Experimental and Theoretical Study of Zircon and Scheelite Phases of DyVO₄

O. Ermakova, W. Paszkowicz, J. López-Solano, A. Muñoz and H. Darkowsk

1. Introduction

Materials from the family of rare-earth orthovanadates (RVO₄), mineral name wavefieldite (La, Ce, Nd, Y)VO₄, exhibit unique physicochemical and optical properties [1–4]. These properties lead to various possible applications such as components of catalysts [5], lasers [6–9], Raman lasers [10], low-loss optical planar waveguides [11], other optical devices and phosphors [12], etc. Tsipis et al. [13] have noted that rare-earth orthovanadates are interesting for high-temperature electrochemical applications as they offer sufficient stability under the operation conditions. For DyVO₄, a particularly interesting application can be found in the field of photocatalysts [14].

At ambient pressure and temperature, most of the RVO₄ (R = Y, Ce - Lu) compounds adopt the zircon-type structure (space group I₄₁/amd). A study performed for an example of GdVO₄ [15] shows that this phase may be nonstoichiometric, what leads to small but detectable lattice parameter changes of the order of 0.001 Å. The RVO₄ compounds are known to undergo a phase transition to a scheelite-type polymorph (space group I₄₁/a) at pressures below 10 GPa [16, 17] which remains metastable after releasing the pressure. For some of them, in particular for DyVO₄, a mechanochemical way for the scheelite-type phase preparation has been documented [18]. The literature data on the structure of DyVO₄ are scarce: representative ones are included in Table I quoting the data from Refs. [4, 19–27] for zircon-type phase; for scheelite-type phase only a single data set (Ref. [28]) of low-accuracy unit-cell parameters could be found in the literature (see Table II). The reported data involve materials prepared by various methods, two of them have been made on single crystals grown by slow cooling from flux (one of them has been powdered). As for the structure refinement, only three datasets have been found, with mostly single crystal structure refinement used. The aim of the present investigation was to experimentally determine the structure of zircon-type dysprosium orthovanadate through Rietveld refinement of the X-ray diffraction data and to compare this structure with the results of density functional theory (DFT) calculations for this material.

2. Experimental

A DyVO₄ single crystal was grown by slow cooling method from PbO/PbF₂ flux, following the recipe for other rare-earth orthovanadates [29]. For powder diffraction experiments, this monocrystal was ground in anagate mortar. The resulting fine powder was studied using a laboratory Bragg-Brentano powder diffractometer (Phillips X’Pert Pro MPD Alpha1, supplied by Phillips/Panalytical) equipped with an incident beam Ge(111) Johannson monochromator and a strip detector. Cu Kα₁ radiation was used in the diffraction experiment. The obtained X-ray diffraction pattern served for the structure refinement of the sample.
Structural data for zircon-type DyVO₄. Lattice parameters a and c, unit cell volume V, and oxygen atoms coordinates x, y and z are provided.

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<th>y(O²)</th>
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Abbreviations: H1 — sample form or preparation, H2 — measurement/calculation, H3 — unit cell/structure refinement method or calculation model, XRDP — X-ray powder diffraction, SIRPD — single crystal diffraction, NPD — neutron powder diffraction, LSQ — least squares refinement, RT — Rietveld refinement, SCR — single crystal refinement, PBE — DFT calculations performed within the PBE XC functional, PBEsol — DFT calculations performed within the PBEsol XC functional, SCF — a single crystal grown from flux, n.r. — not reported. For (A), (B), (C) — see text.

Structural data for scheelite-type DyVO₄. Lattice parameters a and c, unit cell volume V, and oxygen atom coordinates x, y and z are provided.

<table>
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<tr>
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<th>c/a</th>
<th>V [Å³]</th>
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XRPDG — X-ray powder diffraction using a Gandolfi camera, for other abbreviations see Table I.

3. Density functional theory calculations

Density functional theory calculations were performed with the VASP ab initio code [30]. Projector augmented-wave pseudopotentials [31, 32] with valence configurations 5p⁶ 4f¹ 6s² for Dy, 3p⁶ 3d⁸ 4s² for V, and 2s² 2p⁶ for O were used. Calculations within the Perdew-Burke-Ernzerhof (PBE) [33] and the more recent PBEsol [34] generalized gradient approximations of the exchange-correlation (XC) energy functional were performed. An energy cutoff of 520 eV and dense Monkhost-Pack [35] grids appropriate to the zircon-type and scheelite-type structures ensured a total energy convergence of 1 meV per formula unit. Full optimization of the lattice parameters and atomic positions at constant volume was performed, resulting in a diagonal hydrostatic stress tensor with differences of less than 0.1 GPa between its components and atomic forces smaller than 0.005 eV/Å. Zero point motion, temperature and magnetic effects were not included in this work.

4. Results

Phase analysis performed on the basis of powder X-ray diffraction data ("set I") showed that the DyVO₄ crystal is a single phase of zircon-type. The data were treated by the Rietveld procedure, with 19 parameters (2 lattice parameters, 2 oxygen positions parameters, 3 isotropic atomic displacement parameters, 5 profile shape and width parameters, 1 preferred orientation parameter, 1 scale factor, 1 systematic error parameter, 4 peak-asymmetry parameters), assuming valencies of +3, +5 and −2 for dysprosium, vanadium and oxygen, respectively. The refined profile is displayed in Fig. 1. To check the preferred orientation effect, various orientation directions were tried using the exponential model implemented in the Fullprof software. The effect of the preferred orientation is found to be minor, the best direction was [100], in agreement with the [100] cleavage plane of other compounds of the same family, such as YVO₄ and LuVO₄ [36, 37]. The refinement results show that the studied DyVO₄ crystal has the lattice parameters
\( a = 7.14811(4) \, \text{Å}; \ c = 6.30825(4) \, \text{Å} \) and unit cell volume \( V = 322.323(3) \, \text{Å}^3 \), with the following atomic positions: Dy\( ^{3+} \) at (0; 0.75; 0.125), V\( ^{5+} \) at (0; 0.25; 0.375), O\( ^{2-} \) at (0; 0.4300(4); 0.2082(4)). Refined isotropic temperature factors for Dy\( ^{3+} \), V\( ^{5+} \) and O\( ^{2-} \) are equal to 0.74(1), 0.42(3) and 0.90(7), respectively; they partially differ from the respective values (0.1, 0.49, 0.58) determined by neutron diffraction in Ref. [38]. The density derived from the unit cell is 5.71725(5) g/cm\(^3\).

![Graph](image)

Fig. 1. Rietveld refinement for zircon-type DyVO\(_4\). Crosses represent the experimental points, the solid line stays for the fitted pattern, the difference pattern is shown in the lower part of the figure. Lower vertical bars represent the Bragg reflection positions.

It is worth noting, that our result derived from the laboratory data is, as far as we know, the first published structure refinement for zircon type DyVO\(_4\), based on powder X-ray diffraction data. Very small values of the standard deviations of the presently determined lattice parameters \( \ll 1 \times 10^{-4} \) Å reflect both, the high quality of the crystal studied and the very good precision of the experimental setup used. This could be achieved due to the excellent statistics and resolution connected with the use of the strip detector, a device proposed for application in Bragg-Brentano diffractometers and tested by Zięba and coworkers [39, 40] and, starting from year 2000, developed commercially by various suppliers. For this polymorph, ten datasets from earlier studies are cited in Table I. Generally, the discrepancies between the absolute values of lattice parameters are relatively large, within ±0.01 Å, i.e. they are quite big as compared with standard deviations. Various factors may contribute to these discrepancies, such as the preparation method, nature of the sample (single crystal, polycrystal, nanocrystal), purity, kind of experiment (X-ray single diffraction, powder X-ray diffraction, neutron diffraction), etc. It will be useful to distinguish three data groups: the powder diffraction data with reported small lattice-parameter standard deviations (group I with standard-deviation values below 5 \( \times 10^{-4} \) Å, denoted by “A” in Table I), single crystal diffraction data (denoted as “B”) and remaining ones (“C”). The observation that the data of group A differ within the error margin demonstrates that carefully conducted experiments lead to consistent unit cell sizes, irrespectively the Rietveld refinement or least squares refinement is used. The data from set B show lower absolute values, despite the good sigmas, whereas data of group C display a larger scatter of values. It is thus reasonable to state that the lattice parameters within the group A are the most reliable ones for zircon type DyVO\(_4\). A similar conclusion has been recently presented for the particularly difficult case of CaMnO\(_3\) compound, where such analysis could be done on the basis of still larger number of literature datasets [41].

As described in Sect. 3, the density functional theory \( \textit{ab initio} \) calculations were conducted using both the PBE and PBEsol XC functionals. For the zircon-type structure at zero pressure, the PBE calculations provide \( a = 7.2035 \) Å, \( c = 6.3233 \) Å, \( V = 328.119 \, \text{Å}^3 \), \( y(O^{2-}) = 0.4344, \ z(O^{2-}) = 0.2002 \), and the PBEsol ones \( a = 7.1174 \) Å, \( c = 6.2466 \) Å, \( V = 316.436 \, \text{Å}^3 \), \( y(O^{2-}) = 0.4351, \ z(O^{2-}) = 0.1990 \). The difference between the calculated and measured lattice parameters is below 1%, the PBE values being overestimated and the PBEsol underestimated, following the trend already described for other bulk solids [42]. It is worth noting that
the dimensionless quantities connected with the structure, namely the axial ratio and the oxygen atom coordinates, are quite accurately calculated using both XC functionals and that the difference between the oxygen position parameters obtained by the two computational approaches is negligible (cf. Table 1).

The scheelite-type structure has also been considered in the present DFT study. The following structure parameters were obtained for zero pressure: \( a = 5.0725 \, \text{Å}, c = 11.3078 \, \text{Å}, \) \( V = 290.953 \, \text{Å}^3, x(O^{2-}) = 0.2551, y(O^{2-}) = 0.1051, z(O^{2-}) = 0.0446 \) for the PBE XC functional, and \( a = 5.0126 \, \text{Å}, c = 11.1252 \, \text{Å}, V = 279.534 \, \text{Å}^3, x(O^{2-}) = 0.2553, y(O^{2-}) = 0.1033, z(O^{2-}) = 0.0435 \) for the PBEsol. A comparison of calculated lattice parameters with a low-precision experimental dataset from Ref. [28] (cf. Table II) shows that theory and experiment agree within 2%. Also for this phase the difference between the oxygen position parameters calculated using the PBE and PBEsol XC functionals is marginal. It should be noted that in the PBE and PBEsol calculations the total energy of the scheelite-type phase is respectively 270 and 136 meV per formula unit above that of the zircon-type, thus confirming the latter as the stable ambient pressure phase from the theoretical point of view.

5. Summary

In the present study, the structure is determined both experimentally and theoretically for zircon-type \( \text{DyVO}_4 \) and for the metastable scheelite-type \( \text{DyVO}_4 \). The results achieved using X-ray diffraction and \textit{ab initio} DFT calculations, demonstrate a good agreement between the measured and calculated parameters of both crystal structures. In the experimental part, Rietveld refinement provided the crystal structure parameters for zircon-type \( \text{DyVO}_4 \), in particular the lattice parameter values \( a = 7.14811(4) \, \text{Å}, c = 6.30825(4) \, \text{Å} \). These values have a markedly higher accuracy than those determined in previous studies, thus being, to the best of our knowledge, the first refinement of the crystal structure by the Rietveld method for this rare material. An excellent consistency of the present experimental data with specific earlier data is attributed to the choice of favourable diffraction-experiment conditions.

Despite the approximations used in the present DFT study, there is a good overall agreement between \textit{ab initio} and experimental data for both zircon-type and scheelite-type \( \text{DyVO}_4 \) polymorphs, with discrepancies that do not exceed 2%. For the scheelite-type phase, theoretical information on the experimentally unknown oxygen atom position is presented here for the first time, the PBE and PBEsol calculations providing fairly similar values: \( x(O^{2-}) = 0.2551, y(O^{2-}) = 0.1051, z(O^{2-}) = 0.0446 \) and \( x(O^{2-}) = 0.2553, y(O^{2-}) = 0.1033, z(O^{2-}) = 0.0435 \), respectively.

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References