

Crystal structure and thermal expansion studies of α -VO(PO₃)₂

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Abstract

In this manuscript the details of the crystal structure and thermal expansion characteristics of the α -VO(PO₃)₂ are being discussed. Pale blue-colored sample of VO(PO₃)₂ has been prepared by solid-state reaction of V₂O₅ and (NH₄)₂HPO₄ at elevated temperature and analyzed by the Rietveld refinement of the observed ambient temperature powder X-ray diffraction (XRD) data for the phase purity and crystal structure. The observed unit cell parameters for α -VO(PO₃)₂ at ambient temperature are: $a = 15.0924(4)$, $b = 4.1919(1)$, $c = 9.5706(3)$ Å, $\beta = 126.464(2)^\circ$ and $V = 486.95(3)$ Å³, $Z = 4$ (space group: $C2/c$, no. 15). In the temperature range of 25–900 °C, the high-temperature behavior of this compound has been studied by an *in situ* high-temperature X-ray diffraction (HTXRD). This compound shows a significantly higher thermal expansion with the increase in temperature. The observed unit cell parameters at 900 °C are: $a = 15.508(1)$, $b = 4.3527(3)$, $c = 9.8234(9)$ Å, $\beta = 127.759(6)^\circ$, $V = 524.26(7)$ Å³. The typical thermal expansion coefficient of unit cell volume (α_v) is $89.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. The further details of the high-temperature behaviors are explained in this manuscript.

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1. Introduction

Thermal expansion is an important property, generally considered for any material to be used at elevated temperatures. An increase in an-harmonic potential with increasing temperature causes a thermal expansion of chemical bonds, which in turn results in dilation of the crystal lattice. However, there are several unusual examples where despite the expansion of the chemical bonds, there is either an overall contraction in the lattice (negative thermal expansion, NTE) or a very small or no expansion at all (low or zero thermal expansion, LTE or ZTE). Such anomalous thermal expansion behavior has been reported for several phosphates, tungstates and molybdates [1–7]. The study of thermal expansion and structural variation of various silicates, phosphates, molybdates, and tungstates is a strong motivation for us in order to correlate the crystal structure and thermal expansion behavior. It has been demonstrated that the inter-polyhedral (M–O–M') bond angles, metal oxygen (M–O) bond strength, arrangements of the polyhedral units and distortions in the unit cell have a tremendous effect on the lattice thermal expansion

behavior of the crystalline materials. An understanding of the correlation of crystal structure and thermal expansion will be useful in designing materials of desired thermal expansion or zero thermal expansion.

Vanadium phosphate and their hydrate products remained in interest for chemists for a long time due to their interesting catalytic properties [8–10] as well as their interesting structural features in particular of vanadium oxygen polyhedral unit [11,12]. Recently, one-dimensional magnetic chain has been observed in several low valent vanadium phosphates which further add to the importance of fundamental research [13–15] in these systems. In addition, phosphates of metal ions, like, ThP₂O₇, UP₂O₇, ZrP₂O₇, NbOPO₄, VOPO₄, etc., show anomalous thermal expansion, like low or negative thermal expansion behavior [16–22]. At higher temperature, low thermal expansion behavior of cristobalite type phosphates is also reported [23]. The crystal structures of these phosphates undergo a continuous change in structure leading to different structures under pressure or temperature [24–27]. Thus, these broad interests make the vanadium phosphorus oxide system important classes of material to further investigate.

At ambient temperature VO(PO₃)₂ is known to exist in two crystalline modification (α monoclinic, PDF 77-0998, space group: $C2/c$ and β tetragonal, PDF 84-0048, space group: $I-42d$)

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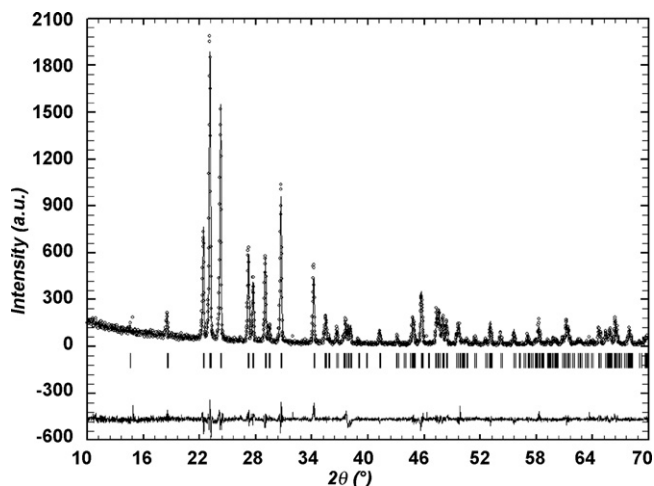


Fig. 1. Typical Rietveld plot for α -VO(PO₃)₂ at ambient temperature. (Observed pattern is shown as circles and calculated pattern is shown as continuous line. Difference between observed and calculated data is shown below. The lower vertical marks indicate the Bragg positions.)

depending on the synthesis procedure and annealing temperature. The details of the crystal structures of both modifications have been reported earlier [28,29]. A comparison of these two structures suggest that both the modifications are closely related and both the structures consists of the chains of PO₄ tetrahedral and V forms a highly distorted octahedra, which can be more closely explained as VO₅ square pyramids. In both the polymorphs, the base of the square pyramid is capped with the apex oxygen of another VO₅ square pyramid and thus making as apex sharing chain of VO₆ octahedra. These chains are separated by the double chains of the PO₄ tetrahedra. In the both structures two PO₄ tetrahedra are the repeating units. Later another polymorph of VP₂O₇ (monoclinic, P2₁) has been obtained by a topotactic de-intercalation of Li from LiVP₂O₇ [30]. The structure of this polymorph bears a significant difference from the earlier reported α and β structures. This new polymorph has isolated VO₆ octahedra similar to the parent LiVP₂O₇ lattice and each apex oxygen atom of the VO₆ octahedra share with the PO₄ tetrahedral units. The crystal structures of all the polymorphs show a very low dense packing of the polyhedra and thus interesting structural changes are expected at higher temperature. Recently, the high-temperature studies on (VO)₂P₂O₇ showed a transformation to another modification with different thermal expansion coefficients than the ambient modification [31]. The differential thermal analysis on the VO(PO₃)₂ shows no phase transition up to 1000 °C. However, a partial reduction of V⁴⁺ before its incongruent melting was reported [32]. Therefore, in order to conclude any absence of low energy displacive transition an *in situ* diffraction study seems to be an ideal technique. Thus, we have carried an *in situ* high-temperature diffraction study on α -VO(PO₃)₂ and the crystal structure and thermal expansion are reported in this paper.

2. Experimental

The title compound was prepared by solid-state reaction of appropriate amounts of V₂O₅ and (NH₄)₂HPO₄. The homogenous mixture of the reactants

Table 1

Refined crystallographic parameters for α -VO(PO₃)₂ at ambient temperature

Atom	Site	<i>x</i>	<i>Y</i>	<i>z</i>
V	4e	0	0.2551(4)	0.25
P	8f	0.3290(1)	0.0067(4)	0.8468(2)
O1	8f	0.4105(4)	0.159(1)	0.8307(8)
O2	8f	0.2376(4)	0.253(1)	0.8061(5)
O3	8f	0.3674(5)	−0.147(1)	0.0125(5)
O4	4e	0	−0.1342(4)	0.25

Monoclinic, space group: C2/c (no. 15). $B_{\text{overall}} = 1.83(7) \text{ \AA}^2$. $a = 15.0924(4)$, $b = 4.1919(1)$, $c = 9.5706(3) \text{ \AA}$, $\beta = 126.464(2)^\circ$, $V = 486.95(3) \text{ \AA}^3$. R_p : 10.8%, R_{wp} : 14.9%, R_{exp} : 11.5%, χ^2 : 1.68, R_B : 6.04%, R_F : 5.19%. The typical interatomic distances (Å) and inter-polyhedral angles (°). V–O1 = 1.946(7) × 2, V–O3 = 1.983(4) × 2, V–O4 = 1.632(3), V–O4 = 2.560(3), P–O1 = 1.473(7), P–O2 = 1.575(6), P–O2 = 1.593(5), P–O3 = 1.475(5), V–O1–P = 160.2(4), V–O3–P = 143.8(3) and P–O2–P = 130.3(3).

was heated initially at 200 °C for 2 h for the decomposition of (NH₄)₂HPO₄ in a platinum boat and then reground and further heated at 650 °C for 12 h. The pale blue-colored product obtained was characterized by powder XRD patterns recorded on a Philips Powder X-ray diffractometer (model PW1710) using the

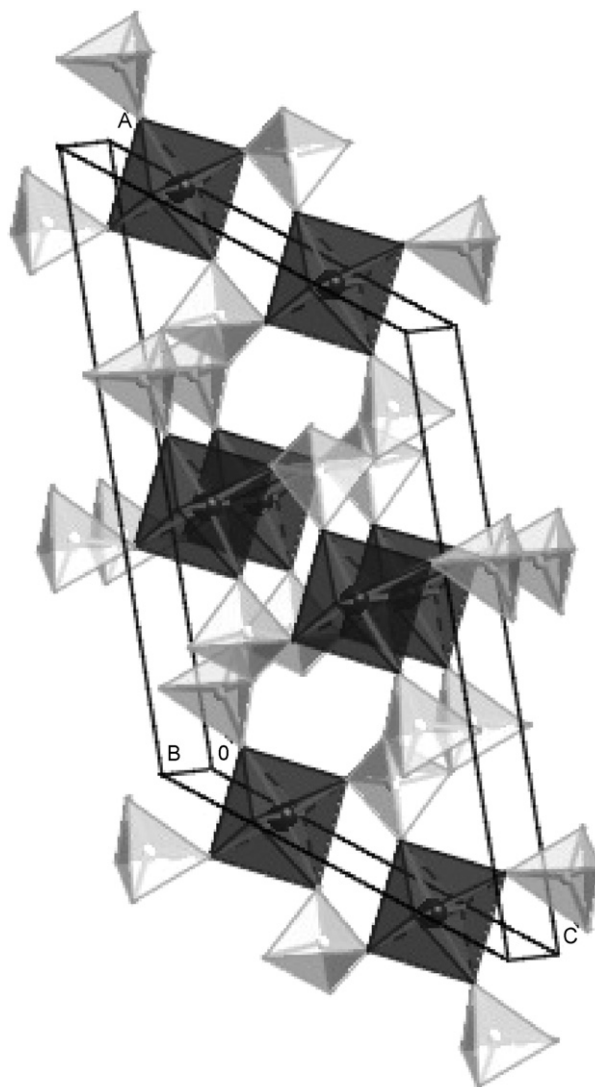


Fig. 2. The typical three-dimensional representation of α -VO(PO₃)₂ at ambient temperature. (The distorted VO₆ octahedra and PO₄ tetrahedra are shown.)

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