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On reduction behavior of $Al_2(WO_4)_3$: A combined powder XRD and temperature programmed reduction (TPR) studies

S.N. Achary, S. Varma, A.K. Tyagi*

Applied Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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Abstract

In this manuscript, we report the reduction behavior of $Al_2(WO_4)_3$ as observed from the temperature programmed reduction (TPR) studies. The title compound crystallizes in orthorhombic lattice with unit cell parameters: 12.6011(2), 9.0622(2), 9.1427(2) Å and $V=1044.03(3)$ $(Å)^3$, $Z=4$ (space group: Pbcn). This compound can be reduced by hydrogen to $AlWO_4$ above 800 °C, which is otherwise prepared under high pressure and high temperature and thus indicates an alternate route for the synthesis of $AlWO_4$ at ambient pressure. On prolonged reduction or increasing the temperature of reduction metallic tungsten is observed. The details of the results of the TPR studies are discussed.

Keywords: A. Inorganic compound; A. Oxides; C. X-ray diffraction; D. Thermodynamic properties

1. Introduction

The metal tungstates have drawn a significant interest after the discovery of a negative thermal expansion in ZrW_2O_8, $Sc_2(WO_4)_3$ and other similar compounds [1–3]. Besides, the trivalent metal ion conduction, in various tungstates and molybdates with $Sc_2(WO_4)_3$ structure [4–6] draws further attraction to them. These trivalent metal ion tungstates of $M_2(WO_4)_3$ type are reported to have different crystal structures depending upon the radii of the trivalent cation. The larger metal ion tungstates are reported to have a monoclinic $Eu_2(WO_4)_3$ structure, and the smaller metal ion tungstates have an orthorhombic structure similar to $Sc_2(WO_4)_3$ [7]. $Al_2(WO_4)_3$ is reported to exist in $Sc_2(WO_4)_3$ type structure.

In the phase diagram of Al_2O_3–WO_3 [8], a congruently melting compound with compositions $2Al_2O_3$–$5WO_3$ had been reported earlier, which was later identified as $Al_2(WO_4)_3$. The crystal data reported by Craig et al. [9] shows that it has an orthorhombic structure and there is no phase transition up to its melting point. Later, the crystal structure was re-determined by de Boer [10], Hanuja et al. [11] and Woodcock et al. [12]. Below ambient temperature, Sleight et al. have reported a displacive phase transition in $Al_2(WO_4)_3$ [13]. The low temperature structure was reported as monoclinic, which is very closely related to the orthorhombic structure [11]. It is also reported that the transition from monoclinic to orthorhombic structure in $Al_2(WO_4)_3$ and in analogous tungstates and molybdates is accompanied by a significant volume expansion [11,13,14]. Earlier we had reported a limited stability of $Al_2(WO_4)_3$ under high pressure and high temperature conditions [15]. This compound decomposes to $AlWO_4$ and other WO_{3-x} phases beyond a limiting pressure and temperature [15]. In addition, at about 5 Kbar pressure and room temperature, a reversible phase transition in this compound was recently reported from the electrical conductivity measurements and high pressure X-ray diffraction [16,17].

The compounds with low valent transition metal ions have interesting magnetic as well as electrical properties. In Al–W–O systems, several compositions with lower valent tungsten, like, $AlWO_4$, $AlWO_3$ etc. have also been reported in literature [18]. Under the high-temperature and high-pressure conditions, several other new reduced tungsten oxides, namely, tetragonal, orthorhombic, monoclinic type phases have also been observed [15]. In order to study the reduction behavior and to explore the possibility of existence of new compositions with lower valent tungsten, the temperature programmed reductions (TPR) are carried

* Corresponding author. Fax: +91 22 2550 5151.
E-mail address: aktyagi@magnum.barc.ernet.in (A.K. Tyagi).

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out on $Al_2(WO_4)_3$. The residue obtained after various TPR experiments were analyzed by XRD.

2. Experimental

The title compound was synthesized by a conventional solid-state reaction of the preheated Al_2O_3 and WO_3 at 1000 and 1100 °C for 30 and 18 h, respectively. A colorless product was obtained, which was characterized by powder XRD and compared with the reported JCPDS data (JCPDS 24–1101). Philips powder XRD unit (model PW 1710) with Ni filtered Cu Kα radiation ($K\alpha_1 = 1.5406$ and $K\alpha_2 = 1.5444$ Å) source was used for powder XRD studies. The XRD data collected in the range 10.010–89.990°, step width = 0.020°, step time = 2.0 s was used for profile refinement. The sample was subjected to TPR study using a Thermoquest, Italy, TPDRO-1100 analyzer, in a flowing 5% H_2 in argon atmosphere (flow rate = 20 ml/min). The out gas was passed through soda lime trap and H_2 concentration was monitored with thermal conductivity detector. About 30 mg sample was heated from room temperature to higher temperature and the product obtained after the experiments were analyzed by powder XRD.

3. Results and discussion

The powder XRD data shows that the $Al_2(WO_4)_3$ crystallizes in an orthorhombic unit cell (Sp. Gr.: Pbcn). The phase purity of the sample was ascertained by profile refinement of the observed powder XRD data by Rietveld method using the Fullprof 2000 software [19]. The observed unit cell parameters for this phase are 12.6011(2), 9.0622(2), 9.1427(2) Å and $V = 1044.03(3)$ (Å)^3, $Z = 4$ (Space group: Pbcn No. 60). The observed and calculated powder profiles along with the difference plot are shown in Fig. 1. The crystal structure analysis of the $Al_2(WO_4)_3$ reveals the presence of AlO_6 octahedra and two types of

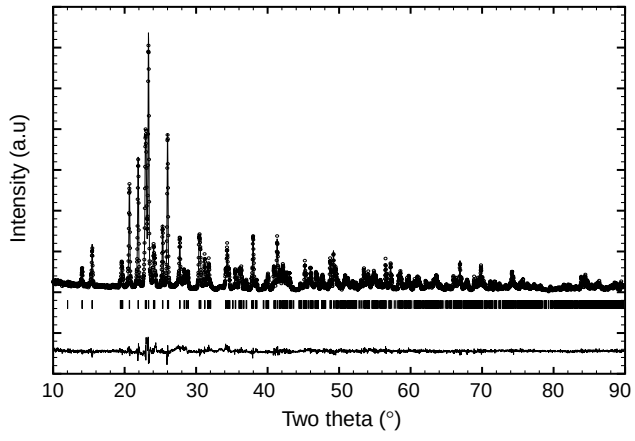

Fig. 1. Typical observed and calculated powder XRD plot for $Al_2(WO_4)_3$.

Table 1
Summary of phases identified at different reduction conditions

S. No.	Exptal. conditions			Phases found
	Max. temp. (°C)	Heating rate (°C/min)	Composition of atmospheric gas	
1	Starting materials			$Al_2(WO_4)_3$
2	1080	10	5% H_2:Ar	$AlWO_4 + WO_{3-x} + W$
3	1080 and held at this temp	10	5% H_2: Ar	$AlWO_4 + WO_{3-x} + W$
4	860	2	5% H_2: Ar	$Al_2(WO_4)_3$, $AlWO_4$, WO_{3-x}
5	1050	2	5% H_2:Ar	$AlWO_4 + W$
6	1108	2	5% H_2:Ar	Only W
7[a]	1080	2	5% H_2:Ar 5% O_2: He	WO_3

[a] Products are analyzed after re-oxidation in 5% O_2 in Helium of the residue in the reverse cycle.

WO_4 tetrahedra namely, $W(1)O_4$ and $W(2)O_4$ in the lattice. The AlO_6 octahedra and the WO_4 tetrahedra share their corners in forming the extended network structure. The further details of crystal structure were reported in literature [9–12,17].

The temperature programmed reductions (TPR) were carried out under various experimental conditions. The phases formed after the reduction were analyzed by recording the powder XRD pattern of the residuals obtained after each experiments. The summary of the various experimental results is given in Table 1. A typical temperature programmed reduction plot for the sample is shown in Fig. 2. It is seen that the reduction of $Al_2(WO_4)_3$ starts at about 800 °C as observed from the onset of the peak. The maximum hydrogen consumption occurs in the temperature range of 800–1000 °C, with a peak temperature of about 960 °C. (Fig. 2). The hydrogen consumption is used

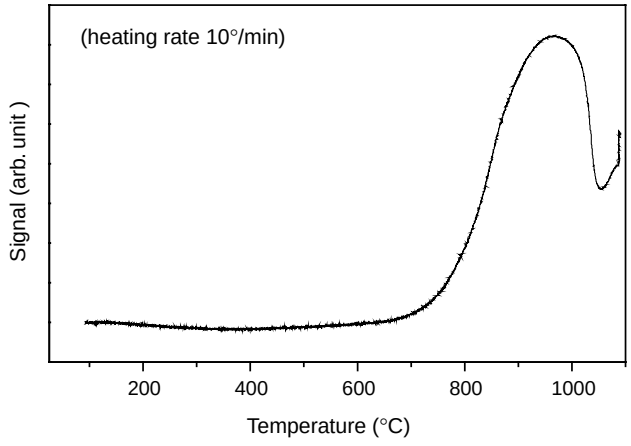

Fig. 2. TPR profile for $Al_2(WO_4)_3$ at heating rate of 10 °C (Sample is heated to 1080 °C, Expt. No.1 of Table 1).