omega_6 = 1.55 \times 10^{-20} \text{ cm}^2$				

## 4 Summary and outlook

We have successfully prepared lanthanoids orthoniobates single crystals from polycrystalline rods by a laser-heated miniature floating zone technique. The single crystals are obtained in the form of minirods with 0.6 - 0.7 mm diameter and 10 - 30 mm long. Optimized pulling and feeding rates for this family of materials were found in the range 0.3 - 0.7  $\text{mm min}^{-1}$ , while the stoichiometric mixture of starting reagents showed to be appropriate enough to obtain single phase crystals in most cases.  $\text{Er}^{3+}$ -doped  $\text{LaNbO}_4$  grows preferentially in the [1 0 0] direction, solidifies in its high-temperature phase, presents remarkable high absorption coefficient and spectral parameters  $\Omega_i$ , and exhibits strong luminescence when pumped at about 514 nm. A detailed study of this luminescence will be reported separately.

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