JOURNAL OF MATERIALS SCIENCE **37** (2002) 2501 – 2509

Preparation, thermal expansion, high pressure and high temperature behavior of $Al_2(WO_4)_3$

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The titled compound $Al_2(WO_4)_3$ was synthesized by a conventional solid state reaction and characterized by powder XRD. It crystallizes in an orthorhombic (Pbcn, No. 60) lattice, with unit cell parameters as 12.582(2), 9.051(1), 9.128(2) Å, and $V = 1039.5(3)$ (Å)^3. The compound was found to show negative thermal expansion (NTE) behavior in the temperature range of 25 to 850°C. The average linear NTE coefficient (α_1), in this temperature range, was -1.5×10^{-6} K^{-1}. The effect of pressure at ambient temperature, was studied by a Bridgman Anvil (BA) apparatus, to reveal that there is no irreversible phase transition up to 8 GPa. The effect of high pressure and high temperature on this compound was studied by a Toroid Anvil (TA) apparatus. This compound has a limited stability under high pressure and temperature, as it undergoes a decomposition to $AlWO_4$ and WO_{3-x} with a partial oxygen loss. As an off-shoot of this work, certain new modifications of WO_{3-x} under pressure and temperature were observed, viz., monoclinic, tetragonal and an orthorhombic modifications at 5 GPa/1400°C, 3 GPa/900°C and 1.8 GPa/1030°C, respectively. The detailed XRD studies of the products are presented here. *© 2002 Kluwer Academic Publishers*

1. Introduction

Thermal expansion is an important property, generally considered for any material to be used at an elevated temperature. An increase in an-harmonic potential with increasing temperature causes the 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 or a very small, or no expansion at all. These special cases of expansion are classified as negative thermal expansion (NTE) or low or zero thermal expansion (LTE, ZTE). Such thermal expansion behavior was reported in some of the tungstates and molybdates [1]. In the tungstate family, very large NTE coefficient is observed for ZrW_2O_8 [2]. By now it is, in general, believed that the negative expansion behavior in tungstate or molybdate or phosphate are due to the transverse vibrations of the bridging oxygen, in M-O-M′ [3]. The negative thermal expansion behavior can also be expected in less dense framework structured compounds, within which the polyhedra can undergo different orientations [3]. The negative thermal expansion behavior is also reported in silica [4], ice [5] and zeolites [6].

Negative expansion ceramic materials are likely to have a probability for tunable thermal expansion (TE) behavior. The ceramic materials with NTE or ZTE have a wide ranging applications e.g., as stress absorbing materials. They can have applications as buffer to compensate the unwanted expansion in the both mechanical and electronics components, e.g., ZrW_2O_8 : Cu composite is used for electronic applications [7]. The NTE materials can be used as an additive in the common house-hold components like oven, dishes, and cooking-wares [8]. However, almost all the applications essentially require the retention of its structure through out the application conditions. It is known that under the pressure of about 2–3 kbar, the cubic ZrW_2O_8 undergoes a phase transition to the orthorhombic modification [9]. This transition is reported to be irreversible but and can be reverted back by heating above 100°C. This cubic to orthorhombic phase transition has been shown to accompany by a reduction in volume, and also it was reported that both the mentioned phases exist in a range of pressure of about 0.2–0.3 GPa [10]. The orthorhombic-ZrW_2O_8 has, however, a negative thermal expansion below room temperature and positive thermal expansion above room temperature. Above room temperature, a continuous negative expansion is reported. It was reported to become amorphous at higher pressure [11]. The amorphization of such a loosely connected polyhedra containing structures with pressure has been well reported in phosphates [12]. Thus the pressure has a pronounced effect in these compounds. Hence, a fresh interest has been invoked in the study of effect of pressure on such network compounds. In this communication, we report the effect of pressure and temperature on $Al_2(WO_4)_3$.

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In the phase diagram of Al_2O_3-WO_3 [13], a congruently melting compound with compositions $2Al_2O_3$-$5WO_3$ has been reported, which was later identified as $Al_2(WO_4)_3$. The crystal data reported by Craig *et al.* [14] shows that it has an orthorhombic structure and there is no phase transition up to the melting point. From the crystal structure data, Craig *et al.* [14] established its composition as $Al_2(WO_4)_3$. Sleight *et al.* have reported that it undergoes a displacive phase transition below room temperature [15]. The low temperature structure was reported as monoclinic which is very closely related to the orthorhombic structure [16]. They also mentioned that the transition from monoclinic to orthorhombic structure is accompanied by a volume expansion. Besides this, it has an anomalous thermal expansion behavior e.g., NTE [1]. $Al_2(WO_4)_3$ is one of the rare compounds to show trivalent ion (Al^{3+}) ion conduction [17]. Hence, it is worth while to examine its behavior under pressure and temperature, to predict its applicability under pressure or temperature or both. Herein, we report some results under Bridgman Anvil and Toroid Anvil experiments.

2. Experimental

The titled compound was prepared by heating an intimate mixture of appropriate amounts of well dried Al_2O_3 and WO_3, at 900°C for 42 hrs followed by 1000°C for 30 hrs with intermittent grindings. The product was characterized by powder XRD for its phase purity. The powder XRD data was collected using a Philips PW1710 model diffractometer in the two theta range 10 to 90°, with Ni filtered Cu K_α radiation. The powder XRD pattern of the starting material $Al_2(WO_4)_3$ is shown in Fig. 1. The powdered product was palletized and sintered for 18 hrs at 1100°C. A dense pellet (~12 mm diameter and 10 mm height) with approximately 88% of theoretical density could be obtained by this heat treatment. The thermal expansion behavior was studied using a dilatometer model LKB 3185. A fused quartz push rod was used to transmit the expansion or contraction to the transducer, i.e., a dial gauge. The percent linear thermal expansions, at various temperatures were given in Fig. 2. The high pressure and room temperature experiments were carried out with a Bridgman Anvil (BA) apparatus (ϕ of face 12.7 mm) [18], in which the sample was pressed inside a pyrophilite gasket by two faces of the Anvil. The sample was held at 8 GPa for 48 hrs and then retrieved after releasing the pressure. The high pressure and high temperature experiments were carried out with Toroid Anvil (TA) Apparatus [19] (ϕ face 31 mm, ϕ cavity 13.5 mm). The sample was heated in a BN sample holder encapsulated inside a graphite resistive heater. The desired pressure was attained gradually within a span of about 30 minutes. The temperature was subsequently increased gradually to the desired value where the sample was held for 8–10 min., and then quenched, by cutting off the power. The pressure was then released slowly. The products thus obtained were characterized

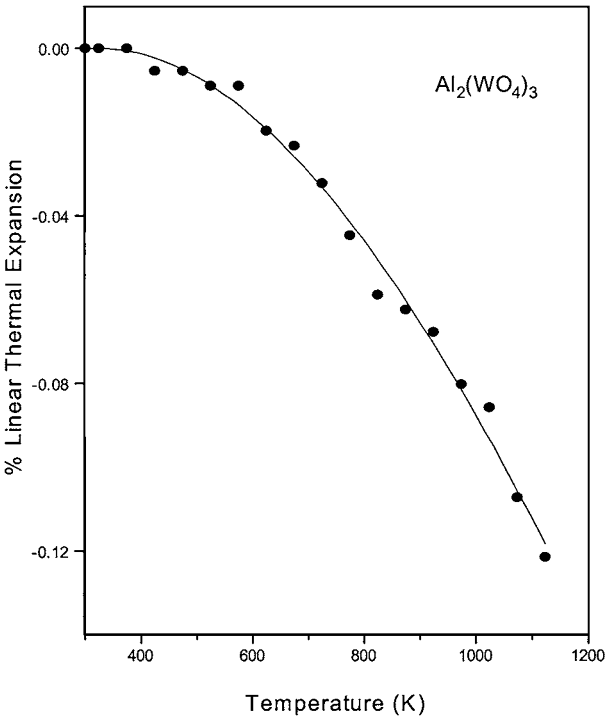

Figure 2 Variation of percent linear thermal expansion versus temperature.

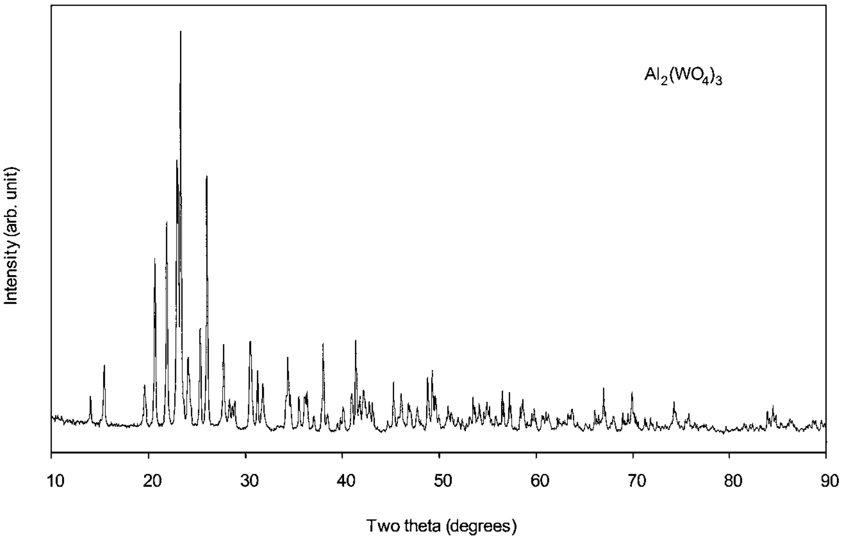

Figure 1 Powder XRD pattern of $Al_2(WO_4)_3$.

by powder XRD in the two-theta range of 10–70° for the phase analysis.

3. Results and discussion

The compound synthesized at 1000°C is found to be phase pure (JCPDS 24-1101). The observed reflections were indexed on an orthorhombic (Pbcn, No. 60) unit cell with lattice parameters as 12.582(2), 9.051(1), 9.128(2) Å, and $V = 1039.5(3)$ (Å)^3. The structure of this compound is iso-structural [14] to $Sc_2(WO_4)_3$ [20]. Thus, the orthorhombic $Al_2(WO_4)_3$ (O-$Al_2(WO_4)_3$) structure is built with W(1)O_4 and W(2)O_4 tetrahedra and Al(1)O_6 octahedra. The AlO_6 octahedra share each of their corners with WO_4 tetrahedra and each of the WO_4 tetrahedra share corners with the AlO_6 octahedra to build the three dimensional open network. The $Sc_2(WO_4)_3$ structure is known to be adopted in tungstates [20] with heavier lanthanides. On other hand, the tungstates of Fe^{3+} have a low temperature monoclinic modification of $Sc_2(WO_4)_3$ [21]. However, $Al_2(WO_4)_3$, is an stable compound with smaller metal ion like Al^{3+}, with an orthorhombic $Sc_2(WO_4)_3$ structure.

The negative thermal expansion behavior was revealed from the plot of % linear thermal expansion versus temperature (Fig. 2). It was observed that the % linear thermal expansion of $Al_2(WO_4)_3$, remains constant initially and then it starts decreasing. Thus the titled compound shows negative thermal expansion in the region of 25 to 850°C. The coefficient of average linear thermal expansion (α_l) is -1.5×10^{-6} C. It may be added here that the thermal expansion behavior of O-$Al_2(WO_4)_3$ is controversial till date. Initially the α_l value (from dilatometric study) for this compound was shown to be about -3×10^{-6} C [1]. However, on the basis of the diffraction studies, this compound was shown to have an anisotropic expansion with a net positive volume expansion, $\alpha_v = +2.2 \times 10^{-6}$ C [1], $+4.5 \times 10^{-6}$ C [22]. The present dilatometric study shows that $Al_2(WO_4)_3$ have negative thermal expansion behavior. However, the contribution of micro-cracks and defects to NTE cannot be ignored. The magnitude of negative expansion is very small as compared to that of $Sc_2(WO_4)_3$ [23] or $Y_2(WO_4)_3$ [22] structure. It may be noted that the anisotropic expansion has been reported in most of the compounds with $Sc_2(WO_4)_3$ type structure [24].

In the Bridgman Anvil experiment, the sample was held under a static pressure of 8 GPa for 48 hrs. The sample was retrieved after releasing the pressure very slowly. The recovered sample was examined by powder XRD. The observed XRD pattern along with the starting phase (O-$Al_2(WO_4)_3$) has been shown in Fig. 3. The observed reflections could be indexed on an orthorhombic unit cell with lattice parameters 12.577(3), 9.044(3) and 9.128(2) Å, and volume 1038.3(5) (Å)^3. It may be mentioned that at this pressure the sharp diffraction lines are getting broadened, as seen from Fig. 3. However, we did not observe any split reflections attributable to monoclinic modification of $Al_2(WO_4)_3$ [16]. A comparison of the unit cell parameters of the samples, before and after subjecting to pressure shows them to be very similar. Hence, it was inferred that there is no irreversible change in the structure. The structures of $Al_2(WO_4)_3$, both in orthorhombic and monoclinic phases are quite similar, hence distinction of the two structures from the conventional powder XRD is a bit difficult. Therefore, at this stage it was concluded that there is no irreversible structural change under BA experimental condition. However, any reversible pressure induced transition could not be ruled out. It has been reported earlier that the cubic ZrW_2O_8 undergoes an irreversible phase transition [10] and also amorphization under pressure [11]. The amorphization of ZrW_2O_8 is also an irreversible transition. However, in this particular experiment on $Al_2(WO_4)_3$, no such irreversible transformation was observed up to 8 GPa. Thus, a remarkable conclusion can be drawn that $Al_2(WO_4)_3$ has an excellent chemical stability under pressure.

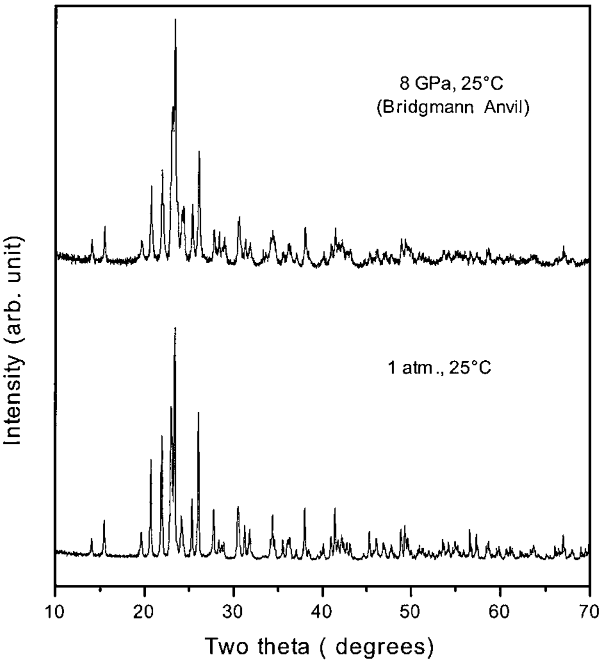

Figure 3 Powder XRD patterns of $Al_2(WO_4)_3$ at pressure of 1 atm. and 8 GPa (BA).

Amorphization of the crystalline materials under pressure is mainly due to the lowering of distances between atoms below a limiting distance [11, 25]. The striking difference in the ZrW_2O_8 and $Al_2(WO_4)_3$ structure is that, in the later all the WO_4 tetrahedra are isolated, while in the former structure one corner of WO_4 tetrahedra remains free. This pattern of arrangements of WO_4 tetrahedra in ZrW_2O_8, makes the structure flexible. In addition, the WO_4 tetrahedra of ZrW_2O_8 are arranged in such a fashion so as to have a W···O–W type linkage, parallel to the three fold axis. The distance between W-W is reduced by the application of pressure due to the deformation of the W···O–W link. Thus, the application of pressure can reduce the distance between two W^{6+} causing the destabilization, which leads to disordered structure. Such close contact links are absent in the $Al_2(WO_4)_3$. The typical shortest W-W bond length in ZrW_2O_8 is about 4.16 Å, while the typical shortest W-W separation in $Al_2(WO_4)_3$ is about 4.39 Å. In the O-ZrW_2O_8 the typical minimum separation comes to about 3.84 Å. Also,

TABLE I Summary of phases identified at different pressures and temperatures

S. No.	P (GPa)	T (°C)	Phases found
1	Room pressure	25	O[a]
2	8 (BA)	25	O
3	5	1400	$AlWO_4 + WO_{3-x}$
4	5	900	”
5	5	750	”
6	5	700	O
7	5	600	O
8	3	900	$AlWO_4 + WO_{3-x}$
9	3	600	O
10	1.8	1030	$AlWO_4 + WO_{3-x}$
11	1.5	900	”
12	1.7	750	O

[a] O = Orthorhombic $Al_2(WO_4)_3$ phase.

the WO_4 tetrahedra in $Al_2(WO_4)_3$ is rigid and hence would need still higher pressure to make the changes in them, responsible for amorphization. Thus the destabilization leading to amorphous structure in $Al_2(WO_4)_3$, may occur at very high pressure, whereas the pressure used in the present study might be insufficient.

The high temperature and high pressure experiments were carried out in a toroid anvil apparatus. The effect of temperature was studied by performing experiments at various temperatures at a particular pressure. Also, the similar study was repeated at different pressures. The summary of various experiments and their phase analyses are given in Table I.

The initial experiments were carried out at a higher temperature and higher pressure. Then the pressure and temperature were decreased in successive experiments. The sample was quenched from the desired temperature and pressure, and analyzed by powder XRD. The results are shown in Figs 4–7, for the experiments carried out at different temperature and pressure. It was observed that above certain temperature, at a particular pressure, the $Al_2(WO_4)_3$ phase decomposes.

The XRD patterns of the retrieved samples from the experiments conducted at 5 GPa and various temperatures are given in Fig. 4. It was observed that the products of the experiment below 750°C, at 5 GPa indicate the retention of the $Al_2(WO_4)_3$. The XRD pattern of products obtained from the experiments carried out at 700 and 600°C shows that although the peak positions remain same compared to that in the parent phase, however, the peak profiles of XRD pattern, observed in the temperature range 600 to 700°C, are broadened implying that there is a tendency towards amorphization. Therefore, it may be suggested that at a relatively lower temperature and higher pressure the sample may get amorphize. In the present experiments, the sample is not completely transformed to an amorphous phase due to the insufficient time. The XRD pattern of the samples at 900° and 1400°C shows that the parent phase is not retained, and new peaks are observed. A complete XRD analyses of the sample obtained from 1400°C and 5 GPa pressure are given in Table II and Fig. 5. A comparison of the observed reflections and the assigned reflections is given in Table II. The presence of phases like $AlWO_4$ [JCPDS 34-1226, 29-96], and BN [JCPDS 34-421] is inferred from the analysis of XRD pattern. Also, an additional phase, which is closely similar to $WO_{2.92}$ [JCPDS 30-1387], has been observed. It may be mentioned here that the residual BN comes from the BN cup, which was difficult to separate from the sample after the experiment. It also signifies the inertness of BN towards $Al_2(WO_4)_3$, compared to its high reactivity with nano-crystalline Fe_2O_3, Y_2O_3 [26]. A comparison of the XRD patterns of the sample of the experiments at 1400 and 900° shows that the reflections corresponding to $AlWO_4$ phase remain identical. It needs to be mentioned that $WO_{2.92}$ reflections are not exactly matching as represented in the Table II. Hence, it may be concluded that the second phase in addition to $AlWO_4$, which is supposed to be WO_3, undergoes different extent of oxygen losses depending on temperature and pressure. Hence, the additional phase is designated as WO_{3-x}. Thus a partial reduction of W^{6+} in WO_3 leads to the formation of some WO_{3-x} (the value of x depends on temperature and pressure).

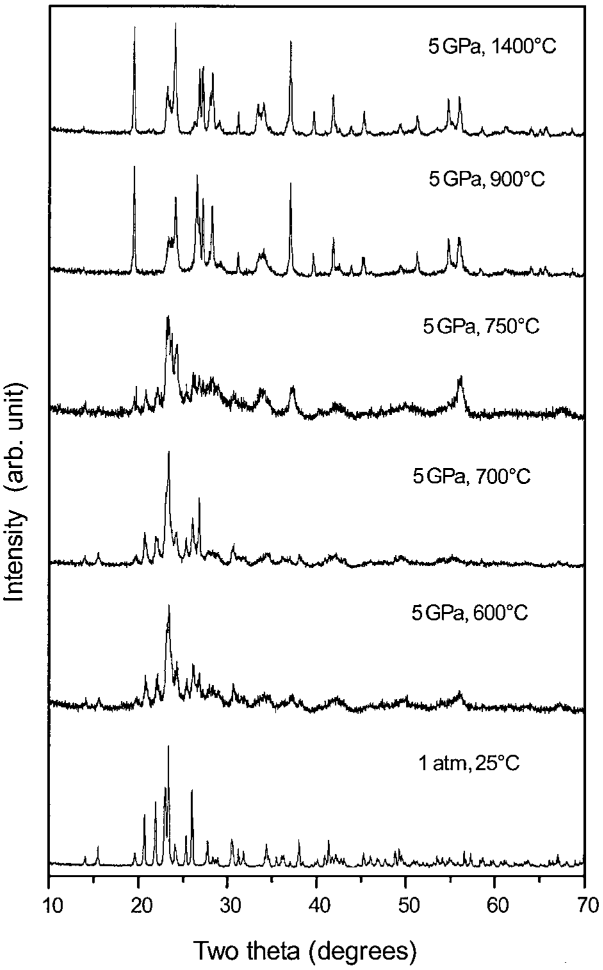

Figure 4 Powder XRD patterns of $Al_2(WO_4)_3$ of sample from TA experiments at 5 GPa, and different temperatures.

The XRD patterns of the products obtained from the toroid anvil experiments at 3 GPa are given in Fig. 6. The phase analysis reveals that at the pressure of 3 GPa at 900^{o}C, $Al_2(WO_4)_3$ decomposes to $AlWO_4$ and WO_{3-x} type phases. But the experiment carried out at about 600°C shows that the parent phase is retained. The experiment at 3 GPa pressure and temperature 900°C shows the complete decomposition. Thus to

TABLE II Phases formed at 5 GPa and 1400°C

			WO_{3-x}		$AlWO_4$			
	Observed data		$WO_{2.92}$ (30-1387)[a]		(34-1226)[a]		(29-96)[a]	
S. no.	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)	d (Å)	I/I_0 (%)
1	4.551	95			4.57	100	4.53	90
2	3.838	43	3.820	100				
3	3.695	100	3.680	78				
4	3.404	9						
5	3.328	60	BN	34-421				
6	3.278	63			3.29	70	3.27	100
7	3.188	37						
8	3.153	56			3.16	65	3.15	100
9	3.076	10						
10	2.870	22			2.876	10	2.861	5
11	2.693	24	2.710	40				
12	2.639	33	2.650	38				
13	2.586	7						
14	2.427	94			2.432	60	2.421	20
15	2.273	24			2.276	30	2.267	30
			3.20					
16	2.159	42			2.161	30		
17	2.145	10					2.149	10
18	2.123	7			2.122	3		
19	2.065	12			2.067	10	2.060	15
20	2.002	21			2.002	25	1.995	40
21	1.847	10						
22	1.782	20			1.785	16	1.776	5
23	1.714	6	1.71, 1.70					
24	1.676	39	1.69, 1.68		1.681	30	1.672	15
25	1.642	39			1.646	40	1.635	50
26	1.639	34						
27	1.577	9			1.580	9	1.571	15
28	1.516	10			1.516	8	1.510	5
29	1.455	8			1.455	9		
30	1.435	8			1.435	4		
31	1.423	3			1.421	9		
32	1.3846	7						
33	1.3689	9			1.370	4		

[a] Corresponding JCPDS numbers.

know the minimum pressure required for decomposition, the experiments were carried out at the relatively lower pressure in the toroid anvil and the results are shown in Fig. 7. The similar kind of decomposition was observed even at pressure of about 1.5, 1.8 GPa, but at a relatively higher temperature, viz. about 900°C. A comparison of pressure at about a constant temperature is shown in Fig. 8. It was observed that at 1.7 GPa

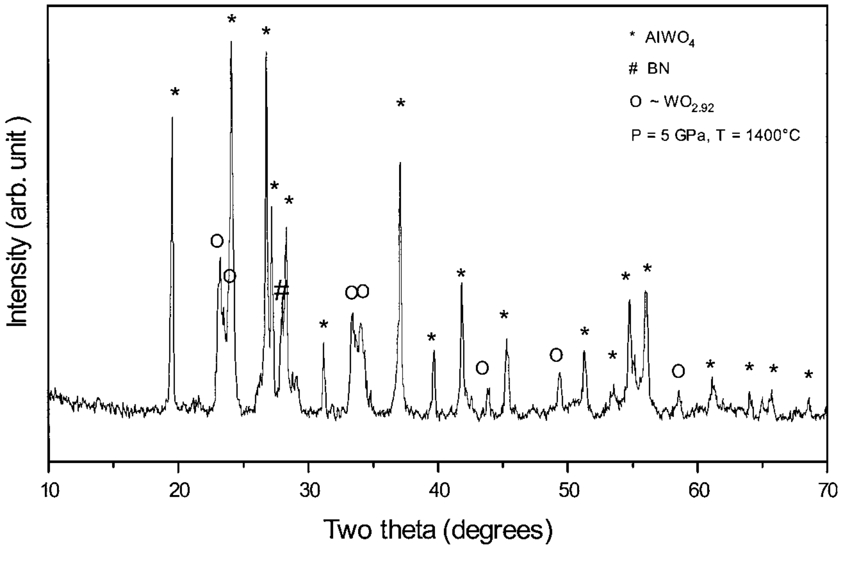

Figure 5 Powder XRD patterns of $Al_2(WO_4)_3$ of samples from TA experiment at 5 GPa, 1400°C.

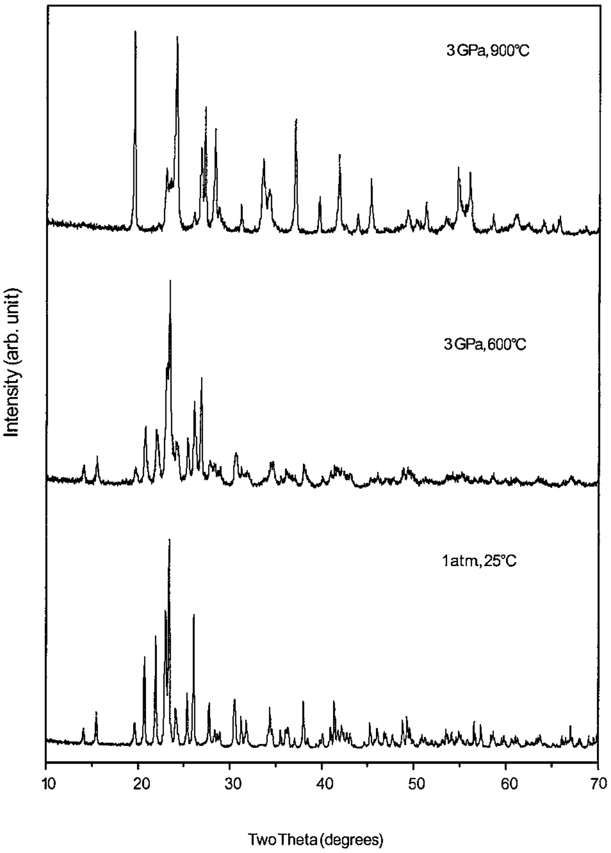

Figure 6 Powder XRD patterns of $Al_2(WO_4)_3$ of sample from TA experiments at 3 GPa, and different temperatures.

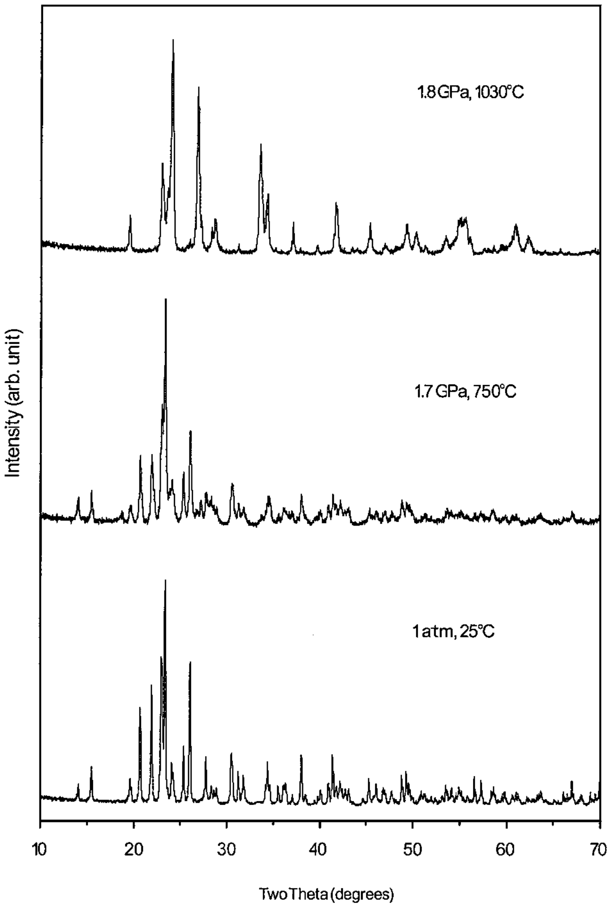

Figure 7 Powder XRD patterns of $Al_2(WO_4)_3$ of sample from TA experiments at <2 GPa, and different temperatures.

pressure the parent phase is retained even up to about 750°C. The decomposition is thus found to be temperature and pressure dependent. Another striking observation is that the decomposition temperature increases with decreasing pressure.

The structure of $AlWO_4$ reported by Doumerc *et al.* [27] with a monoclinic unit cell with lattice parameters 9.069(5), 5.705(6), 4.541(5) Å, $\beta = 92.3(0)°$, and volume 234.8 $(Å)^3$ for $Z = 4$. Later, this compound was reported by Vishnevskii *et al.* [28] to have an orthorhombic unit cell with lattice parameters 6.573, 6.319, 2.874 Å, and volume 119.4 $(Å)^3$ for $Z = 2$. Doumerc *et al.* had used high pressure and high temperature technique for the preparation of $AlWO_4$ starting from Al_2O_3, WO_3 and WO_2 whereas the later authors prepared it using Al_2O_3 and WO_3 under an argon atmosphere with low oxygen partial pressure. In the present study, the observed reflections assigned to $AlWO_4$ phase are given in Table III. The selected observed reflections could be indexed on a monoclinic unit cell with lattice parameters are 4.552(1), 2.870(1), 4.545(2) Å, and $\beta = 92.19(2)°$, $V = 59.34(4)$ $(Å)^3$. The observed unit cell volume in the present study is about half of the value reported by Vishnevskii *et al.* [28] and about one fourth of the volume reported by Doumerc *et al.* [27]. Thus, the unit cell represented by these authors might have also accounted for some other weaker reflections observed by them. The identified reflections for $AlWO_4$, from the sample obtained from 5 GPa and 1400°C are marked in Fig. 5.

The XRD patterns of the $Al_2(WO_4)_3$ phases retained in various experiments were indexed and the refined lattice parameters are given in Table IV. It was observed that the unit cell volume remains almost unaltered after these experiments. However, sharp new peaks are seen to develop with increasing temperature. Similarly the observed reflections assigned to $AlWO_4$ type phase in

TABLE III Typical reflections assigned for $AlWO_4$ type phase (5 GPa, 1400°C)

S. no.	d_{obs} (Å)	d_{cal} (Å)	I/I_0 (%)	$h\ k\ l$
1	4.551	4.548	100	1 0 0
2	3.278	3.277	66	−1 0 1
3	3.153	3.154	59	1 0 1
4	2.870	2.870	23	0 1 0
5	2.427	2.427	100	0 1 1
6	2.273	2.274	25	2 0 0
7	2.159	2.159	44	−1 1 1
8	2.123	2.123	7	1 1 1
9	2.065	2.065	13	−2 0 1
10	2.002	2.003	22	2 0 1
11	1.782	1.783	21	2 1 0
12	1.676	1.677	41	−2 1 1
13	1.642	1.643	41	2 1 1
14	1.639	1.639	34	−2 0 2
15	1.577	1.577	9	2 0 2
16	1.516	1.516	10	3 0 0
17	1.455	1.455	8	−3 0 1
18	1.435	1.435	8	0 2 0
19	1.423	1.423	3	3 0 1
20	1.369	1.369	9	0 2 1

Typical monoclinic unit cell parameters 4.552(1), 2.870(1), 4.545(2) Å, $\beta = 92.19(2)°$, $V = 59.34(4)$ $(Å)^3$.

TABLE IV Typical unit cell parameters of $Al_2(WO_4)_3$ phases in different temperature and pressure experiments

S. no	P (GPa)	T (°C)	a (Å)	b (Å)	c (Å)	V (Å)^3
1	Ambient pressure	27	12.582(2)	9.051(1)	9.128(2)	1039.5(3)
2	8 (BA)	27	12.577(3)	9.044(3)	9.128(2)	1038.3(5)
3	3	600	12.582(4)	9.057(3)	9.124(4)	1039.7(7)
4	1.7	750	12.594(4)	9.049(2)	9.133(3)	1040.8(5)

TABLE V Typical unit cell parameters of $AlWO_4$ phases in different temperature and pressure experiments

S. no	P (GPa)	T (°C)	a (Å)	b (Å)	c (Å)	β (°)	V (Å)^3
1	5	1400	4.552(1)	2.870(1)	4.545(2)	92.19(2)	59.34(4)
2	3	900	4.551(1)	2.869(1)	4.542(2)	92.23(3)	59.26(4)
3	1.8	1030	4.556(3)	2.870(2)	4.533(5)	92.14(6)	59.23(8)

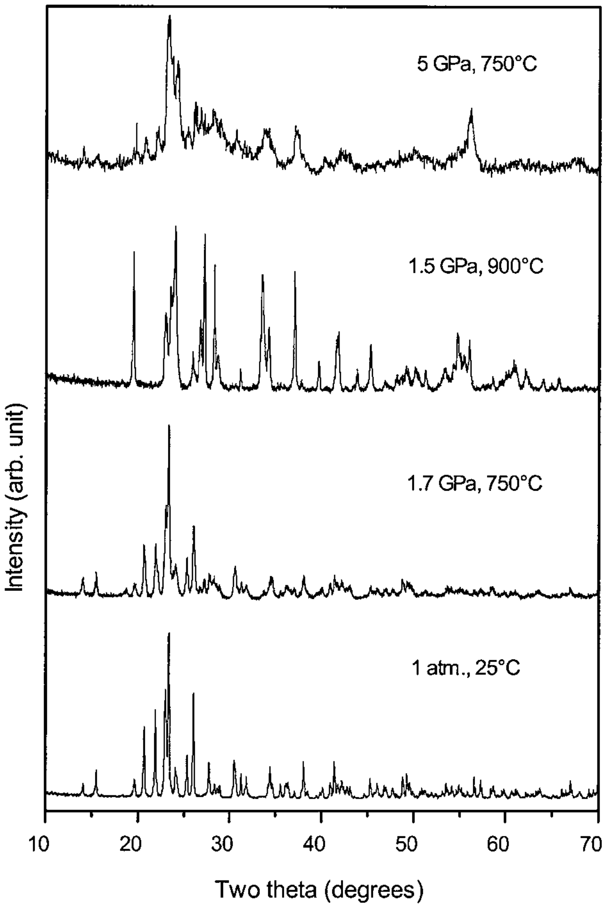

Figure 8 A comparison of XRD patterns at different pressure and temperature.

various experiments are given in the Table V. Similar comparison of volumes of the different phases shows them to be almost identical. Therefore, it can be inferred that the stoichiometry of $Al_2(WO_4)_3$ and $AlWO_4$ remains same under various temperature and pressure.

The $Al_2(WO_4)_3$ structure has Al^{3+} in octahedral coordination whereas the coordination of both kinds of W^{6+} is tetrahedral. The structure of $AlWO_4$ in monoclinic unit cell has been shown [27] to consist of AlO_6 and WO_6 octahedra. These units share their corners to form the three dimensional network. The synthesis of $AlWO_4$ has been reported [27, 28] by the reaction of stoichiometric amounts of Al_2O_3, WO_3 and WO_2 at the high pressure and high temperature. The partial reduction of $Al_2(WO_4)_3$ unit causes the decomposition. It is known that the WO_3 structure consists of WO_6 octahedra [29]. The temperature can cause the partial reduction of W^{6+}, as the reduction of Al^{3+} is not expected. The decomposition of $Fe_2(WO_4)_3$ structure to Fe_2WO_6 [30] and WO_3 [29] was reported [21] at ambient pressure at relatively lower temperature i.e., about 600°C. Thus an insight of the decomposition of $Al_2(WO_4)_3$, based on the above reports, indicates it to be driven by the increase in the coordination number of tungsten polyhedra from four to six. The preparation of $Cr_2(WO_4)_3$ at about 900°C always ends in Cr_2WO_6 and WO_3, which further more signifies the importance of the stability of octahedral tungsten under certain conditions. In the present case of $Al_2(WO_4)_3$, tungsten has a tetrahedral environment, as in ZrW_2O_8 which undergoes decomposition to ZrO_2 and WO_3 at elevated temperature. This further supports for the stability of octahedral tungsten. It is well known that the application of pressure in general leads to increase in the coordination number. Thus the decomposition of $Al_2(WO_4)_3$ might be due to the lowering of the free energy, with the formation of $AlWO_4$ and WO_{3-x} phases, in which the cations have stable coordination. Therefore, it is not surprising to observe the decomposition of $Al_2(WO_4)_3$ under stringent experimental conditions employed in the present investigation, although it melts congruently under ambient pressure.

The temperature assisted formation of WO_{3-x}, in an oxygen deficient atmosphere was initially reported by Magneli [31]. These oxygen deficient WO_{3-x} phases were explained by the different crystallographic shear, which is well known both theoretically [31] and experimentally [32]. Since the observed reflections assigned to WO_{3-x} do not exactly match to the reported WO_{3-x} phases, they were considered as some distinct oxygen deficient phases. However, at this stage the exact compositions of WO_{3-x} phases, observed in the present investigations, could not be concluded. XRD data of some the new modifications of WO_{3-x} are given in Table VI. It is known [29] that WO_3 structure is built from corner sharing WO_6 octahedra, similar to ReO_3. However, depending on the temperature, these octahedra tend to share their edges leading to the formation of different shear planes, which leads to the formation of different structures [32]. Therefore,

TABLE VI WO_{3-x} phases at different temperature and pressure

$P = 5$ GPa, 1400°C				$P = 3$ GPa, 900°C				$P = 1.8$ GPa, 1030°C			
d_{obs} (Å)	d_{cal} (Å)	I/I_0	*h k l*	d_{obs} (Å)	d_{cal} (Å)	I/I_0	*h k l*	d_{obs} (Å)	d_{cal} (Å)	I/I_0	*h k l*
3.838	3.839	43	1 1 0	3.869	3.865	28	0 0 1	3.864	3.864	42	1 1 0
3.695	3.695	100	0 1 1	3.693	3.694	100	1 1 0	3.776	3.777	29	0 1 1
3.404	3.404	9	0 0 2	3.107	3.107	12	1 0 1	3.691	3.691	100	2 1 0
3.188	2.185	37	−1 0 2	2.669	2.671	37	1 1 1	3.148	3.150	14	5 0 3
3.076	3.065	10	1 0 2	2.613	2.612	20	2 0 0	3.109	3.108	16	3 0 4
2.693	3.692	24	0 1 2	1.849	1.847	11	2 2 0	2.817	2.821	2	7 0 2
2.639	3.642	33	−2 0 2	1.518	1.519	9	3 1 1	2.678	2.680	50	5 1 2
2.586	2.580	7	−1 1 2					2.612	2.613	30	4 1 3
2.145	2.150	10	1 0 3					2.494	2.491	2	6 0 4
1.847	1.848	10	0 2 2					2.168	2.165	25	10 0 0
1.714	1.714	6	4 1 1					2.085	2.082	4	4 1 5
								1.985	1.985	3	7 1 4
$a = 7.834(9)$ Å				$a = 5.225(2)$ Å				1.937	1.937	4	6 0 6
$b = 4.400(5)$ Å				$c = 3.865(3)$ Å				1.899	1.899	3	3 0 7
$c = 6.817(6)$ Å				$V = 105.5(1)$ (Å)^3				1.848	1.850	15	4 0 7
$\beta = 93.0(1)°$				(Tetragonal)				1.813	1.812	10	9 0 5
$V = 235.6(4)$ (Å)^3								1.714	1.713	8	4 2 3
(Monoclinic)								1.676	1.675	18	3 0 8
								1.652	1.653	16	13 0 1
								1.640	1.641	9	4 0 8
								1.576	1.575	4	10 0 6
								1.558	1.559	4	7 2 3
								1.521	1.521	16	9 2 0
								1.484	1.483	6	11 1 5
											$a = 21.648(7)$ Å
											$b = 3.927(2)$ Å
											$c = 13.777(4)$ Å
											$V = 1171.2(7)$ Å
											(Orthorhombic)

often the WO_{3-x} phases have octahedral and trigonal bipyramids, which share both corners and edges, leading to dense structures. There are few high pressure and high temperature phases of WO_{3-x} [33–35]. The structures of these phases were obtained by high resolution electron microscope and powder XRD. In the present experiments, it was found that the WO_{3-x} phases formed from different temperature and pressure conditions have different reflections, but their unit cell parameters (Table VI) are, however, closely related to either WO_3 or some other modifications of WO_{3-x} or tungsten bronze compounds.

The observed reflections assigned for WO_{3-x} at 5 GPa and 1400°C were found similar to that of $WO_{2.92}$. However, there are some extra reflections, which could not be accounted by $WO_{2.92}$ [JCPDS-30-1387]. A complete list of the observed reflections and their comparison with the closely reported reflections for $WO_{2.92}$ is given in Table II. Hence, this phase was believed to be a new phase, and the observed reflections were indexed on a monoclinic unit cell with parameters 7.864(9), 4.400(5), 6.817(6) Å and $\beta = 93.0(1)°$, $V = 235.6(4)$ (Å)^3. This unit cell would be a basis cell for this phase. However, the exact structure and unit cell has to be derived from HREM. The monoclinic phase reported for $WO_{2.92}$ [JCPDS 30-1387] has the lattice parameters as 11.93, 3.82, and 59.72 Å with $\beta = 98.3°$. There are a number of monoclinic phases reported in W-O system, viz. $WO_{2.90}$ [JCPDS 5-386], WO_3 [JCPDS 43-1035], $WO_{2.72}$ [JCPDS-5-392]. The unit cell parameters reported for $WO_{2.90}$ are 12.05, 3.767, 23.59 Å and $\beta = 94.72$; for WO_3 are 7.297, 7.539, 7.688 Å, $\beta = 90.91$; for $WO_{2.72}$ 18.28, 3.775, 13.98 Å and $\beta = 115°$. A comparison of the observed lattice parameters for WO_{3-x} in the present investigation and these reported unit cell parameters show that there exists a close similarity in all these phase. Hence, the unit cell parameter for the present phase may be the correct unit cell or the basis cell for a new phase observed in the present investigations.

In a similar way, we have separated the peaks for WO_{3-x} phase obtained at 3 GPa, and 900°C, and the list of assigned reflections is also included in Table VI. This phase could be indexed on a tetragonal unit cell with cell parameters 5.224(2) and 3.865(3) Å. There are several reported bronze structures of tungsten, viz. $Na_{0.10}WO_3$ [36], $Li_{0.95}WO_3$ [37], $H_{0.23}WO_3$ [38] reported to have a similar kind of tetragonal unit cell. Also, WO_3 has a polymorph [39] with similar kind of tetragonal unit cell. It may be mentioned that $WO_{2.90}$ is reported to crystallize in a similar tetragonal unit cell, however, it has tetragonal unit cell at the composition $WO_{2.80}$ with about four fold magnification of the given '*a*' axis. Hence, it is inferred that under these experimental conditions, there is a formation of certain composition of WO_{3-x} phase with a tetragonal unit cell. The tetragonal phases have been reported either in metal/hydrogen intercalated tungsten oxides, or reduction of WO_3. Therefore, it can be further ascertained that there is also a tetragonal phase of WO_{3-x} under high pressure and temperature. Similar comparative selection of WO_3 like phases from the product of the experiments at

1.8 GPa and 1030°C, yet another new WO_{3-x} phase was found, which could be indexed on an orthorhombic unit cell with lattice parameters as 21.648(7), 3.927(2) and 13.777(4) Å and $V = 1171.2(7)$ (Å)^3. It is reported [34] that a high-pressure form of tungsten oxide, with composition $WO_{2.625}$, in W-O system, has a quite closely related orthorhombic unit cell. The unit cell parameters for this reported phase [34] has been given as 21.431, 17.766, 3.783 Å. The observed unit cell parameters for the present phase seems to be closely related in two axes, and difference in the third axis shows that there may be a different kind of periodicity. The heavily reduced phase obtained at high pressure and temperature [33] namely $WO_{1.09}$ also has an orthorhombic structure with unit cell parameters 17.16, 10.32, and 3.78 Å. Here it is shown that another WO_{3-x} phase with closely related to the above structure also exists in W-O system, under high pressure and temperature.

4. Conclusion

XRD analyses of samples from TA experiment showed that $Al_2(WO_4)_3$ has a limited stability under pressure and temperature. At a given pressure and beyond certain temperature, it decomposes to $AlWO_4$ and WO_{3-x} type phase, accompanied by a loss of oxygen, leading to reduction of W^{6+} to lower valency. The left-over WO_3 undergoes a partial oxygen loss, forming WO_{3-x}. A smaller monoclinic unit cell is proposed for the $AlWO_4$ type phase. A series of experiments at a varying pressure and temperature shows that the decomposition temperature increases as the pressure decreases. At the pressure of 1.5 GPa, temperature of about 900°C is sufficient to cause the decomposition. Several new modifications of WO_{3-x} have been shown to exist in the high pressure and high temperature conditions. However, their detailed structure are yet to be ascertained. In the present study on $Al_2(WO_4)_3$, no irreversible phase transition was observed under pressure alone. It has an excellent stability up to a significantly high pressure (i.e., up to 8 GPa) at room temperature. $Al_2(WO_4)_3$ has limited stability under pressure and temperature. No amorphization was observed in any experiments which is in complete contrast to ZrW_2O_8, which amorphizes at lower pressure.

Acknowledgements

The authors thank to Dr. N. M. Gupta, Head, Applied Chemistry Division, and Dr. B. K. Godwal, Head, High Pressure Physics Division, B. A. R. C., for their support to this work. Dr. M. D. Mathews, Applied Chemistry Division is thanked for the help in thermal expansion measurements.

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Received 24 April 2001
and accepted 14 February 2002