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Neutron powder diffraction investigations of pure and deuterated $Ti_3PO_{0.58}$.

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Abstract

The crystal structures of $Ti_3PO_{0.58}$ and $Ti_3PO_{0.58}D_{0.37}$ have been refined from neutron powder diffraction room temperature data using the Rietveld method. $Ti_3PO_{0.58}$ crystallizes in the filled Re_3B type structure, space group *Cmcm*, with the unit cell dimensions $a=3.2934(2)$ Å, $b=9.8978(6)$ Å and $c=7.7143(4)$ Å, $Z=4$. The dissolved deuterium atoms in $Ti_3PO_{0.58}D_{0.37}$ occupy two different types of interstices between the metal atoms, one position octahedrally surrounded by six titanium atoms and one position with four close titanium neighbours in a tetrahedral arrangement. The unit cell dimensions increase to $a=3.2975(5)$ Å, $b=9.9028(9)$ Å and $c=7.7596(8)$ Å.

Keywords: Ti_3PO_{1-x}; Crystal structure; Metal hydride; Neutron diffraction

1. Introduction

The occurrence of a ternary phase, Ti_3PO_{1-x}, was reported previously in connection with investigations of the Ti_3P–D system [1]. It was indicated that Ti_3PO_{1-x} is isostructural with $Zr_3PO_{0.42}$, which crystallizes in the filled Re_3B type structure [2–4]. Ti_3PO_{1-x} was found to absorb appreciable amounts of deuterium in a solid solution. There are various types of interstices between the metal atoms that might accommodate the deuterium atoms. The present investigation was therefore undertaken to verify the previous structure proposal and to locate the deuterium positions.

2. Experimental

2.1. Sample preparation

Rods of titanium, red phosphorus and titanium oxide (TiO_2) powder, with the claimed purities 99.9%, 99.999% and 99.9%, respectively, were used as starting materials. Mixtures of titanium turnings and red phosphorus were heated at 900 °C in evacuated silica tubes for three days. The product and appropriate amounts of titanium oxide powder were arc-melted and subsequently annealed at approximately 1350 °C for 10 h in a high-frequency induction furnace in a purified argon atmosphere. The sample was crushed and ground to a fine powder. X-ray powder diffraction films showed that there were a few very weak lines of TiO_y in addition to Ti_3PO_{1-x}. The deuterium solution was formed by reacting the powder with deuterium at a pressure of 90 kPa at 650 °C for 2 h followed by slow cooling to room temperature.

2.2. X-ray diffraction

Phase analyses and determinations of the unit cell dimensions of the pure and deuterated samples were carried out using a Guinier–Hägg type focusing camera with strictly monochromatic $CuK\alpha_1$ radiation and silicon ($a=5.431028$ Å at 22 °C) as internal calibration standard.

2.3. Neutron powder diffraction

Neutron powder diffraction intensities were recorded at room temperature at the R2 reactor, Studsvik, Sweden. The neutron beam was monchromated from two copper (220) single crystals in a parallel arrangement giving a wavelength of 1.467(1) Å and a neutron flux at the sample of $\sim 10^6$ neutrons cm^{-2} s^{-1}. A multidetector system with ten separate detectors mounted 3.12° apart recorded the intensities in 2θ-steps of 0.08° in the range 0.20–128.04°. No corrections for absorption effects were made since the

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observed μ-values were less than 0.20 cm^{-1} as obtained from transmission measurements at $2\theta=0$.

3. Structure analysis and refinements

Structure refinements were based on the Rietveld method [5] using the program FULLPROF [6]. The powder diffraction profile used in the refinements covered the 2θ-range 15.40–128.04°. The diffraction peaks were described by a pseudo-Voigt function including a Lorentzian contribution to the Gaussian peak shape. Peak asymmetry corrections were made for angles below $2\theta=40°$. The neutron scattering lengths used were Ti: −3.438, P: 5.130, O: 5.803 and D: 6.671 fm.

3.1. Ti_3PO_{1-x}

Earlier work has indicated that the crystal structure of Ti_3PO_{1-x} is isostructural with Zr_3PO_{1-z}, therefore, the atomic coordinates of $Zr_3PO_{0.42}$ were used as initial parameters in the refinements of Ti_3PO_{1-x}. The values of the occupancy and the temperature factor are strongly correlated and therefore the temperature factor of the oxygen position was fixed to the value obtained from the single crystal structure determination of $Zr_3PO_{0.42}$. The impurity phase was identified to $TiO_{0.45}$ by comparing the obtained unit cell dimensions from X-ray powder photographs ($a=2.9639(2)$ Å, $c=4.8211(10)$ Å), with composition-unit cell parameters relations earlier reported [7]. The scale factor was the only varied parameter of $TiO_{0.45}$. A total of 22 parameters were refined in the last refinement cycles: scale factors (2), 2θ zero-point (1), background parameters (6), half-width parameters (3), asymmetry parameter (1), Lorentzian profile shape parameter (1), wavelength (based on the X-ray unit cell dimensions) (1), atomic coordinates (4), isotropic temperature factors (2) and occupancy of oxygen (1).

3.2. $Ti_3PO_{1-x}D_u$

Approximate deuterium positions were located with difference Fourier syntheses where the Ti_3PO_{1-x} contributions were subtracted. The difference maps showed significant maxima corresponding to two non-equivalent atomic positions. Deuterium atoms in these positions were included in the structure refinements. The temperature factors of the deuterium atoms were fixed at the values obtained in $Ti_3PD_{2.4}$ [1]. Structural parameters of deuterated $TiO_{0.45}$ were taken from Ref. [8]. The scale factor and the deuterium occupancy of the impurity phase were varied. A total number of 25 parameters were refined in the final refinement cycles: scale factors (2), 2θ zero-point (1), background parameters (6), half-width parameters (3), asymmetry parameter (1), Lorentzian profile shape parameter (1), wavelength (based on the X-ray unit cell dimensions) (1), atomic coordinates (5), isotropic temperature factors (2) and occupancy of deuterium (3).

Table 1
Final structure parameters for $Ti_3PO_{0.58}$ and $Ti_3PO_{0.58}D_{0.37}$

$Ti_3PO_{0.58}$, space group *Cmcm* (No. 63)
$a=3.2934(2)$ Å, $b=9.8978(6)$ Å, $c=7.7143(4)$ Å
$R_p=0.054$, $R_{wp}=0.070$, R_B (155 refl.)=0.086, $R_{exp}=0.054$

Atom	Position	x	y	z	B_{iso}	Occupancy (%)
Ti1	8f	0	0.1399(5)	0.0528(6)	0.77(5)	100
Ti2	4c	0	0.4445(6)	1/4	0.77(5)	100
P	4c	0	0.7494(5)	1/4	0.60(6)	100
O	4b	0	1/2	0	0.30	58.1(2)

$Ti_3PO_{0.58}D_{0.37}$, space group *Cmcm* (No. 63)
$a=3.2975(5)$ Å, $b=9.9028(9)$ Å, $c=7.7596(8)$ Å
$R_p=0.051$, $R_{wp}=0.068$, R_B (156 refl.)=0.081, $R_{exp}=0.040$

Atom	Position	x	y	z	B_{iso}	Occupancy (%)
Ti1	8f	0	0.1413(6)	0.0542(5)	0.65(7)	100
Ti2	4c	0	0.4425(7)	1/4	0.65(7)	100
P	4c	0	0.7512(5)	1/4	0.78(8)	100
O	4b	0	1/2	0	0.30	58.1
D1	4b	0	1/2	0	1.10	29.9(3)
D2	4c	0	0.034(5)	1/4	1.10	7.0(2)

Estimated standard deviation within parentheses.

4. Results and discussion

The composition of the investigated samples were refined to $Ti_3PO_{0.58}$ and $Ti_3PO_{0.58}D_{0.37}$. The structure parameters and the agreement factors are listed in Table 1. Selected distances are listed in Table 2. The observed and calculated neutron diffraction profiles are plotted in Fig. 1 and a projection of the crystal structure along the *a*-axis is shown in Fig. 2. The amounts of $TiO_{0.45}$ was estimated to be less than 4% and the composition of the deuterated sample was refined to $TiO_{0.45}D_{0.24}$.

$Ti_3PO_{0.58}$ crystallizes in the filled Re_3B type structure, space group *Cmcm* (No. 63). This structure has been thoroughly described and discussed in several earlier papers [9–11]. The two types of non metal atoms occupy two different types of interstices between the metal atoms. The larger phosphorus atoms are situated in triangular

Table 2
Selected interatomic distances shorter than 3.2 Å for $Ti_3PO_{0.58}D_{0.37}$

D1	2 Ti2	2.022(2)	D2	2 Ti1	1.85(3)
	4 Ti1	2.203(4)		2 Ti2	1.88(2)
	4 D2	2.569(6)		8 O	2.569(6)
	2 P	3.155(4)		2 P	2.71(4)
				P	2.81(5)

Estimated standard deviations within parentheses.

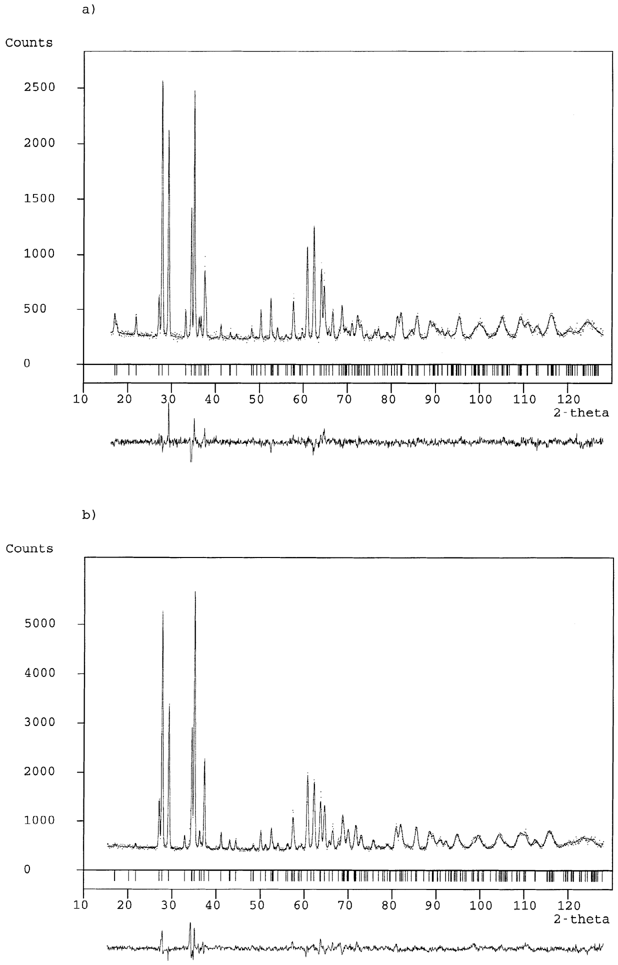

Fig. 1. Final observed (dots) and calculated (full line) neutron powder diffraction patterns. (a) $Ti_3PO_{0.58}$ and $TiO_{0.45}$; (b) $Ti_3PO_{0.58}D_{0.37}$ and $TiO_{0.45}D_{0.24}$.

prismatic interstices and the oxygen atoms in octahedral interstices.

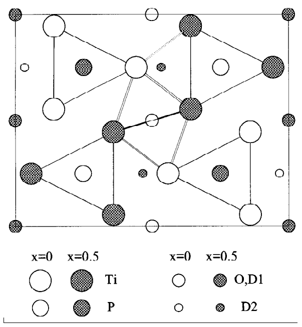

Fig. 2. The crystal structure of $Ti_3PO_{0.58}D_{0.37}$ projected along the *a*-axis. The columns of triangular prisms are shown. The octahedral environment of one D1 atom and the tetrahedral surrounding of one D2 atom are indicated.

$Ti_3PO_{0.58}$ absorbs deuterium forming a solid solution, and the host lattice remains essentially unchanged upon moderate deuterium absorption. The volume expansion was 1.2 Å^3 per deuterium atom. At higher deuterium contents the formation of a hydride phase was indicated. Two independent deuterium positions were found in the structure. A 4b-site (D1, occupation 32%) is equivalent to the octahedral interstices that are partly filled with oxygen, i.e., the empty holes accommodate deuterium atoms. The D1 atoms are coordinated by two Ti2 atoms at distances of 2.02 Å and four Ti1 atoms at 2.20 Å. The shortest P–D1 and O–D1 distances are 3.15 and 3.30 Å, respectively. The second independent deuterium site is a 4c-site: D2, occupation 7%. D2 is coordinated by four near titanium atoms in a tetrahedral arrangement, with the distances D2–2Ti1 1.85 Å and D2–2Ti2 1.88 Å. The tetrahedral site is less favourable than the octahedral site probably due to close O–D2 contacts at 2.57 Å and P–D2 contacts at 2.70 Å. Similar tetrahedral deuterium environments has also been observed in the deuterium solid solution and the hydride phase of Ti_3P, where the shortest P–D distances were 2.5–2.6 Å [1,12].

Acknowledgments

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