**High pressure studies of $A_2Mo_3O_{12}$ negative thermal expansion
materials ($A_2 = Al_2, Fe_2, FeAl, AlGa$)**

Lindsay Young, Jennifer Gadiant, Xiaodong Gao, Cora Lind

*Department of Chemistry and Biochemistry, The University of Toledo, Toledo, OH 43606-
3390, USA*

*Corresponding author:

Address: Department of Chemistry and Biochemistry, MS 602
The University of Toledo
Toledo, OH 43606
USA

Phone: +1 419 530 1505

Fax: +1 419 530 4033

E-mail: cora.lind@utoledo.edu

Abstract

High pressure powder X-ray diffraction studies of several $A_2Mo_3O_{12}$ materials ($A_2 = Al_2, Fe_2, FeAl,$ and $AlGa$) were conducted up to 6-7 GPa. All materials adopted a monoclinic structure under ambient conditions, and displayed similar phase transition behavior upon compression. The initial isotropic compressibility first became anisotropic, followed by a small but distinct drop in cell volume. These patterns could be described by a distorted variant of the ambient pressure polymorph. At higher pressures, a distinct high pressure phase formed. Indexing results confirmed that all materials adopted the same high pressure phase. All changes were reversible on decompression, although some hysteresis was observed. The similarity of the high pressure cells to previously reported $Ga_2Mo_3O_{12}$ suggested that this material undergoes the same sequence of transitions as all materials investigated in this paper. It was found that the transition pressures for all phase changes increased with decreasing radius of the A-site cations.

Keywords Negative thermal expansion; high pressure; synchrotron radiation; *in-situ* studies; phase transitions; scandium tungstate family

1. Introduction

The thermal expansion coefficient of a material describes the magnitude of the change in length or volume of a material as a function of temperature. Most materials display positive thermal expansion, and expand with increasing temperature. When the thermal expansion of two materials are mismatched, thermal cycling can cause degradation or failure of materials and their interfaces. This can be a major concern in a range of engineering fields. In recent years, it has been proposed that negative thermal expansion (NTE) materials may offer a solution to these challenges when used as fillers in composites. This has been demonstrated for optical fiber coatings consisting of ceramic composites of zirconia and the NTE material zirconium tungstate [1]. However, other attempts to prepare composites with this NTE material have failed due to the irreversible formation of high pressure phases. For example, a Cu/ZrW₂O₈ composite displayed irreproducible expansion behavior between different cycles due to formation of an orthorhombic high pressure phase with positive volume expansion [2].

The A₂M₃O₁₂ family, also known as the scandium tungstate family, is known for its NTE behavior. Scandium tungstate materials can adopt a wide range of elemental compositions, in which A is a trivalent cation that can range from Al³⁺ to the smaller lanthanides, and M can be Mo or W. These materials form corner-sharing networks of AO₆ octahedra and MO₄ tetrahedra, which can support concerted tilting motions of the polyhedra that may result in NTE. These materials can crystallize in monoclinic (α -A₂M₃O₁₂) or orthorhombic (β -A₂M₃O₁₂) structures, where NTE is only observed in the orthorhombic phase. The orthorhombic structure is favored at higher temperatures, and many compositions undergo a reversible phase transition between the two structures. The phase transition temperature is highly dependent on elemental composition, with scandium tungstate retaining the orthorhombic structure to at least 10 K[3],

while gallium molybdate remained monoclinic up to its decomposition temperature of 600 °C [4].

NTE materials included in a composite may need to withstand high pressures and temperatures during production and regular use of the composite. The open crystalline framework of these materials makes them susceptible to temperature and pressure induced phase transitions or pressure-induced amorphization. Because NTE behavior is intrinsic to the orthorhombic crystal structure, the denser amorphous or crystalline high pressure phases are not expected to exhibit NTE behavior. It is therefore important to determine whether reversible or irreversible transitions occur upon compression before NTE materials can be used in composites.

Considering the number of reported $A_2M_3O_{12}$ compositions, the collective published high pressure studies are sparse. Some compositions have been studied extensively while many are uncharacterized. Due to variations in data quality and experimental parameters, this also includes conflicting results for the same material. The high pressure behavior remains largely unpredictable, as only a few compounds convert to similar high pressure polymorphs. Among the few exceptions is the observation that compositions that adopt the orthorhombic β -structure at room temperature undergo a phase transition to the denser monoclinic α - $A_2M_3O_{12}$ structure below 0.5 GPa [5-13]. Generally, at least one additional phase transition occurs at higher pressures between 1 and 4 GPa. Amorphization is commonly reported, which can be reversible or irreversible and show onsets as low as 2.3 GPa or higher than 10 GPa [4-6, 10, 14-25].

In this paper, we report on a family of four compounds that undergo the same sequence of high pressure phase transitions, and show that the same sequence of phases was observed for at least one previously reported material. Trends that correlated phase transition pressures to

properties of the A^{3+} cations could be established. While the starting phase of all compositions studied here is the positive expansion monoclinic structure, the observed phase transition behavior may still be applicable to other compositions in the $A_2M_3O_{12}$ family that are orthorhombic under ambient conditions.

2. Materials and Methods

All materials were synthesized using the non-hydrolytic sol-gel (NHSG) method as described previously [4, 26-31]. *In situ* high pressure powder X-ray diffraction (PXRD) synchrotron studies of $Al_2Mo_3O_{12}$, $Fe_2Mo_3O_{12}$, $FeAlMo_3O_{12}$, and $AlGaMo_3O_{12}$ were conducted at beamline 17-BM at the Advanced Photon Source at Argonne National Laboratories. This beamline is a dedicated powder diffraction instrument for parametric studies capable of rapid 2-D data acquisition. Data were collected with a Perkin Elmer a-Si C-window CCD detector using a wavelength of 0.72959 Å. A detector distance of 600 mm was used. The setup allowed high quality *in situ* data collection in which even subtle changes in the PXRD pattern could be seen.

The materials were finely ground in a mortar and pestle in an approximately 3:1 ratio with sodium chloride as an internal pressure calibrant. A membrane diamond anvil cell with a diamond culet face measuring 500 microns was used. This DAC used 300 micron thick steel gaskets, which were pre-indented to a thickness of 100 microns. The sample was packed into the 250 micron sample chamber, flooded with anhydrous 4:1 methanol:ethanol (hydrostatic limit: 10.2 GPa) as a pressure transmitting fluid, and the DAC was quickly sealed. An “as closed” pattern was collected before attaching a stainless steel diaphragm to the cell, and a programmable methanol pump was used to gradually increase the pressure to values between 6.5 and 7.3 GPa while collecting data at pressure increments of approximately 0.02 to 0.2 GPa

(Table 1). After the highest pressure was reached, files were collected during decompression in approximately 1.0 GPa steps. A “decompressed” pattern was collected after opening the cell.

Table 1: Pressure ranges for all experiments and pressure induced phase transitions.

Material	Pressure Range (GPa)	α'-transition (GPa)	γ-transition (GPa)	δ-transition (GPa)	Appearance of α-phase on decompression (GPa)
Al ₂ Mo ₃ O ₁₂	0.03 - 6.68	3.0	4.6-4.9	5.7-6.1	3.6
AlGaMo ₃ O ₁₂	0.09 - 6.54	2.0, 2.9	4.1-4.4	5.0-5.3	3.5 - 2.2
FeAlMo ₃ O ₁₂	0.18 - 7.28	1.7	3.2	3.9-4.2	2.8 - 1.5
Fe ₂ Mo ₃ O ₁₂	0.18 - 6.92	1.5	2.7-2.9	3.5-3.7	2.6 - 1.5
Ga ₂ Mo ₃ O ₁₂ [4]	0.19 - 10.2	NA	3.3*	4.2*	NA

*First pressure at which phase was observed. Due to much larger pressure steps, the exact transition pressure could not be determined.

The 2-D data were integrated using GSAS-II. A pattern of NIST LaB₆ collected in the DAC was used to calibrate accurate detector distance and determine the penetration correction, which was necessary to correct a slight non-linear distortion of the data due to penetration of X-rays into the detector. The patterns were refined using Topas Academic, and consecutive refinements were conducted using MultiTopas. New phases were indexed by fitting peaks in MDI Jade, and then indexing the peak list in Topas Academic. Rietveld refinements were used for all known phases, while new high pressure phases were refined by the Pawley method using the best possible unit cell obtained from indexing. The pressure for each scan was determined from the refined NaCl lattice parameters using the equation of state published by Birch [32]. This approach requires calculation of Eulerian strain using equation (1):

$$f = \frac{(v / v_o^{-2/3}) - 1}{2} \quad (1)$$

where f is the Eulerian strain, v is the cell volume at pressure P , and v_o is the ambient pressure volume. The value for v_o was determined to be $179.5864 \text{ \AA}^3$. The calculated values for f can then be used to determine pressure using equation (2):

$$P = 3K_o f(1 + 2f)^{5/2} * (1 + af) \quad (2)$$

where K_o is the bulk modulus at ambient temperature and a is a constant that depends on temperature. Literature values for K_o (239.9 kbar at 25 °C) and a (1.796 at 25 °C) were used [32].

Principal axis compressibilities were calculated using PASCAL [33] and are summarized in the supporting information. Bulk moduli were also estimated in PASCAL using a 3rd order Birch-Murnaghan equation of state. For all high pressure phases, the lowest pressure at which the polymorph existed as a pure phase was used as a critical pressure.

3. Results and Discussion

All materials investigated in this study adopt the monoclinic α - $A_2M_3O_{12}$ structure (space group $P2_1/a$, Fig. 1) under ambient conditions. Visual inspection of the data suggested similar behavior for all materials, with the occurrence of several phase transitions (Fig. 2) in all datasets. At low pressures, the α -phase peaks shifted gradually to higher angles as pressure was increased. At a certain pressure threshold, anisotropic peak shifts, peak splitting and peak coalescence were observed. At higher pressures, an abrupt change with discontinuous peak shifts occurred. All datasets collected at pressures below the abrupt phase transition could be refined using the monoclinic α -phase structure as a starting model. All changes were reversible upon decompression, although some hysteresis was observed.

Figure 1: Structure of $\alpha\text{-Al}_2\text{Mo}_3\text{O}_{12}$ viewed down the b -axis. Pale octahedra represent AlO_6 , dark tetrahedra represent MoO_4 .

Figure 2: Fit2D overlay of $\text{Al}_2\text{Mo}_3\text{O}_{12}$ datasets.

The patterns collected at the lowest pressures were subjected to 2-phase Rietveld refinements using Topas Academic. Full structural refinements were carried out, in which the atomic positions and isotropic displacement parameters were allowed to vary to obtain the best possible fit. Starting files for MultiTopas batch runs were then set up using these results.

Figure 3: Relative compressibilities of (a) unit cell parameters and (b) volume of $\text{Al}_2\text{Mo}_3\text{O}_{12}$ extracted using the $\alpha\text{-Al}_2\text{Mo}_3\text{O}_{12}$ structure. Filled symbols correspond to values extracted by MultiTopas, while values for open symbols were obtained by individual refinements.

Atomic positions were fixed before running MultiTopas to avoid potentially disastrous changes during the sequential refinements. To confirm that MultiTopas gave reliable results, every fifth scan of the $\text{Al}_2\text{Mo}_3\text{O}_{12}$ dataset was refined individually for comparison purposes, allowing the atomic positions to vary. Lattice constants extracted by both approaches were indistinguishable (Fig. 3). The data for $\text{FeAlMo}_3\text{O}_{12}$ were refined by the Pawley method, as graininess problems resulted in intensities that could not easily be accounted for by structural refinements.

All four materials studied here showed very similar behavior. For simplicity, a thorough discussion of aluminum molybdate will be presented, and quantitative results for the other compositions will be compared at the end of each paragraph. Pressures for the different phase transitions are given in Table 1, and unit cell constants and compressibilities for all materials and phases are summarized in Tables 2 and 3. Compressibilities of the principal axes are summarized in the supporting information, while compressibilities of unit cell axes will be

compared here due to the close structural relationships between the majority of phases. Bulk moduli and V_0 values for all phases can be found in Table 4.

A refinement of the as closed pattern confirmed that $\text{Al}_2\text{Mo}_3\text{O}_{12}$ adopts the monoclinic (α) structure at ambient pressure (Fig. 4). MultiTopas was used to conduct Rietveld refinements up to 6.16 GPa, and lattice constants were extracted as a function of pressure. Up to 3 GPa, the axial compressibility was close to isotropic, with relative compressibilities of $\beta_{\alpha,a} = 0.93 \pm 0.01 \times 10^{-2} \text{ GPa}^{-1}$, $\beta_{\alpha,b} = 1.07 \pm 0.01 \times 10^{-2} \text{ GPa}^{-1}$, $\beta_{\alpha,c} = 0.99 \pm 0.01 \times 10^{-2} \text{ GPa}^{-1}$, and $\beta_{\alpha,v} = 2.76 \pm 0.04 \times 10^{-2} \text{ GPa}^{-1}$. The bulk modulus was found to be 26.4 GPa. Above 3 GPa, a change in slopes of the compressibility curves took place, and the axial compressibility became anisotropic. This indicated that a subtle structural change occurred, which coincided with the pressure range where peak splitting and coalescence were observed in the 2D data overlays. As the patterns could still be described with the structural model for $\alpha\text{-A}_2\text{M}_3\text{O}_{12}$, this will be referred to as the α' -phase transition. For the α' region (3-4.5 GPa), the compressibility constants were $\beta_{\alpha',a} = 0.96 \pm 0.02 \times 10^{-2} \text{ GPa}^{-1}$, $\beta_{\alpha',b} = 0.98 \pm 0.01 \times 10^{-2} \text{ GPa}^{-1}$, $\beta_{\alpha',c} = 0.66 \pm 0.01 \times 10^{-2} \text{ GPa}^{-1}$, and $\beta_{\alpha',v} = 2.46 \pm 0.05 \times 10^{-2} \text{ GPa}^{-1}$, indicating that the change caused stiffening of the c-axis, while the a- and b-axes retained comparable compressibility to the α -phase, resulting in an overall decrease in volume compressibility and a small increase in B_0 to 31.6 GPa. The observation of approximately isotropic compressibility in the α -phase extended to $\text{AlGaMo}_3\text{O}_{12}$, $\text{FeAlMo}_3\text{O}_{12}$ and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ as well (Table 3). Comparable bulk moduli of 28.3, 26.9 and 25.4 GPa were observed for these materials (Table 4). All compositions displayed considerable stiffening of the c-axis at the onset of anisotropic compressibility (α' -phase), but differed in the behavior of the a- and b-axes. While $\text{AlGaMo}_3\text{O}_{12}$ showed slight stiffening of these axes and a resulting decrease in volume compressibility, the a- and b-axes

softened significantly in $\text{FeAlMo}_3\text{O}_{12}$ and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, giving rise to slightly higher volume compressibility and smaller B_0 values in the α' -phase compared to the α -phase. Such behavior is intriguing, as phase transitions under pressure generally result in denser, less compressible phases. The material $\text{AlGaMo}_3\text{O}_{12}$ was unique, as it showed two subtle transitions that caused changes in linear compressibility, resulting in an additional α'' -phase. The α'' -phase showed slight softening of the a- and b-axes, combined with further slight stiffening of the c-axis. These changes are also reflected in the behavior of the principal axes, which show approximately isotropic compressibility in the α -phase for all materials, followed by slight stiffening of one principal axis in the α' - phase.

After the α' -transition, another change was observed in the compressibility plots at 4.6 GPa, which resulted in a sudden, stepwise change in several lattice constants and a 1% decrease in unit cell volume. Surprisingly, the patterns above this stepwise change could still be described by the $\alpha\text{-A}_2\text{M}_3\text{O}_{12}$ structure model in space group $\text{P2}_1/\text{a}$, although some distortion of the polyhedra was observed. It was thus initially unclear whether the drop in unit cell volume corresponded to the formation of a distinct new phase. However, close inspection of the patterns for $\text{Al}_2\text{Mo}_3\text{O}_{12}$ in this pressure range clearly revealed that new peaks had emerged, resulting in a pressure range in which two phases that produced similar but shifted patterns coexisted (Fig. 5). These patterns were fitted by adding a second phase of identical structure with smaller lattice constants, which will be designated as γ -phase.¹ The two distinct phases coexisted between 4.63 and 4.89 GPa. Above these pressures, only peaks belonging to the γ -phase were present (Fig. 6). Surprisingly, the b-axis was found to soften significantly, while the other two axes became less compressible. This behavior is even more evident when inspecting

¹ All compositions reported in this paper adopt the orthorhombic $\text{Sc}_2\text{W}_3\text{O}_{12}$ structure at high temperatures, which constitutes the β -polymorph.

Figure 4: Rietveld plot of α - $\text{Al}_2\text{Mo}_3\text{O}_{12}$ at 0.04 GPa using the ambient pressure structure. Circles represent data points, the calculated pattern corresponds to the overlaid solid line, and the difference curve is shown below the pattern. Tick marks indicate $\text{Al}_2\text{Mo}_3\text{O}_{12}$ (top) and NaCl peaks (bottom).

Table 2: Unit cell constants of ambient and high pressure phases, and relative volume changes during phase transitions. Cell constants are reported for the lowest pressure at which each phase is observed unless indicated otherwise.

A_2	α -phase (ambient)	γ -phase	δ -phase	$V_{\alpha', \text{last}}/V_0$	$V_{\gamma, \text{tvr}}/V_0$, $V_{\gamma, \text{last}}/V_0$	$V_{\delta, \text{init}}/V_0$
Al_2	$a = 15.38 \text{ \AA}$, $b = 9.04 \text{ \AA}$ $c = 17.89 \text{ \AA}$, $\beta = 125.4^\circ$ $V = 2028.0 \text{ \AA}^3$	$a = 14.65 \text{ \AA}$, $b = 8.53 \text{ \AA}$ $c = 17.08 \text{ \AA}$, $\beta = 124.5^\circ$ $V = 1760 \text{ \AA}^3$	$a = 14.04 \text{ \AA}$, $b = 8.28 \text{ \AA}$ $c = 13.47 \text{ \AA}$, $\beta = 101.9^\circ$ $V = 1532.6 \text{ \AA}^3$	0.88	0.87, 0.84	0.76
AlGa	$a = 15.43 \text{ \AA}$, $b = 9.07 \text{ \AA}$ $c = 17.91 \text{ \AA}$, $\beta = 125.3^\circ$ $V = 2044.6 \text{ \AA}^3$	$a = 14.76 \text{ \AA}$, $b = 8.59 \text{ \AA}$ $c = 17.21 \text{ \AA}$, $\beta = 124.6^\circ$ $V = 1798.1 \text{ \AA}^3$	$a = 14.16 \text{ \AA}$, $b = 8.32 \text{ \AA}$ $c = 13.62 \text{ \AA}$, $\beta = 102.2^\circ$ $V = 1567.6 \text{ \AA}^3$	0.89	0.88, 0.85	0.77
FeAl	$a = 15.51 \text{ \AA}$, $b = 9.13 \text{ \AA}$ $c = 18.02 \text{ \AA}$, $\beta = 125.3^\circ$ $V = 2082.3 \text{ \AA}^3$	$a = 14.94 \text{ \AA}$, $b = 8.71 \text{ \AA}$ $c = 17.48 \text{ \AA}$, $\beta = 124.4^\circ$ $V = 1877.0 \text{ \AA}^3$	$a = 14.20 \text{ \AA}$, $b = 8.36 \text{ \AA}$ $c = 13.57 \text{ \AA}$, $\beta = 102.0^\circ$ $V = 1575.7 \text{ \AA}^3$	0.91	0.90, 0.88	0.76
Fe_2	$a = 15.71 \text{ \AA}$, $b = 9.23 \text{ \AA}$ $c = 18.20 \text{ \AA}$, $\beta = 125.3^\circ$ $V = 2155.2 \text{ \AA}^3$	$a = 15.06 \text{ \AA}$, $b = 8.79 \text{ \AA}$ $c = 17.63 \text{ \AA}$, $\beta = 124.6^\circ$ $V = 1922.2 \text{ \AA}^3$	$a = 14.46 \text{ \AA}$, $b = 8.48 \text{ \AA}$ $c = 13.77 \text{ \AA}$, $\beta = 102.0^\circ$ $V = 1652.7 \text{ \AA}^3$	0.90	0.89, 0.87	0.77
$\text{Ga}_{2[4]}$	$a = 15.63 \text{ \AA}$, $b = 9.14 \text{ \AA}$ $c = 18.05 \text{ \AA}$, $\beta = 125.5^\circ$ $V = 2100.3 \text{ \AA}^3*$	$a = 15.24 \text{ \AA}$, $b = 8.68 \text{ \AA}$ $c = 17.44 \text{ \AA}$, $\beta = 126.1^\circ$ $V = 1865.2 \text{ \AA}^3\&$	$a = 14.45 \text{ \AA}$, $b = 8.34 \text{ \AA}$ $c = 13.71 \text{ \AA}$, $\beta = 101.3^\circ$ $V = 1620.5 \text{ \AA}^3*$	NA	0.89**	0.77**

*Results from reference 4 included for comparison purposes. The “ δ - phase” was originally designated γ - $\text{Ga}_2\text{Mo}_3\text{O}_{12}$, and was preceded by a different high pressure phase between 3.3 and 4.2 GPa. Re-analysis of the data during this work showed that the intermediate phase can be described by the α -phase cell, similar to the γ -phase of other materials reported here.

**First pressure at which phase was observed. Due to much larger pressure steps, exact values could not be determined.

&Results from reanalyzing 2005 data.

Table 3: Compressibility constants of all phases.

Material	Phase	β_a (GPa ⁻¹)	β_b (GPa ⁻¹)	β_c (GPa ⁻¹)	β_v (GPa ⁻¹)	Pressure of Extraction (GPa)
Al ₂ Mo ₃ O ₁₂	α	0.93×10^{-2}	1.07×10^{-2}	0.99×10^{-2}	2.76×10^{-2}	0.04-3.0
	α'	0.96×10^{-2}	0.98×10^{-2}	0.66×10^{-2}	2.46×10^{-2}	3.1-4.5
	γ	0.81×10^{-2}	1.33×10^{-2}	0.60×10^{-2}	2.07×10^{-2}	4.9-5.7
	δ^*	0.22×10^{-2}	0.38×10^{-2}	0.41×10^{-2}	1.01×10^{-2}	6.2-6.5
AlGaMo ₃ O ₁₂	α	1.01×10^{-2}	1.15×10^{-2}	1.10×10^{-2}	3.04×10^{-2}	0.1-1.9
	α'	0.93×10^{-2}	1.03×10^{-2}	0.75×10^{-2}	2.52×10^{-2}	2.0-2.9
	α''	1.02×10^{-2}	1.08×10^{-2}	0.71×10^{-2}	2.60×10^{-2}	3.0-4.0
	γ^*	0.94×10^{-2}	1.39×10^{-2}	0.65×10^{-2}	2.36×10^{-2}	4.3-5.0
FeAlMo ₃ O ₁₂	δ^*	0.48×10^{-2}	0.38×10^{-2}	0.54×10^{-2}	1.36×10^{-2}	5.3-6.7
	α^*	1.14×10^{-2}	1.21×10^{-2}	1.14×10^{-2}	3.31×10^{-2}	0.2-1.7
	α'^*	1.31×10^{-2}	1.52×10^{-2}	0.90×10^{-2}	3.51×10^{-2}	1.9-3.1
	γ^*	1.27×10^{-2}	1.95×10^{-2}	1.00×10^{-2}	3.42×10^{-2}	3.2-3.8
Fe ₂ Mo ₃ O ₁₂	δ^*	0.55×10^{-2}	0.48×10^{-2}	0.53×10^{-2}	1.56×10^{-2}	4.5-6.4
	α	1.28×10^{-2}	1.27×10^{-2}	1.15×10^{-2}	3.50×10^{-2}	0.2-1.5
	α'	1.45×10^{-2}	1.75×10^{-2}	0.92×10^{-2}	3.78×10^{-2}	1.6-2.7
	γ	1.45×10^{-2}	2.38×10^{-2}	0.94×10^{-2}	3.72×10^{-2}	2.8-3.5
Ga ₂ Mo ₃ O ₁₂	δ^*	0.59×10^{-2}	0.47×10^{-2}	0.55×10^{-2}	1.59×10^{-2}	3.9-6.2
	$\alpha^* \&$	0.79×10^{-2}	0.85×10^{-2}	1.20×10^{-2}	2.90×10^{-2}	0.2-3.3
	$\alpha^* \& \dagger$	0.48×10^{-2}	0.37×10^{-2}	0.16×10^{-2}	0.94×10^{-2}	4.2-7.9

*Compressibility estimated via Pawley refinement.

&May contain contributions from α' phase.

† This phase was named " γ - Ga₂Mo₃O₁₂" in the original publication, but the pattern corresponds to the δ -phase patterns discussed in this work. It is referred to as " δ -phase" here for more streamlined discussion.

Table 4: Bulk moduli (in GPa) and V_0 (in Å³) of all phases.

Material	$B_0(\alpha)$	$B_0(\alpha')$	$B_0(\gamma)$	$B_0(\delta)$	$V_0(\alpha)$	$V_0(\alpha')$	$V_0(\gamma)$	$V_0(\delta)$
Al ₂ Mo ₃ O ₁₂	26.4	31.6	40.5	84.6	2033	1863	1762	1534
AlGaMo ₃ O ₁₂	28.3	30.8*	36.9	54.8	2051	1880	1792	1568
FeAlMo ₃ O ₁₂	26.9	22.8	25.7	53.9	2132	2020	1899	1638
Fe ₂ Mo ₃ O ₁₂	25.4	21.5	21.2	52.9	2161	2043	1924	1663

*Values for α' -AlGaMo₃O₁₂, which resemble the α' -phase of other compositions more closely.

the compressibility of the principal axes, which showed significant softening of the principal axis corresponding to the b-axis combined with rapid stiffening of the least compressible axis. The compressibility constants for the γ -phase were extracted from 4.9 to 5.7 GPa to avoid non-linear regions, and were found to be $\beta_{\gamma,a} = 0.81 \pm 0.01 \times 10^{-2}$ GPa⁻¹,

Figure 5: High pressure diffraction patterns of $\text{Al}_2\text{Mo}_3\text{O}_{12}$ around the α' - to γ -phase transition pressure, showing coexistence of both phases: (a) 4.31 GPa, (b) 4.41 GPa, (c) 4.51 GPa, (d) 4.63 GPa, (e) 4.77 GPa, (f) 4.89 GPa, (g) 5.10 GPa, and (h) 5.14 GPa.

Figure 6: Rietveld plot of $\gamma\text{-Al}_2\text{Mo}_3\text{O}_{12}$ at 3.0 GPa using the ambient pressure structure. Circles represent data points, the calculated pattern corresponds to the overlaid solid line, and the difference curve is shown below the pattern. Tick marks indicate $\text{Al}_2\text{Mo}_3\text{O}_{12}$ (top) and NaCl peaks (bottom).

$\beta_{\gamma,b} = 1.33 \pm 0.01 \times 10^{-2} \text{ GPa}^{-1}$, $\beta_{\gamma,c} = 0.60 \pm 0.01 \times 10^{-2} \text{ GPa}^{-1}$, and $\beta_{\gamma,v} = 2.07 \pm 0.03 \times 10^{-2} \text{ GPa}^{-1}$. Distinct phase coexistence was not observed for the other compositions, but a similar stepwise drop in cell volume by about 1% occurred for all compounds, accompanied by significant softening of the b-axis. The behavior of the a-axis (slight stiffening for $\text{AlGaMo}_3\text{O}_{12}$ and $\text{FeAlMo}_3\text{O}_{12}$, no change for $\text{Fe}_2\text{Mo}_3\text{O}_{12}$) and c-axis (slight stiffening for $\text{AlGaMo}_3\text{O}_{12}$, slight softening for $\text{FeAlMo}_3\text{O}_{12}$ and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$), combined with changes in the β -angle, determined the ultimate effect on volume compressibility, which decreased for $\text{Al}_2\text{Mo}_3\text{O}_{12}$ and $\text{AlGaMo}_3\text{O}_{12}$, but remained similar for $\text{FeAlMo}_3\text{O}_{12}$ and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$. Consequently, the bulk

moduli for $\gamma\text{-Al}_2\text{Mo}_3\text{O}_{12}$ ($B_0(\gamma) = 40.5$ GPa) and $\gamma\text{-AlGaMo}_3\text{O}_{12}$ ($B_0(\gamma) = 36.9$ GPa) are larger than for the corresponding α -phases, while those for the iron containing compositions are smaller (25.7 and 21.2 GPa for $\text{FeAlMo}_3\text{O}_{12}$ and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, respectively). The γ -phase persisted until a major phase transition resulting in abrupt changes in the diffraction pattern occurred, which resulted in similar patterns for all compositions (Fig. 7). This new phase will be referred to as $\delta\text{-Al}_2\text{Mo}_3\text{O}_{12}$. Coexistence of the γ - and δ -phases was observed between 5.7 and 6.1 GPa (Table 1). Individual scans in the range of the discontinuity were closely inspected to determine the best quality phase pure scan for indexing the δ -phase. Indexing was conducted using Topas, and multiple monoclinic solutions were found. For all indexing cell lists, there were no unindexed lines in the top results.

Pawley fits of the most highly ranked cells were conducted, and the fits were inspected to determine the best cell based on the quality of the fit for the entire pattern. Fitting statistics for the top cells were similar, however, most cells failed to fit one or two peaks that were not used for indexing. Only one cell ($a = 14.04$ Å, $b = 8.28$ Å, $c = 13.47$ Å, $\beta = 101.9^\circ$, $V = 1532.6$ Å³) provided a fit with no discrepancies for $\text{Al}_2\text{Mo}_3\text{O}_{12}$ (Fig. 8). Very similar unit cells were found during indexing for all compositions investigated. The top result in the indexing list for $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ ($a = 14.20$ Å, $b = 8.36$ Å, $c = 13.57$ Å, $\beta = 102.0^\circ$, $V = 1575.7$ Å³) had a significantly higher figure of merit than any other cell. Inspection of the fit of this cell compared to other results showed that this cell accounted for all peaks, while cells with lower figures of merit failed to fit some peaks. While the figure of merit did not indicate a strong preference for a specific cell for $\text{AlGaMo}_3\text{O}_{12}$, it was found that a cell resembling the other best indexing results ($a = 14.16$ Å, $b = 8.32$ Å, $c = 13.62$ Å, $\beta = 102.2^\circ$, $V = 1567.6$ Å³) provided a fit with no discrepancies, whereas other cells failed to fit at least one peak. Finally, the indexing results of

Figure 7: XRD patterns of the δ -phase of (a) aluminum molybdate at 6.2 GPa, (b) iron molybdate at 4.1 GPa, (c) iron aluminum molybdate at 6.5 GPa, and (d) aluminum gallium molybdate at 5.5 GPa.

Figure 8: Pawley fit of δ - $\text{Al}_2\text{Mo}_3\text{O}_{12}$ at 6.23 GPa. Circles represent data points, the calculated pattern corresponds to the overlaid solid line, and the difference curve is shown below the pattern. Tick marks indicate $\text{Al}_2\text{Mo}_3\text{O}_{12}$ (top) and NaCl peaks (bottom).

$\text{FeAlMo}_3\text{O}_{12}$ gave several cells with comparable figures of merit, all of which were permutations of the same cell and could account for all peaks ($a = 14.20 \text{ \AA}$, $b = 8.36 \text{ \AA}$, $c = 13.57 \text{ \AA}$, $\beta = 102.0^\circ$, $V = 1575.7 \text{ \AA}^3$). Based on these results, it was concluded that this cell was the most likely unit cell of the δ -phase. Optimized unit cell constants (Table 2) and compressibilities were estimated via Pawley refinements (Table 3). For all materials, the δ -phase is considerably less compressible than the previous phases, which is typical for dense

high pressure phases, giving bulk moduli twice as large as the γ -phases (Table 4). Due to limited data quality at high pressure, structure solution could not be attempted.

No further changes were observed during compression. Refinement of patterns collected during decompression indicated that the transition to the δ -phase was reversible, although considerable hysteresis was observed (Table 2). The back-transformation pressure was determined by visual inspection of the patterns collected during decompression, as the phase change was quite obvious. Because the pressure steps between files were much larger during decompression, the transformations generally occurred between two scans, and phase coexistence was rarely observed. The only exception was the 3.6 GPa scan for $\text{Al}_2\text{Mo}_3\text{O}_{12}$, for which the δ -phase was the major phase, with a small amount of the lower pressure phase starting to form. This pressure is 2.1 GPa lower than the first pressure at which the δ -phase was observed during compression. For the next dataset collected at 2.5 GPa, the lattice constants of $\text{Al}_2\text{Mo}_3\text{O}_{12}$ ($a = 15.02 \text{ \AA}$, $b = 8.80 \text{ \AA}$, $c = 17.45 \text{ \AA}$, $\beta = 125.1^\circ$) were consistent with the values found for the α -phase during compression at the same pressure. No phase coexistence was observed in any of the other compositions, which makes it impossible to determine the exact pressure of the back-transition. These materials still contained pure δ -phase at pressures that were 0.9 to 1.5 GPa lower than the first pressure where the phase formed during compression, while α -structure type was observed at pressures 2.4 to 2.8 GPa below the transition pressure during compression. The large pressure steps between patterns during decompression make it difficult to determine whether the structure immediately goes back to the α -phase, or whether the γ - and α' -phases are formed first. For $\text{FeAlMo}_3\text{O}_{12}$ and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, the first observation of an α -structure type pattern during decompression occurs at a pressure (1.5 GPa) below the α' -transition during compression. The lattice constants at this pressure are smaller than those

observed for the α -phase during compression. This is especially evident in the b-lattice parameter. The observed cell volumes could be equally well accounted for by extrapolation of data for the γ - or α' -phases. However, the individual lattice constants are in better agreement with extrapolations of the α' -phase for each composition. Like $\text{Al}_2\text{Mo}_3\text{O}_{12}$, the lattice constants match those of the α -phase after complete decompression. In contrast, $\text{AlGaMo}_3\text{O}_{12}$ reverted between 3.5 and 2.2 GPa, which is above the α' transition pressure for this material. Close inspection of the $\text{AlGaMo}_3\text{O}_{12}$ data set revealed that the lattice constants first seen on decompression ($a = 15.09 \text{ \AA}$, $b = 8.84 \text{ \AA}$, $c = 17.50 \text{ \AA}$, $\beta = 125.0^\circ$) resembled those of the α' -phase at the same pressure. This suggests that the materials may be transforming back to the α' -phase and then the α -phase during decompression, as all transition pressures lie below the values where the γ -phases are formed during compression.

The phase transition pressures showed a clear trend with respect to average A-site cation size. The radii of Al^{3+} , Ga^{3+} , and Fe^{3+} in octahedral coordination are 54 pm, 62 pm, and 65 pm, respectively. This gives average A-site radii of 54 pm ($\text{Al}_2\text{Mo}_3\text{O}_{12}$, $V = 2028.0 \text{ \AA}^3$), 58 pm ($\text{AlGaMo}_3\text{O}_{12}$, $V = 2039.2 \text{ \AA}^3$), 59.5 pm ($\text{FeAlMo}_3\text{O}_{12}$, $V = 2082.8 \text{ \AA}^3$), and 65 pm ($\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $V = 2155.5 \text{ \AA}^3$). The unit cell volume of the ambient phase monoclinic cell increases with increasing A-site cation radius, while all phase transition pressures decrease (Table 1). The highest transition pressures are observed for $\text{Al}_2\text{Mo}_3\text{O}_{12}$, with the α' -, γ -, and δ -transitions occurring at 3.0, 4.6-4.9, and 5.7-6.1 GPa, respectively. The equivalent transitions in $\text{AlGaMo}_3\text{O}_{12}$ are observed at lower pressures of 2.0, 4.1-4.4, and 5.0-5.3 GPa, $\text{FeAlMo}_3\text{O}_{12}$ displays them at 1.7, 3.2, and 3.9-4.2 GPa, and $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ undergoes the transitions at 1.5, 2.7-2.9, and 3.5-3.7 GPa, respectively. The phase transition pressures seem to be related to the compressibility of each material, as the onset of peak splitting (α' -transition) occurred after an

approximately 5% reduction in unit cell volume for all materials. After 10 to 13% overall volume reduction, a stepwise reduction of 1% was observed during the formation of the γ -phase. Similarly, the initial volume of the δ -phase corresponded to relative cell volumes of 76 to 77% compared to the respective ambient pressure phases (Table 2). It is well known that larger cations tend to form softer polyhedra that can be more easily distorted [34, 35], which leads to more compressible phases. However, this also results in lower phase transition pressures when the atomic arrangement becomes thermodynamically unfavorable with the decrease in unit cell size.

Our results led us to revisit previously collected data on gallium molybdate, as this material underwent two pressure induced phase transition, with a final high pressure cell (designated ' γ - $\text{Ga}_2\text{Mo}_3\text{O}_{12}$ ' by Gates et al., as $\text{Ga}_2\text{Mo}_3\text{O}_{12}$ does not adopt an orthorhombic structure) that resembled the δ -phase found in this work. This suggested that the material may undergo the same sequence of pressure induced phase transitions as the compositions discussed in this manuscript. The gallium molybdate data were collected with pressure steps of 0.3 to 1.0 GPa, resulting in a limited number of patterns. As a result, subtle changes such as an α' transition would not be detectable, and the anisotropic peak shifts may be interpreted as the occurrence of new peaks corresponding to a different structure. While the highest pressure phase was well described by the proposed cell, the patterns corresponding to the intermediate pressure phase could not be fully described. The current findings led us to suspect that the γ -transition may have occurred for gallium molybdate as well, and that the considerable anisotropic peak shifts obscured the fact that a monoclinic cell closely related to the ambient pressure phase could provide a good fit. It was found that this phase could indeed be better described by such a cell (Fig. 9), demonstrating that gallium molybdate displays the same high pressure behavior as the

Figure 9: Pawley fit for $\text{Ga}_2\text{Mo}_3\text{O}_{12}$ data at 3.8 GPa using the ambient pressure structure with a significantly smaller cell volume (“ γ -phase” for materials studied in this paper). Circles represent data points, the calculated pattern corresponds to the overlaid solid line, and the difference curve is shown below the pattern. Tick marks indicate $\text{Ga}_2\text{Mo}_3\text{O}_{12}$ peaks (top), and MoO_3 an impurity phase (bottom).

group of materials discussed here. Exact phase transition pressures for $\text{Ga}_2\text{Mo}_3\text{O}_{12}$ are not known due to the larger pressure steps, but the first occurrence of the high pressure phases (at 3.3 and 4.2 GPa, respectively) agrees with the cation size/pressure trends observed in this work.

4. Conclusions

The high pressure study of $\text{Al}_2\text{Mo}_3\text{O}_{12}$, $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, $\text{AlFeMo}_3\text{O}_{12}$ and $\text{AlGaMo}_3\text{O}_{12}$ showed that these materials undergo the same sequence of high pressure phase transitions from the monoclinic $\text{P2}_1/\text{a}$ structure under ambient conditions (α -phase, isotropic compressibility) to two closely related structures (α' -phase, anisotropic compressibility; γ -phase, 1% smaller volume) to a distinct high pressure phase (δ -phase). One material behaved slightly differently; $\text{AlGaMo}_3\text{O}_{12}$ had a second α' -prime transition in which the compressibility curves of all unit cell parameters softened slightly. Surprisingly, the γ -phase transition was accompanied by a notable softening of the b-axis in all materials, however, volume compressibility became slightly smaller than in the α' -phase.

A decrease in all phase transition pressures was observed with increasing A-site cation radius, suggesting that softer, more distortable polyhedra result in lower transition pressures. Interestingly, the relative unit cell sizes at each transition were similar for all compositions, indicating a possible thermodynamic intersection in volume-stability curves for the different polymorphs. The γ -phase transition was preceded by about a 10% reduction in volume, and a stepwise decrease of 1% accompanied this transformation. After an additional compression by 2-3%, the volume collapsed by another 10%, resulting in the δ -phase, which was 23-24% denser than the ambient pressure cell. Thus, the pressure at which transitions occur is strongly related to the compressibility of the material. All materials showed hysteresis during decompression, but reverted to the original α -phase.

Based on these results, we conclude that these compositions belong to a "group" of $A_2M_3O_{12}$ materials displaying identical high pressure behavior, and that other $A_2M_3O_{12}$ materials that have yet to be fully characterized could also belong to this group. This was already demonstrated by reevaluating previously published data for $Ga_2Mo_3O_{12}$. It is currently unclear what properties of the A-site cations causes the common behavior trends, and additional high pressure studies will be necessary to obtain a more complete picture on a larger number of compounds.

Acknowledgments

This work is based upon research conducted at the Argonne National Laboratory Advanced Photon Source, which is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The authors acknowledge NSF Grants DMR-0545517 and CRIF-0840474 for providing funds for this research.

References

- [1] D.A. Fleming, D.W. Johnson, P.J. Lemaire, Article Comprising a Temperature Compensated Optical Fiber Refractive Index Grating, Lucent Technologies, USA, 1997.
- [2] H. Holzer, D.C. Dunand, Phase transformation and thermal expansion of Cu/ZrW₂O₈ metal matrix composites, J. Mater. Res., 14 (1999) 780-789.
- [3] J.S.O. Evans, T.A. Mary, A.W. Sleight, Negative Thermal Expansion Materials, Physica B, 241-243 (1998) 311-316.
- [4] S.D. Gates, J.A. Colin, C. Lind, Non-Hydrolytic Sol-Gel Synthesis, Properties, and High-Pressure Behavior of Gallium Molybdate, J. Mater. Chem., 16 (2006) 4214-4219.
- [5] T. Varga, A.P. Wilkinson, C. Lind, W.A. Bassett, C.S. Zha, High Pressure Synchrotron X-ray Powder Diffraction Study of Sc₂Mo₃O₁₂ and Al₂W₃O₁₂, J. Phys.-Condens. Mat., 17 (2005) 4271-4283.
- [6] W. Paraguassu, M. Maczka, A.G. Souza, P.T.C. Freire, J. Mendes, F.E.A. Melo, L. Macalik, L. Gerward, J.S. Olsen, A. Waskowska, J. Hanuza, Pressure-Induced Structural Transformations In the Molybdate Sc₂(MoO₄)₃, Phys. Rev. B, 69 (2004) 094111.
- [7] M. Cetinkol, A.P. Wilkinson, K.W. Chapman, Scandium Tungstate Above 2.5 GPa, Solid State Commun., 148 (2008) 511-515.
- [8] T. Varga, A.P. Wilkinson, J.D. Jorgensen, S. Short, Neutron Powder Diffraction Study of the Orthorhombic to Monoclinic Transition in Sc₂W₃O₁₂ On Compression, Solid State Sci., 8 (2006) 289-295.

- [9] T. Varga, A.P. Wilkinson, C. Lind, W.A. Bassett, C.S. Zha, *In Situ* High-Pressure Synchrotron X-ray Diffraction Study of $\text{Sc}_2\text{W}_3\text{O}_{12}$ At Up To 10 GPa, *Phys. Rev. B*, 71 (2005) 214106.
- [10] N. Garg, C. Murli, A.K. Tyagi, S.M. Sharma, Phase Transitions In $\text{Sc}_2(\text{WO}_4)_3$ Under High Pressure, *Phys. Rev. B*, 72 (2005) 064106.
- [11] C. Lind, Two Decades of Negative Thermal Expansion Research: Where Do We Stand?, *Materials*, 5 (2012) 1125-1154.
- [12] T. Varga, Materials That Shrink On Heating: Pressure-Induced Phase Transitions In Negative Thermal Expansion Materials, and Their Energetics, in: J.C. Taylor (Ed.) *Advances in Chemistry Research*, Nova Publishers, 2011, pp. 1-54.
- [13] M. Maczka, A.G. Souza, W. Paraguassu, P.T.C. Freire, J. Mendes, J. Hanuza, Pressure-Induced Structural Phase Transitions and Amorphization In Selected Molybdates and Tungstates, *Prog. Mater. Sci.*, 57 (2012) 1335-1381.
- [14] N. Garg, C. Murli, B. Taru, S. Karmakar, A.K. Tyagi, S.M. Sharma, Pressure Induced Phase Transitions In $\text{Sc}_2(\text{WO}_4)_3$ and $\text{Al}_2(\text{WO}_4)_3$, *Solid State Phys.*, 45 (2001) 39-40.
- [15] N. Garg, V. Panchal, A.K. Tyagi, S.M. Sharma, Pressure-Induced Phase Transitions in $\text{Al}_2(\text{WO}_4)_3$, *J. Solid State Chem.*, 178 (2005) 998-1002.
- [16] R.A. Secco, H. Liu, N. Imanaka, G. Adachi, Pressure-Induced Amorphization In Negative Thermal Expansion $\text{Sc}_2(\text{WO}_4)_3$, *J. Mater. Sci. Lett.*, 20 (2001) 1339-1340.
- [17] R.A. Secco, H. Liu, N. Imanaka, G. Adachi, Anomalous Ionic Conductivity of $\text{Sc}_2(\text{WO}_4)_3$ Mediated By Structural Changes At High Pressures and Temperatures, *J. Phys.-Condens. Mat.*, 14 (2002) 11285-11289.

- [18] R.A. Secco, H. Liu, N. Imanaka, G. Adachi, M.D. Rutter, Electrical Conductivity and Amorphization Of $\text{Sc}_2(\text{WO}_4)_3$ At High Pressures and Temperatures, *J. Phys. Chem. Solids*, 63 (2002) 425-431.
- [19] G.D. Mukherjee, V. Vijaykumar, S.N. Achary, A.K. Tyagi, B.K. Godwal, Phase Transitions In $\text{Al}_2(\text{WO}_4)_3$: High Pressure Investigations of Low Frequency Dielectric Constant and Crystal Structure, *J. Phys.-Condens. Mat.*, 16 (2004) 7321-7330.
- [20] T.I. Baiz, C.P. Heinrich, N.A. Banek, B.L. Vivekens, C. Lind, *In Situ* Non-Ambient X-ray Diffraction Studies of Indium Tungstate, *J. Solid State Chem.*, 187 (2012) 195-199.
- [21] S. Karmakar, S.K. Deb, A.K. Tyagi, S.M. Sharma, Pressure-Induced Amorphization In $\text{Y}_2(\text{WO}_4)_3$: *In Situ* X-ray Diffraction and Raman Studies, *J. Solid State Chem.*, 177 (2004) 4087-4092.
- [22] H. Liu, R.A. Secco, N. Imanaka, G. Adachi, X-ray Diffraction Study of Pressure-Induced Amorphization in $\text{Lu}_2(\text{WO}_4)_3$, *Solid State Commun.*, 121 (2002) 177-180.
- [23] A.K. Arora, R. Nithya, T. Yagi, N. Miyajima, T.A. Mary, Two-Stage Amorphization of Scandium Molybdate At High Pressure, *Solid State Commun.*, 129 (2004) 9-13.
- [24] A.K. Arora, T. Yagi, N. Miyajima, T.A. Mary, Amorphization and Decomposition of Scandium Molybdate At High Pressure, *J. Appl. Phys.*, 97 (2005).
- [25] A.C. Torres Dias, C. Luz Lima, W. Paraguassu, K. Pereira da Silva, P.T.C. Freire, J. Mendes Filho, B.A. Marinkovic, K.J. Miller, M.A. White, A.G. Souza Filho, Pressure-Induced Crystal-Amorphous Transformation In $\text{Y}_2\text{Mo}_3\text{O}_{12}$, *Vib. Spectrosc.*, 68 (2013) 251-256.
- [26] S.D. Gates, C. Lind, Polymorphism in Yttrium Molybdate $\text{Y}_2\text{Mo}_3\text{O}_{12}$, *J. Solid State Chem.*, 180 (2007) 3510-3514.

- [27] S.D. Gates, Cation Influence of Negative Thermal Expansion In the $A_2M_3O_{12}$ Family, Ph.D. thesis, Department of Chemistry, The University of Toledo, Toledo, OH, 2008.
- [28] T.I. Baiz, A.M. Gindhart, S.K. Kraemer, C. Lind, Synthesis of $MgHf(WO_4)_3$ and $MgZr(WO_4)_3$ using a non-hydrolytic sol-gel method, J. Sol-Gel Sci. Technol., 47 (2008) 128-130.
- [29] T.I. Baiz, Non-Hydrolytic Sol-Gel Synthesis and Characterization of Materials of the Type $AA'M_3O_{12}$, Ph.D. thesis, Department of Chemistry, The University of Toledo, 2010.
- [30] A.M. Gindhart, Synthesis and Characterization of $AA'W_3O_{12}$ Compounds, M.S. thesis, Department of Chemistry, The University of Toledo, Toledo, OH, 2007.
- [31] A.M. Gindhart, C. Lind, M. Green, Polymorphism In the Negative Thermal Expansion Material Magnesium Hafnium Tungstate, J. Mater. Res., 23 (2008) 210-213.
- [32] F. Birch, Equation of State and Thermodynamic Parameters of NaCl to 300-kbar In the High-Temperature Domain, J. Geophys. Res.-Solid, 91 (1986) 4949-4954.
- [33] M.J. Cliffe, A.L. Goodwin, PASCAL: a principal axis strain calculator for thermal expansion and compressibility determination, Journal of Applied Crystallography, 45 (2012) 1321-1329.
- [34] A.W. Sleight, L.H. Brixner, New Ferroelastic Transition in Some $A_2(MO_4)_3$ Molybdates and Tungstates, J. Solid State Chem., 7 (1973) 172-174.
- [35] J.S.O. Evans, T.A. Mary, A.W. Sleight, Negative Thermal Expansion In A Large Molybdate and Tungstate Family, J. Solid State Chem., 133 (1997) 580-583.

Graphical Abstract

Overlay of variable pressure X-ray diffraction data of $\text{Al}_2\text{Mo}_3\text{O}_{12}$ collected in a diamond anvil cell. Both subtle and discontinuous phase transitions are clearly observed.