Equation of State of Zircon-Type TbVO$_4$

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High-pressure energy-dispersive X-ray diffraction study were performed on zircon-type phase of terbium orthovanadate, TbVO$_4$, in the pressure range up to 7 GPa. For analysis of the collected diffraction spectra, Le Bail refinements were performed. The values of bulk modulus and its pressure derivative ($B_0 = 121$ GPa, $B' = 4.1$) were obtained from fitting of the second-order Birch–Murnaghan equation of state. The equation of state derived for TbVO$_4$, is compared with earlier data based on the Raman spectroscopic studies and with data of several other rare-earth orthovanadates.

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1. Introduction

Zircon-type rare-earth orthovanadates (RVO$_4$) exhibit physical properties that may lead to a number of applications. Known examples are the europium and neodymium doped YVO$_4$ crystals used as phosphor and laser materials, respectively. Some compounds of this family are considered as being suitable for optical waveguides and polarizers, they can be used for remote thermometry, as catalysts for oxidative dehydrogenation, and are candidates for advanced bio-imaging phosphors and as components of toughened ceramic composites.

RVO$_4$ (with R = Sc, Y, La–Lu) orthovanadates belong to a large class of ABO$_4$ type ternary oxides that typically adopt the structures of zircon, scheelite, fergusonite, monazite, wolframite, CrVO$_4$, ZnSO$_4$ and rutile types [1–3]. For RVO$_4$, R = Pr to Lu, the ambient-pressure structure is of zircon type, space group $I4_1/amd$. This latter structure can be also obtained for R = La using special preparation methods. Phase relationships in this class, observed as a function of pressure have been systematized by Fukunaga and Yamaoka [2] and Errandonea and Manjón [4] (for all possible ABO$_4$ compounds), and by Kolitsch and Holtstam [3] for RBO$_4$ compounds (B = P, As, V).

A number of RVO$_4$ oxides have been studied at high-pressure conditions using mostly the *ex situ* X-ray diffraction and other methods, showing that under pressure of several GPa, these materials undergo an irreversible phase transition to scheelite-type structure. Only for some of them, *in situ* methods have been applied resulting in a more precise knowledge of the phase diagrams and of the bulk-modulus values. Duclos et al. [5]

on the basis of earlier published elastic constants have evaluated the bulk modulus of TbVO$_4$ to be 126 GPa. Using the results of the Raman spectroscopy studies presented in the cited paper, Chen et al. [6] have fitted the evaluated by them $V(p)/V(0)$ points using the second-order Murnaghan EOS assuming a fixed pressure derivative of the bulk modulus of 6.5. This B' value has been predetermined through analysis of the pulse repetition frequencies measurements of non-metamict single crystal zircon [7]. The resulting bulk modulus value equals 149 GPa, being greater than that obtained by Duclos et al. Up to now the equation of state has not been determined by diffraction methods. In this work, we performed *in situ* X-ray diffraction experiments in order to determine the bulk modulus of the zircon-type phase of this material.

2. Experimental

The investigated terbium orthovanadate (TbVO$_4$) powder was prepared, using a mortar, from a small single crystal grown from PbO/PbF$_2$ flux by the slow cooling method. The *in situ* X-ray diffraction experiments were conducted using the energy-dispersive method at the F2.1 beamline (Hasylab/DESY) equipped with a large-anvil diffraction press, MAX80. The sample was mounted in a cylindrical sample container (inner diameter 1 mm) constructed from hexagonal boron nitride (hBN), inserted into a cube fabricated from a mixture of boron and epoxy resin. To achieve the pseudo-hydrostatic compression conditions and to reduce the strain, the studied polycrystalline material was mixed with vaseline. The measurements were performed in the range from 0 to 7.28 GPa, with the temperature fixed at 303($\pm$2) K. The pressure was calibrated using NaCl (mounted separately within the same hBN container).

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The accuracy of pressure determination is evaluated to be ± 0.05 GPa. The diffraction angle was fixed at $7.616°$.

Diffraction patterns were fitted by the whole-pattern decomposition procedure (Le Bail method [8]) with the help of Fullprof.2k (v. 2.70) program [9]. The bulk modulus (B_0) as well as its pressure derivative were calculated by fitting the second order Birch–Murnaghan [10] equation of state to the experimental data, using the EOS program [11].

3. Results

The typical energy-dispersive X-ray diffraction data collected for $TbVO_4$ at ambient pressure and at 6.5 GPa are shown in Fig. 1. The spectrum is composed of the diffraction lines of $TbVO_4$ and of those due to the container material (hexagonal boron nitride), as well as the X-ray fluorescence line for terbium. Above 5 GPa, some

(progressively growing with rising pressure) broadening of diffraction lines, well visible for the first four separate lines, is attributed to the strain appearing due to not fully hydrostatic conditions at the highest pressures. At ambient pressure, the lattice parameters of zircon-type $TbVO_4$ are $a = 7.178(2)$ Å, $c = 6.326(2)$ Å, giving a volume (V_0) of 325.9(2) Å^3 and axial ratio $c/a = 0.8813(4)$. The observed variation of lattice parameters with pressure (cf. Table I) is relatively smooth, as shown in Fig. 2. The c parameter behaves linearly whereas the a parameter is slightly nonlinear. The increase of the axial ratio with increasing pressure is about 0.56% within the investigated range. This is apparently a smaller decrease than that for YVO_4 [6] (0.70%), showing that the compression anisotropy is less pronounced for the presently studied $TbVO_4$. In the pressure range up to 7.28 GPa, the phase transition to scheelite is not observed.

TABLE I

Lattice parameters and relative volume of $TbVO_4$ as a function of pressures.

Pressure [GPa]	a [Å]	c [Å]	V_p/V_0	Pressure [GPa]	a [Å]	c [Å]	V_p/V_0
0	7.178(2)	6.326(2)	1	4.55	7.085(2)	6.271(2)	0.9659
0.48	7.172(2)	6.320(2)	0.9976	4.99	7.077(2)	6.265(3)	0.9628
0.82	7.159(2)	6.316(2)	0.9931	5.55	7.070(3)	6.259(3)	0.9598
1.44	7.145(2)	6.307(2)	0.9880	5.94	7.056(3)	6.253(3)	0.9553
1.97	7.138(2)	6.302(2)	0.9851	6.48	7.049(3)	6.247(3)	0.9525
2.58	7.123(2)	6.294(2)	0.9799	6.80	7.045(3)	6.240(3)	0.9501
3.20	7.106(2)	6.288(2)	0.9746	7.28	7.041(4)	6.235(4)	0.9484
3.86	7.097(2)	6.275(2)	0.9697				

TABLE II

Bulk moduli and their derivatives for RVO_4 phases.
XPD = X-ray photoelectron diffraction.

Compound	B_0 [GPa]	B'	Method	Ref.	Year
YVO_4	130(3)	4.4(10)	XPD	[12]	2004
$TbVO_4$	126		evaluation from elastic constants	[5]	1989
$TbVO_4$	149	6.5 (fixed)	Raman	[6]	1992
$TbVO_4$	121(5)	4.1(1.9)	XPD	this work	2010
$DyVO_4$	160	6.5 (fixed)	Raman	[6]	1992
$LuVO_4$	147	4.3	XPD	[13]	2008
$LuVO_4$	166	4.8	theoretical value	[13]	2008

Figure 3 shows the experimental reduced volume (V/V_0) versus pressure. A comparison with the points derived from the Raman spectroscopy data [6] shows

that there is a difference in compression behaviour between these two datasets. The zero-pressure bulk modulus (B_0) determined for $TbVO_4$ is 121(5) GPa and its
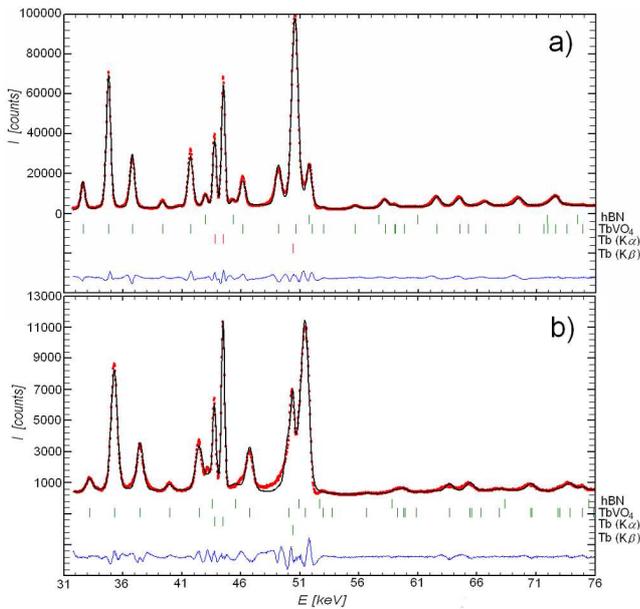
Fig. 1. (color online) Examples of X-ray diffraction spectra (doted line) collected at the ambient (a) and 6.5 GPa (b) pressures, and fitted (solid line) using the Le Bail method. The markers below refer to the hBN phase of the container, the studied $TbVO_4$ phase and Tb fluorescence lines, respectively. The weak intensity of diffraction peaks above 52 keV is due to the strong absorption above the terbium K absorption edge at 52.0 keV.
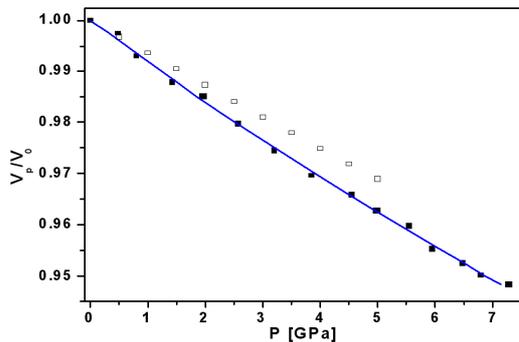

Fig. 3. Experimental relative volume compression of $TbVO_4$ as a function of pressure (■). The solid line represents the fitted Birch–Murnaghan equation of state. The literature data of Chen et al. [6] are displayed for comparison (□).

pressure derivative B' is 4.1(1.9). The present B_0 value is apparently closer to that of 126 GPa evaluated directly from elastic constants (see Table II); it seems that the Raman-method based value of 149 GPa is thus slightly overrated. As for B', the present result ($B' = 4.1$) is comparable to those of XRD measurements and calculations for several related materials (for details see Table II).
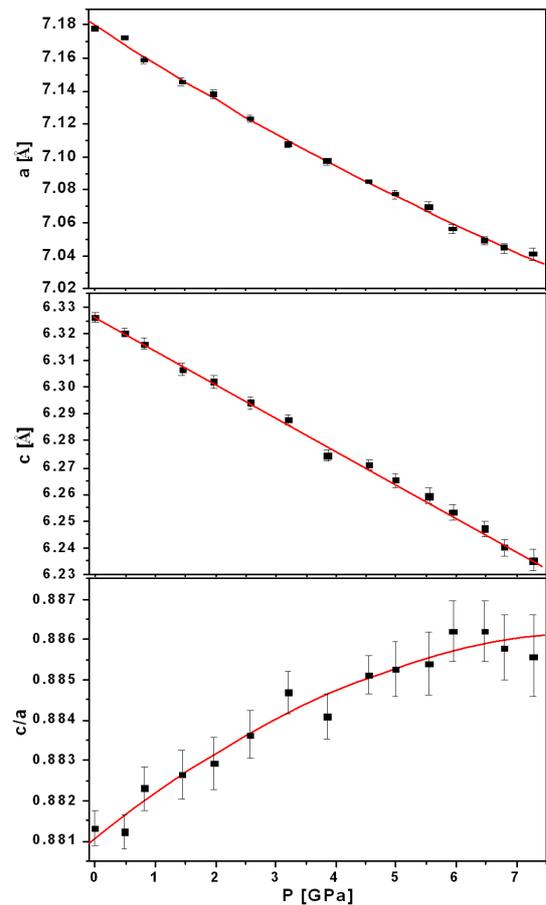

Fig. 2. Experimental pressure dependence of the a and c lattice parameters, and of the axial ratio for the zircon-type terbium orthovanadate (filled squares). The solid lines are a guide to eye.

4. Summary

In summary, the present study provides a new quantitative information about unit-cell behaviour of terbium orthovanadate under high pressure up to 7.28 GPa. For the first time the Birch–Murnaghan type equation of state of the studied material were determined using energy-dispersive X-ray diffraction. The values of bulk modulus and its pressure derivative were determined to be 121 GPa, and 4.1, respectively, the volume at zero pressure is 325.9(2) Å³. Based on the difference of axial-ratio pressure dependence for $TbVO_4$ and YVO_4, one can expect that the compression anisotropy varies among RVO_4 orthovanadates.

Acknowledgments

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