

Dilatometric studies of $Y_2W_3O_{12}$ with added Al_2O_3 [†]

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Abstract. $Y_2W_3O_{12}$ exhibits negative thermal expansion along the three crystallographic directions due to the transverse thermal vibrations perpendicular to the Y–O–W linkage. It is highly hygroscopic and forms a trihydrate structure at room temperature. Dilatometric studies of $Y_2W_3O_{12}$ show large thermal expansion hysteresis due to large grain size and a large initial positive thermal expansion due to the removal of water molecules. Al_2O_3 has been added to $Y_2W_3O_{12}$ up to 10 wt% in an attempt to overcome the hygroscopicity and reduce the particle size and thereby the thermal expansion hysteresis. Thermo gravimetric, dilatometric and electron microscopic studies are presented to support these observations.

Keywords. Corner shared structure; negative thermal expansion; dilatometric studies.

1. Introduction

Negative thermal expansion has been observed in many molybdates and tungstates of $A_2M_3O_{12}$ type.^{1–5} These compounds have a corner-shared network of octahedral and tetrahedral sites. Atom A is octahedrally coordinated, while atom M is tetrahedrally coordinated with oxygen. Negative thermal expansion occurs due to the transverse thermal vibrations perpendicular to the A–O–M linkage. Bulk thermal expansion of these molybdates and tungstates has been reported⁶ during heating cycles on some members.

$Y_2W_3O_{12}$ belonging to this series of tungstates exhibits negative thermal expansion of $-7.0 \times 10^{-6} K^{-1}$ from 15 to 1373 K⁴ as inferred by X-ray diffraction studies. The transverse thermal vibrations perpendicular to the Y–O–W linkage cause negative thermal expansion. $Y_2W_3O_{12}$ is highly hygroscopic and forms a trihydrate structure at room temperature.⁷ Though the phenomenon of negative thermal expansion has been amply demonstrated by diffraction studies, bulk materials aspects like microstructure, sintering etc have not been reported.

The hygroscopic nature and tungsten loss at high temperature limits the formation of strong sintered pellets for dilatometric studies. In our earlier studies it was shown that sintering the material in a W-rich atmosphere at 1473 K leads to large grain size of 100 nm.⁸ Due to large particle size and anisotropy in thermal contraction, large thermal expansion hysteresis is observed in $Y_2W_3O_{12}$. In addition, the water molecules present in the material cause a large initial expansion and only after the complete removal of the water molecules the material exhibits negative thermal expansion. It was shown that the

[†]Dedicated to Professor C N R Rao on his 70th birthday

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negative thermal expansion range of the bulk material could be extended up to room temperature by encapsulating the material with a coating of glaze.⁸

In this article an attempt has been made to overcome the hygroscopicity of $Y_2W_3O_{12}$ by incorporating additional cations either as substituents or as additives. Compositions of $A_2W_3O_{12}$ for $A = Al, Fe$ and light rare earths have similar framework features but either show positive or weak negative expansion behaviour. Preliminary results on Al substituted $Y_2W_3O_{12}$ do not show solid solution formation but indicate a decrease in particle size of $Y_2W_3O_{12}$. It was therefore decided to add Al_2O_3 to $Y_2W_3O_{12}$ as a grain growth inhibitor. Presence of Al_2O_3 along the grain boundaries could cover each $Y_2W_3O_{12}$ grain and reduce the hygroscopicity. The samples were hot-pressed to get dense ceramic pellets for dilatometric studies. Thermo gravimetric and dilatometric studies have been carried out on $Y_2W_3O_{12}$ with added Al_2O_3 .

2 Experimental

$Y_2W_3O_{12}$ was prepared by solid-state technique using Y_2O_3 (Fluka) and H_2WO_4 (SD Fine) as starting materials. Appropriate quantities of the reactants were intimately ground for 2 h and heat treated at 1173 K for 24 h. Al_2O_3 (1, 3, 5 and 10 wt%) was added to 1173 K heat-treated mixture of $Y_2W_3O_{12}$. As the phase formation of $Y_2W_3O_{12}$ begins at 1173 K, aluminum is incorporated at this temperature to inhibit the grain growth. For better dispersion of Al_2O_3 particles, it was added in the form of $Al(NO_3)_3 \cdot 9H_2O$ solution. Aluminum-added $Y_2W_3O_{12}$ was further heat-treated at 1273 K for 24 h. X-ray powder diffraction was obtained from a Philips (Model PW 1050/37) diffractometer using $CuK\alpha$ radiation. $Y_2W_3O_{12}$ mixture with 1 and 3 wt% Al_2O_3 addition were hot-pressed at 25 MPa and 1273 K using an induction furnace arrangement whereas 5 and 10 wt% Al_2O_3 -added $Y_2W_3O_{12}$ was sintered at 1273 K at ambient pressure. Thermal expansion studies were done on a home-built dilatometer having horizontal geometry, from 300–1100 K using a LVDT-based push rod type quartz cell dilatometer. Thermal expansion was measured on pellets of 12 mm diameter heated at a rate of 2 K min^{-1} . Thermo gravimetric analysis was done (Perkin–Elmer) from room temperature to 773 K. Heating rate of 10 K was maintained during the experiment. The microstructure on the fractured surface of hot-pressed and sintered samples with conducting gold coating was recorded on a JEOL scanning electron microscope (JSM-840A).

3 Results

3.1 X-ray diffraction studies

The room temperature XRD pattern of $Y_2W_3O_{12}$ can be indexed to an orthorhombic trihydrate structure with a unit cell of $a = 10.098(1)\text{ \AA}$, $b = 13.315(3)\text{ \AA}$, $c = 9.691(4)\text{ \AA}$ and $V = 1303.5(4)\text{ (\AA)}^3$. The X-ray diffraction pattern of $Y_2W_3O_{12}$ heat-treated at 1173 K and Al_2O_3 -added $Y_2W_3O_{12}$ is shown in figure 1. The phase formation of $Y_2W_3O_{12}$ starts at 1173 K and so the Al_2O_3 was added at this stage and heat-treated to 1273 K for 24 h. As the Al_2O_3 addition increases there is no change in the diffraction line positions of $Y_2W_3O_{12}$ phase. However additional peaks due to Al_2O_3 are seen to emerge with increasing concentration of aluminum (figure 1).

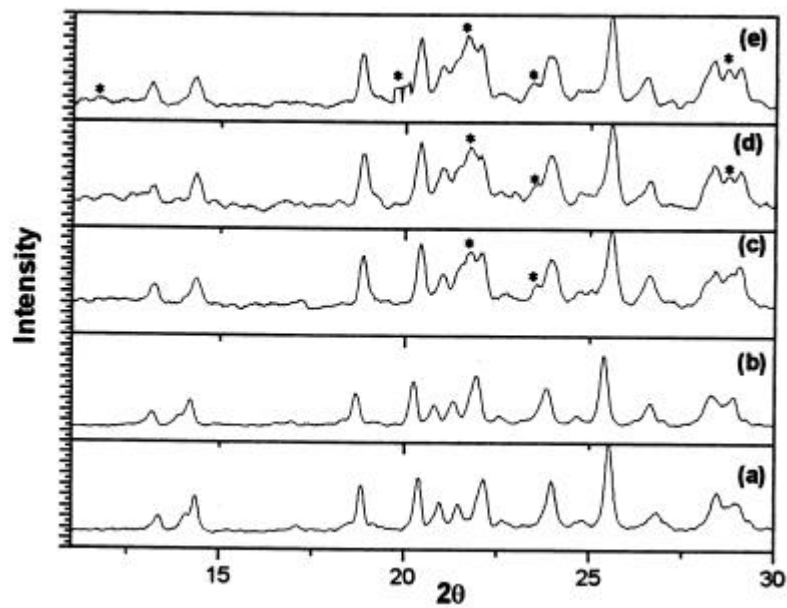


Figure 1. X-ray powder diffraction pattern of (a) $Y_2W_3O_{12}$ heat treated at 1173 K (b) 1 wt% Al_2O_3 added, (c) 3 wt% Al_2O_3 added, (d) 5 wt% Al_2O_3 added, (e) 10 wt% Al_2O_3 added $Y_2W_3O_{12}$ (*indicates the positions of Al_2O_3 peaks).

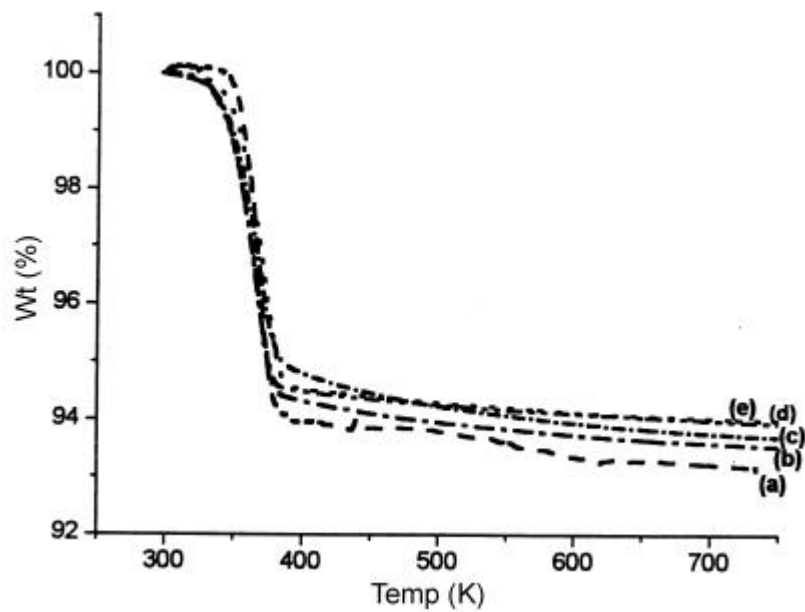


Figure 2. Thermogravimetric studies of (a) $Y_2W_3O_{12}$, (b) 1 wt% Al_2O_3 added, (c) 3 wt% Al_2O_3 added, (d) 5 wt% Al_2O_3 added, (e) 10 wt% Al_2O_3 added $Y_2W_3O_{12}$.

3.2 Thermogravimetric studies

Thermogravimetric studies of $Y_2W_3O_{12}$ and Al_2O_3 added $Y_2W_3O_{12}$ is shown in figure 2. The general features of Al_2O_3 -added $Y_2W_3O_{12}$ are similar to that of $Y_2W_3O_{12}$. $Y_2W_3O_{12}$ loses the water of hydration from 333 to 393 K. About 6 wt% loss can be attributed to 3 water molecules. It is seen that Al_2O_3 -added $Y_2W_3O_{12}$ is also hygroscopic and loses the

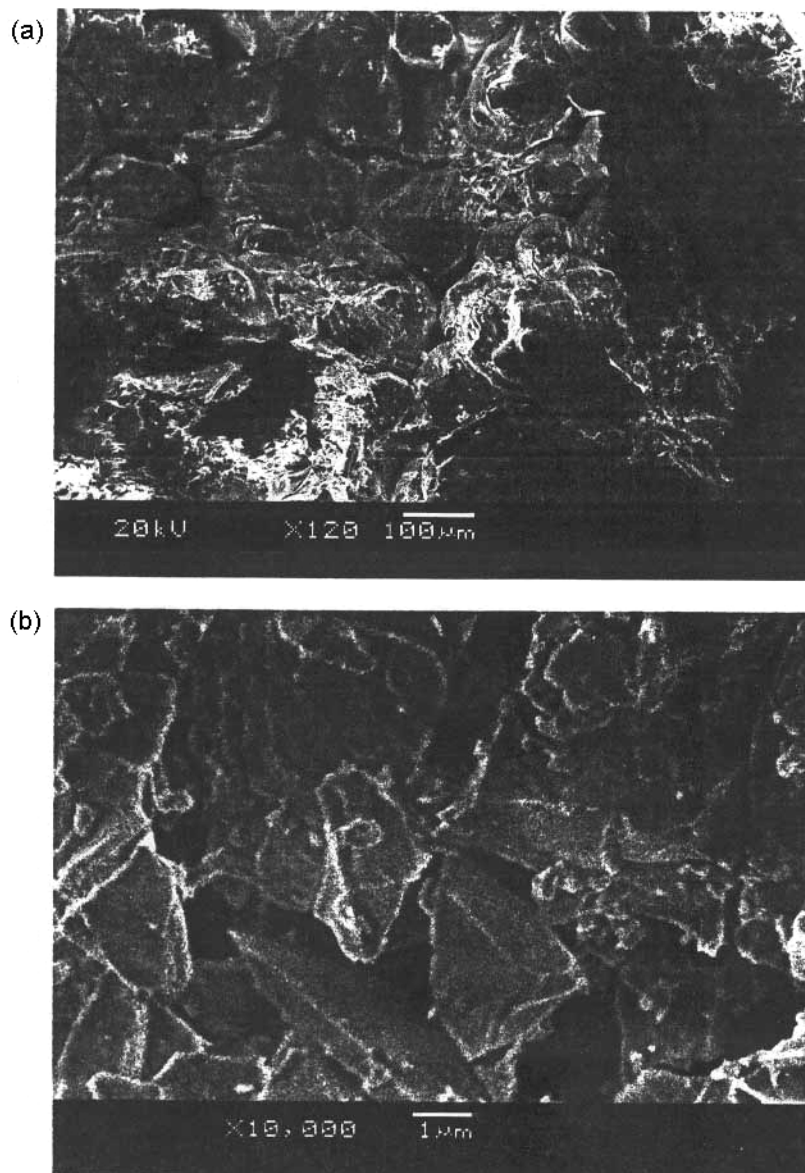


Figure 3. Scanning electron micrograph of $Y_2W_3O_{12}$, (a) sintered at 1473 K in a tungsten rich atmosphere, (b) hot-pressed at 25 MPa and 1273 K.

water of hydration in a similar temperature range. A very marginal reduction in hygroscopicity is observed in Al_2O_3 -added $Y_2W_3O_{12}$ though it is not a very significant change.

3.3 Microscopic studies

The scanning electron micrograph of $Y_2W_3O_{12}$ sintered in tungsten-rich atmosphere and hot-pressed is shown in figures 3a and b respectively. $Y_2W_3O_{12}$ sintered at 1473 K in a tungsten-rich atmosphere results in large particle size of $> 100 \mu m$ as compared to smaller particle size of 2–5 μm obtained by hot-pressing at 1273 K. Micrographs of Al_2O_3 -added $Y_2W_3O_{12}$ are shown in figure 4a–d. It is seen that the Al_2O_3 particles do not completely cover the $Y_2W_3O_{12}$ particles but only partially surround the $Y_2W_3O_{12}$ grains. In figure 4a with 1 wt% Al_2O_3 there is no significant reduction in the $Y_2W_3O_{12}$ particle size. As Al_2O_3 addition increases there is a significant reduction in $Y_2W_3O_{12}$ particle size.

3.4 Dilatometric studies

Dilatometric studies on sintered $Y_2W_3O_{12}$ at 1473 K show negative thermal expansion after the complete removal of water molecules, but owing to its large particle size the material exhibits thermal expansion hysteresis and in addition softening of the material is

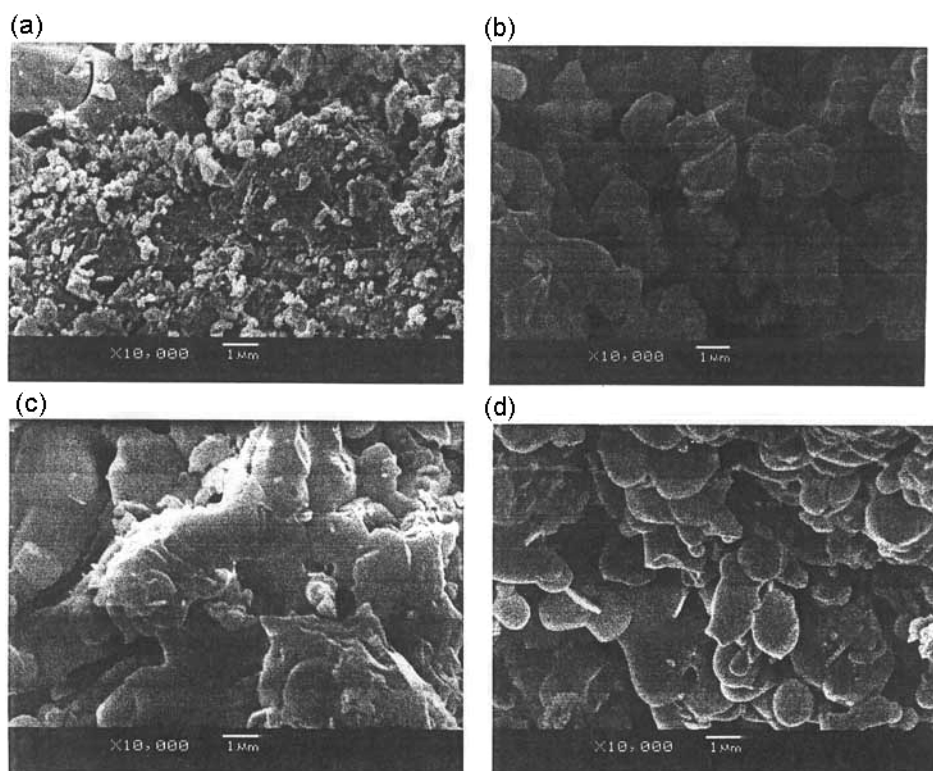


Figure 4. Scanning electron micrograph of (a) 1 wt% Al_2O_3 added, (b) 3 wt% Al_2O_3 added (c) 5 wt% Al_2O_3 added, (d) 10 wt% Al_2O_3 added $Y_2W_3O_{12}$.

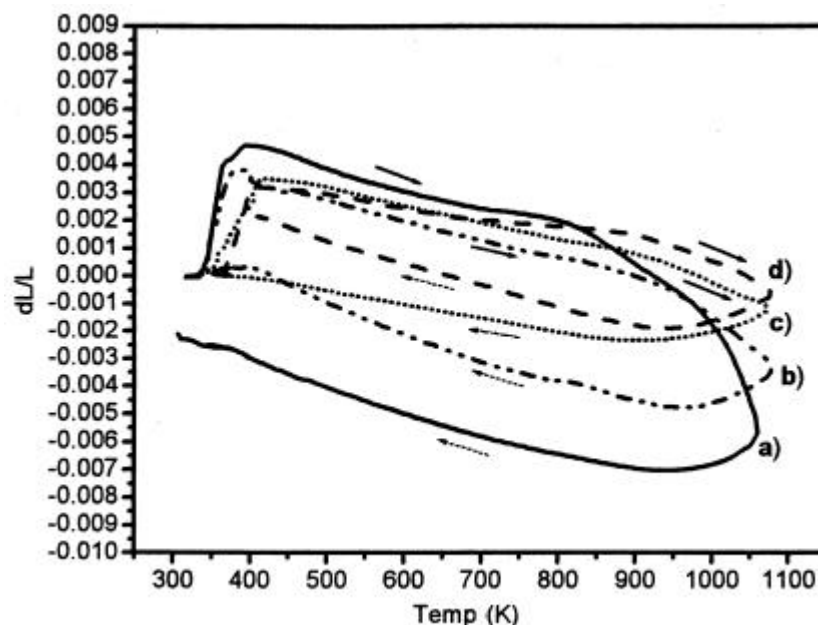


Figure 5. Dilatometric studies of (a) $Y_2W_3O_{12}$ hot-pressed at 25 MPa and 1273 K, (b) 1 wt% Al_2O_3 added $Y_2W_3O_{12}$ hot-pressed at 25 MPa and 1273 K, (c) 5 wt% Al_2O_3 added $Y_2W_3O_{12}$ sintered at 1273 K, (d) 10 wt% Al_2O_3 added $Y_2W_3O_{12}$ sintered at 1273 K.

observed at high temperature.⁸ Dilatometric studies on hot-pressed $Y_2W_3O_{12}$ and Al_2O_3 -added $Y_2W_3O_{12}$ also show initial expansion and then contraction after the complete removal of water molecules (figure 5). Al_2O_3 addition does not eliminate hygroscopicity in the material.

$Y_2W_3O_{12}$ with 1 and 3 wt% Al_2O_3 addition showed poor sinterability and hence they were hot pressed at 25 MPa and 1273 K. Al_2O_3 addition of 5 and 10 wt% improved the sinterability of $Y_2W_3O_{12}$ and the pellets could be sintered in air at 1273 K.

Enhanced contraction above 873 K in $Y_2W_3O_{12}$ is due to softening of the material at high temperature. The horizontal spring loaded push rod makes point contact with the sample and at high temperature the material softens and creeps. This leads to enhanced contraction at high temperature and while cooling back the material regains strength and shows expansion up to room temperature. As Al_2O_3 addition increases, the softening nature of $Y_2W_3O_{12}$ reduces as seen in figure 5. Due to reduction in particle size with Al_2O_3 addition, the hysteresis in the material due to microcracking is also reduced.

4 Discussion

$Y_2W_3O_{12}$ is highly hygroscopic and forms a trihydrate structure at room temperature. It exhibits negative thermal expansion after the complete removal of water molecules beyond 393 K. Al_2O_3 added at 1173 K with further heat treatment at 1273 K inhibits the grain growth. The Al_2O_3 addition reduces the particle size as seen from the microscopic

studies but the hygroscopicity in the material still remains. Even for 10 wt% addition of Al_2O_3 , the hygroscopicity in the material is seen from thermogravimetric studies.

The reduction in particle size with the increase in Al_2O_3 addition is reflected in the reduction of thermal expansion hysteresis. Though a reduction in particle size of about 2–5 μm is obtained on hot-pressed $Y_2W_3O_{12}$, the thermal expansion hysteresis and softening nature is still observed. Only reduction in thermal expansion hysteresis can be achieved by Al_2O_3 addition.

5 Conclusions

$Y_2W_3O_{12}$ exhibits negative thermal expansion after the complete removal of water molecules. Al_2O_3 addition to $Y_2W_3O_{12}$ inhibits the grain growth and reduces the particle size for higher percentage of Al_2O_3 . Aluminum addition helps in lowering the thermal expansion hysteresis by reducing microcracking and creep effects of the material beyond 873 K. However, the hygroscopicity in the material still remains a problem to be solved.

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