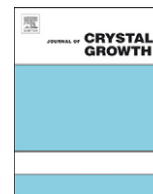




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journal homepage: www.elsevier.com/locate/jcrysgrGrowth and characterization of high quality LuVO₃ single crystalsPaolo Ghigna^{a,*}, Alice Garberi^a, Michele Zema^b, Serena C. Tarantino^b, Claudio Mazzoli^c^a Dipartimento di Chimica, Università di Pavia, V.le Taramelli 16, I27100 Pavia, Italy^b Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, via Ferrata 1, I27100 Pavia, Italy^c ESRF, 6, Rue Jules Horowitz, F38043 Grenoble, France, and Dipartimento di Fisica, Politecnico di Milano, Piazza L. Da Vinci, 32, I20133 Milano, Italy

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ABSTRACT

The floating zone method using an image furnace under reducing atmosphere has proven successful in growing high-quality LuVO₃ single crystals with the largest dimensions to date. Crystals of several mm³ in dimension, and thus large enough for Resonant X-ray Scattering measurements have been obtained, and the growth strategy, described in detail, could be in principle easily extendable to other members of the REVO₃ perovskite class. Crystal quality was checked by Laue photographs and structural analysis of LuVO₃ was performed by single-crystal X-ray diffraction.

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1. Introduction

Rare earth vanadates of general formula REVO₃ form a homogenous class of perovskite materials. The crystal structure is described in the *Pnma* space group (no. 62), due to the tilting of the octahedra, that in the Glazer classification scheme [1] is *a⁺b⁻b⁻*. The interest in this class of compounds is related to their magnetic properties, in particular to the presence of the so-called anomalous diamagnetism in some of the members [2]. The members with RE=Y, La and Lu are of particular interest, in this respect, since the RE(III) ions in these cases carry no magnetic moment, and therefore they cannot interact with the VO₃ framework. As a matter of fact, YVO₃ and LuVO₃ show a complex physics with a sequence of phase transitions on cooling, in particular, a second order orbital order–disorder transition, associated with a structural phase transition to *P2₁/c*, is observed at *T*_{OO}; lowering the temperature, a second order antiferromagnetic transition occurs at *T*_N. A first order spin and orbital re-ordering transition follows at *T*_{GC}, giving the symmetry change back to *Pnma* [3–5].

Such a complex phenomenology asks for high quality and large single crystals for applying up-to-date techniques for magnetic and orbital ordering investigations, such as Resonant X-ray Scattering. Although several papers in the literature describe

experiments with single crystals of members of the class, to our knowledge a detailed method for preparation has not been described yet, except for La_{1-x}Sr_xVO₃ [6].

The aim of this work is to illustrate in an exhaustive way how very high quality and the largest to date single crystals of LuVO₃ can be efficiently prepared by the floating zone method using an image furnace. The method here described can be easily extended to other members of the class.

2. Experimental

2.1. Synthesis

Powders of LuVO₃ were obtained by solid state reaction. In particular, an equimolar mixture of V₂O₅ (Alfa Aesar, 99.8%) and Lu₂O₃ (Aldrich, 99.9%) was suspended in CHCl₃ and stirred overnight, until the CHCl₃ had completely evaporated. The mixture was then pressed to pellets and then put in an alumina boat. The reacting mixture was fired at 1350 °C under flowing Ar+5% H₂, for a total time of 48 h, with several intermediate re-grindings. The phase purity of the final product was checked by X-ray Powder Diffraction, using a D8 Bruker powder diffractometer equipped with a Cu anticathode, an incident slit of 0.5°, an antiscatter slit of 0.5°, a detector slit of 1 mm, and a graphite monochromator in the diffracted beam. The powder diffraction pattern of the starting material for the crystal growth is shown in Fig. 1. To check for hydrogen impurities, the powder sample has

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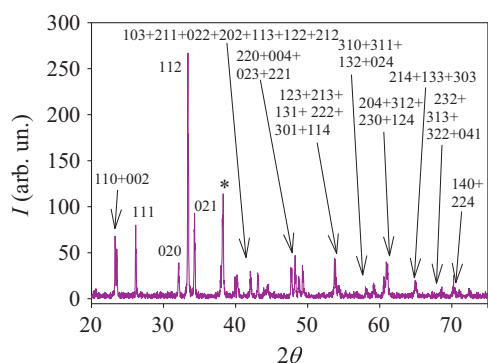


Fig. 1. Diffraction pattern of the LuVO_3 powders used as starting material for the crystal growth. The indexing is according to the perovskite structure [10]. The peak marked with a * is due to the Al sample holder.

been analyzed with a thermogravimetric apparatus (TA, TGA 2950), in flowing nitrogen (2 l/h). We detected no weight losses within the accuracy of the instrument up to 600 °C.

The powders (ca. 10 g) were then inserted in a cylindrical silicone mold, with an internal hollow space of 5 mm in diameter and 5 cm in length, and then hydrostatically pressed at 2500 bar for 20 min. The rod thus obtained was then sintered using the same conditions as for the synthesis, and then cut into two equal parts. The two rods were then mounted in a Cyberstar image furnace, equipped with two 2 kW halogen lamps. The growth was performed in flowing $\text{Ar}+5\% \text{H}_2$. The lamp power was linearly increased until a droplet of liquid was observed to form at the bottom of the upper rod, and then kept constant. The lower rod was raised to touch the liquid, and the liquid zone was allowed to move at 1 mm/h in the vertical direction, at a rotation speed of 1 round per minute. The crystal was allowed to grow for 9 h.

3. X-ray single-crystal diffraction

Several fragments were checked for crystal quality by X-ray single-crystal diffraction and all showed sharp and narrow diffraction profiles. The structural analysis was performed on a grain of $0.14 \times 0.18 \times 0.24$ mm in size. Intensity data were obtained at room temperature on a Bruker-AXS Smart Apex three-circle diffractometer equipped with a CCD detector. Data collection was carried out with operating conditions 50 kV and 30 mA and graphite monochromatized Mo- $K\alpha$ radiation ($\lambda=0.71073$ Å). The Bruker SMART system of programs was used for preliminary crystal lattice determination and X-ray data collection. A total of 7200 frames (resolution: 512×512 pixels) were collected with eight different goniometer settings ($\varphi=0^\circ, 90^\circ, 180^\circ, 270^\circ$ with CCD camera at $2\theta=-32^\circ$ and -64°) using the ω -scan mode (scan width: $0.2^\circ\omega$; exposure time: 5 s/frame; detector-sample distance: 5 cm). Completeness of measured data was achieved up to $46.8^\circ\theta$. The Bruker program SAINT+ was used for the data reduction including intensity integration, background and Lorentz-polarization corrections. Final unit-cell parameters were obtained by the Bruker GLOBAL least-squares orientation matrix refinement procedure based on the positions of all measured reflections and are reported in Table 1. The semi-empirical absorption correction of Blessing [7], based on the determination of transmission factors for equivalent reflections, was applied using the Bruker program SADABS [8]. The values of equivalent reflections were averaged and the resulting discrepancy factors are reported in Table 1. Structure refinement was carried out in space group $Pnma$ by full-matrix least-squares using SHELXL-97

Table 1
Crystal and refinement data.

Chemical formula	LuVO_3
Formula weight	273.41
Crystal shape	Prism
Crystal size (mm)	$0.14 \times 0.18 \times 0.24$
Crystal system	Orthorhombic
Space group	$Pnma$
a (Å)	5.5727(1)
b (Å)	7.5410(1)
c (Å)	5.2167(1)
V (Å ³)	218.34(1)
Z	4
D_{calc} (g cm^{-3})	8.332
T (K)	298(3)
μ (mm^{-1})	48.909
θ max ($^\circ$)	46.86 (completeness 99.9%)
Index ranges	$-11 \leq h \leq 11, -15 \leq k \leq 15, -10 \leq l \leq 10$
Reflns measured	10100 (5794 after merging identical reflns)
R_{int}	0.0471 (1036 unique reflns)
Refinement type	F^2
R_1^a	0.0258
R_{all}	0.0269
wR_2	0.0621
$\text{GO}F^b$	1.122
Refined parameters	29
(shift/e.s.d.) _{max}	0.000
max, min $\Delta\rho$ ($\text{e} \times \text{Å}^{-3}$)	4.35, -6.51

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ (calculated on 1004 reflections with $I > 2\sigma_I$).

^b $\text{GO}F = S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{0.5}$, where n is the number of reflections and p is the total number of parameters refined.

[9], starting from the structural model given by Martínez-Lope et al. [10]. The atomic scattering curves were taken from the *International Tables for X-ray Crystallography* [11]. Structure factors were weighted according to $w = 1 / [\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2) / 3$, and A and B were chosen to produce a flat analysis of variance in terms of F_c^2 as suggested by the program. An extinction parameter x was refined to correct the structure factors according to the equation: $F_o = F_c k [1 + 0.001x F_c^2 \lambda^3 / \sin 2\theta]^{-1/4}$ (where k is the overall scale factor). All parameters, including anisotropic displacement parameters and an isotropic extinction parameter, were refined simultaneously. Final discrepancy factors, together with the goodness of fit S and the number of total and unique reflections, are reported in Table 1. Bond distances and other geometrical parameters are given in Table 2. Fractional coordinates and displacement parameters, observed and calculated structure factors are available from the authors.

4. Results and discussion

The central part of the boule was made up of quite large single crystals: one of them is shown in Fig. 2(A), after mounting it on the sample stage of a Laue camera. The Laue photograph, shown in Fig. 2(B), demonstrated the single crystal nature of the sample, and that the c axis of the crystal was nearly perpendicular to the plane of the sample stage. The dimensions of the crystal are perfectly suitable for performing resonant X-ray scattering measurements [12]. The crystal quality of the sample shown in Fig. 2 was checked by high resolution X-ray diffraction, performed by synchrotron radiation at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. ID20 magnetic scattering beam-line optics were tuned close to the the V-K edge resonance (wavelength of 2.273 Å) and the single crystal was installed on the vertical diffractometer hosted in EH1. Impinging X-ray beam

Table 2
Bond distances and selected geometrical parameters.

Lu–O1 (Å)	2.186(3)
Lu–O1 (Å)	2.251(3)
Lu–O2 (Å) × 2	2.227(2)
Lu–O2 (Å) × 2	2.463(2)
Lu–O2 (Å) × 2	2.672(2)
<Lu–O> (Å)	2.395
Polyhedral volume (Å ³)	23.10
Average edge length (Å)	2.938
V–O1 (Å) × 2	2.006(1)
V–O2 (Å) × 2	2.008(2)
V–O2 (Å) × 2	2.022(2)
<V–O> (Å)	2.012
Polyhedral volume (Å ³)	10.84
Average edge length (Å)	2.845
V–O1–V (deg.)	140.0(2)
V–O2–V (deg.)	142.5(1)
OAV	4.007
OQE	1.0011

Note: Standard deviations are in parentheses. OAV and OQE are the octahedral angle variance and the mean octahedral quadratic elongation, respectively [12].

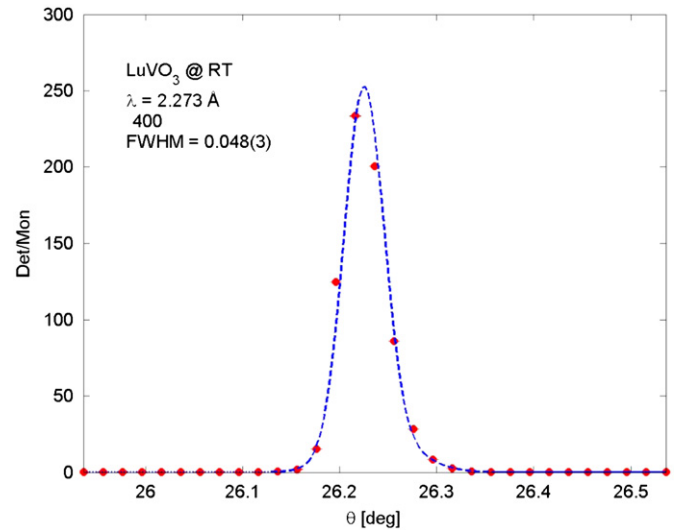


Fig. 3. 400 reflection of the crystal shown in Fig. 2, as measured on the ID20 beamline at the ESRF at room temperature.

of horizontal polarization was shaped to 0.2×0.2 mm at the sample by incident slits. A Kapton™ foil seen at 90° by an APD diode was used as an intensity monitor between the slits and the sample.

Fig. 3 shows a representative reflection profile (dots are experimental data) acquired by the detector (APD diode) and normalized to the monitor, together with a fit by an asymmetric pseudo Voigt function (dashed line). Its total FWHM of $0.048(3)^\circ$ proves the high crystal quality of our sample (for the use of the FWHM of a diffraction effect see for example [15], and references therein). By sample translations the FWHM has been checked over an area of ~ 1 mm² without detecting appreciable deviations. Further details on Q resolution corresponding to the selected experimental conditions can be found on the beamline document [12].

By moving from the center of the boule, increasingly smaller crystals were found, and some of them were collected for performing structural analysis as described in the experimental section. Nearly 4 mm from the center of the boule, the rod was found still to be a powder.

The crystal structure of LuVO₃ is reported in Fig. 4(A). Results of the single-crystal X-ray diffraction experiment are in good agreement with previously published data from neutron powder diffraction [10,13]. As displayed in Fig. 4(B), Lu³⁺ ions are coordinated by eight oxygen atoms with an average bond distance of 2.395 Å. Four oxygen atoms lie at longer distances, between 3.202 and 3.603 Å. V³⁺ ions are in a regular octahedral coordination as indicated by the angular distortion parameter OAV (Octahedral Angle Variance) [14] reported in Table 2, with fairly similar V–O distances, ranging between 2.006 and 2.022 Å.

Finally, it would be interesting to compare the results presented here with that obtained for the growth of single crystals of the LuVO₄ compound with the zircon type structure (see for example [16] and references therein). Larger (10 mm in size) crystals of LuVO₄ can be easily grown. This is possibly due to the fact that stabilization of V(III) in the LuVO₃ perovskite requires a reducing atmosphere, and therefore the use of an H₂ in Ar mixture. The high thermal conductivity of this gas mixture, if compared to the air atmosphere in which LuVO₄ single crystals are usually grown, can be the source of temperature gradients that do not allow growing crystals with a size larger than that reported here.

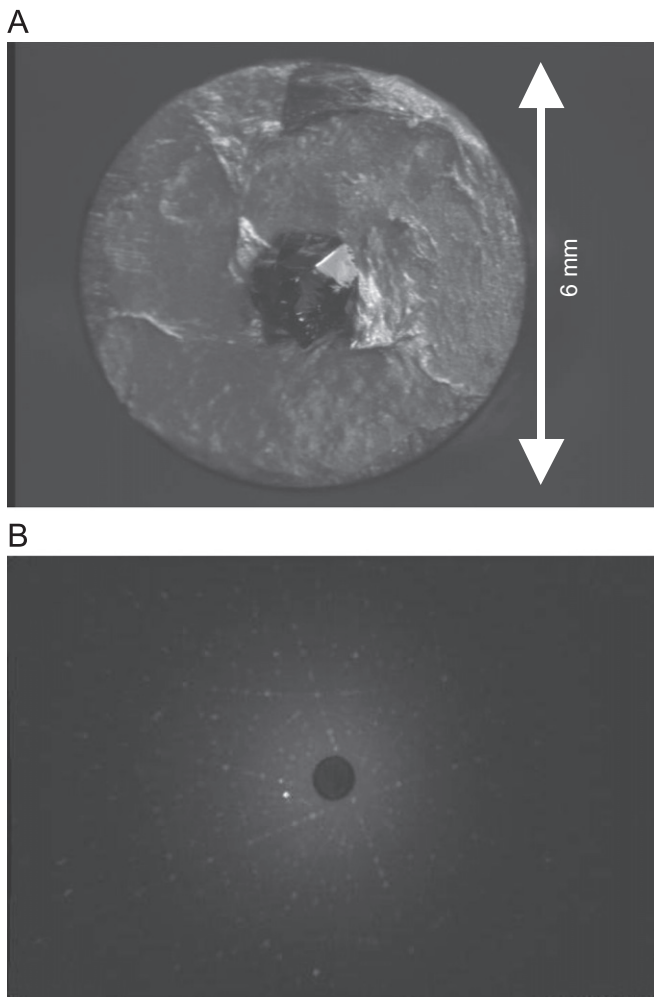


Fig. 2. (A) Large single crystal of LuVO₃, as mounted on the sample stage of a Laue camera. (B) Corresponding Laue photograph.

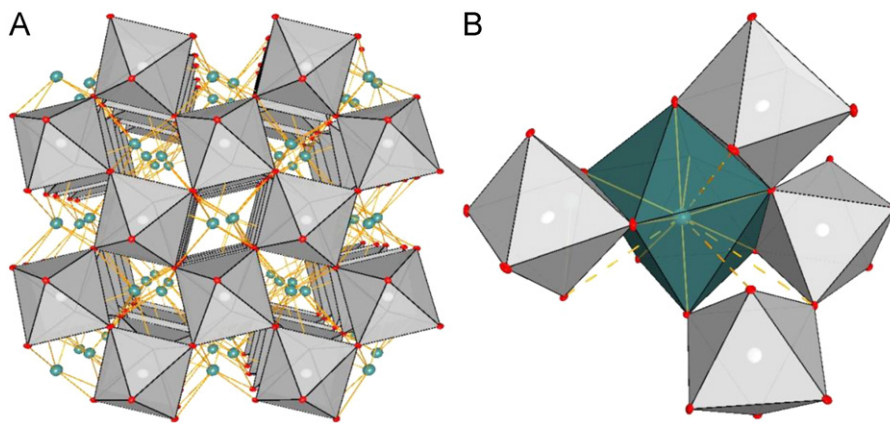


Fig. 4. (A) Perspective view of LuVO₃ perovskite along *b*. (B) coordination polyhedron around Lu³⁺ ion (green) completed by four oxygen atoms at longer distances (dashed bonds). Octahedra around V³⁺ ions are reported in grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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