Structural and optical properties of LuVO4 single crystals

Structural and optical properties of $LuVO_4$ 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 $LuVO_4$ 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 Å, b = 7.0236 Å, c = 6.2293 Å, volume = 307.30(3) $Å^3$ are measured. The crystals composition as well as vanadium oxidation state were measured in order to confirm that the crystal phase is mainly $LuVO_4$. Optical transmission and Raman Spectroscopy are further performed on $LuVO_4$ single crystal to reveal the optical quality and structure details

1. Introduction

Rare-earth orthovanadates (RVO_4, 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, RVO_4 are potential candidates for optical isolators, circulators, beam displacers, and components for polarizing optics [1].

Up to now, crystal growth process of RVO_4 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 RVO_4 melts congruently and although the melting temperatures are as high as 1400 °C and above, and consequently large crystals were not obtained.

Among RVO_4 single crystals, $LuVO_4$ 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 $LuVO_4$ crystals and study of their structural and optical properties.

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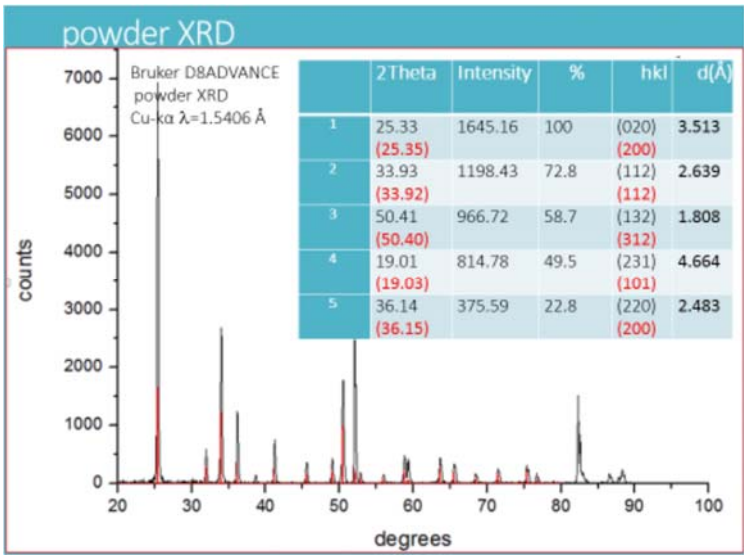
2. Experimental details and discussion

2.1. Crystal growth, structural analysis and composition

Single crystals of $LuVO_4$ were grown by high temperature solution growth method. As a first step, polycrystalline $LuVO_4$ was synthesized by the solid state reaction. Stoichiometric amounts of Lu_2O_3 and V_2O_5 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 V_2O_5 flux in V_2O_5: $LuVO_4$ =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 $LuVO_4$ single crystals with high optical quality have tetragonal rectangular shape and typical size of 6 x 8 x 0.5 mm.



	2Theta	Intensity	%	hkl	d(Å)
1	25.33 (25.35)	1645.16	100	(020) (200)	3.513
2	33.93 (33.92)	1198.43	72.8	(112) (112)	2.639
3	50.41 (50.40)	966.72	58.7	(132) (312)	1.808
4	19.01 (19.03)	814.78	49.5	(231) (101)	4.664
5	36.14 (36.15)	375.59	22.8	(220) (200)	2.483

Figure 1: Powder XRD of $LuVO_4$ 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 $LuVO_4$ powder prepared from single crystal sample. The powder diffraction pattern and main peaks assignments (inset) are shown in figure1.

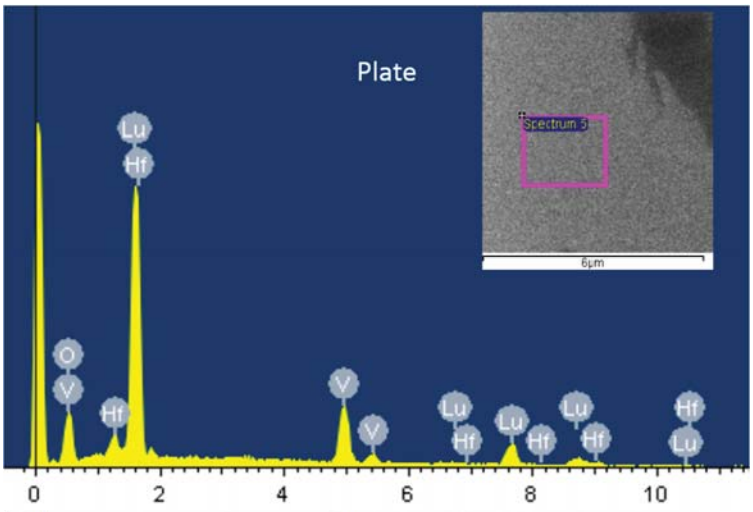
A single crystal $LuVO_4$ specimen was used for the X-ray crystallographic analysis The X-ray intensity data were measured at room temperature using Bruker-AXS Smart Apex three-circle diffractometer equipped with a CCD detector which verified that the grown crystals possess centrosymmetric tetragonal structure with the point group symmetry D4h 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 $Å^3$ 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, $LuVO_4$. 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 $LuVO_4$ single crystals prepared by our method.



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	25.18	0.7718	17.45	1.05	60.37
V K	33.33	1.0129	17.60	0.62	19.12
Lu M	104.59	0.9650	57.95	1.30	18.34
Hf M	6.47	0.4941	7.00	1.55	2.17
Totals			100.00		

Figure 2: EDS spectra and composition data of $LuVO_4$ single crystal plate

For $LuVO_4$, the oxidation state of vanadium ion is very close to V^{5+}, since its V-L2,3 X-ray Absorption Spectroscopy (XAS) spectra (figure 3) is very similar to the spectra of reference V_2O_5, V2p and O1s spectra shown on figure 3 top (adapted from [9]) as well as $Ni_3V_2O_8$ [11], $Co_3V_2O_8$ [10], and YVO_4 [11]. Moreover, if there were V^{4+}, an enhancement of the structures below the main peaks will be observed, as observed for example in beta-$Sr_{0.17}V_2O_5$ [12]. However, this effect is absent in our single crystal $LuVO_4$. Therefore, we could conclude that V in $LuVO_4$ is in 5+ state.

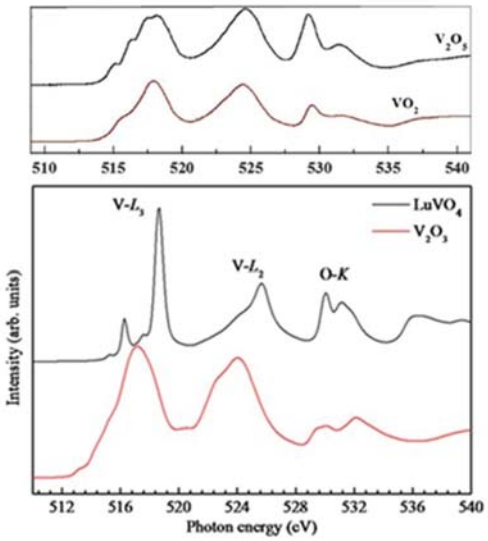


Figure 3: XAS spectra of $LuVO_4$ single crystal

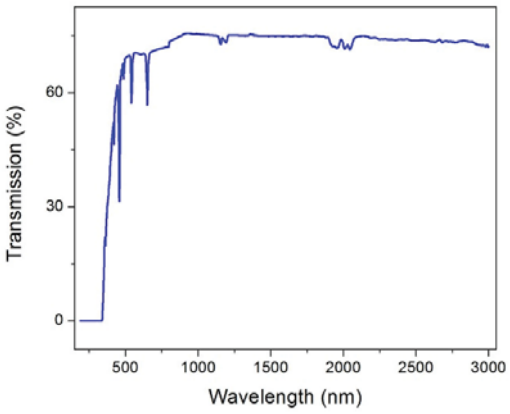


Figure 4: Optical Transmission of $LuVO_4$ single crystal 200-3000 nm

2.2. Optical transmittance and Raman spectroscopy analysis

The $LuVO_4$ 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 $LuVO_4$ crystallizes in a centrosymmetric tetragonal structure with the point group symmetry D4h and space group I41/amd (zircon-type structure). The structure consists of Lu^{3+} ions and VO_4^{3-} tetrahedra that can be approximately regarded as separate units due to the strong internal bonds within each tetrahedron. Therefore, the lowest-frequency vibrations of $LuVO_4$ comprise translations and librations of the VO_4^{3-} tetrahedrons as rigid units against the Lu^{3+} ions. The higher-frequency phonons, on the other hand, are almost entirely due to internal vibrations of the VO_4^{3-} 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 $LuVO_4$ 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 simple. 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 $LuVO_4$ 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.

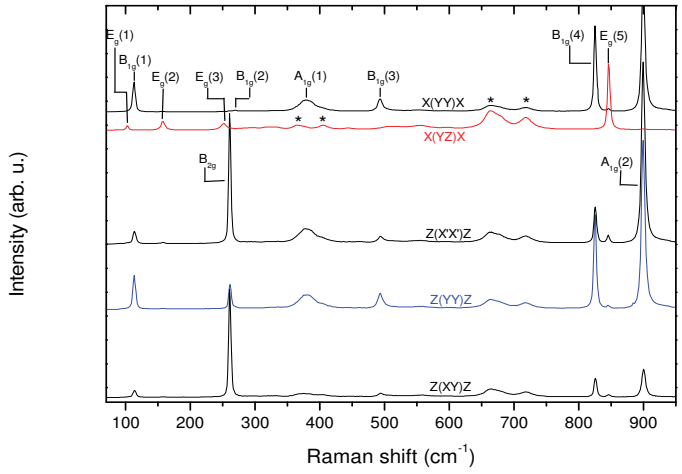


Figure 5: Raman spectra with mode assignment of $LuVO_4$ single crystal in different polarization configurations given in Porto notations. Features stemming from impurities or second-phase inclusions are marked with asterisks

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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