

Negative thermal expansion in rare earth molybdates

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Abstract

Negative thermal expansion in rare earth molybdates of $A_2M_3O_{12}$ family ($A = Y, Er, Yb$ and Lu) is measured by high temperature X-ray diffraction and dilatometry. Rare earth molybdates which are isostructural with the corresponding rare earth tungstates, also exhibit this phenomena attributed to transverse acoustic vibrations. The rare earth molybdates of $A_2M_3O_{12}$ family with an orthorhombic structure ($A = Y, Er, Yb$ and Lu) are highly hygroscopic and exhibit negative thermal expansion after the complete removal of water molecules. Axial thermal expansion co-efficient calculated from high temperature X-ray diffraction (RT-1073K) shows rare earth size effect. As the 'A' cation decreases in size, the thermal expansion co-efficient along 'b' axis and the linear thermal expansion co-efficient become less negative. The thermal expansion behaviour of the tetragonal $La_2Mo_3O_{12}$ is also reported to demonstrate the effect of crystal structure.

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1. Introduction

Various tungstates and molybdates of $A_2M_3O_{12}$ group are known to exhibit unusual thermal expansion. Negative thermal expansion (NTE) has been observed in a group of rare earth tungstates [1–4] with specific crystal structure. NTE has been reported in $Sc_2Mo_3O_{12}$ [5] and very recently in $Y_2Mo_3O_{12}$ [6]. The $A_2W_3O_{12}$ group of materials crystallize either in an orthorhombic or monoclinic symmetry. Only the orthorhombic corner shared polyhedral network shows significant negative thermal expansion behaviour. The difference in the thermal expansion behaviour in this series of tungstates is due to the difference in the crystal structure. The orthorhombic structure has an open framework structure with $A-O-M$ linkages, which can accommodate for transverse thermal vibrations responsible for negative thermal expansion. The monoclinic modifications in $A_2W_3O_{12}$ family of oxides have an edge shared structure, which are more densely packed and cannot accommodate for transverse thermal vibrations. The correlation between the crystal structure and thermal expansion in $A_2W_3O_{12}$ series has been reported [7,8].

The rare earth tungstates with 'A' cation ranging in size from Y to Lu are highly hygroscopic and exhibit negative thermal expansion only after the complete removal of water molecules. Negative thermal expansion in rare earth tungstates and the effect of 'A' cation size on thermal expansion coefficient has been reported by us [8]. It was hypothesized that the presence of water molecules could hinder the rocking motion of the corner-shared polyhedra's and cause a positive thermal expansion [9]. It is reported that the corresponding rare earth molybdates ranging in size from Y to Lu are also highly hygroscopic [10] and crystallize in an orthorhombic structure. These molybdates are isostructural with the rare earth tungstates. In rare earth molybdates also there exists a structural dissimilarity as a function of A cation size. The molybdates with A cation ranging in size from La to Gd adopt a tetragonal structure at high temperature, but their room temperature structure is unknown. Tb and Dy molybdates adopt a tetragonal structure at room temperature.

Several members of this family are known to undergo volume reducing displacive phase transitions to monoclinic structure at low temperatures. $Sc_2Mo_3O_{12}$ which exhibits negative thermal expansion [5] undergoes a volume reducing displacive phase transition. This phase transition is accompanied by 1.4% increase in the volume per formula unit. Below 178 K $Sc_2Mo_3O_{12}$ has a monoclinic structure and it shows a positive

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thermal expansion with $\alpha_v = 2.19 \times 10^{-5}/\text{K}$ and above 180 K it transforms into an orthorhombic structure which shows negative thermal expansion with $\alpha_v = -6.3 \times 10^{-6}/\text{K}$. The monoclinic to orthorhombic displacive phase transition induces some structural flexibility, which is essential for negative thermal expansion.

In another article by Tyagi et al. [11], it has been reported that the typical monoclinic ($P2_1/a$) cell for all the $A_2\text{Mo}_3\text{O}_{12}$ with $A = \text{Al, Cr and Fe}$ shows positive thermal expansion until transition. Beyond phase transition, these materials transform into an orthorhombic structure ($Pnca$) and show negative thermal expansion. This structural change is termed as a ferroelastic phase transition. Ferroelastic phase transition was reported in $A_2M_3O_{12}$ ($A = \text{Al, In, Fe, Sc, Cr and } M = \text{W, Mo}$) by Sleight and Brixner [12] and the transition temperatures of these compounds, as observed from DSC studies is also reported. The ferroelastic transition temperature in the rare earth molybdates increases with the increasing electronegativity of the A cation. In a ferroelastic transition observed in the molybdates from $P2_1/a$ to $Pnca$, the point group changes from $2/m$ to mmm and in such crystals the spontaneous polarization can be achieved by mechanical stress [13]. Further studies, have been carried out to understand the vibrational modes of $A_2B_3O_{12}$ ($A = \text{Sc, In, Al, Cr; } B = \text{Mo, W}$) and their temperature dependence [14]. The preliminary bulk thermal expansion data by dilatometry has been reported for some members of this family of tungstates, molybdates and their solid solutions during the heating cycle by Mary and Sleight [15].

In this paper, we report the thermal expansion of rare earth molybdates with A cation ranging in size from Y to Lu , which are isostructural to the corresponding rare earth tungstates. Axial thermal expansion coefficients from high temperature X-ray diffraction, thermogravimetric analysis to indicate the presence of water and bulk dilatometric expansion experiments are performed. The tetragonal $\text{La}_2\text{Mo}_3\text{O}_{12}$ has been studied for thermal expansion by high temperature X-ray diffraction and dilatometry.

2. Experimental

The rare earth molybdates were synthesized by the conventional solid-state synthesis with preheated oxides (Fluka) and ammonium dihydrogenmolybdate (S.D. Fine). Appropriate quantities of these oxides were ground and preheated at 773 K. Further calcination was done at 1173 K for 24 h with one intermittent grinding. Final calcination was carried out at 1273 K for 24 h.

The high temperature X-ray data was collected on Scintag-2000 diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with a Buhler high temperature attachment. The room temperature unhydrated pattern of the rare earth hygroscopic molybdates was recorded by heating the sample in HTXRD sample chamber to 473 K, followed by cooling the sample in vacuum to prevent any moisture absorption. The cell parameters of the room temperature hydrated molybdates were calculated from the autoindexing CRYSFIRE [16] program. The cell parameters obtained from the autoindexing program were further refined

by a standard refinement program PROSZKI [17]. The same program was used to get the cell parameters of the expanding $\text{La}_2\text{Mo}_3\text{O}_{12}$.

Thermogravimetric analysis was carried out in the temperature range 300 to 773 K in (SDTQ600) at a heating rate of 10 K/min. The trihydrate structure of the hygroscopic molybdates (except $\text{La}_2\text{Mo}_3\text{O}_{12}$ which is non-hygroscopic) was obtained by storing the samples over saturated NH_4Cl solution.

Strong ceramic pellets of all the molybdates, for dilatometric studies were obtained by hot pressing at 1273 K under 25 MPa uniaxial pressure in an argon atmosphere using an induction furnace heating arrangement for 15 minutes.

Dilatometric studies were carried out in the temperature range from (300–1100 K) using a homemade LVDT based push-rod dilatometer [18]. Thermal expansion was measured on pellets of 12 mm diameter heated at a rate of 2 K/min. Data was collected during heating and cooling cycles.

3. Results and discussions

3.1. Phase formation

The X-ray diffraction pattern of the room temperature hydrated and unhydrated pattern of $\text{Y}_2\text{Mo}_3\text{O}_{12}$ is shown in Fig. 1. The difference in XRD pattern between the hydrated and unhydrated pattern indicates a different crystal structure for the two different phases. The room temperature XRD pattern of the hygroscopic molybdates corresponds to the hydrated $\text{Er}_2\text{Mo}_3\text{O}_{12}$ data reported by Nassau et al. [10]. The cell volume of the hydrated molybdates is less than the unhydrated cell volume at room temperature. A similar trend has been observed in the corresponding rare earth tungstates [7]. The room temperature cell volume of the hydrated and unhydrated pattern for the molybdates and corresponding tungstates is tabulated in Table 1. The expected lanthanide contraction is observed in these rare molybdates for both the hydrated and unhydrated phases.

3.2. Thermogravimetric analysis

The rare earth hygroscopic molybdates were stored under saturated NH_4Cl solution for the complete formation of trihydrate structure. Stable trihydrate structure in the hygroscopic orthorhombic molybdates and tungstates is obtained only when stored under saturated NH_4Cl solution.

Table 1
Variation of unit cell parameters of $A_2\text{Mo}_3\text{O}_{12}$ as a function of A cation size for hydrated and unhydrated phase

Rare earth molybdates	a (Å)	b (Å)	c (Å)	Vol. (Å ³)
$\text{Y}_2\text{Mo}_3\text{O}_{12} \cdot 3\text{H}_2\text{O}$	9.799(4)	9.799(4)	13.969(3)	1341.4(1)
$\text{Er}_2\text{Mo}_3\text{O}_{12} \cdot 3\text{H}_2\text{O}$	9.752(1)	9.752(1)	13.932(2)	1335.1(5)
$\text{Yb}_2\text{Mo}_3\text{O}_{12} \cdot 3\text{H}_2\text{O}$	9.684(3)	9.684(3)	13.870(5)	1300.7(8)
$\text{Lu}_2\text{Mo}_3\text{O}_{12} \cdot 3\text{H}_2\text{O}$	9.681(7)	9.681(7)	13.873(8)	1300.3(7)
$\text{Y}_2\text{Mo}_3\text{O}_{12}$	10.044(3)	13.889(4)	9.954(2)	1388.6(6)
$\text{Er}_2\text{Mo}_3\text{O}_{12}$	10.025(6)	13.845(8)	9.918(3)	1376.6(1)
$\text{Yb}_2\text{Mo}_3\text{O}_{12}$	9.975(5)	13.774(8)	9.841(3)	1352.1(9)
$\text{Lu}_2\text{Mo}_3\text{O}_{12}$	9.915(7)	13.702(1)	9.833(4)	1335.9(2)

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