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Crucibleless crystal growth and Radioluminescence study of calcium tungstate single crystal fiber

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ABSTRACT

In this article, single phase and high optical quality scheelite calcium tungstate single crystal fibers were grown by using the crucibleless laser heated pedestal growth technique. The as-synthesized calcium tungstate powders used for shaping seed and feed rods were investigated by X-ray diffraction technique. As-grown crystals were studied by Raman spectroscopy and Radioluminescence measurements. The results indicate that in both two cases, calcined powder and single crystal fiber, only the expected scheelite $CaWO_4$ phase was observed. It was verified large homogeneity in the crystal composition, without the presence of secondary phases. The Radioluminescence spectra of the as-grown single crystal fibers are in agreement with that present in Literature for bulk single crystals, presented a single emission band centered at 420 nm when irradiated with β-rays.

1. Introduction

Scheelite calcium tungstate ($CaWO_4$) is one of the most widely used phosphor in industrial radiology and medical diagnosis [1]. It can be employed for a variety of applications such as tunable fluorescence [1], optical storage [2], sensor for dark matter search [3], X-rays and gamma-rays sensors in medical applications [4], plasma display panels and advertising signs fluorescent tubes [5]. Their luminescence properties have been investigated extensively using several radiations fonts (X-rays, beta-rays, ultraviolet light, gamma-rays, synchrotron radiation, etc.) [3,4,6]. Its recent use in medicine and dark matter search has prompted a renewed research interest aimed at a comprehensive characterization of their physical properties and crystal growth conditions [3,4,7].

Bulk $CaWO_4$ single crystals are mostly grown by the Czochralski method [8,9] whose the main disadvantage are the contaminated with the crucible material, besides this growth method can cause strains, cracks, low-angle grain boundaries, gas bubble entrapment, among other undesirable effects in produced crystals [10]. Crucibleless growth techniques could be useful to growth single phase scheelite $CaWO_4$, with advantages like geometry and low contamination of shaped crystals. Fiber-like shaped single crystals of some tungstates [11], for example, have been demonstrated in efficient stimulated Raman scattering [12] and could be proposed for high performance scintillating screens [13].

Conventional LHPG concentrates a previously expanded CO_2 laser beam into a single small region centered in the focal point of a spherical mirror [14,15]. When the seed and feed rods are vertically aligned and their closer ends brought into the growth region, steeped temperature gradients are developed in the axial direction around the formed liquid–solid interfaces. These gradients can be as high as 1000 °C/mm, depending on the thermophysical properties of the growing material and the way of focusing the laser beam onto the melting region. However, the large temperature gradients are a drawback for the growth of materials with tendency to evaporate or decompose due to overheating, like $CaWO_4$.

Therefore, in this work, we have reported the growth of scheelite $CaWO_4$ single crystal fibers by using the crucibleless laser-heated pedestal growth (LHPG) technique with a modification in the way of heating both needed seed and feed rods. To the best of our knowledge this is the first time this technique with the mentioned modification is reported to be useful to grow high quality scheelite $CaWO_4$ single crystal fibers.

2. Experimental procedure

2.1. Seed and feed rods preparation

Scheelite $CaWO_4$ powders was synthesized by solid-state reaction using as precursor materials $CaCO_3$ (Merck) and 99.9% WO_3

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(Merck). The starting materials were mixed according to the stoichiometric ratio of $CaWO_4$ and homogenized in agate mortar for 20 min. Soon after, the powder was calcined in air at 800 °C for 2 h following a heating rate of 10 °C/min. Next, the powder was mixed with a binder solution of polyvinyl alcohol in a concentration of 0.1 g ml^{-1} to form a soft paste that was extruded into cylindrical rods of 1.0 mm diameter and 50–100 mm length. The extruded bodies were dried in air for 4 h and then used in the crystal growth experiments as feed and seed rods.

2.2. Experimental setup for crystal growth

The main features of our approach for crystal growth by the LHPG technique are shown in Fig. 1. In order to decrease the temperature gradient in the liquid–solid interfaces, a focusing mirror was modified to generate two foci separated by 1.0 mm. This bifocal spherical mirror was made by slicing a spherical copper mirror into eight sectors, and displacing alternate sectors by 1.0 mm along the growth direction. The lowered symmetry of the heating beam did not harmfully reduce the heating uniformity in the molten zone. The relative surface areas of the two sets of displaced mirror sectors (approximately 3:1) define the relative amounts of laser power focused on the melt and on the after heated region. This approach has been used before by us for the successful growth of large diameter $LiNbO_3$ single crystal minirods, with measured temperature gradients significantly reduced (to approximately 300 °C/mm) relative to the standard LHPG method [14].

2.3. Crystal growth procedure

The experiments were fully carried out in air atmosphere at room pressure, with partially automated control of the laser power, pulling and feeding rates, without the rotation of the seed or feed rods. After the alignment of the seed and feed rods, they were maintained in rest and separated around the region of the crystal growth. A first dome-shaped molten zone was formed by focusing the laser beam on the top of the feed rod. Soon after, the seed rod was dipped and held into the first melt up to the formation of a molten zone with the shape of a liquid bridge. When the molten zone became stable, both seed and feed rods were displaced upwards with equal pulling and feeding rates in the range of 0.5–0.7 mm/min. The growing crystal to feed rod diameters ratio was fixed in this way close to unity.

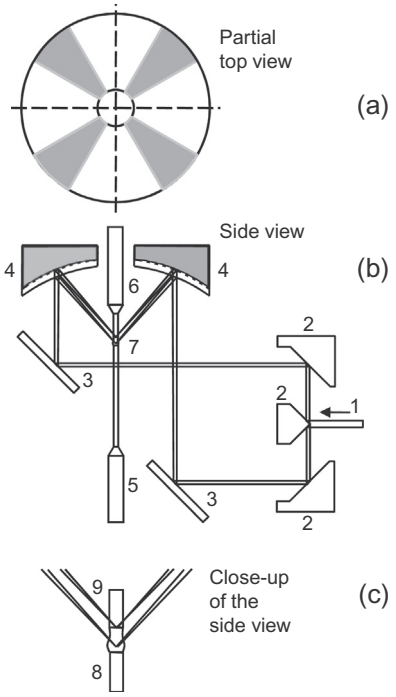

Fig. 1. Schematic representations of main modifications made in a LHPG system for the growth of $CaWO_4$ single crystal fibers. All components found 1.0 mm higher in height appear shadowed. (a) Top view of the bifocal spherical mirror. (b) Side view of the main setup: (1) CO_2 laser beam, (2) reflection, (3) flat mirror, (4) bifocal spherical mirror, (5) feed rod holder, (6) seed rod holder, (7) crystal growth region. (c) Close view of the crystal growth region: (8) feed rod, (9) seed rod.

2.4. Feed material and crystal characterization

X-ray diffraction technique (XRD) was used to study the phase formation of the calcined $CaWO_4$ powder. XRD data were collected in a Rigaku RINT 2000/PC diffractometer, using Cu Kα radiation in continuous scan mode, at rate of 2°/min, and 2θ range from 20° to 60°. Raman spectroscopy was employed to investigate the existing phases and the homogeneity of the as-grown crystals. Unpolarized Raman spectra were measured using a Bruker Senterra spectrometer with a 532 nm laser excitation source operated at 10 mW, with a 50× objective, collecting the data by averaging 10 acquisitions, each one lasting for 4 s, with a resolution of 1–15 cm^{-1}. Radioluminescence (RL) spectra were recorded at 20 K and 300 K using β radiation from a $^{90}Sr/^{90}Y$ source. The RL curve of the crystal was detected using a Hamamatsu R928 photomultiplier tube (PMT) and a monochromator (FUNBEC Unicrom 100). The PMT and $^{90}Sr/^{90}Y$ source were positioned along perpendicular axes forming each 45° with the horizontal plane.

3. Results and discussion

Fig. 2 shows the XRD pattern of the powder calcined at 800 °C for 2 h. The peaks are indexed according to JCPDS database (PDF #77-2233). As can be seen, only the scheelite $CaWO_4$ phase was observed and none trace of a probable secondary phases, like WO_3, was detected.

Fig. 3 shows a typical transparent and crackless as-grown $CaWO_4$ single crystal fiber, with a piece of feed rod in the bottom left side. The high transparency is characteristic of minimal or none oxygen-deficiency stoichiometry.

Fig. 4 presents the Raman spectra measured along the length of the as-grown single crystal fiber. All analyzed regions show only the peaks of the tetragonal scheelite $CaWO_4$ phase [15,16]. The

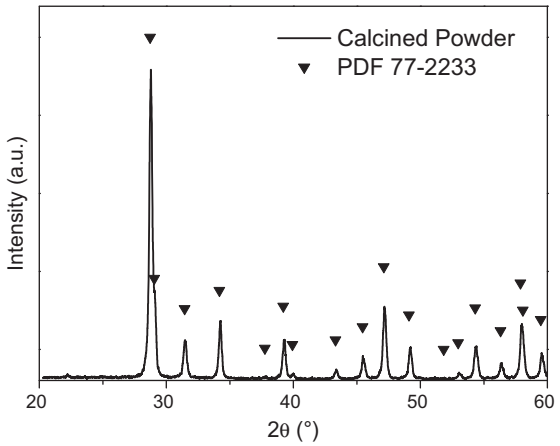

Fig. 2. X-ray diffraction pattern of as-synthesized powder, calcined at 800 °C/2 h, used for the growth of the $CaWO_4$ single crystal fiber. Reflection peaks were indexed according to inorganic crystal structure database – PDF – 77-2233 – $CaWO_4$.

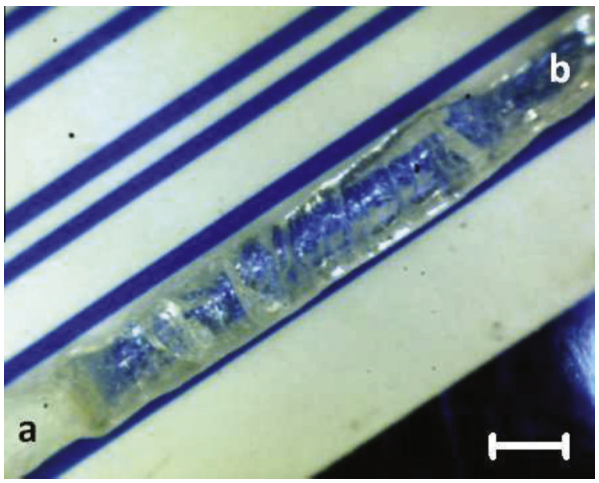

Fig. 3. As-grown $CaWO_4$ single crystal fiber. A piece of feed rod (a) and the region close to the last mm of grown crystal (b) are indicated. Scale bar at the right bottom side scales 1.0 mm.

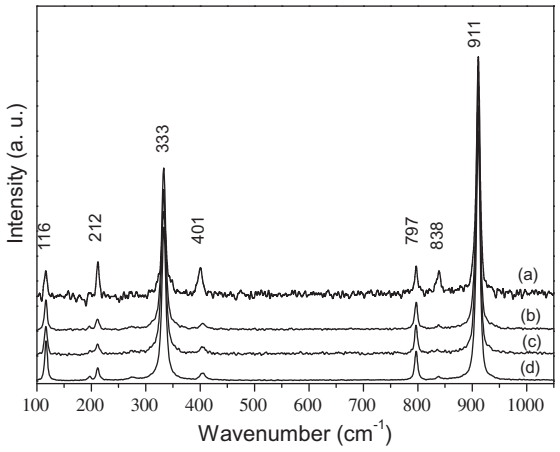

Fig. 4. Raman spectra along the length of the as-grown $CaWO_4$ single crystal fiber. (a) Close to the seed–crystal interface; (b–d) spectra measured every 3 mm along the fiber.

absence of Raman bands in the 500–700 cm^{-1} region and vibrational modes at 270, 715, 805 cm^{-1} reflect the absence of bridging W–O–W bonds and of the WO_3 group, respectively, thus demonstrating the phase purity and compositional homogeneity of the produced fiber [17]. The stronger Raman band found at 911 cm^{-1} (A_g) and other bands at 838 (B_g), 797 (E_g), 401 (B_g), and 333 cm^{-1} ($E_g + B_g$) correspond to internal covalent vibrational modes of the single slightly irregular WO_4 unit. Bands below 250 cm^{-1} correspond to the external optical modes, with the band at 212 cm^{-1} (A_g) assigned to the rotational modes, and the band at 116 cm^{-1} (E_g) is attributed to the translational modes [16]. Additionally, the Raman spectra in Fig. 4 (b-d) contain predominately only lines 797 cm^{-1} (E_g) and 911 cm^{-1} (A_g) in the high frequencies region, while in the spectrum of Fig. 4a, in addition to these two lines, the line 838 cm^{-1} (B_g) also arises. Such spectrum corresponds to the fiber orientation only along the C_{4h}-axe of the Scheelite structure and for a use of the scattering geometry with the vector *E*-direction of the excitation light along the C_{4h}-axe as well. Other growth directions and the scattering geometry views would result in a presence of either the three lines (797 cm^{-1} (E_g), 838 cm^{-1} (B_g) and 911 cm^{-1} (A_g)) or of the two (797 cm^{-1} and 911 cm^{-1}) lines in the Raman spectra. Such case is seen very well in Fig. 4a, that in our samples corresponds to the polycrystalline seed and contained three lines (797 cm^{-1} (E_g), 838 cm^{-1} (B_g) and 911 cm^{-1} (A_g)).

Fig. 5 presents the emission spectral of $CaWO_4$ measured under β irradiation at 20 and 300 K. The emission band is centered at 420 nm and remains constant when the temperature increases. This band is due to electronic transitions of the charge transfer type within the $(WO_4)^{2-}$ anion complex and is interpreted as an emission of self-trapped molecular excitons [9,18].

Fig. 6 presents the scintillation light output of $CaWO_4$ as a function of the temperature. The scintillation yields were obtained measuring the polychromatic isothermal emission. It is clear that the light output intensity, and thus the scintillating efficiency, decreases as the temperature increases, presenting a slight reduction up to 220 K (~3%) and since than a faster decline up to 400 K (~40%). According to Mikhailik et al. [18], at high temperatures (>220 K) the light output is dominated by thermal quenching, and as the probability of nonradiative decays increases strongly with temperature, the emission intensity decreases. The results presented in Figs. 5 and 6 is in agreement with previous reports onto the luminescence properties of $CaWO_4$ bulk single crystal [9,18]. It is evident that for future applications more detailed studies are needed, however the results presented here confirm LHPG as an effective technique to growth $CaWO_4$ single crystalline fibers with suitable properties.

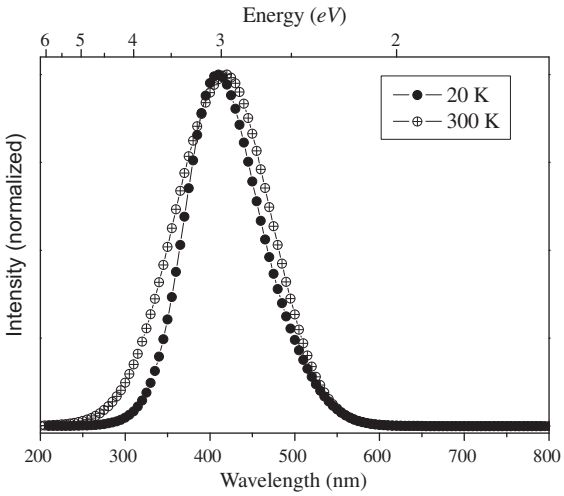

Fig. 5. Radioluminescence spectra of $CaWO_4$ single crystal fiber under excitation with a $^{90}Sr/^{90}Y$ source, at 20 and 300 K. Both curves are normalized.

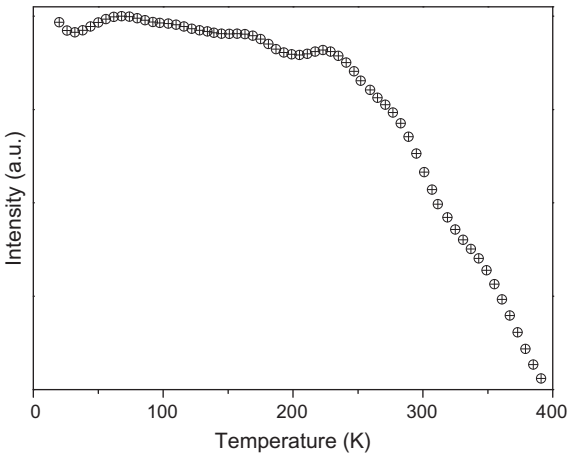

Fig. 6. Total scintillation yield (normalized to the yield at 20 K) under β radiation as a function of the temperature.

4. Conclusions

An efficient method of growing crackless, single phase and high optical quality scheelite $CaWO_4$ single crystal fibers involving the use of crucibleless LHPG technique was described. The prepared samples, synthesized powder and single crystal fibers, show presented single $CaWO_4$ phase, confirmed by X-ray diffraction and Raman results. During the single crystal fibers growth, beyond the adequate feeding and pulling speeds and the stoichiometric composition of seed and feed rods, the success of our crystal growth can be also attributed to the temperature gradient control around the solid–liquid interfaces, which reduces the $CaWO_4$ evaporating and decomposition by overheating. It is expected that the current approach can be applicable to the successful crystal growth of other materials having similarities with $CaWO_4$. The single crystal fibers exhibit comparable luminescence features reported for bulk single crystals with emission band centered at 420 nm and remains constant when the temperature increases.

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