

Growth, structural characterization and thermal analysis of LiLa(WO₄)₂ crystalline fibers

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Abstract

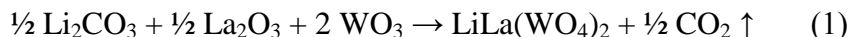
Crystal fibers of LiLa(WO₄)₂ (LLW) obtained through the micro-pulling-down method from starting materials of different compositions (La-deficient, stoichiometric composition and La-enriched) were examined by differential thermal analysis (DTA) and powder X-ray diffraction (XRD). La-deficient melts allowed the crystallization of stoichiometric LLW crystals; stoichiometric melt lead initially to the solid solution and then the stoichiometric LLW phase crystallization; and from the La-enriched melt only an opaque La-rich solid solution of LLW was possible to be grown. All results are discussed based on the melt behavior observations and they are consistent with the phase diagram data of the system LiLa(WO₄)₂ – La₂(WO₄)₃.

Introduction

LiLa(WO₄)₂ has been presented recently as a promising solid state laser matrix showing for this application thermo-mechanical and optical properties comparable to the other tungstates/oxides [1-4]. However, very few information is available in the literature concerning their growth process from the melt either by bulk (Czochralski) or by fiber growth methods (micro-pulling-down) [5-6]. The thermal data available give information regarding the system LiLa(WO₄)₂ – La₂(WO₄)₃ reporting the formation of solid solution phases as concentration of La₂(WO₄)₃ decreases [7]. However, the phase relations between LiLa(WO₄)₂ and Li₂WO₄ are not given; such data are described only to systems in which La is replaced by other rare earth ions such as Yb, Sm, Dy and Tb. Despite the fact that there is no data available for LLW melt vaporization, several works suggest that Li and W present high evaporation rates during the growth process without experimental evidence [8], however a conclusive report was not found. In a previous work de Moraes *et al.* [5-6] reported that the moisture adsorption of the La₂O₃ reagent must be avoided to obtain single phase compounds of NaLa(WO₄)₂ (NLW) and LiLa(WO₄)₂ (LLW). In the case of La deficiency, the formation of the phased Na₂W₄O₁₃ and Li₂W₄O₁₃ were observed in both materials respectively. In this work, an investigation of the melt behavior and the crystallization process of the LLW growth by the micro-pulling-down (μ -PD) method were carried out. The μ -PD method [9] is an excellent method to obtain samples more quickly than other growth methods and it requires only small amounts of materials for the experiments performed for these investigations.

Experimental Setup

Starting materials for fiber growth were synthesized in a resistive furnace equipped with a temperature controller, model 2416, from Eurotherm. The synthesis process occurred through solid state reactions as was performed in previous works [5-6]. The initial analytical grade chemicals La₂O₃, WO₃ and Li₂CO₃, were carefully mixed in an agate mortar in the appropriate molar ratios - considering a La-deficiency (~15% weight), no La-deficiency and a La-enriched (~15% weight) composition - in accordance with the reaction:



The reagent powder mixtures were annealed in a single step under air atmosphere. The treatment of the material was performed in alumina crucibles. The powder was heated at a rate of 50°C/h to 750°C, treated at this temperature for a period of 48 h and then cooled down to room temperature at a rate of 50°C/h.

The crystal fiber growth experiments were performed in a modified commercial resistive μ -PD system from Linn High Therm. The starting materials were melted in Pt-Au 5% handmade crucibles. The fibers were pulled through a micro nozzle made in the bottom-center of the crucible (nozzle diameter/length - 0.8/1.2 mm) at a pulling rate of 0.06 mm/min under air atmosphere using a LLW crystal fiber seed.

The fibers were analyzed through a video-microscope to evaluate macroscopic defects and segregation. XRD analyses of the starting materials and the fibers were carried out in a Bruker AXS model A8 Advance diffractometer, equipped with a Ni filtered Cu cathode ($\lambda_{\text{K}\alpha} = 1.5406 \text{ \AA}$). Data were collected at room temperature in the range of 15° to 80° with a step scan rate of 0.02°/5s. All measurements were performed with powders. Experimental data and the LLW XRD pattern from ICSD were compared. The lattice parameters were determined through the Rietveld method using GSAS software [10]. Thermal analysis was accomplished in a simultaneous TG/DTA system of TA Instruments, model SDT2960 or in a TG/DSC system of NETZSCH, model STA 409 PC/PG with a heating rate of 10°C/min under Ar flow of 100 mL/min in alumina pans. Pieces from the fibers were used as samples with a average weight of 19.0 mg.

Results and Discussion

Phase identification of synthesized materials by XRD analysis (Table 1) indicates that only the LLW phase was formed for the stoichiometric case and the LLW plus the secondary phases $\text{Li}_2\text{W}_4\text{O}_{13}$ and $\text{La}_2(\text{WO}_4)_3$ for the La-deficient and La-enriched cases, respectively. Fibers crystallized in different ways depending on the melt composition (Table 1) and these results can be interpreted based in the equilibrium phase diagram reported by Evdokimov *et al.* [7] as discussed next.

Table 1. Crystal fiber's chemical composition as function of melt composition.

synthesized powder XRD (fig. 3)	LLW + $\text{Li}_2\text{W}_4\text{O}_{13}$	LLW	LLW + $\text{La}_2(\text{WO}_4)_3$
synthesized	$a = 5.3359$	$a = 5.3272$	$a = 5.3250$
LLW cell parameters	$c = 11.6061$	$c = 11.5452$	$c = 11.5416$
melt composition	La-deficient	stoichiometric composition	La-enriched
during growth fiber aspect	transparent	transparent becomes opaque + transparent at the end	transparent becomes opaque
as-grown fiber aspect	transparent (Fig. 1c) [no cracks – except for segregation (Fig. 1b)]	<u>from</u> opaque <u>to</u> transparent (no cracks)	opaque (no cracks) (Fig. 1a)
crystal fiber composition by XRD (fig. 4)	stoichiometric LLW	<u>from</u> La-rich LLW solid solution <u>to</u> stoichiometric LLW	La-rich LLW solid solution
LLW crystal cell parameters	-	<i>stoichiometric</i> $a = 5.3365$ $c = 11.6726$	<i>La-rich</i> $a = 5.3406$ $c = 11.6905$

Li-enriched melt induced the crystallization of a single phase LLW (Fig 1). Despite the fact that Zharikov [8] misunderstood Huang's reports [3], LLW does not show a polymorphic transition from the tetragonal phase to any other crystallographic system as was verified by Evdokimov et al. [7] and in this work (Fig. 2) as well. Depending on the stability of the growth process segregation of extraneous phases may occur (Fig. 1a). Although the segregations' exact composition was not identified, DTA analysis revealed two endothermic peaks (700°C and 1125°C) that differ from the LLW melt peak (approximately 1050°C) implying the presence of a distinct phase other than LLW (Fig. 2).

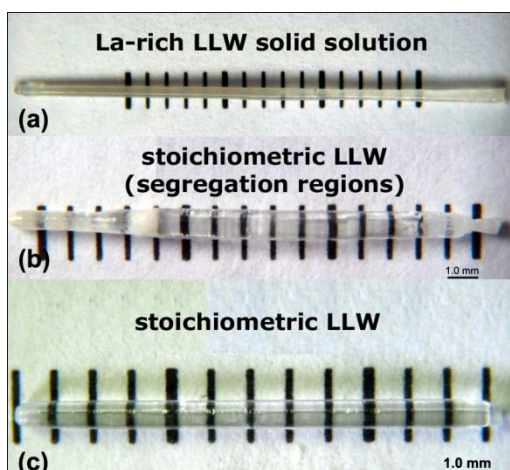


Figure 1: LLW crystal fibers grown from (a) La-rich, (b) and (c) stoichiometric melt compositions.

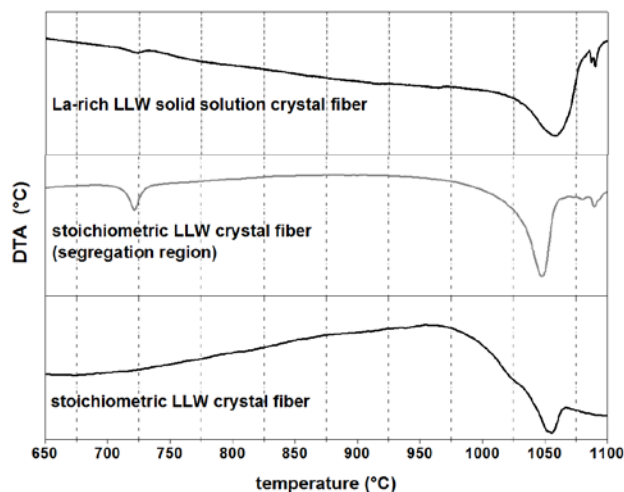


Figure 2: DTA of LLW crystal fibers grown from different melt compositions.

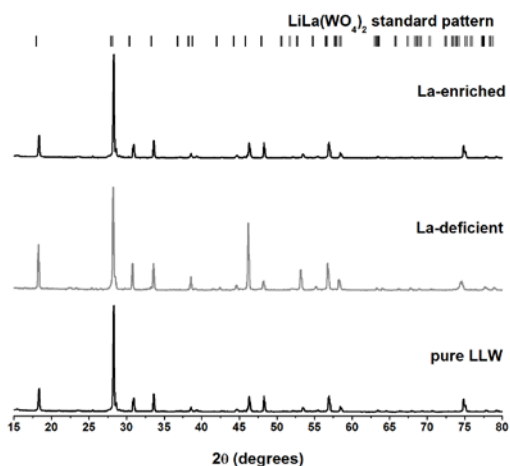


Figure 3: XRD of synthesized LLW powders.

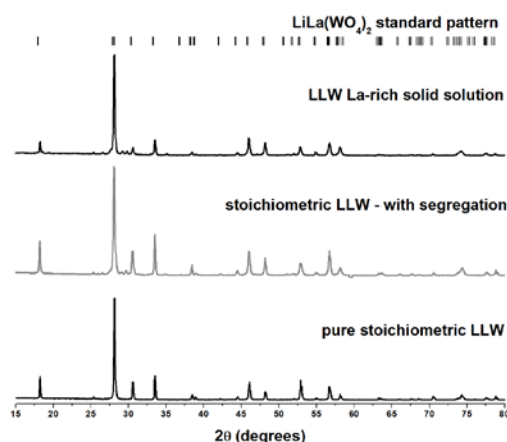


Figure 4: XRD of LLW crystal fibers powders

The melt of stoichiometric composition lead to the crystallization of a transparent phase that becomes opaque and at the end of the growth a stable transparent region is crystallized. A hypothesis can be drawn to explain this behavior: an intense but slow Li evaporation simultaneous to the fast crystallization of the La-enriched melt. The opaque

crystal is therefore formed until the Li-evaporation/La-excess-crystallization ratio becomes close to the unit. Nevertheless no significant mass loss was detected by TG analyses despite the fact that a white film was deposited on the top surface of the chamber throughout all of the growth experiments. This is consistent with a more pronounced evaporation of lithium since this element's mass is extremely small in comparison to some of the others' (La and W) and negligible mass loss during thermal analysis could still lead to significant composition change in a sample. In this case, the opaque crystal is a La-rich solid solution of LLW (according to the phase diagram [7]) and the transparent region is closer in composition to the stoichiometric LLW.

La-enriched melts lead to the crystallization of an opaque fiber throughout its entire length (Fig. 4), even though the growth interface presented itself as a transparent meniscus in the growing crystal. XRD data reveals the presence of reflection peaks differing from the LLW phase and it may indicate the crystallization of a La-rich LLW solid solution, as proposed by Evdokimov [7].

Conclusions

La-deficient (or Li-rich) melt allows the crystallization of stoichiometric LLW crystals; stoichiometric melt leads initially to the La-rich LLW solid solution and then the stoichiometric LLW fiber crystallization; and from the La-enriched melt only an opaque La-rich LLW solid solution of was possible to be grown. All results are discussed based on the melt behavior observations and they are consistent with the phase diagram data of the system $\text{LiLa}(\text{WO}_4)_2 - \text{La}_2(\text{WO}_4)_3$ proposed by Evdokimov.

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