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In situ high-pressure synchrotron X-ray diffraction study of the structural stability in $NdVO_4$ and $LaVO_4$

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ABSTRACT

Room-temperature angle-dispersive X-ray diffraction measurements on zircon-type $NdVO_4$ and monazite-type $LaVO_4$ were performed in a diamond-anvil cell up to 12 GPa. In $NdVO_4$, we found evidence for a non-reversible pressure-induced structural phase transition from zircon to a monazite-type structure at 6.5 GPa. Monazite-type $LaVO_4$ also exhibits a phase transition but at 8.6 GPa. In this case the transition is reversible and isomorphic. In both compounds the pressure induced transitions involve a large volume collapse. Finally, the equations of state and axial compressibilities for the low-pressure phases are also determined.

1. Introduction

Orthovanadates are technologically important materials with applications in existing and future technologies. In particular, recently they have attracted considerable attention due to potential applications in renewable energy and alternative green technology [1]. Orthovanadates are also used as laser-host materials [2,3] and exhibit properties like luminescence, chemical stability, and non-toxicity. Because of these properties, they as nanoparticles are promising materials for biomedical applications [4]. $NdVO_4$ and $LaVO_4$ belong to the orthovanadate family. $NdVO_4$ crystallizes in the tetragonal zircon-type structure (space group: $I4_1/amd$, $Z = 4$) [5] shown in Fig. 1. $LaVO_4$ adopts the monoclinic monazite-type structure (space group: $P2_1/n$, $Z = 4$) [6] also illustrated in Fig. 1.

High-pressure studies on rare-earth orthovanadates have received large interest in the last decade [7–20]. In particular, several pressure-induced transitions have been reported. Zircon-type vanadates with a small rare-earth cation (e.g. Tb and Sm) transform into the tetragonal scheelite-type structure (space group: $I4_1/a$, $Z = 4$) around 6–8 GPa [7,17]. However, those with a large rare-earth cation transform into the monazite-type structure at similar pressures [7,17].

Among rare-earth orthovanadates, $NdVO_4$ and $LaVO_4$ are two of the less studied compounds under pressure. Zircon-type $NdVO_4$ has been studied only by optical-absorption experiments and ab initio calculations [13]. Monazite-type $LaVO_4$ has not been studied yet under compression, but its electronic, optical, and vibrational properties have been recently theoretically explored at ambient pressure [21]. Therefore, it is interesting to investigate the structural high-pressure (HP) behavior of $NdVO_4$ and $LaVO_4$. Additional interest of the study of $LaVO_4$ comes from the fact that isomorphic transition has been observed in other monazite-structured oxides [22,23].

In order to shed more light on the HP structural behavior of rare-earth vanadates, we have studied $NdVO_4$ and $LaVO_4$ up to 12 GPa by means of synchrotron powder X-ray diffraction (XRD). Pressure induced phase transition and the structure of the HP

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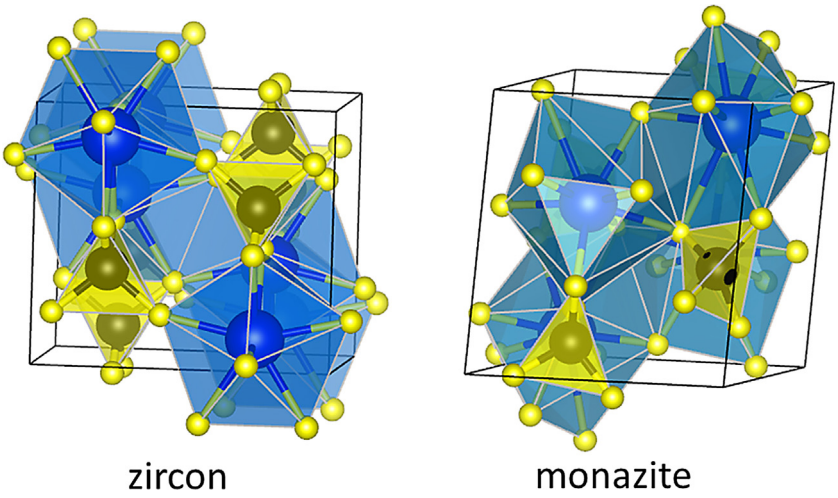

Fig. 1. Schematic view of the zircon and monazite structures. Large blue spheres: rare-earth atom. Medium-size black spheres: V. Small yellow spheres: O. The coordination polyhedra are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

phases have been identified. The pressure dependences of unit-cell parameters of the different phases and the equations of state (EOS) of the low-pressure phases have been determined.

2. Experimental details

Powder samples used in the experiments were obtained from single crystals of $LaVO_4$ and polycrystalline $NdVO_4$. $LaVO_4$ crystals were prepared by the flux growth method using $Pb_2V_2O_7$ as solvent. Pure La_2O_3, V_2O_5, PbO, and $Na_2B_4O_7$ were the starting materials. The composition of the growth mixture was (in molar % ratio): La_2O_3:V_2O_5:PbO:$Na_2B_4O_7$ = 2.3:31.5:62.9:3.3. The mixture of reactants was transferred to a Pt crucible, heated to 1270 °C in a horizontal programmable furnace, and maintained at this temperature for 12 h. It was then cooled to 800 °C at a rate of 1.8 °C/h and finally to room temperature at a rate of 15 °C/min. Transparent crystals in the form of platelets (average size 0.5 mm × 2 mm × 2 mm) were separated from the flux by dissolving it in hot diluted HNO_3. $NdVO_4$ was prepared by solid-state reaction of appropriate amounts of predried Nd_2O_3 (Indian Rare Earth Ltd. 99%) and V_2O_5 (Alfa-Aesar 99%). Homogeneous mixtures of the reactants were pelletized and heated at 800 °C for 24 h and then cooled to ambient temperature. Further, the pellets were reground and heated again at 1100 °C for 24 h.

Room-temperature HP angle-dispersive XRD studies were conducted in a diamond-anvil cell (DAC) up to 12 GPa. Experiments were performed at the MSPD beamline of ALBA synchrotron [24] with a 15 × 10 μm-focused incident monochromatic beam of λ = 0.4246 Å. The powder samples were loaded in a 150 μm-diameter hole of an Inconel X750 gasket pre-indented to a thickness of 50 μm. A 16:3:1 methanol–ethanol–water mixture was used as pressure-transmitting medium. The maximum pressure was limited to 12 GPa to avoid the influence of deviatoric stresses on the studies [25,26]. Pressure was measured using ruby fluorescence [27] and the EOS of Cu [28]. The maximum pressure uncertainty was 0.1 GPa. Data reduction was done using Fit2D [29]. The indexing and refinement of XRD patterns were performed using FULLPROF [30], GSAS [31], and POWDERCELL [32]. Equations of state were fitted using EosFit [33].

3. Results and discussion

XRD measurements at ambient conditions confirmed a single phase with the zircon structure for $NdVO_4$, a = 7.334(1) Å and c = 6.436(1) Å, and with the monazite structure for $LaVO_4$, a = 7.047(1) Å, b = 7.286(1) Å, c = 6.725(1) Å, and β = 104.8(1)°. Figs. 2 and 3 show XRD patterns collected upon compression in $NdVO_4$ and $LaVO_4$, respectively. In $NdVO_4$ the reflections in the XRD patterns up to 6.1 GPa could be well indexed with the zircon structure. A typical Rietveld refinement fit for the pattern measured at 0.3 GPa for $NdVO_4$ is shown in Fig. 2. Since the occupancy and the atomic displacement factors are correlated and sensitive to background subtraction [34], in the structural refinement (to reduce the number of free parameters) the occupancy was constrained to 1 for all atoms, as established by stoichiometry, and the isotropic displacement parameters (B) were constrained to 0.5 $Å^2$ [34]. In addition to the unit-cell parameters, the atomic positions of O (the only not fixed in the zircon structure) were refined. At 0.3 GPa we got a = 7.360(1) Å and c = 6.471(1) Å. The O atoms are at the Wyckoff position *16h* (0, 0.4325(8), 0.2035(6)). The quality if the refinement is illustrated by the small R-factors and reduced χ^2; R_p = 2.06%, R_{wp} = 2.95%, R_F^2 = 1.92%, and χ^2 = 1.88. Refinements of similar quality were obtained for the zircon structure up to 6.1 GPa. At 6.5 GPa, additional peaks are observed in the diffraction pattern of $NdVO_4$. They indicate the onset of a pressure-induced phase transition. The intensities of

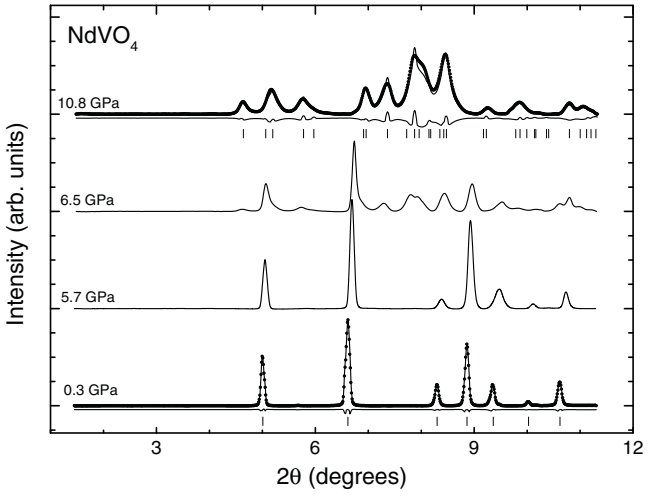

Fig. 2. Selection of XRD patterns for $NdVO_4$. Pressures are indicated. The background was subtracted. At 0.3 (10.8) GPa the residuals of the Rietveld (LeBail) refinement are shown. The dots represent the measured pattern and the solid lines the calculated profiles. Ticks indicate the position of Bragg reflections. Experimental patterns at 5.7 and 6.5 GPa are shown with solid lines.