Growth and characterization of single crystal fibers of Nd$^{3+}$:NaLa(WO$_4$)$_2$

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Abstract. Single crystal fibers of pure and Nd$^{3+}$-doped NaLa(WO$_4$)$_2$ were grown by the micro-pulling down method ($\mu$PD) under air atmosphere. The starting materials were synthesized through solid state reaction. Inductive and resistive configurations of $\mu$PD systems were tested. The control of the growth process was better achieved through the resistive mode than in the inductive one. Optical and structural properties are compatible with the data already reported in the literature for bulk crystals of this host.

1. Introduction
Recently, there has been an increasing interest in the production of single-crystalline fibers of many different compounds. Their unique properties make their use in a variety of optical and electronic devices possible. Additionally, the growth of single crystalline fibers is fast and relatively low-cost compared to others crystal growth techniques from the melt, making their production a very suitable tool in the search for new materials.

In these last decades several works were reported regarding the properties of alkali rare earth tungstates - A(RE)(WO$_4$)$_2$, where A= K, Na, Li, and (RE) = rare earth elements. They are promising materials for optical applications due to their excellent luminescence properties, particularly as laser hosts, when doped with optically active rare earth ions [1]. In special, Nd$^{3+}$ was the first of the trivalent rare earth ions to be used in a laser, and remains by far the most important element in this group. Stimulated emission has been obtained with this ion incorporated in at least 100 different host materials, and a higher power level has been obtained from Nd lasers than from any other four-level material [2]. Recent spectroscopic studies of Nd$^{3+}$:NaLa(WO$_4$)$_2$ crystals have shown high luminescent quantum efficiency, moderate emission cross-section and FWHM large emission in the 1.06 and 1.35µm regions, making this material a promising active host for tunable solid state laser [3-4].

Many reports about Czochralski growth (CZ) of Na(RE)(WO$_4$)$_2$ and TSSG of K(RE)(WO$_4$)$_2$ crystals have already been published. However, very little investigations were performed on single crystal fiber growth of these materials. In fact, only one report was found on fiber growth of NaGd(WO$_4$)$_2$ and NaY(WO$_4$)$_2$ [5].

In this work, the preparation of pure and Nd$^{3+}$-doped NaLa(WO$_4$)$_2$ (NLW) compounds through solid state reaction and the growth process of single crystal fibers through the micro-pulling down
method (µPD) was studied. NaLa(WO₄)₂ crystals are isostructural with scheelite tetragonal structure (CaWO₄ – space group $\text{Ce}_{4h}^{-I}F_a/a$). They melt congruently at 1253°C [6]. In the µPD method, the fiber growth stability is controlled through the capillarity effect where the meniscus shape must be carefully controlled so that an uniform fiber pulling process occurs [7]. Details about µPD method can be found in the refs. [8,9,10].

2. Experimental procedure
Starting materials for fiber growth experiments were synthesized in a kanthal resistive furnace equipped with a temperature controller model 2416 from Eurotherm. The synthesis process was realized through solid state reaction as described in the literature by Serrano et al. [11] which is summarized as follows.

The initial chemicals of analytical grade – La₂O₃, Nd₂O₃, WO₃ and Na₂CO₃ – were carefully mixed in an agate mortar, in the appropriate molar ratio in accordance with the reaction

$$\text{Na}_2\text{CO}_3 + (1-x) \text{La}_2\text{O}_3 + x \text{Nd}_2\text{O}_3 + 4 \text{WO}_3 \rightarrow 2 \text{NaLa}_{1-x}\text{Nd}_x(\text{WO}_4)_2 + \text{CO}_2 \uparrow \quad (x = 0, 0.01, 0.02) \quad (1)$$

to obtain NaLa₁₋ₓNdₓ(WO₄)₂ compounds. The powder mixture was annealed in two steps under air atmosphere. The treatment of the material was performed with alumina or platinum crucibles. Firstly, the powder was heated at a rate of 50°C/h to 750°C and treated in this temperature for a period of 18h. After cooled down to room temperature the product of reaction was mixed in an agata mortar and submitted to a second heating step at a rate of 100°C/h to 850°C and held at this temperature for 24h.

X-ray diffraction (XRD) analyses of the synthesized tungstates were carried out with a Bruker AXS A8 Advance diffractometer with a Cu cathode ($\lambda = 1.054\text{Å}$). The data were collected using a Ni filtered Cu-target tube at room temperature in the 2θ range of 15–80°, step 0.02°/5s. XRD patterns of pure and doped compounds were compared and lattice parameters were determined through the Rietveld method using the DBWS software [12].

Single crystal fibers growth experiments were performed in a commercial resistive µPD system from Linn High Therm and in a homemade inductive µPD system equipped with an induction Versa Power (5KW 10-50KHz) InductoTherm frequency converter. The visual control of the experiments was performed with a stereo microscope. The starting materials were manually pressed into cylindrical pellets of 3.0mm of diameter and 10.0mm in thickness and placed in Pt crucibles in both cases.

Micro-EDX analyses were performed in order to characterize the Nd³⁺ incorporation. The measurements were taken longitudinally using a fluorescence spectrometer µEDX 1300, Shimadzu Inc. The scanning was done with steps of 1.0mm and count time of 100s per point. Absorption spectroscopy was performed at room temperature in the VIS and near IR range (450-950nm) with a CARY-17 Spectrophotometer, Conversion OLIS Inc.

3. Results and discussion
3.1. Starting material synthesis and characterization
Evaluation of X-ray powder diffraction reveals that the obtained polycrystalline compounds, when annealed in an alumina or platinum crucible, are formed by a main phase NaLa(WO₄)₂ (84wt%) and a secondary phase Na₃W₂O₁₃ (16wt%). A non-stoichiometric reaction is probably the reason of the secondary phase formation.

The high temperature may result in evaporation of one or more components resulting non-stoichiometric reactions. Analyzing the synthesis equation (1), the formation of Na₃W₂O₁₃ phase can be only explained if we consider a lower concentration of La₂O₃ during the processing of the samples, stimulating the occurrence of a secondary reaction with Na₂CO₃ + 4WO₃ resulting in Na₃W₂O₁₃ compound. The presence of this secondary compound was not detected in grown fibers.

Figure 1 shows the XRD patterns, analyzed by DBWS software, of a pure synthesized powder identified as the scheelite tetragonal NLW (main phase).
Lattice parameters were obtained for all NLW compounds as shown in table 1. The decrease of the cell parameters due to the La substitution by Nd ions can be observed in figure 2. This result is justified since ionic radii of Nd is smaller (109.0pm) than of La$^{3+}$ (118.0pm) and Na$^+$ (116.0pm) [13] for octahedral coordination [14] as in this case. The calculated values are comparable with those observed in bulk crystals [15].

Table 1. Lattice parameters of pure and Nd-doped NLW powders.

| compound               | a (Å)    | c (Å)    | volume (Å$^3$) |
|------------------------|----------|----------|----------------|
| bulk crystal [15]      | 5.349    | 11.628   | 332.7          |
| NaLa(WO$_4$)$_2$       | 5.3661(1)| 11.6735(2)| 336.13(1)      |
| NaLa$_{0.99}$Nd$_{0.01}$(WO$_4$)$_2$ | 5.3634(4) | 11.6681(9) | 335.65(5)      |
| NaLa$_{0.98}$Nd$_{0.02}$(WO$_4$)$_2$ | 5.3627(4) | 11.6655(9) | 335.48(5)      |

3.2. Crystal fiber growth through the μPD method

In order to obtain seeds, fiber growth tests in an inductive μPD system were first performed using as starting materials pieces of CZ crystals of Nd:NLW. The initial seed was an arbitrary oriented piece of crystal grown through the CZ method. The growth conditions are summarized in table 2.

Table 2. Growth conditions of Nd-doped NLW in the inductive μPD system.

|                      |                        |
|----------------------|------------------------|
| crucible (cylindrical)| Pt (3.0 cm$^3$)        |
| nozzle diameter      | 0.6mm                  |
| pulling rate         | 0.3-0.5mm/min          |
| atmosphere           | air                    |

Power control on this system was observed to be very critical at the start of the growth process. Variations of about 0.1kW in the radio frequency system result in significant changes in the growth interface as the liquid quickly flows to the exterior side of crucible. An appropriate control was only obtained with power variations of about 0.05kW which is very close to the limit of this equipment.
Such small variations make it possible to obtain controlled concave and convex liquid drops in the nozzle facilitating the seeding process. Once a stable meniscus was formed, Nd-doped NLW fibers with ~1.0mm in diameter and 10mm in length were obtained. All of them are transparent and uniform as showed in the figures 3.

![Figure 3.](a) As-grown Nd:NLW fiber obtained through inductive μPD and (b) its optical zoom.

Growth experiments were also performed in a μPD resistive mode. In this system there are two heater components (main and after heater – figure 4) that can be fitted to provide an ideal temperature gradient for stable crystallization conditions. The control of the process was better achieved through this system than in the inductive one. By adjusting the distances between the main and after heaters and also between the after heater spirals a better temperature control was obtained. Fiber growth parameters are summarized in table 3.

**Table 3.** Growth conditions of pure and Nd-doped NLW in the resistive μPD system.

| Parameter          | Values                                      |
|--------------------|---------------------------------------------|
| Crucible           | Pt (15.0 x 4.0 x 1.0mm³)                    |
| Nozzle diameter    | 0.8 and 1.0mm                               |
| Pulling rate       | 0.2-0.4mm/min                               |
| Atmosphere         | Air                                         |

In the growth process a constant and uniform meniscus, which is essential to produce regular fibers in diameter, was obtained through the temperature control of the crucible and after heater. Once a stable flat crystallization interface was achieved, no more changes of the pulling rate and main and after heater temperatures were necessary. The dimensions of the growth zone were measured through video microscope images during the crystal growth process as shown in figure 5. The meniscus height is given by the following empiric equation [16]:

\[
H_{max} \approx \frac{D_{fiber}}{2} = R_{fiber}
\]  

The control of the temperature of the after heater (Pt wire – figure 4) allowed the pulling of free crack fibers of all the grown compositions. Transparent and uniform fibers with 0.8mm in diameter and 15mm in length were pulled (figure 6-8). Doped fibers showed transparent purple color.
Nd-doped NaLa(WO$_4$)$_2$ single-crystalline fiber during growth process. Note: 0.8mm diameter of the crystal as scale reference.

Figure 5. Meniscus shape during Nd-doped NaLa(WO$_4$)$_2$ single-crystalline fiber growth process.

Figure 6. Stoichiometric NaLa(WO$_4$)$_2$ single-crystalline fiber.

Figure 7. As grown NaLa$_{0.99}$Nd$_{0.01}$(WO$_4$)$_2$ single-crystalline fiber.

Figure 8. As grown NaLa$_{0.98}$Nd$_{0.02}$(WO$_4$)$_2$ single-crystalline fiber.

3.3. Fiber characterization

The main fluorescence lines of La and Nd elements are very close, which complicates the determination of the real dopant concentration in NLW crystals through the μEDX technique. Due to this, the data was obtained taking into account the quantification of La atoms with Na atoms and the (WO$_4$)$_2$ group fixed, and using the Nd element as measurement balance. It was also considered that the Nd ions occupy La sites due to their similar valence and ionic radii, as discussed in the 3.1 section of this work. The average concentrations in the fibers are summarized in the table 4.

| nominal concentration (mol%) | measured concentration (mol%) |
|------------------------------|--------------------------------|
| 1.0                          | 1.58(28)                       |
| 2.0                          | 1.98(19)                       |

The absorption spectrum (figure 9) showed absorption bands of the neodymium trivalent cation (Nd$^{3+}$) in the NLW host (in the single-crystalline fiber shape) in accordance with data already reported at literature for bulk crystals [4]. All of the observed transitions were identified.
4. Conclusions
The ideal conditions to obtain single-crystalline fibers of pure and Nd-doped NaLa(WO$_4$)$_2$ compounds with good optical quality for optical properties evaluation were established. The control of the growth process in the μPD system was better achieved through the resistive mode than in the inductive one. Optical properties are compatible with the data already reported in the literature for bulk crystals of this host. In addition, the results show that the incorporation of neodymium trivalent cation (Nd$^{3+}$) by the NLW host is relatively easy.

Acknowledgments
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