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High-pressure XRD study of β -Na_{0.33}V₂O₅

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We have investigated the pressure-dependent structural properties of the quasi-one-dimensional metal β -Na_{0.33}V₂O₅ at room temperature by high-resolution angle-dispersive powder X-ray diffraction. According to our structural data, the crystal lattice of β -Na_{0.33}V₂O₅ remains monoclinic (space group $C2/m$) up to 20 GPa. The smallest compressibility is found along the conducting b -axis. We observe an anomaly in the pressure dependence of the lattice parameters and the volume of the unit cell in the range 12–15 GPa, in agreement with the pressure-dependent optical properties.

Keywords: low-dimensional transition-metal oxide; crystal structure; β -vanadium bronzes

1. Introduction

The low-dimensional β -vanadium bronzes β -A_{0.33}V₂O₅ with monovalent A¹⁺ (A = Li, Na, and Ag) are typical examples of highly correlated electron systems. They have attracted great interest because of their remarkable physical properties, such as temperature-induced metal-insulator transition, charge ordering, and pressure-induced superconductivity [1]. Superconductivity under pressure in β -vanadium bronzes was first discovered for β -Na_{0.33}V₂O₅ for pressures between 7 and 9 GPa and for temperatures below ≈ 9 K [2]. The superconducting phase is adjacent to a charge-ordered phase, which suggests an important role of charge fluctuations for the superconductivity. According to the recently investigated pressure–temperature phase diagram, the superconducting state competes with a new non-superconducting metallic state under pressure, in addition to the charge-ordered state [1]. Infrared and Raman measurements on β -Na_{0.33}V₂O₅ single crystals at room temperature found anomalies in the pressure dependence of the phonon modes and the emergence of new excitations at ≈ 12 GPa [3,4]. The observed changes were attributed to a redistribution of charge with a possible relation to structural changes.

The β -vanadium bronzes β -A_{0.33}V₂O₅ show a quasi-one-dimensional metallic character, which is intimately linked to their monoclinic tunnel-like crystal structure (space group $C2/m$) built

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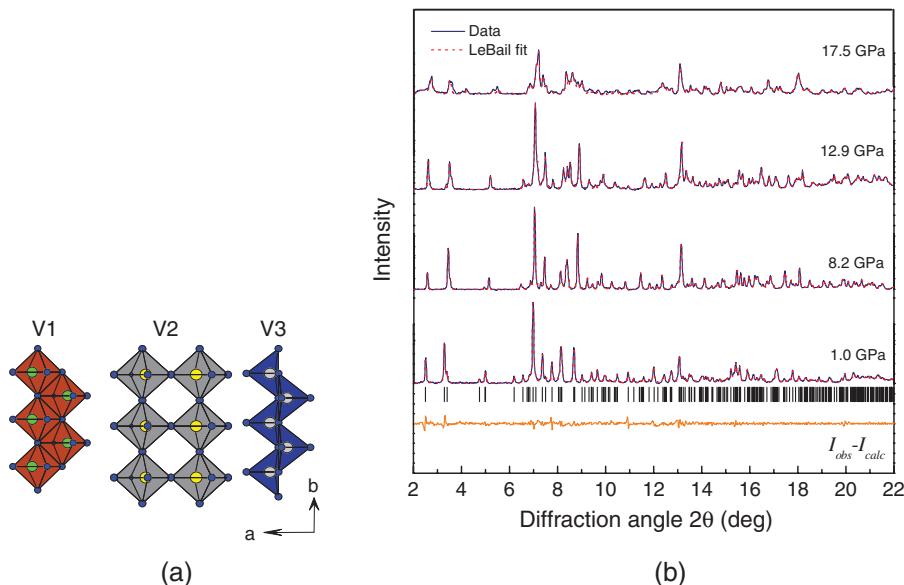


Figure 1. (a) Structural subunits of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$: zigzag chains of edge-sharing (V1) O_6 octahedra; two-leg ladders of corner-sharing (V2) O_6 octahedra; zigzag chains of (V3) O_5 polyhedra. (b) Room-temperature powder XRD diagrams of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ as a function of pressure together with the LeBail fits. For the lowest applied pressure (1.0 GPa), the difference curve ($I_{\text{obs}} - I_{\text{calc}}$) between the diffraction diagram and the LeBail fit is shown. Markers depict the calculated peak positions for the ambient-pressure phase.

by three kinds of chains along the b -axis, consisting of three inequivalent vanadium sites (Figure 1(a)): zigzag chains of edge-shared (V1) O_6 octahedra, two-leg ladders of corner-sharing (V2) O_6 octahedra, and zigzag chains of (V3) O_5 polyhedra. There are two possible sodium sites located in the tunnels along the b -axis, which can be represented as a two-leg ladder. For an A stoichiometry of 0.33, half of the sites are occupied.

For an understanding of the pressure-induced changes in the electronic properties, knowledge about the alterations of the crystal lattice under pressure is highly desirable. However, detailed information about the crystal structure of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ at high pressures is lacking so far.

2. Experiment

Single crystals of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ were grown by a flux method, as described in [5]. The structural properties of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ were studied at room temperature by high-resolution angle-dispersive powder X-ray diffraction (XRD). The measurements were carried out at the beamline ID09A of the European Synchrotron Radiation Facility (ESRF) in Grenoble. A crystal was ground into fine powder and loaded in a diamond anvil cell (DAC) with helium as a pressure-transmitting medium to assure good hydrostatic conditions up to the highest investigated pressure of 20 GPa. The ruby luminescence method was used for pressure determination [6]. The XRD patterns were collected by an image plate MAR345 detector with a focused monochromatic beam ($\lambda = 0.41142 \text{ \AA}$). The images were integrated by using the FIT2D software [7] to yield one-dimensional intensity versus 2θ patterns. The DAC was rotated by $\pm 3^\circ$ during the exposure to improve the powder averaging. We carried out LeBail fits of the diffraction data using the Jana2000 software [8], in order to determine the lattice parameters as a function of pressure.

3. Results and discussion

Room-temperature powder XRD diagrams of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ as a function of pressure together with the LeBail fits are depicted in Figure 1(b). For the fitting of the lowest-pressure data, we assumed the ambient-condition monoclinic unit cell with space group $C2/m$ containing two formula units, with the parameters $a = 15.44 \text{ \AA}$, $b = 3.61 \text{ \AA}$, $c = 10.08 \text{ \AA}$, and $\beta = 109.6^\circ$. The results of the fitting of the diffraction diagrams for all studied pressures are summarized in Figure 2, where we show the lattice parameters and unit cell volume as a function of pressure. Below the critical pressure $P_c \approx 12 \text{ GPa}$, the lattice parameters a , b , and c decrease monotonically with increasing pressure, while the monoclinic angle β slightly increases. The smallest compressibility is found along the conducting b direction, consistent with earlier reports [9]. The diffraction diagrams could be well fitted with the ambient-pressure crystal structure ($C2/m$) up to the highest applied pressure of 20 GPa. However, we observe an anomaly in the pressure dependence of all lattice parameters in the range 12–15 GPa. The anomaly is followed by a monotonic decrease in the parameters a , b , and c and an increase in the angle β . We also carried out fits of the X-ray data for $P > 15 \text{ GPa}$, assuming other crystal symmetries and also other space groups within the monoclinic system. The corresponding quality of the fits was, however, significantly worse.

From the lattice parameters, the pressure dependence of the unit cell volume V was obtained. In Figure 2(b), we plot $V(P)$ together with the fitting curves in the low- and high-pressure range according to the Murnaghan equation [10]:

$$V(P) = V_0 \left[\left(\frac{B'}{B_0} \right) P + 1 \right]^{-1/B'} \quad (1)$$

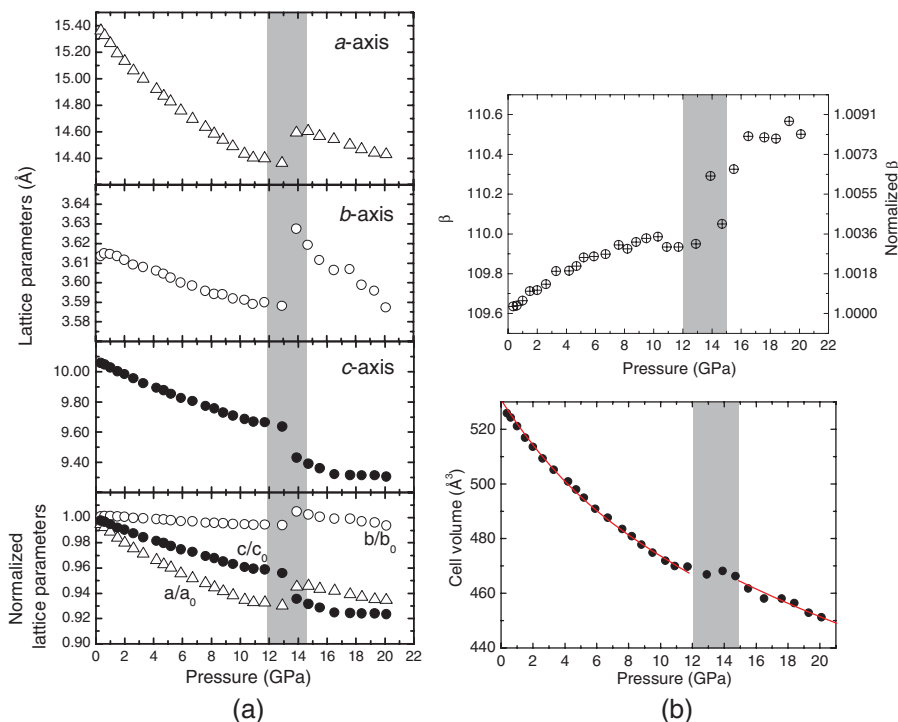


Figure 2. Lattice parameters and unit cell volume of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ as a function of pressure at room temperature. The gray bars mark the pressure range of the anomaly. The full lines in (b) are fits according to Equation (1).

with the bulk modulus $B_0 = -dP/d \ln V$ and its derivative B' at zero pressure. The ambient-pressure unit cell volume V_0 was kept fixed at the experimental value of 531.23 \AA^3 . For $P < P_c$, the bulk modulus B_0 evaluated according to the Murnaghan equation is 53.8 ± 1.5 and its derivative B' is 7.8 ± 0.5 . One notices that the pressure derivative B' is significantly larger compared to the value $B' \approx 4$ typically found for three-dimensional solids with isotropic elastic properties. The enhanced value of B' thus suggests anisotropic compression properties of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$. For $P > 15 \text{ GPa}$, we find the values $B_0 = 72.0 \pm 8.0$ and $B' = 6.1 \pm 1.3$. Hence, the anisotropic compression seems to be reduced above P_c .

We now want to discuss the implications of our findings. One interesting result of our analysis is the extremely small compressibility along the b direction, *i.e.* along the polyhedral chains. Accordingly, the chains can be viewed as rigid objects. Applying pressure basically reduces the distance between the chains – as signalled by the decrease of the lattice parameters a and c – but leaves them intact. Owing to the reduced distance, an enhanced interaction between the chains is expected, which should promote the charge transfer between them.

Furthermore, $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ keeps the ambient-pressure crystal structure up to 20 GPa according to our structural data. This finding is in full agreement with optical studies, which showed that all spectroscopic signatures are present up to high pressure [3,4]; hence, the structural units (V-O polyhedra) remain intact up to 20 GPa. The anomalies observed in the optical response at $\approx 12 \text{ GPa}$ [3,4] also fully agree with our finding of anomalies presented here. The sudden drop in the lattice parameter c at P_c (Figure 2(a)) reduces the distance between the (V1)O₆ and (V3)O₅ polyhedra (see [3] for a detailed view of the crystal structure). The transfer of charge between the V1 and V3 sites could thus be enhanced above P_c , consistent with the earlier interpretation of the pressure-dependent Raman data [3]. Additionally, the anisotropic compression is reduced above P_c , which is consistent with a pressure-induced increase in dimensionality proposed earlier [11]. According to the highest pressure diagram (Figure 2(b)), strong changes in the peak intensities and the appearance of new peaks at small diffraction angles occur at P_c . These findings evidence that the pressure application induces important structural modifications at P_c .

4. Summary

Our powder XRD measurements show that the room-temperature crystal structure of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ remains monoclinic with space group $C2/m$ up to 20 GPa. The main effect of pressure is a decrease in the distance between the chains of V-O polyhedra. We observe anomalies for all lattice parameters in the pressure range 12–15 GPa, in full agreement with recent optical data.

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