

A thermal dehydration study of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$

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Abstract. Step-wise thermal dehydration of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ has been investigated and the various hydrated tungsten trioxide phases characterized. A cubic phase of tungsten trioxide with 0.36 moles of water is obtained by heating $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ to 498 K.

Keywords. Thermal dehydration; tungsten trioxide dihydrate; cubic phase.

1. Introduction

Solid state reactions which are topochemically controlled bear orientational relationship between the parent and product phases. Except for changes in dimension in one or more directions, the atomic arrangement in the reactant crystal remains largely unaffected during the course of a topotactic solid state reaction (Rao and Raveau 1995). Gunter (1972) showed that one such reaction is the dehydration of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ to give MoO_3 and WO_3 respectively. The structural feature common to various allotropic modifications of tungsten trioxide and several of its hydrates is the presence of W^{6+} in octahedral environment (Figlarz *et al* 1990). But the great number of possible arrangements of these octahedra, their distortions and the ease of hydration of WO_3 either by substitution of one oxygen of the octahedra by H_2O or by intercalation of H_2O between the sheets of the layered structure leads to a large number of structures. Among these hydrates the existence and structure of the tungsten trioxide dihydrate and monohydrate are known by the comparison of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ (Krebs 1972) and $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (Boudjada *et al* 1993).

In the course of a study on the reactivity of tungsten trioxide hydrates, Gerard *et al* (1981) obtained a new tungsten trioxide hydrate characterized as $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ which had similarities with the sodium octatungstate with large variations in the compositions. This hydrate crystallizes in the orthorhombic system with infinite plane of WO_6 octahedra sharing their corners and forming six-membered rings, which had structural relationships with the product of dehydration, a new anhydrous hexagonal tungsten trioxide (Seguin *et al* 1983). This hexagonal WO_3 phase turns irreversibly into the thermodynamically stable monoclinic WO_3 phase at about 673 K. A recent investigation involving the preparation and dehydration of $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ has shown the presence of sodium as a requirement, with a minimum concentration of as much as 160 ppm, for the stabilization of $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ (Pfeifer *et al* 1995). A new form of WO_3 with a pyrochlore-type structure was reported by Coucou and Figlarz (1988). This new oxide was prepared in three steps involving the thermal treatment of ammonium tungstate in acidic solution of ethylene glycol. The pyrochlore hydrate, $\text{W}_2\text{O}_6 \cdot x\text{H}_2\text{O}$,

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was then obtained by ion exchange in acidic solutions. Dehydration of these hydrates at about 373 K led to WO_3 in the pyrochlore structure.

From 0 K to 1273 K stoichiometric tungsten trioxide, WO_3 , was reported to have undergone many phase transformations in the solid state (Rao and Rao 1974). Below 1173 K, WO_3 was tetragonal in the space group $P4/nmm$ (Kehl *et al* 1952) and transformed at about 1013 K into an orthorhombic modification with space group $Pmnb$. Between 290 K and 603 K, WO_3 exhibited monoclinic symmetry in the space group $P2_1/n$ (Loopstra and Rietveld 1977). Below 290 K, WO_3 was triclinic with the space group $P1$ (Diehl *et al* 1978) and transformed into another monoclinic phase with the space group Pc at 233 K. These WO_3 related phases had distorted ReO_3 type crystal structures in common.

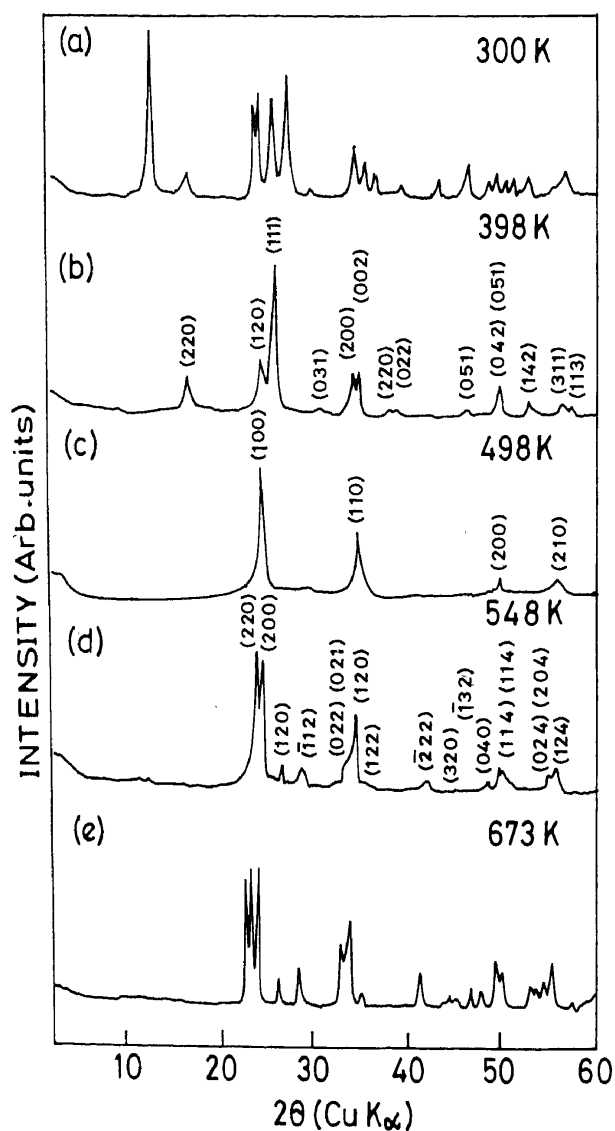


Figure 1. X-ray powder diffraction pattern of (a) $\text{WO}_3 \cdot 2\text{H}_2\text{O}$, (b) $\text{WO}_3 \cdot \text{H}_2\text{O}$, (c) $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$, (d) WO_3 (monoclinic) and (e) WO_3 (mixture of monoclinic and triclinic).

Although the tungstic acids or tungsten trioxide hydrates systems and their dehydration products have been extensively investigated for some time, the existence of some of the intermediate hydrate phases remains to be understood. With this interest, we have carried out the stepwise dehydration of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ and studied the topotactic mechanism involved in the reaction.

2. Experimental

Preparation of the $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ was carried out by following the procedure reported by Freedman (1959). Fifty ml of 1.0 M Na_2WO_4 was pipetted into 450 ml of 3.0 N HCl at 373 K. The initial yellow solution turned turbid and later to a characteristic yellow precipitate. The mixture was heated for 30 min and allowed to settle and washed repeatedly with 0.1 N HCl at room temperature. The slurry was filtered and dried at 373 K for 2 h to obtain orange-yellow powder of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$. Atomic absorption spectroscopy was performed to confirm the absence of Na in the final product (<1 ppm). X-ray diffraction experiments at various temperatures were performed using a STOE/STADIP high resolution powder X-ray diffractometer. Thermogravimetric

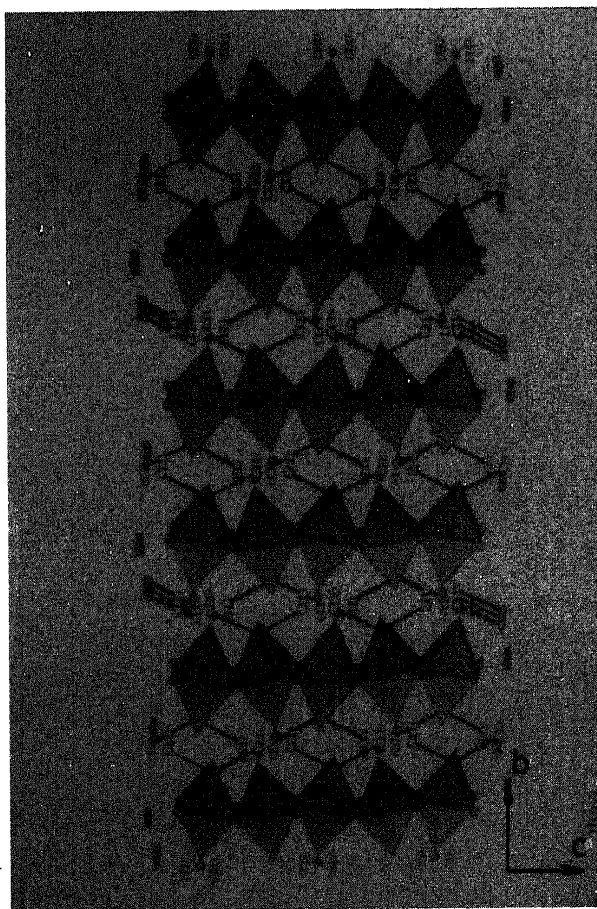


Figure 2. Structural projection of $\text{WO}_3 \cdot \text{H}_2\text{O}$.

analysis of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ and other hydrated products was performed using POLYMER (Model STA 1500) TGA setup. Infrared spectra were recorded using the Perkin-Elmer (Model 580) spectrometer.

3. Results and discussion

High-resolution X-ray powder diffraction data of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ were collected at various temperatures. Figure 1 shows that at around 398 K the tungsten trioxide dihydrate loses one H_2O molecule and converts to $\text{WO}_3 \cdot \text{H}_2\text{O}$. The X-ray diffraction

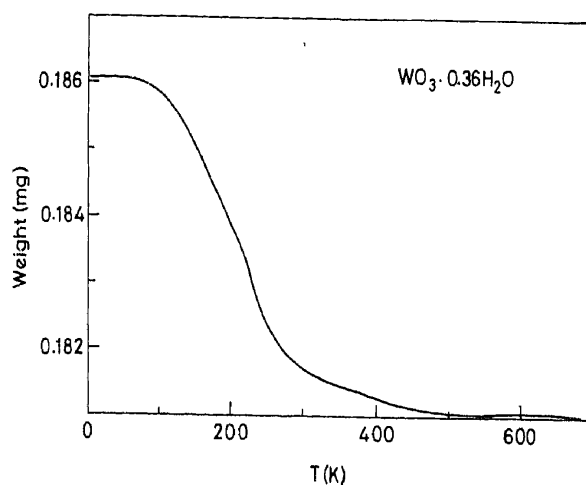


Figure 3. Thermogravimetric analysis plot for $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$.

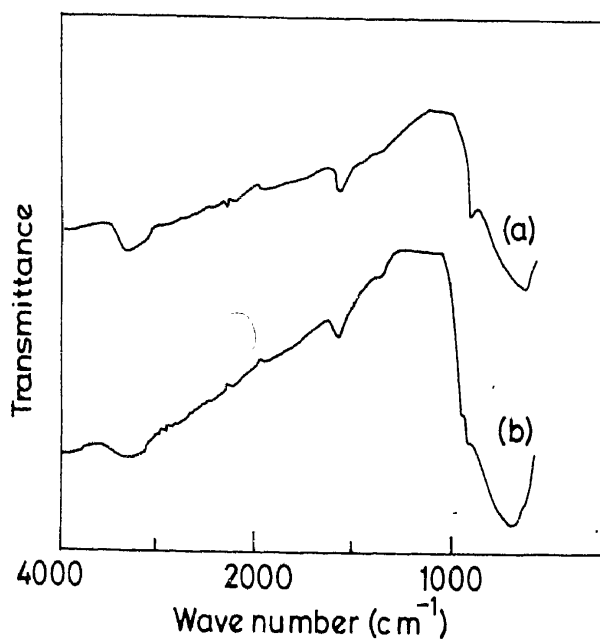


Figure 4. Infrared spectra of (a) $\text{WO}_3 \cdot \text{H}_2\text{O}$ and (b) $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$.

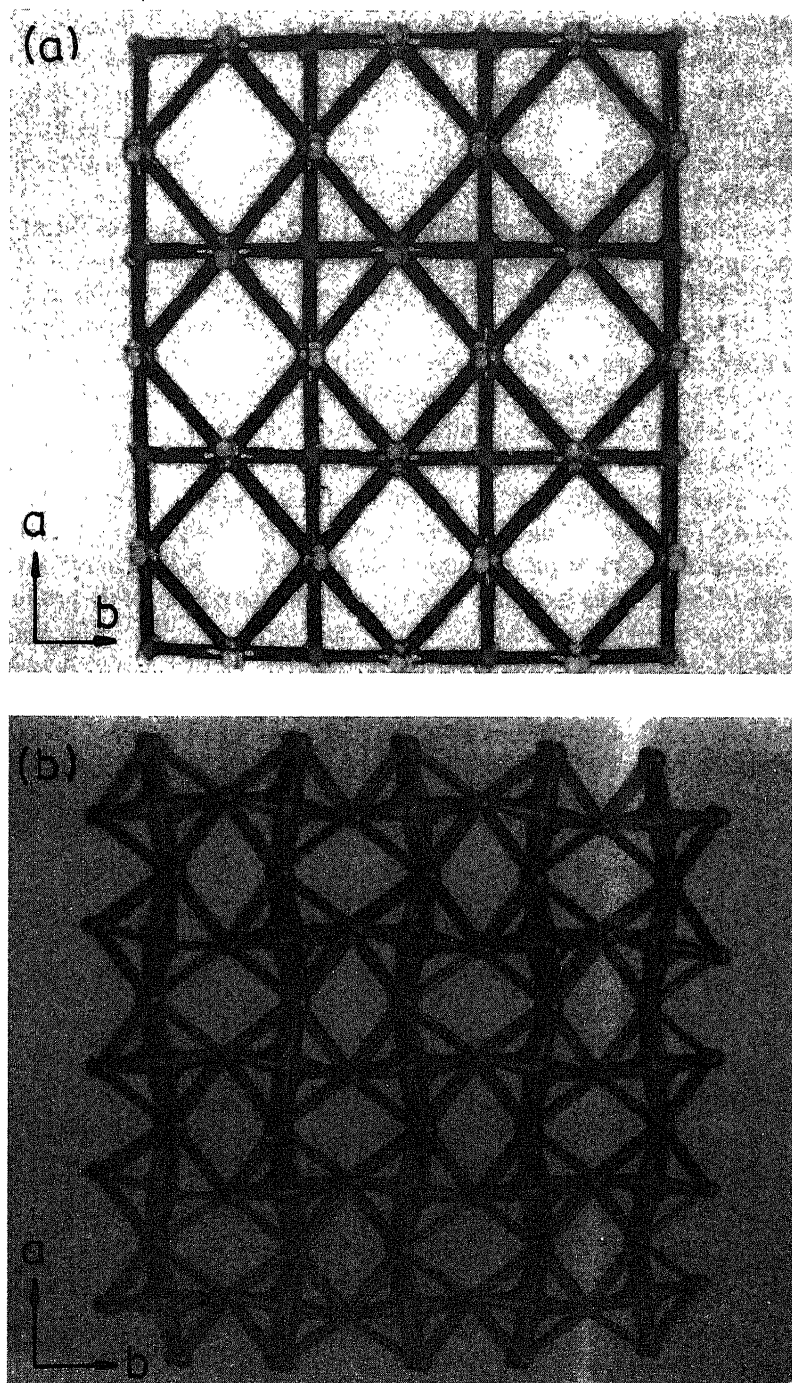


Figure 5. Structural projections of (a) $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ and (b) WO_3 with monoclinic distortion.

pattern of $\text{WO}_3 \cdot \text{H}_2\text{O}$ (figure 1b) could be indexed in the orthorhombic system (space group $Pmnb$) (Boudjada *et al* 1993) with the cell dimensions $a = 5.228$, $b = 10.680$ and $c = 5.128$ Å. The structure of $\text{WO}_3 \cdot \text{H}_2\text{O}$ consists of WO_6 octahedra which are stacked in sheets at $y = 1/4$ and $3/4$ sharing four corners in the equatorial plane, and the water

oxygen atoms alternate on the axial corners along [100] and [001] directions (figure 2). All the sheets are linked by hydrogen bonds involving the water molecules and two octahedra of neighbouring sheets. Heating $\text{WO}_3 \cdot \text{H}_2\text{O}$ to 498 K results in $\text{WO}_3 \cdot x\text{H}_2\text{O}$. The X-ray diffraction pattern of $\text{WO}_3 \cdot x\text{H}_2\text{O}$ (figure 1c) could be indexed in the cubic system with the space group $Pm\bar{3}m$ with the cell dimension $a = 3.675 \text{ \AA}$.

Thermogravimetric analysis (figure 3) of $\text{WO}_3 \cdot x\text{H}_2\text{O}$ showed weight loss corresponding to 0.36 moles of H_2O at 575 K. In figure 4, we compare the infrared spectra of $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ with that of $\text{WO}_3 \cdot \text{H}_2\text{O}$ (Daniel *et al* 1987). The infrared spectrum of $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ shows a broad band around 3350 cm^{-1} corresponding to O–H stretching and a pronounced H–O–H deformation band at 1615 cm^{-1} (figure 4). The X-ray diffraction pattern corresponds to the ReO_3 structure consisting of corner linked WO_6 octahedra forming an infinite 3D network of interconnecting tunnels (figure 5a). The structure with layered sheets of WO_6 octahedra interleaved with H_2O molecules in $\text{WO}_3 \cdot \text{H}_2\text{O}$ changes to a structure with a 3D network of WO_6 octahedra in $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$. The nature of the coordination of water molecule in $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ can only be studied through neutron diffraction. Heating $\text{WO}_3 \cdot 0.36\text{H}_2\text{O}$ to 548 K results in the complete loss of water molecule. The X-ray diffraction pattern of the product heated at 548 K (figure 1d) corresponds to that of the stable monoclinic WO_3 with the space group $P2_1/n$ with the cell dimensions $a = 7.508$, $b = 7.296$, $c = 7.691 \text{ \AA}$ and $\beta = 90.49^\circ$. The structure of the monoclinic phase consists of distorted corner-linked WO_6 octahedra with the displacement of tungsten ions from the centre of the octahedra. Further heating of WO_3 to 673 K and then quenching it to room temperature, gives a mixture of monoclinic and triclinic phases (figure 1e). The structural projection with the monoclinic distortion is shown in figure 5b.

In summary, the present study shows that the thermal dehydration of tungsten trioxide dihydrate proceeds in three steps. All the hydrated and the final dehydrated phases have tungsten in octahedral coordination in common. The intermediate tungsten trioxide with 0.36 moles of water has a cubic symmetry.

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