

Structure of the hydrated pyrochlore $\text{NaW}_2\text{O}_6 \cdot n\text{H}_2\text{O}$ Gordon J. Thorogood^{a,b}, Brendan J. Kennedy^{b,*}, Victor Luca^a^aInstitute of Materials and Engineering Science, Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights, NSW 2234, Australia^bSchool of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

Abstract

The structure of the non-stoichiometric pyrochlore $\text{NaW}_2\text{O}_6 \cdot n\text{H}_2\text{O}$ has been refined from powder neutron diffraction data using the Rietveld method. The stoichiometry found from the structural refinements is $\text{Na}_{0.85(2)}\text{W}_{2.02(2)}\text{O}_6 \cdot 0.92(5)\text{H}_2\text{O}$ in good agreement with other analytical studies. The Na cation is seven-coordinated bonding to six framework oxygen atoms and one oxygen atom from the water. The refinements show a disordered H_2O molecule to be present with the O(2) on a 32e site and the H(1) 48f site. Crown Copyright © 2006 Published by Elsevier B.V. All rights reserved.

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Introduction

The structural, electrical and physical properties of pyrochlore-type oxides have long been of interest in materials chemistry [1]. Following the earlier work of Moller [2] on the use of pyrochlores as ion exchangers to remove radioactive Sr-90 and Cs-137 from intermediate level liquid waste, we have been interested in the ion-exchange properties of a number of defect tungsten pyrochlores of the type $\text{NaW}_2\text{O}_6 \cdot n\text{H}_2\text{O}$.

The pyrochlore structure has cubic symmetry (space group $\text{Fd}\bar{3}\text{m}$) with a stoichiometry of $\text{A}_2\text{B}_2\text{X}_6\text{X}'$ where A is a large low-valence cation and B is a smaller cation which is capable of octahedral coordination (e.g. Ti^{4+} , Zr^{4+} , W^{6+} , Sb^{6+}). The X anion site is usually occupied by O^{2-} as is the X' site, although this latter site may also be occupied by other anions such as OH^- or F^- . The pyrochlore structure contains two weakly interacting interpenetrating sublattices, a cuprite-like $\text{A}_2\text{X}'$ lattice and a B_2X_6 framework built from corner sharing BX_6 octahedra. Vacancies on the $\text{A}_2\text{X}'$ sublattice are commonly observed and the stoichiometry can be expressed as $\text{A}_{2-x}\text{B}_2\text{X}_6\text{X}'_{1-x/2}$ [1]. When the crystallographic origin is at $\bar{3}\text{m}$ the B-type cation is located at 16c

Wycoff position (0,0,0) and the X-type anion occupies the 48f site $(x, \frac{1}{8}, \frac{1}{8})$. In the ideal cubic structure, there is only one variable positional parameter, x . If $x > 0.3125$ the octahedra are compressed in the [111] direction, and if $x < 0.3125$ the octahedra are elongated in the same direction.

The most promising ion-exchange materials are produced using hydrothermal methods; these have small particle sizes, high surface areas and tend to contain additional water molecules within the structure. A number of studies aiming to establish the distribution of the water molecules in the pyrochlore form of antimonic acid and pyrochlores of other compositions have been reported [3–7]. The role of these water molecules in influencing the favorable ion-exchange properties of $\text{NaWO}_6 \cdot n\text{H}_2\text{O}$ is unknown and a crucial first step in understanding this is establishing the precise structure of this material.

In this report, we describe powder neutron diffraction structural studies of $\text{NaW}_2\text{O}_6 \cdot n\text{H}_2\text{O}$ and the nature of cation/water distribution within the pyrochlore channels.

Experimental

Powder neutron diffraction data were collected on the medium resolution powder diffractometer (MRPD) instrument ($\lambda = 1.6649 \text{ \AA}$) at the HIFAR facility, of the Australian Nuclear Science and Technology Organisation

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(ANSTO). The sample, prepared using D₂O as solvent, was sealed into a vanadium sample can and placed into a closed cryostat. A powder neutron diffraction pattern was collected at 10 K, over the angular range of 6–132° in increments of 0.1°. The structure was refined by the Rietveld method [8] with RIETICA [9].

The structure model was based on that described by Slade et al. [10] for antimonite acid [HSbO₃·0.5H₂O]. Initial refinements were carried out with a fixed *x* value of 0.3139 for O(1) and 0.4214 for H(1). Only once the refinement had converged was the position and occupancy of the water molecule allowed to vary in the refinements.

Results

The refined cubic lattice parameter for NaW₂O₆·*n*H₂O is 10.339(1) Å, the larger than usual error in this being a consequence of the broadening of the diffraction peaks apparent in Fig. 1. The high background is a result of partial exchange of the D by H upon standing, the ratio of D to H is ~1:10.

It was rapidly established during the refinements that the Na site was not fully occupied, with the refined occupancy being around 50%. There was no indication from the refinements for any positional disorder of the Na cations (Table 1).

The W–O(1) distance is similar to that observed in other W^{VI} oxides and is very similar to the Sb–O distance observed in antimonite acid, 1.974(1) Å, as expected from the similarities in the ionic radii of the two cations W^{VI} and Sb^V, both being given as 0.60 Å. The W–O–W angle is larger than that observed in antimonite acid, 136.4°. The small but significant differences in the W–O distances and angles of the W₂O₆ framework possibly reflect the importance of the channel water molecules.

Analysis of the pattern indicates that the oxygen atom from the water is located on a 32e site with *x* = 0.393(3).

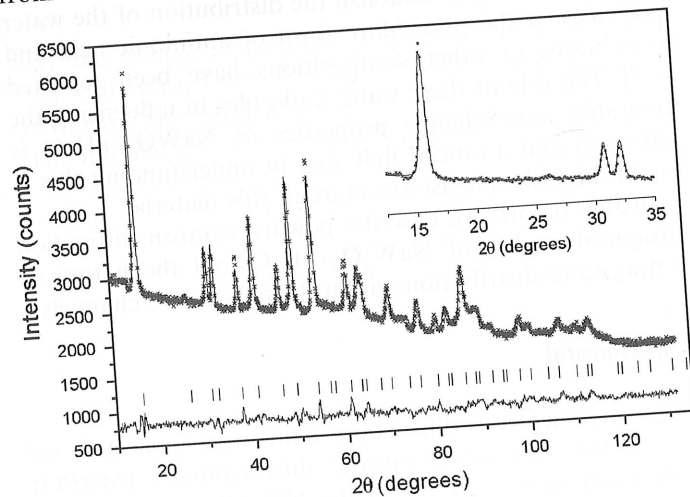


Fig. 1. Observed, calculated and difference neutron diffraction profiles for NaW₂O₆·*n*H₂O using neutron diffraction data at 10 K. The Bragg positions (|) are indicated. The inset highlights the broadening of low angle peaks.

Table 1
Atom parameters, selected interatomic distances and bond angles for NaW₂O₆·*n*H₂O (space group Fd3̄m) at 10 K

Atom	Site	<i>x</i>	<i>y</i> = <i>z</i>	<i>N</i>
W	16c	0.000	0.000	0.083(0)
Na	16d	0.500	0.500	0.035(1)
O(1)	48f	0.3145(3)	0.125	0.250(0)
O(2)	32e	0.393(2)	0.393(2)	0.041(3)
H(1)	48f	0.521(3)	0.125	0.067(4)
Framework atoms				
W–O(1)	<i>x</i> 6	1.947(1) Å	BVS W 6.0	
W–O–W		139.7°(2)		
Interstitial species				
Na–O(1)	<i>x</i> 6	2.647(2) Å	BVS Na 1.1	
Na–O(2)		2.06(6) Å		
H–O(1)		2.08(3) Å		
H–O(2)		0.96(4) Å		

$R_p = 1.77\%$; $R_{wp} = 2.34\%$; $R_{exp} = 0.98\%$; $R_B = 16.21\%$; $\chi^2 = 5.65\%$. The refined value of *x* for the O(1) site indicates compression of the octahedra in the (111) direction.

The O can be described as being disordered from an 8b site at $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$ by displacement of ~0.32 Å in the 111 direction. This site is only partially occupied, the occupancy corresponding to approximately one water molecule per 16d site. As noted above, approximately 50% of the 16d sites are vacant and it appears reasonable to suppose that the Na atoms are seven-coordinate, bonding to six O(1) atoms from the W₂O₆ network with Na–O(1) 2.647(2) Å and the one O(2) from the water molecule at 2.06(6) Å. This gives an effective bond valence of the Na ions of 1.1. The H atoms from the water molecule are directed towards the O(1) atoms although the shortest H–O(1) distance of 2.08(3) Å demonstrates there is little H bonding between the water and W₂O₆ framework.

The distribution of the Na and water molecules within the channels are highlighted in Fig. 2.

Thermo gravimetric analysis shows the sample loses ~5% of weight when heated to 812 °C (Fig. 3). A broad continuous weight loss from room temperature corresponding to a weakly bonded (and presumably non-structural) component, is observed, together with a more rapid loss near 250 °C corresponding to the more tightly bound structural water.

The stoichiometry of the sample based on the Rietveld refinement is Na_{0.85(2)}W_{2.02(2)}O₆·0.92(5)H₂O. The expected weight loss of this composition would be 3.3%, in good agreement with the observed TGA results. This Na:W ratio is in good agreement with the results of X-ray microanalysis that gave a Na:W ratio of 0.99:2.

In their study of antimonite acid, Slade et al. [10] found two crystallographically unique water molecules. Attempts to place another H₂O molecule in the structure of NaW₂O₆·*n*H₂O yielded unstable refinements, so it is apparent that NaW₂O₆·*n*H₂O contains less H₂O than the pyrochlore form of antimonite acid studied by Slade.

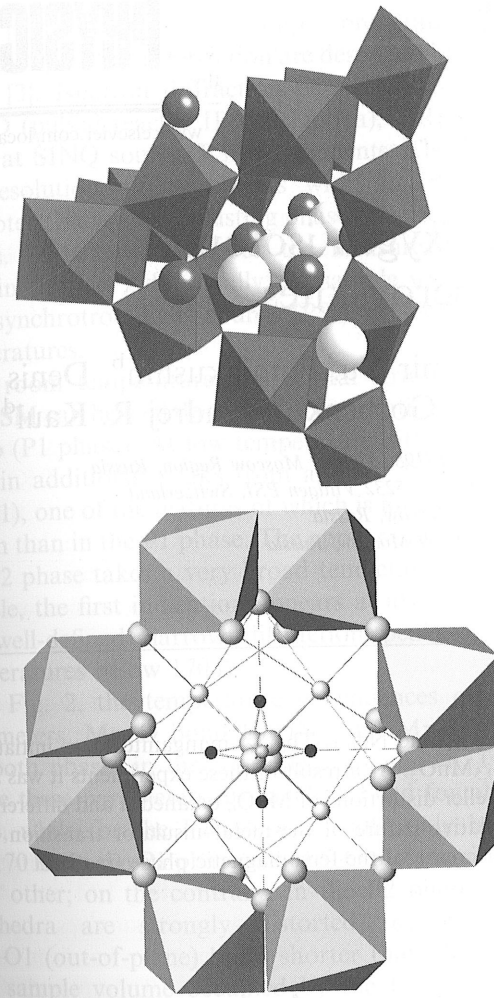


Fig. 2. Top: representation of NaW₂O₆·*n*H₂O perpendicular to [111] showing the arrangement of the WO₆ octahedra and the general locations of H₂O (dark sphere) and Na (light sphere) in the channels. Note the zigzag arrangement in the channels of H₂O. Bottom: representation showing the possible positions of the O(2) (centre) and possible hydrogen bonds (- -) to O(1) located on octahedra vertices.

Conclusion

Structural studies of the defect pyrochlore NaW₂O₆·*n*H₂O have revealed that the Na cations and water

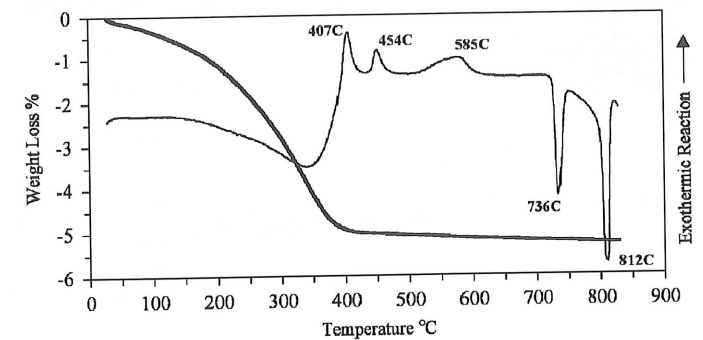


Fig. 3. Results of the thermo gravimetric analysis of NaW₂O₆·*n*H₂O, showing ~5% weight loss by 400 °C, before the first phase transformation at 407 °C. Two additional phase changes occur at 454 and 585 °C with two melting events at 736 and 812 °C.

molecules both reside in the channels that form in the 111 direction of the W₂O₆ network. While the water molecule is strongly bonded to the Na cations, it only weakly interacts with the W₂O₆ framework. The importance of the water molecule in influencing the ion exchange properties of this material is yet to be fully established; however, the weakness of the interaction with the W₂O₆ framework suggests that this group may be highly mobile.

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