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Structural and optical properties of LuVO₄ single crystals

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Abstract. The synthesis of large single crystals with good optical quality which is a preliminary condition for the practical applications of these materials frequently is complicated. It is found that large LuVO₄ single crystals with high optical quality are possible to be prepared using high temperature solution growth method. It is obtained by X-ray crystallographic analysis that the grown crystals possess centrosymmetric tetragonal structure with the point group symmetry D_{4h} and space group I41/amd (zircon-type structure). The unit cell parameters of $a = 7.0236 \text{ \AA}$, $b = 7.0236 \text{ \AA}$, $c = 6.2293 \text{ \AA}$, volume = $307.30(3) \text{ \AA}^3$ are measured. The crystals composition as well as vanadium oxidation state were measured in order to confirm that the crystal phase is mainly LuVO₄. Optical transmission and Raman Spectroscopy are further performed on LuVO₄ single crystal to reveal the optical quality and structure details

1. Introduction

Rare-earth orthovanadates (RVO₄, where R = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) compounds demonstrate diverse applications in various fields. Due to their exceptional optical properties, as wide optical transparency and large birefringence, RVO₄ are potential candidates for optical isolators, circulators, beam displacers, and components for polarizing optics [1].

Up to now, crystal growth process of RVO₄ has been attempted by several methods. Slow cooling from solution [2], the Czochralski process [3], top-seeded solution growth [4], the laser-heated pedestal growth method [5], the floating-zone (FZ) method [6] and the micro-FZ method [7] have been already reported. All those methods offer single crystals with excellent quality, however with relatively small sizes. The reason is that RVO₄ melts congruently and although the melting temperatures are as high as 1400 °C and above, and consequently large crystals were not obtained.

Among RVO₄ single crystals, LuVO₄ is one with a particular interest as a laser host material due to the larger absorption cross section near 800 nm and larger emission cross section at 1.064 μm in comparison with other vanadate crystals [8]. These features are very desirable for diode pumped solid-state lasers, as they make it feasible to achieve highly efficient pumping and to realize low threshold



laser operation with high optical-to-optical efficiency. The synthesis of large single crystals with good optical quality which is a prerequisite for the practical applications however is quite complicated. This paper reports the crystal growth process of large, high quality LuVO₄ crystals and study of their structural and optical properties.

2. Experimental details and discussion

2.1. Crystal growth, structural analysis and composition

Single crystals of LuVO₄ were grown by high temperature solution growth method. As a first step, polycrystalline LuVO₄ was synthesized by the solid state reaction. Stoichiometric amounts of Lu₂O₃ and V₂O₅ with minimum purity of 99.99% were mixed, compacted, and then calcinated in oxygen at 650 °C for 48 h. The reacted product was ground and mixed with V₂O₅ flux in V₂O₅: LuVO₄ =12:1 ratio. The mixture was melted and heated to 1100 °C for 48 h in a platinum crucible of 50 mm diameter and 60 mm depth, covered with a platinum lid. Single crystals were obtained by cooling the solution from 1100 to 700 °C at a cooling rate of 1 °C/h. The residual flux was separated from the as-grown crystals by decanting. The obtained crystals remained on the bottom and the walls of the crucible. The LuVO₄ single crystals with high optical quality have tetragonal rectangular shape and typical size of 6 x 8 x 0.5 mm.

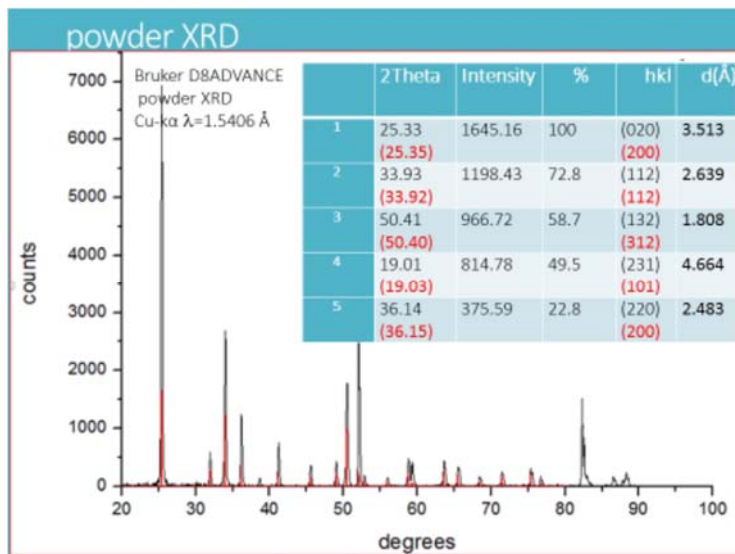


Figure 1: Powder XRD of LuVO₄ crystal (inset: main peaks assignment)

X-ray Powder Diffraction, using a D8 Bruker powder diffractometer equipped with a Cu anticathode, an incident slit of 0.51, an anti-scatter slit of 0.51, a detector slit of 1mm, and a graphite monochromator in the diffracted beam was performed on LuVO₄ powder prepared from single crystal sample. The powder diffraction pattern and main peaks assignments (inset) are shown in figure1.

A single crystal LuVO₄ specimen was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at room temperature using Bruker-AXS Smart Apex three-circle diffractometer equipped with a CCD detector which verified that the grown crystals possess centrosymmetric tetragonal structure with the point group symmetry D_{4h} and space group I4₁/amd (zircon-type structure).

Table 1: Single crystal data

Chemical formula	LuVO ₄	Unit cell dimensions	a=7.0236(3) Å
Formula weight	289.91		b=7.0236(3) Å
Temperature	296(2) K		c=6.2293(4) Å
Wavelength	0.71073 Å		α=90°, β=90°, γ=90°
Crystal system	tetragonal	Volume	307.30(3) Å ³
Space group	I 41/amd	Z	4
F(000)	504	Density(calculated)	6.266 g/cm ³
Absorption coefficient	34.794 mm ⁻¹		

In this structure, the vanadium atom is in tetrahedral coordination, while the trivalent R cation is coordinated by eight oxygen atoms. The unit cell parameters of a = 7.0236(3) Å, b = 7.0236 Å, c = 6.2293 Å, volume = 307.30 Å³ are measured. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group I41/amd, with Z = 4 for the formula unit, LuVO₄. A selection of the data obtained is shown in table 1.

The single crystals composition and the valence state of vanadium were further verified with EDAX Energy Dispersive Spectrometry and X-ray Absorption Spectroscopy (XAS) respectively. EDAX data (shown on figure 2) revealed some hafnium impurities in the LuVO₄ single crystals prepared by our method.

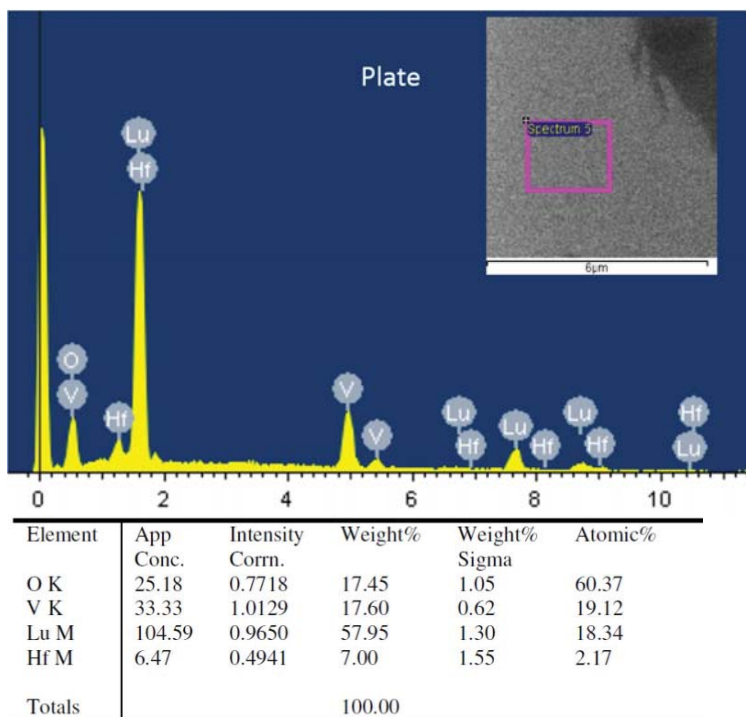


Figure 2: EDS spectra and composition data of LuVO₄ single crystal plate

For LuVO₄, the oxidation state of vanadium ion is very close to V⁵⁺, since its V-L2,3 X-ray Absorption Spectroscopy (XAS) spectra (figure 3) is very similar to the spectra of reference V₂O₅, V2p and O1s spectra shown on figure 3 top (adapted from [9]) as well as Ni₃V₂O₈ [11], Co₃V₂O₈ [10], and YVO₄ [11]. Moreover, if there were V⁴⁺, an enhancement of the structures below the main peaks will be observed, as observed for example in beta-Sr_{0.17}V₂O₅ [12]. However, this effect is absent in our single crystal LuVO₄. Therefore, we could conclude that V in LuVO₄ is in 5+ state.

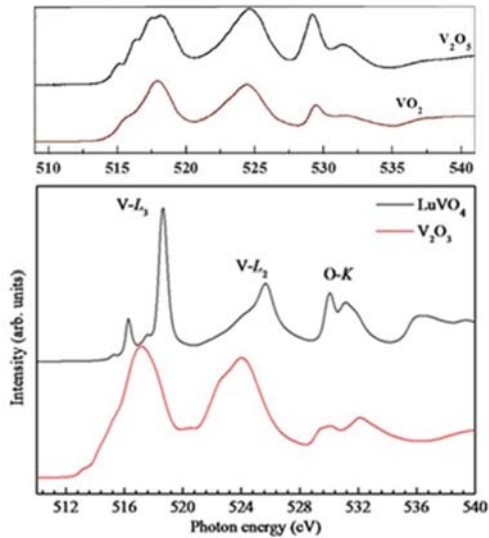


Figure 3: XAS spectra of LuVO₄ single crystal

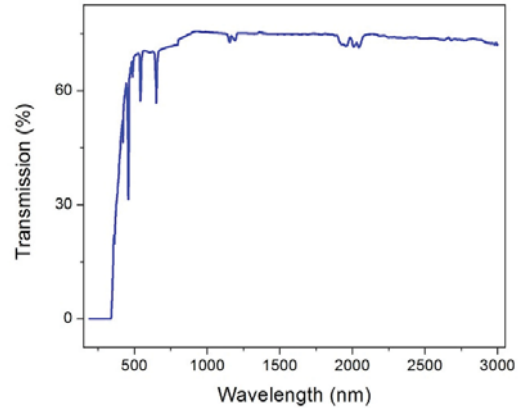


Figure 4: Optical Transmission of LuVO₄ single crystal 200-3000 nm

2.2. Optical transmittance and Raman spectroscopy analysis

The LuVO₄ single crystals are moreover analysed by Optical spectroscopy and Raman spectroscopy methods.

Optical transmission spectra were measured on crystal polished plate using Cary 5E UV-VIS spectrophotometer. As it seen from figure 4, the obtained crystal shows high transparency in a wide spectral range from 500 to 3000 nm. The absorption bands in the spectral interval 500-750 nm could be due to the hafnium impurities as shown in EDAX/EDS data.

For the Raman spectroscopic measurements single crystals with elongated shapes along the Z axis with naturally grown {100} and {001} surfaces were selected which additionally displayed well shaped {001} surfaces. The Raman spectra were measured in the range of (80 - 1200) cm⁻¹ on a HORIBA Jobin Yvon LabRAM HR visible spectrometer equipped with a Peltier-cooled CCD detector. The 1.95 eV line of a He-Ne laser was used for excitation, the absolute accuracy being 0.5 cm⁻¹.

Lutetium vanadate LuVO₄ crystallizes in a centrosymmetric tetragonal structure with the point group symmetry D_{4h} and space group I4₁/amd (zircon-type structure). The structure consists of Lu³⁺ ions and VO₄³⁻ tetrahedra that can be approximately regarded as separate units due to the strong internal bonds within each tetrahedron. Therefore, the lowest-frequency vibrations of LuVO₄ comprise translations and librations of the VO₄³⁻ tetrahedrons as rigid units against the Lu³⁺ ions. The higher-frequency phonons, on the other hand, are almost entirely due to internal vibrations of the VO₄³⁻ tetrahedral complexes.

For the polarized Raman measurements, the notations X (100), Y (010) and Z (001) for the main crystal axes as well as X' (110) and Y' (-110) were used. The measured spectra are presented in figure 5 with scattering configurations given in Porto notations. Raman selection rules are clearly discernible despite the considerable depolarisation effects caused by the extremely strong birefringence of the LuVO₄ crystal. These effects leading to partial mixing of allowed and forbidden intensity between different Raman modes [Porto] can be minimized by using focusing/collecting optics with small numerical aperture (N.A.) and keeping short the beam path within the sample. These two requirements were successfully met by using a 20× microscope objective with NA = 0.4. The spectra also contain features from impurities or second-phase inclusions that do not obey the Raman selection rules and obviously do not pertain to the vibrational spectrum of LuVO₄ crystal. Their frequencies lie in most

cases far from LuVO_4 signal and with one exception they posed no obstacle to the assignment of the LuVO_4 modes.

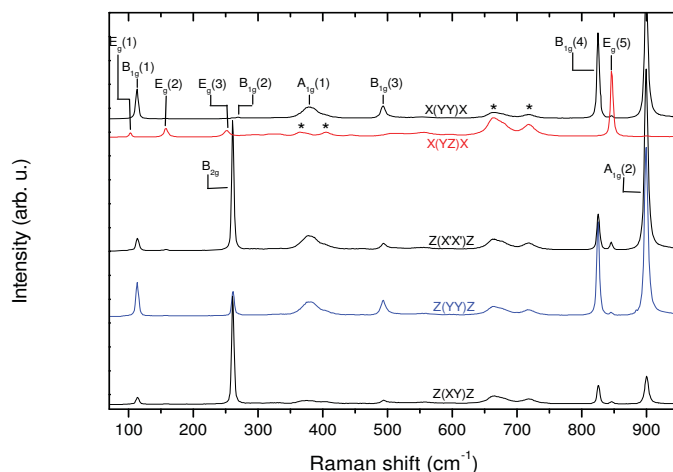


Figure 5: Raman spectra with mode assignment of LuVO_4 single crystal in different polarization configurations given in Porto notations. Features stemming from impurities or second-phase inclusions are marked with asterisks

3. Conclusion

Large, optically homogenous single crystals of LuVO_4 were prepared by using high temperature solution growth method. The single crystal structure quality details as well as composition and oxidation state of vanadium for LuVO_4 crystal phase were confirmed. The samples possess high optical transparency in the spectral interval 500-3000 nm.

Acknowledgements

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