PHASE EQUILIBRIA IN THE In_2O_3 - WO_3 SYSTEM

BY

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Here's to keeping it short and sweet:

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ABSTRACT

Uses of materials in the In_2O_3 - WO_3 system are far reaching. Applications include gas sensing, catalysts, as well as other potential electrical and optical applications. The subsolidus phase relationships in the $\text{In}_2\text{O}_3 - \text{WO}_3$ system at $800 - 1400^\circ\text{C}$ were studied by x-ray diffraction. Two binary oxide phases – $\text{In}_2(\text{WO}_4)_3$ and $\text{In}_6\text{WO}_{12}$ – were found to be stable in air over the temperature range of $800 - 1200^\circ\text{C}$. The structures of the binary oxides were refined using the Rietveld method. Differential thermal analysis data of $\text{In}_2(\text{WO}_4)_3$ showed a large exothermic/endothermic peak upon heating and cooling respectively between 260°C and 240°C . The data was interpreted as a phase transition. Higher-resolution diffraction data of $\text{In}_2(\text{WO}_4)_3$ was taken at 310°C (583K) and 225°C (498K). The structure of $\text{In}_2(\text{WO}_4)_3$ at 310°C (583K) was refined to the $\text{Sc}_2(\text{WO}_4)_3$ -type Pnca space group. The low temperature phase of $\text{In}_2(\text{WO}_4)_3$, x-ray data taken at 225°C (498K), is believed to crystallize in the $\text{Fe}_2(\text{MoO}_4)_3$ - $\text{P } 2_1/\text{a}$ monoclinic space group. Rietveld refinement of bulk powder $\text{In}_6\text{WO}_{12}$ satisfactorily matched single crystal work using the $\text{R } \bar{3}\text{r}$ space group.

1. INTRODUCTION AND LITERATURE REVIEW

Materials in the $\text{In}_2\text{O}_3\text{-WO}_3$ system are interesting because of their potential electrical and optical applications. For example, WO_3 is the most researched inorganic electrochromic material,¹ $\text{In}_2(\text{WO}_4)_3$ is a trivalent cation conductor,² $\text{In}_6\text{WO}_{12}$ has been examined as a potential neutrino detector³ and In_2O_3 is the parent compound for indium tin oxide.

This work investigated phase relationships and crystal structures of two of the binary oxide compounds in the system, namely $\text{In}_2(\text{WO}_4)_3$ and $\text{In}_6\text{WO}_{12}$. Prior to this study, little was known about any of the phase relationships in the $\text{In}_2\text{O}_3\text{-WO}_3$ system, although there had been numerous studies regarding the synthesis and crystal structures of individual phases in the system. This section summarizes the previous literature in this system.

1.1 WO_3

Tungsten oxide is of interest scientifically for the number of stable phases in the region near 75 atomic % oxygen. The base tungsten coordination polyhedron is an octahedron with the tungsten ion at the center. Magnelli found four phases, $\alpha\text{-WO}_x$ ($2.98 < x < 3.0$), $\beta\text{-WO}_x$ ($2.83 < x < 2.90$), $\gamma\text{-WO}_x$ ($2.66 < x < 2.72$) and WO_2 . He was able to relate these known phases using the tungsten – oxygen octahedron and the concept of crystallographic shear.⁴ At one extreme, all octahedra are corner sharing resulting in WO_3 . Pure tungsten oxide, WO_3 , is monoclinic (space group, s.g., $P 2_1/n$) with lattice parameters $a=7.297\text{\AA}$, $b=7.539\text{\AA}$, $c=7.688\text{\AA}$, $\beta=90.91^\circ$.⁵ An alternate stable crystal structure for WO_3 at room temperature is a distorted AlF_3 structure.⁶ The monoclinic $P 2_1/n$ is similar to a distorted perovskite with the A atoms of the perovskite formula ABO_3 missing. A schematic diagram of the WO_3 structure is presented in Figure 1. Molenda *et al.* reported that “pure” WO_3 exists simultaneously as a biphasic mixture of 70 atom % monoclinic phase and the rest orthorhombic.⁷ Through the removal of oxygen, corner shared octahedra become edge sharing resulting in the numerous variable stoichiometric tungsten oxide phases. The most recent delineations are given in the phase diagram, Figure 2.⁸

Figure 1. Schematic diagram of pseudo cubic WO_3 . Figure was generated using Ball and Sticks[®] using atomic positions reported by Loopstra *et al.*⁹ Red (smaller) balls represent tungsten atoms and yellow (larger) balls represent oxygen atoms.

Figure 2. Phase diagram of the W-O system in the region of WO_3 . Figure used with permission of ASM International[®].

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Phases of interest for electrochromic application in the tungsten oxide system have hexagonal symmetry. Hexagonal structures have been reported in the bronze region. They exhibit one-dimensional tunnels. Hexagonal tungsten oxides, h-WO₃, have recently been reported. These compounds are made through reduction processes requiring the use of water for charge neutrality. The resulting compounds have pyrochlore structures with 3-dimensional tunnels.¹

1. 2 Tungsten Bronzes

Tungsten bronzes were first reported in the early 19th century. Tungsten bronzes occur when corner sharing tungsten trioxide octahedra stack in three dimensions forming a tunnel network. Metal atoms, denoted M, can be inserted into these tunnels creating tungsten bronzes with the formula M_xWO₃.⁴ As the M-atoms are inserted, corner-sharing tungsten octahedra flex the tunnel structure to either tetragonal or hexagonal symmetry. Tetragonal indium tungsten bronzes have been reported at compositions of In_{0.02}WO₃ and In_{0.03}WO₃.¹⁰ As the mole fraction of In³⁺ increases, the tunnel sections become either triangular or hexagonal, hence the name hexagonal tungsten bronzes (HTB). HTB are characterized by a deep blue color. As the indium concentration increases, a metallic shine becomes apparent.^{4,10-13} Using geometrical arguments, Bouchard and Gillson indicate x up to 0.33 will form HTB.¹¹⁻¹³ However, HTB have been reported with x equal to 0.40.^{10,14}

1. 3 M₂(WO₃)₄ or M₂O₃ · 3WO₃ Materials

In the mid-60's and 70's, rare-earth metal tungstates and molybdates with the composition of M₂(WO₃)₄ or M₂O₃ · 3WO₃ were studied for their “interesting optical properties.”¹⁵⁻¹⁷ Crystallographic identification of the tungstates indicated three structural classes. These are monoclinic C 2/c (Type I), orthorhombic Pnca (Type II) with the third class projected as either P 4₂2 or P $\bar{4}$ ₂m. Lanthanides, La through Dy, form the Type I tungstates and molybdates. Ho through Lu and trivalent cations such as Y, Sc, In, and Al form the Type II tungstates and molybdates. Dy, Gd, and Tb also crystallize in the Type III structure at high temperatures. Lanthanides crystallizing in the Type III structures have been only reported for molybdates.

Monoclinic C 2/c is described as a distorted scheelite structure (CaWO_4 – s.g. I 4₁/a) with ordered vacancies. Scheelite is a body centered tetragonal crystal. It forms perfect O tetrahedra with W in the center, while Ca occupies an octahedral site. Similar to scheelite, tungsten resides in a tetrahedral site in the C 2/c tungstate structures. The octahedral site is occupied by either an alkali-earth ion or rare-earth ion. In the C 2/c structure, the coordination polyhedra are severely distorted from their ideal shapes. Templeton and Zalkin suggested that it is more accurate to regard the monoclinic C 2/c structure as a double oxide than as a salt of tungstic acid.¹⁶ A visual comparison of the tetragonal scheelite structure to the defect C 2/c structure is given in Figures 3 and 4. Pnca is a non-standard setting of the Pbcn space group in which the order of the measured axes is cab instead of abc. Pnca is not a subgroup of the scheelite (I 4₁/a) space group. The Pnca space group is described as densely populated vertex-sharing layers of WO_4 tetrahedra and MO_6 octahedra.^{2,18,19} A cartoon of the $\text{M}_2(\text{WO}_4)_3$, in the standard setting of Pbcn, is shown in Figure 5. The crystal structure of $\text{In}_2(\text{WO}_4)_3$ is reported to be isostructural with $\text{Sc}_2(\text{WO}_4)_3$. A partial structure determination of $\text{In}_2(\text{WO}_4)_3$ was completed by Trunov and Kovba over the range of 10 - 34° θ in 1967.¹⁹ Whether the rare-earth metal tungstate will crystallize in either the monoclinic form or the orthorhombic form is dependent upon the radius ratio ($r_{\text{M}^{3+}} / r_{\text{O}^{2-}}$). A radius ratio greater than 0.75 will result in stable 8-fold coordination, yielding the Pnca structure. Below this ratio, a 6-fold coordination will result yielding the C 2/c monoclinic structure.²⁰

Figure 3. Tetragonal ($I 4_1/a$) scheelite structure. Figure was generated using Ball and Sticks[®] using atomic positions reported by Hazen *et al.*²¹ Blue (medium sized) balls represent calcium atoms, red (small) balls represent calcium atoms, and yellow (large) balls represent oxygen atoms.

Figure 4. Monoclinic $C 2/c$ structure of $M_2(WO_4)_3$ better described as a double oxide rather than a distorted scheelite. Atom positions were taken from Tempelton and Zelkin.¹⁶ Red (smaller) balls represent tungsten atoms, blue (medium size) balls represent M atoms, and yellow balls (larger) represent oxygen atoms.

[®] Balls and Sticks, ver. 1.48 <<http://www.xbug.org/toycrate>>

Figure 5. Pbcn structure of $M_2(WO_4)_3$. Figure was generated using Ball and Sticks. Woodcock *et al.* reported atomic positions.²² Blue (small) balls represent M atoms, pink (lighter) balls represent tungsten atoms, and yellow (larger) balls represent oxygen atoms.

Most of the early literature about these materials was structural reports on single crystals. However a few of these reports delved into physical and electrical measurements to uncover the “interesting optical properties” that were the original intent stated in the paper’s introductions. Preliminary electrical measurements suggest that $Sc_2(WO_4)_3$ is diamagnetic at room temperature and has a small temperature dependent paramagnetic component, which becomes equal in magnitude at 30K to the diamagnetism.²⁰ Recent reports further explored mechanical and electrical behavior using polycrystalline material. Sleight *et al.* reported $In_2(WO_4)_3$ as having a positive (linear) thermal expansion coefficient,²³ while $Sc_2(WO_3)_4$ had a negative expansion coefficient.²⁴ Koehler *et al.* reported that the ionic conductivity values for $In_2(WO_4)_3$ and $Sc_2(WO_3)_4$ are on the order of $10^{-5} \text{ S cm}^{-1}$ at 600°C. It was also determined that $In_2(WO_4)_3$ is an ionic conductor with the trivalent In as the dominant transport carrier.^{2,18}

1. 4 $3\text{M}_3\text{O}_2 \cdot \text{WO}_3$

Structures with the composition of M_7O_{12} or $3\text{R}_2\text{O}_3 \cdot \text{WO}_3$ are mainly of scientific interest. First they are a defect structure of the parent fluorite structure, space group $\text{m}\bar{3}\text{m}$.²⁵⁻²⁸ The fluorite relationship becomes more visible when M_7O_{12} is re-written as $\text{M}_7\text{O}_{12}\text{V}_2$ where V denotes a structural anion vacancy. These compounds have $1/7^{\text{th}}$ of the oxygen atoms missing from the ideal fluorite structure; this corresponds to 2 oxygen vacancies per formula unit, aligned along the $\langle 111 \rangle$. The ideal construction of M_7O_{12} along the c-axis of a hexagonal cell is shown in Figure 6. The ideal M_7O_{14} fluorite-type structure is shown to highlight the location of the systematic vacancies. The systematic vacancies are believed to cause a consistent lengthening of the metal – metal bonds and a shortening of the oxygen – oxygen bonds. Distortion due to the shortened and lengthened bond changes the space group from cubic to rhombohedral, $\text{R}\bar{3}$. The alignment allows for six other metal atoms surrounding each six metal atoms, 3 above and 3 below in the c_{HEX} direction, which are necessarily 7 coordinated by oxygen. The second reason of interest in these materials was that they revisited the question of required stoichiometry for stable materials to exist.⁴

This material had previously been investigated by Dabney *et al.* as a possible transparent conducting material. Dabney *et al.* reported electrical resistivities of $\text{In}_6\text{WO}_{12}$ between $70 - 720 \text{ }\Omega\text{cm}^{-1}$.²⁹ Gaewdang *et al.* has identified $\text{In}_6\text{WO}_{12}$ as a possible neutrino detector.³ Other tungstates known to form in this structure are yttrium and the rare-earth elements Ho through Lu. Isostructural materials within the III-VI are UR_6O_{12} , $\text{MoN}_6\text{O}_{12}$ where $\text{R} = \text{La, Pr to Lu}$ and $\text{N} = \text{Y and Er to Lu}$. Literature reports of these types of compounds involve mainly structural studies.^{25,26}

Figure 6. The ideal fluorite structure of $\text{M}_7\text{O}_{12}\text{V}_2$ displayed along the $\langle 111 \rangle$ direction. The figure is oriented to emphasize the aligned structural vacancies. Dark circles represent metal atoms, while open circles represent oxygen atoms and the open squares represent vacant oxygen positions in the ideal fluorite structure.

1. 5 In₂O₃

Indium oxide at ambient temperature and pressure crystallizes into the body-centered cubic rare-earth C-type structure (s.g. Ia $\bar{3}$) also known as bixbyite. In₂O₃ has interesting industrial applications as well as scientific interest. Indium oxide doped with tin oxide (ITO) is a well-known transparent conducting oxide. Thin-film ITO can be prepared so that it is about 85 - 90 % transparent to visible light and has a sheet resistance of 10 Ω cm⁻¹.³⁰ The bixbyite structure is also a defect fluorite structure. It has ¼ of the ideal anion positions vacant.⁴

1. 6 Rietveld Refinement

Rietveld analysis is a powerful tool for crystal structure refinement. The advantage of Rietveld refinement over other structure solution methods is the use of full-pattern fitting. All lines for each phase are explicitly considered and even overlapped lines are not problematic. The use of all the lines in a pattern minimizes the uncertainty in the derived weight fractions, and the effects of non-linear detection system. Finally, preferred orientation of crystallites is much less of a problem with full pattern methods.³¹ The term refinement is used instead of “crystal structure solution” because starting parameters such as space group symmetry, atomic positions, site occupancies, and lattice parameters, are needed before the structure can be refined. Least-square refinements are carried out until the best fit is obtained between the entire observed powder diffraction pattern taken as a whole and the entire calculated pattern based on the simultaneously refined models for the crystal structure(s), diffraction optic effects, instrumental factors, and other specimen characteristics (i.e. lattice parameters) as may be desired and can be modeled.³² The best fit is mathematically modeled by the residual, S_y , defined by : $S_y = \sum_i w_i (y_i - y_{ci})$; where w_i is the weight assigned to each step intensity and is typically equal to the inverse of the counting error (usually equal to the square root of the observed intensity) at step i ; y_i is the observed intensity at the i^{th} step; and y_{ci} is the calculated intensity at the i^{th} step.

Two important features of Rietveld analysis are that the process models contributions to the diffraction pattern from the instrument and the structure to all possible hkl reflections at every point, I , in the diffraction pattern as well as giving

feedback during the refinement, between improving knowledge of the structure and improving allocation of observed intensity to partially overlapping individual Bragg reflections.³² The calculated diffraction intensity, y_{ci} , is modeled by,

$$y_{ci} = y_{bi} + s[\sum_{hkl} L_{hkl} |F_{hkl}|^2 \Phi(2\theta_i - 2\theta_{hkl}) P_{hkl} A];$$

where y_{bi} is the background intensity, s is a scale factor, L_{hkl} includes the Lorentz polarization factor and multiplicity factors, F_{hkl} is the structure factor, Φ is the profile (peak shape) function, $2\theta_i$ is the angle corresponding to data point i , $2\theta_{hkl}$ is the Bragg angle, P_{hkl} is preferred orientation function, and A is the adsorption function. These terms encompass a number of refinable parameters. For example, L_{hkl} , F_{hkl} , P_{hkl} and $2\theta_{hkl}$ include lattice parameters and structural parameters such as atom position, site occupancy, and thermal parameters. The profile function, the absorption function, and the background function encompass a number of refinable parameters that are dependent upon the experimental method as well as the sample.

2. EXPERIMENTAL PROCEDURE

2.1 Bulk Phase Analysis

Samples with various indium to tungsten ratios were prepared and characterized as summarized in Table I. Most samples were prepared by solid-state reaction from commercially obtained powders, In_2O_3 (Indium Corporation of America) and WO_3 (>99.99% purity, Aldrich Chemical Co.). Pre-weighed amounts of powders were moistened with acetone and mechanically mixed in an alumina mortar and pestle. Samples of $x_{\text{In}} = 0.4$ were also produced using a solution method, where x_{In} is defined as $[\text{In}]/([\text{In}]+[\text{W}])$. A 1M solution of $\text{In}(\text{NO}_3)_3$ (Indium Corporation of America) and a 1M solution of H_2WO_4 (Kodak) were mixed in an porcelain crucible at a cation ratio of 2In:3W. Excess water and nitrates were removed by heating the solution in an alumina crucible to 750°C. Powders were then ground in an alumina mortar and pestle. All mixed powders were pressed into ½” (12.5mm) diameter pellets by uniaxially applying a force of 2 metric tons, which converts to a pressure of slightly less than 0.1 MPa. The pellets were fired inside alumina crucibles. The pellets were covered with either sacrificial pellets or powders of the same composition to limit volatilization of the constituent oxides. The samples were fired between 800°C and 1200°C at 100°C increments for 50 hours. After firing, the samples were quenched in air, weighed and ground for phase identification using x-ray diffraction (XRD) analysis. The samples were then re-pressed, re-fired, re-weighed, and re-analyzed until consecutive XRD patterns were identical. Select samples were heated at temperatures as high as 1400°C.

XRD analysis of the resulting products was conducted using a Phillips XRG 3100 diffractometer (Phillips Inc., USA) using $\text{Cu K}\alpha$ radiation (40kV, 20mA). Thick samples of the sintered powders were mounted in aluminum holders for phase identification and lattice-parameter measurements. Silicon was used as an internal standard. Diffraction patterns were collected between 10°-70° 2θ at a stepped scan rate of 0.04 per step and a count time of 4 seconds per step. Commercial software (Jade 6.0, Materials Data, Inc.) was used to calculate the positions of the reflections with respect to the Si standard and to determine lattice parameters via a least squares method.

TABLE I. Summary of Samples

Composition		Temperature (°C)	Firing Time (hrs)	Visual Appearance	Xray Phase Assembled
X_{WO_3}	$X_{\text{In}_2\text{O}_3}$				
1.00	0.00	800	50	black	a
		900	50	black	a
		1000	50	black	a
		1100	50	black	a
		1200	50	black	a
		1300	50	black	a
0.83	0.17	1000	168	green	a+b
		1100	50	green	a+b
		1200	50	green	a+b
		1300	50	green	a+b
0.67	0.33	1000	100	white + green	a+b
		1100	100	white + green	a+b
		1200	100	white + green	a+b
0.60	0.40	800	100	yellow + green	a+b
		900	100	yellow	b+c
		1000	100	white	b+c
		1100	100	white	b+c
		1200	100	white	b+c
		1300	100	white + gray	c+d
		1400	100	white + gray	c+d
0.59	0.41	1200	50	white	b+c
		1300	50	white	b+c
0.56	0.44	1200	50	white	b+c
		1300	50	white	b+c
0.50	0.50	800	100	yellow	b+c
		900	100	yellow	b+c
		1000	100	white	b+c
		1100	100	white	b+c
0.33	0.67	900	100	yellow	b+c
		1000	100	yellow	b+c
		1100	100	white	b+c
		1200	100	white	b+c

a=WO₃, b= In₂(WO₄)₃, c= In₆WO₁₂, and d=In₂O₃

TABLE I. Summary of Samples continued

Composition		Temperature (°C)	Firing Time (hrs)	Visual Appearance	Xray Phase Assembled
X_{WO_3}	$X_{\text{In}_2\text{O}_3}$				
0.22	0.78	900	100	yellow	b+c
		1000	100	white	b+c
		1100	100	white	b+c
		1200	100	white	b+c
0.14	0.86	800	100	yellow	a+d
		900	100	yellow	a+c+d
		1000	100	white	c
		1100	100	white	c
		1200	100	white	c
		1300	100	greenish white	c+d
		1400	100	greenish white	c+d
0.10	0.90	1000	100	yellow	c+d
0.08	0.92	1000	100	yellow	c+d
		1200	100	yellow	c+d
0.06	0.94	1000	100	yellow	c+d
0.04	0.96	1000	100	yellow	c+d
0.02	0.98	1000	100	yellow	c+d
0.00	1.00	1000	50	yellow	d
		1200	100	yellow	d
		1400	50	yellow	d

a= WO_3 , b= $\text{In}_2(\text{WO}_4)_3$, c= $\text{In}_6\text{WO}_{12}$, and d= In_2O_3

2.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were made using a Jupiter STA 449C calorimeter, using nitrogen as a purge gas. A sample powder with the composition of $x_{\text{In}} = 0.4$ was heated at a rate of 5°C/minute from room temperature to 500°C. Measurements were taken while heating and cooling.

2.3 Rietveld Refinement

X-ray diffraction data for $\text{In}_2(\text{WO}_4)_3$ were obtained using a horizontal Siemens D500 with an Osmic GO13N parabolic multilayer optic on the incident beam side and a custom flat multilayer optic on the diffracted beam side with attached furnace. The combination of optics provides a highly parallel beam with divergence on the order of 0.033 degrees. The diffraction furnace is of custom design and is similar to the furnace described by Misture.³⁵ A thin sample was cast onto an alumina plate from an acetone slurry. X-rays were generated at settings of 40kV and 30mA. Heating was accomplished using two hemispherical Pt/20% Rh coils mounted in alumina insulation. The temperature was measured by a Pt/Pt-10% Rh thermocouple welded to the heating element. Measurements were made at 310°C and 225°C. Diffraction patterns were collected between 5° – 120° 2 θ at a step rate of 0.02° per step and a count time of 15 seconds per step. Refinement involved 33 structural parameters including one scale factor, twenty-seven atom positions and five thermal parameters. There were 15 refined profile parameters.

Data for Rietveld Refinement of $\text{In}_6\text{WO}_{12}$ were collected using a thick sample mount on a Siemens D500 diffractometer with Bragg-Brentano geometry. X-rays were generated at settings of 40kV and 30mA. Divergence slits were adjusted to 0.3°. Diffraction patterns were collected between 13° – 130° 2 θ at a step rate of 0.02° per step and a count time of 10 seconds per step. Fifteen parameters were refined including one scale factor, twelve atom positions and two thermal parameters.

All refinements were made using the EXPGUI³⁴ version of the GSAS³⁵ suite of programs.

3. RESULTS AND DISCUSSION

The $\text{In}_2\text{O}_3\text{-WO}_3$ system is a part of the $\text{M}_2\text{O}_3 - \text{WO}_3$ tungstate series described by Aitken *et al.*, where M = the lanthanides and the trivalent cations Sc, Y, and Al.²⁶ A summary of previously identified stable phases in the tungstates series is presented in Table II, as a reference for the following discussion. In the following section, phase analysis is described for various compositions where x_{In} refers to $[\text{In}]/([\text{In}]+[\text{W}])$.

3.1 Bulk Phase Identification

3.1.a Samples Prepared with $x_{\text{In}} \leq 0.40$

Tungsten (VI) oxide powders with indium oxide powder additions at concentrations between $0.167 < x_{\text{In}} < 0.287$ were fired for 7 days at 1000°C in air. Two additional samples, $x_{\text{In}} = 0.333$ and $x_{\text{In}} = 0.375$, were also included. As shown in Table II, materials with indium concentrations between $x_{\text{In}}=0.30$ and $x_{\text{In}}=0.40$ [$\text{In}_2(\text{WO}_4)_3$] have not previously been reported. On average all of the samples lost 3.6% of their initial weight. The observed samples were dark green. The pellets' ability to reflect light increased, while remaining green, as the $[\text{In}]/([\text{W}]+[\text{In}])$ cation ratio was increased.

The collected diffraction patterns are shown in Figure 7. In this region, WO_3 was the primary phase in the powders. Peaks corresponding to indium oxide could not be found. At higher x_{In} concentrations, initial peaks corresponding to $\text{In}_2(\text{WO}_4)_3$ became apparent. Outside this region, the peaks of the $x_{\text{In}} = 0.333$ and $x_{\text{In}} = 0.375$ XRD patterns also correspond to either WO_3 or $\text{In}_2(\text{WO}_4)_3$. The relative intensities of $x_{\text{In}}=0.333$ and $x_{\text{In}} = 0.375$, indicate that as the indium concentration increases, $\text{In}_2(\text{WO}_4)_3$ becomes the phase most present. This is visible through the more intense and sharper peaks of Figures 7d and 7e.

Powder samples with $x_{\text{In}}=0.167$ were examined in the temperature range of $1100^\circ\text{C} - 1300^\circ\text{C}$. Each sample was fired at temperature for 50 hours in platinum foil. A weight loss of 0.27% was measured for the powder fired at 1100°C . At higher temperatures, more than 5% of the initial weight was lost during the firing cycle.

TABLE II. Summary of Reported Phases

Cation 3^+	Ionic Radius [^] (Å)	$M_2O_3 \cdot 3WO_3$ $x_M=0.4$	$M_2O_3 \cdot WO_3$ $x_M=0.66$	$7M_2O_3 \cdot 4WO_3$ $x_M=0.77$	$5M_2O_3 \cdot 2WO_3$ $x_M=0.83$	$3M_2O_3 \cdot WO_3$ $x_M=0.86$
Al	0.530	x	x			⊕
Sc	0.745	x				⊕
In	0.800	x				⊕
Lu	0.861	x	♦			
Yb	0.868	x	♦ ∞			⊕
Tm	0.880	x	♦ ∞			⊕
Er	0.890	x	♦ ∞			
Y	0.900	x	♦ ∞	⊗	⊗	⊕
Ho	0.901	x	♦ ∞			⊕
Dy	0.912	• low/x high	♥ ∞			
Tb	0.925	• low/x high	♥ ∞			⊕
Gd	0.938	• low/x high	♥ ∞			⊕
Eu	0.947	•	♥ ∞			◇
Sm	0.958	•	♥ ∞			⊕
Pm	0.970	•	♥ ∞			
Nd	0.983	•	♥ ∞			⊕
Ce	1.010	•				
Pr	1.030	•	♥ ∞			⊕
La	1.045	•	♠ ∞			⊕

Coordination number of all the cations is VI.

Different symbols mean either different phases or different sources of information.

[^] Ref. ³⁶, ♥♦♦ Ref. ³⁷, • Ref. ¹⁵, x Ref. ²⁰, ⊕ Ref. ²⁶, x Ref. ³⁸, ∞ Ref. ³⁹,

◇ Ref. ⁴⁰, ⊗ Ref. ¹⁷.

Figure 7. X-ray diffraction patterns of samples prepared with: a. $x_{\text{In}} = 0.0$, b. $x_{\text{In}} = 0.1667$, c. $x_{\text{In}} = 0.2308$, d. $x_{\text{In}} = 0.2867$, e. $x_{\text{In}} = 0.333$, and f. $x_{\text{In}} = 0.375$ fired for 7 days at 1000°C .

A powder with $x_{\text{In}} = 0.333$ was further tested at higher temperatures. Sample powders were fired at 1000°C , 1100°C , and 1200°C for 50hrs. The diffractograms are shown in Figure 8. The diffraction pattern of WO_3 fired for 50 hours is provided as a visual aid. As the firing temperature of $x_{\text{In}} = 0.333$ was increased, the amount of $\text{In}_2(\text{WO}_4)_3$ formed increased. The WO_3 component subsequently decreased. Pellets removed from the furnace at 1000°C were white around the edges and green towards the center. As the sintering temperature was increased, the white phase migrated farther towards the center; while the green phase became centrally located at the center of the pellet. The migration is also observable in the relative intensities of the WO_3 phase shown in Figure 8. The peaks corresponding to WO_3 become less intense.

Figure 8. X-ray diffraction patterns of samples prepared with a. $x_{\text{In}} = 0.0$ at 1000°C , b. $x_{\text{In}} = 0.333$ at 1000°C , c. $x_{\text{In}} = 0.333$ at 1100°C d. $x_{\text{In}} = 0.333$ at 1200°C and e. $x_{\text{In}} = 0.40$.

Figure 9. X-ray diffraction patterns of $\text{In}_2(\text{WO}_4)_3$ samples prepared by solid state reaction at: a. WO_3 at 1000°C , b. 800°C , c. 1000°C , and d. 1200°C , and e. 1300°C .

3.1.b Samples Prepared with $x_{\text{In}} = 0.4$

3.1.b.i Samples Prepared via Solid-State Reaction

Solid-state reaction was the first method of material processing used in this report due to its simplicity. Figure 9 shows the phase evolution of the samples prepared with $x_{\text{In}} = 0.40$ as the firing temperature is increased from 800 - 1400°C. Peaks in Figure 9 correspond to $\text{In}_2(\text{WO}_4)_3$ (PDF card #49-0337), possibly $\text{In}_6\text{WO}_{12}$, and possibly WO_3 . Filled circles indicate peaks listed in PDF card #49-0337, while open circles were additional peaks. The dashed vertical line Figure 9 is located at the end of the $\text{In}_2(\text{WO}_4)_3$ peak list for PDF card # 49-0337.

Samples at 800°C were yellow and green. The green phase was assumed to be WO_3 . The yellow color of the $\text{In}_2(\text{WO}_4)_3$ pellet fired to 800°C is characteristic of unreacted In_2O_3 . The X-ray diffraction patterns for samples prepared at 1000°C and 1200°C were generally consistent with PDF card #49-0337, which reports reflections over the range 10° to 34° 2 θ Cu-K α . Above 34° 2 θ , the diffraction patterns of the powders fired to 1000°C and 1200°C differ. Both patterns appeared to be crystalline, but the intensity and location of the measured peaks were not all the same. Samples heated at 1300°C and 1400°C exhibited excessive weight loss, i.e. more than 5% of their initial weight. They were gray and white. Development of a second phase was quite evident for $\text{In}_2(\text{WO}_4)_3$ samples heated to 1400°C. On the sample surface, shiny gray filings were visible. XRD patterns of the crushed filings were identical to $\text{In}_6\text{WO}_{12}$, PDF card #74-1410.

A different synthesis method was thought necessary to yield better definition of the measured diffraction profile. Some sample powders had been fired for as long as 150 hours to either complete the reaction or promote grain development without better definition in the measured diffraction pattern. The solid solution method was changed to a solution synthesis process.

3.1.b.ii Samples Prepared via Solution Synthesis

Oxide powders were prepared in solution, reacted and equilibrated at temperatures ranging from 800 – 1300°C. The measured XRD patterns are shown in Figure 10. Similar XRD results from the solution-derived mixed-oxide powders, as

compared, to the solid state derived powders were collected, with a few exceptions. In general, the raw data of Figure 10 has less background noise and the peaks at low angles are sharper. At high angles, the peaks have less intensity and may be overlapped. Samples fired at 800°C were white without any yellow present, suggesting the absence of unreacted In_2O_3 . The XRD pattern of the 800°C sample does not show peaks in the region of $20 - 30^\circ 2\theta$ that are attributed in Figure 9 to WO_3 . This suggested a more phase-pure material. The corresponding SEM micrograph, shown in Figure 11, indicated a relatively homogeneous sample with fine grain size. The micrograph was taken using backscattered electrons. The small grain size was representative of the fragile nature of the material. Samples of $x_{\text{In}} = 0.40$ prepared at 1000°C and 1200°C were also believed to be nominally phase pure. The diffraction peaks of the samples were consistent with regard to peak position and peak height.

Other similarities to the solid state derived powders of interest were the two well-defined, low-intensity peaks at $\sim 25.5^\circ$ and $\sim 30.4^\circ$ in the diffraction patterns shown as Figure 9 b and c. These peaks are not reported in the powder diffraction file for $\text{In}_2(\text{WO}_4)_3$, PDF 49-0337, or those of any other reported WO_3 - In_2O_3 phase. One probable explanation of the feature is that the samples were not, as originally believed, phase pure. Quenching conditions in air were not strictly controlled allowing for partial phase transformations during cooling resulting in a product containing orthorhombic as well as monoclinic $\text{In}_2(\text{WO}_4)_3$. Similar to the solid-solution samples, pellets heated at 1300°C and 1400°C exhibited excessive weight loss and were gray and white. Samples powders fired to 1400°C showed gray sand around the exterior of the pellet instead of the needle-like whiskers formed by solid-state synthesis.

Figure 10. X-ray diffraction patterns of $\text{In}_2(\text{WO}_4)_3$ samples prepared by solution method at: a. WO_3 at 1000°C, b. 800°C, c. 1000°C, d. 1200°C, and e. 1300°C.

Figure 11. SEM image of $x_{\text{In}}=0.40$ prepared by solution method fired to 800°C using back-scattered electrons.

3.1.c Samples Prepared with $x_{\text{In}} = 0.5, 0.67$ and 0.78

Table II documents the plethora of literature on stable oxytungstates with $x_{\text{In}} = 0.5, 0.667$, and 0.778 . Sample oxide powders with $x_{\text{In}} = 0.50, 0.667$, and 0.78 were prepared by solid-state reaction and fired to temperatures between 800°C and 1200°C . Figure 13 shows the diffraction patterns of powders with cation ratios corresponding to $x_{\text{In}} = 0.5$ and 0.778 fired at 900°C . Characteristic of all the samples fired between 800°C and 900°C is that they were yellow after quenching. The yellow color is characteristic of unreacted In_2O_3 . The arrow in Figure 12 indicates the single indium oxide peak detectable in both samples. The rest of the peaks corresponded to either $\text{In}_2(\text{WO}_4)_3$ or $\text{In}_6\text{WO}_{12}$, so labeled in Figure 13. Figure 13 shows the diffraction patterns of powder samples with $x_{\text{In}} = 0.5, 0.667$, and 0.778 fired to 1100°C . All of these samples fired between 1000°C and 1200°C were white. Indium oxide was not detected. Again the distinguishable peaks correspond to either $x_{\text{In}} = 0.40$ [$\text{In}_2(\text{WO}_4)_3$] or $x_{\text{In}} = 0.857$ [$\text{In}_6\text{WO}_{12}$]. Extra peaks corresponding to additional phases such as $\text{In}_2\text{W}_2\text{O}_9$, In_2WO_6 , and $\text{In}_{14}\text{W}_4\text{O}_{33}$ are not present in Figures 12 and 13. This is a rather interesting result given that similar phases have been reported for the smaller Al^{3+} ($0.537\text{\AA}$) cation and the larger Y^{3+} ($0.978\text{\AA}$) cation. The radius of the In^{3+} cation has been measured at $0.800\text{\AA}$ ³⁶

Figure 12. X-ray diffraction patterns of samples prepared with: a. $x_{\text{In}} = 0.500$ and b. $= 0.778$ at 900°C .

Figure 13. X-ray diffraction patterns of samples prepared with: a. $x_{\text{In}} = 0.500$, b. $x_{\text{In}} = 0.667$, and c. $x_{\text{In}} = 0.7787$ at 1100°C .

Powders with $x_{\text{In}} = 0.667$ and 0.778 initially fired to 1200°C were annealed at 900 and 800°C for several days with no evidence of dissociation to either In_2O_3 or WO_3 . Thus, $\text{In}_6\text{WO}_{12}$ and $\text{In}_2(\text{WO}_4)_3$ are assumed to be stable at these temperatures.

3.1.d Samples Prepared with $x_{\text{In}} = 0.86$

The x-ray diffraction patterns presented in Figure 14 are powder data synthesized via solid solution. Similar to the $x_{\text{In}}=0.40$ powders, sample powders fired below 1000°C were yellow. The diffraction pattern of powders fired to 800°C has peaks corresponding to In_2O_3 . Small peaks between 22° and 26° 2θ may correspond to WO_3 . The large mole fraction of In_2O_3 compared to WO_3 may be overshadowing the WO_3 peaks. At 900°C , $\text{In}_6\text{WO}_{12}$ diffraction peaks are visible. Samples heated at 1000°C and 1200°C were white. The corresponding XRD patterns indicated the presence of only $\text{In}_6\text{WO}_{12}$. Figure 15 shows a SEM image of sample powder fired to 1000°C . The region shown is of small grain size with consistent coloration.

Lattice parameter measurements were made on samples fired to 1000°C and 1200°C . Assuming a rhombohedral symmetry, the lattice parameters for powders fired to 1000°C were $a_{\text{R}} = 6.2323(1) \text{ \AA}$ and $\alpha = 99.029(3)^{\circ}$ [hexagonal axes: $a_{\text{HEX}} = 9.4803(4) \text{ \AA}$ and $c_{\text{HEX}} = 8.9414(4) \text{ \AA}$]; for the samples heated to 1200°C $a_{\text{R}}=6.2323(8) \text{ \AA}$ and $\alpha=99.030(1)^{\circ}$ [$a_{\text{HEX}}=9.4804(5) \text{ \AA}$ and $c_{\text{HEX}}=8.9414(7) \text{ \AA}$]. These lattice parameter values were in close agreement to the single-crystal lattice parameters reported by Michel and Kahn.⁴¹ Their values were $a_{\text{R}}=6.2277(9) \text{ \AA}$ and $\alpha=99.01^{\circ}(1)$ [$a_{\text{HEX}}=9.472(5) \text{ \AA}$ and $c_{\text{HEX}}=8.939(2) \text{ \AA}$]. Samples equilibrated at 1200°C were annealed at 800° and 900°C for several days with no evidence of dissociation, indicating that $\text{In}_6\text{WO}_{12}$ is stable at those temperatures. The XRD patterns of samples heated at 1300°C and 1400°C showed evidence of In_2O_3 in addition to $\text{In}_6\text{WO}_{12}$. These samples were greenish yellow throughout the sample.

Figure 14. X-ray diffraction patterns of $x_{\text{In}} = 0.867 \text{ In}_6\text{WO}_{12}$ powders fired at a. 800°C, b. 900°C, c. 1000°C, d. 1200°C and e. 1300°C.

Figure 15. SEM image of $x_{\text{In}} = 0.857 [\text{In}_6\text{WO}_{12}]$ at 1000°C.

These samples though did not exhibit excessive weight loss. Samples heated at 1400°C for an extended period of time did experience excessive weight loss, suggesting that WO_3 is preferentially lost at the higher temperatures.

Sample powders were formed using two different liquid synthesis methods. The first followed the method described by Dabney *et al.*²⁹ The second followed the method described in the experimental section for $x_{\text{In}}=0.40$ using $\text{In}(\text{NO}_3)_3$ and H_2WO_4 . Changes to the ratio of In : W were made accordingly. The diffraction patterns of the powders created by both methods were identical to the diffraction patterns of the powders produced via solid state.

3.1.f Samples Prepared with $x_{\text{In}} = 0.90 - 0.98$

Samples with $x_{\text{In}} = 0.90 - 0.98$ were prepared and characterized to determine whether or not W could be incorporated into the bixbyite structure to form an In_2O_3 solid solution. X-ray diffraction patterns of samples prepared with $x_{\text{In}} = 0.92 - 1.0$ are presented in Figure 16. The $x_{\text{In}} = 0.98$ pattern, Figure 16f, shows the presence of $\text{In}_6\text{WO}_{12}$. This suggests that the solubility limit of W in In_2O_3 has been surpassed. However, Figure 17, which illustrates the lattice parameters of In_2O_3 with increasing W content, shows that the lattice parameter of In_2O_3 increases with increasing W content, above 2 cation %. Such trends often indicate the continued incorporation of a different sized cation into the parent structure. We speculate that the increased $\text{In}_6\text{WO}_{12}$ content with increasing W, is affecting accurate lattice parameter determination because of extensive peak overlap in the two patterns.

Figure 16. X-ray diffraction patterns of samples prepared with: a. $x_{\text{In}} = 0.857$, b. $x_{\text{In}} = 0.90$, c. $x_{\text{In}} = 0.92$, d. $x_{\text{In}} = 0.94$, e. $x_{\text{In}} = 0.96$, f. $x_{\text{In}} = 0.98$.

Figure 17. Measured lattice parameter as a function of tungsten concentration.

Figure 18 is a proposed subsolidus phase diagram for the $\text{In}_2\text{O}_3\text{-WO}_3$ system based on the work presented in the above section. The work was performed in ambient atmosphere using oxide-starting materials.

Figure 18. Proposed formation diagram for the $\text{WO}_3\text{-InO}_{1.5}$ system. Solid circles indicate nominally phase-pure materials identified in this study. Open circles indicate biphasic samples identified in this study.

3.2 Structure Refinement of Stable Phases

In the In_2O_3 - WO_3 system, two binary oxides, $\text{In}_2(\text{WO}_4)_3$ and $\text{In}_6\text{WO}_{12}$, were found to be stable phases in the temperature region of 800-1200°C in air atmosphere. Structure refinement via the Rietveld technique was undertaken to understand the structural principles of the identified materials.

3.2.a Differential Scanning Calorimetry (DSC)

Literature reports by Kohler *et al.* suggested that $\text{In}_2(\text{WO}_4)_3$ exhibited a first order orthorhombic/monoclinic phase change around 250°C.² DSC measurements were made to confirm such a transition. Figure 19 shows DSC data confirming a first order phase transition between 230 °C – 260°C for $\text{In}_2(\text{WO}_4)_3$.

Figure 19. Differential scanning calorimetry curve of $\text{In}_2(\text{WO}_4)_3$.

3.2.b $\text{In}_2(\text{WO}_4)_3$ at 310°C (583K)

Rietveld analysis was conducted on x-ray data for the high temperature, orthorhombic phase, of $\text{In}_2(\text{WO}_4)_3$. Many literature reports have identified $\text{In}_2(\text{WO}_4)_3$ as being isostructural with $\text{Sc}_2(\text{WO}_4)_3$.^{2,15,18} The refined XRD data measured at 310°C is shown in Figure 20. The sample powder used was prepared by solution-synthesis and fired at 800°C. Refinement was based upon 5600 measured reflections. Initial atom positions were taken from the reported positions by Evans *et al.* for $\text{Sc}_2(\text{WO}_4)_3$ at 300K.²⁴ Initial lattice parameters were taken from indexing the pattern using the Jade® software package. A 7-variable shifted-Chebyshev polynomial of the first kind described the background. Peak profiles were described using the pseudo-Voigt function described by Thompson *et al.*³⁵ The refined profile parameters were LX, LY, the transparency, the asymmetry and the zero shift due to the improved resolution of a multilayer optic diffractometer. Oxygen thermal parameters were constrained to 0.01. In_2O_3 was refined as a minor phase. Refinement of the above parameters resulted in residual values of: $\chi^2 = 1.9$, wRp = 12%, and Rp = 9%.

$\text{In}_2(\text{WO}_4)_3$ has previously been studied by several investigators with conflicting results. Swanson and Anderson describe single crystals of $\text{In}_2(\text{WO}_4)_3$ as orthorhombic with unit cell dimensions $a=10.72$ (2) Å, $b=13.04$ (2) Å, and $c=10.35$ Å.⁴² Nassau *et al.* also report an orthorhombic unit cell for $\text{In}_2(\text{WO}_4)_3$ powder, but with cell dimensions of $a=9.3$ Å, $b=13.3$ Å, and $c=9.3$ Å.¹⁵ The refined lattice parameters of this data were: $a=9.7125$ (5) Å, $b=13.3823$ (6) Å, $c=9.6141$ (5) Å, which are in closer agreement to those of Nassau *et al.*

Details of the orthorhombic Pnca structure with 4 molecules per unit cell for $\text{Sc}_2(\text{WO}_4)_3$ have been given by Evans *et al.*²⁴ The structure is constructed by corner-sharing layers of WO_4 tetrahedra and ScO_6 octahedra extended along the [100] and [001] directions. The 2D polyhedra layers build up a 3-D network of $\text{Sc}_2\text{W}_3\text{O}_{18}$ tunnel units.¹⁸ Evans *et al.* uses the term “lantern like” to describe the open framework. These open frameworks are linked via oxygen atoms, O(3), parallel to the b-axis. The resulting 3D structure contains open tunnels in which ionic conduction of M^{3+} ions has been known to occur.^{2,18}

Tables III, IV, and VI contain the refined atomic positions, bond lengths, and bonding angles. The atomic coordinates are in close agreement with the published work of Evans *et al.* Further refinement of the profile may be necessary. Table V shows selected bond distances of $\text{Sc}_2(\text{WO}_4)_3$ at 300K. The bond length data of $\text{In}_2(\text{WO}_4)_3$ presented in Table IV, are in close agreement to Table V. Factors mitigating the observed differences are the radius size difference between In^{3+} and Sc^{3+} as well as the sample temperature at measurement difference. The data reported here was taken at approximately 583K as compared to 300K. $\text{In}_2(\text{WO}_4)_3$ is a positively expanding material compared to $\text{Sc}_2(\text{WO}_4)_3$ which is negatively expanding material.²³ Comparable bond angle data was not available. However, similar factors affecting the bond differences should account for differences in bond angles.

Lambda = 1.540562, L-S Cycle 389

Hist #1

Observ & Diff data

Figure 20. Observed (+), calculated (line), and difference (lower line) of $\text{In}_2(\text{WO}_4)_3$ heated to 310°C (598K). The samples was synthesized via solution-method and re-fired to 800°C (1073K). Tick marks represent predicted peak positions of $\text{In}_2(\text{WO}_4)_3$ (higher) and In_2O_3 (lower).

TABLE III. Atomic Coordinates and Anisotropic Thermal Parameters of $\text{In}_2(\text{WO}_4)_3$ at 310°C (583K)

(Space Group Pnca ; $a = 9.71181$ (17) Å, $b = 13.38098$ (24) Å, $c = 9.61325$ (18) Å)

Atom	Position	x	y	z	U*100
In	8d	0.4674 (3) [0.46688 (22)]	0.3816 (2) [0.38110 (17)]	0.2495 (4) [0.24937 (31)]	0.12 (2)
W1	4c	0.2500000 (0) [0.25]	0.000000 (0) [0.0]	0.4719 (4) [0.4743 (8)]	0.016 (2)
W2	8d	0.1164 (3) [0.1188 (6)]	0.3551 (2) [0.3557 (4)]	0.3942 (3) [0.3949 (5)]	0.016 (2)
O1	8d	0.112 (3) [0.0917 (5)]	0.148 (2) [0.14199 (39)]	0.091 (27) [0.0770 (5)]	1.0 ^a
O2	8d	0.142 (3) [0.1302 (5)]	0.066 (2) [0.06284 (35)]	0.351 (3) [0.3693 (5)]	1.0 ^a
O3	8d	-0.022 (3) [0.0118 (5)]	0.272 (2) [0.26323 (38)]	0.317 (3) [0.3215 (5)]	1.0 ^a
O4	8d	0.333 (2) [0.3358 (5)]	0.391 (2) [0.41072 (35)]	0.062 (2) [0.0787 (5)]	1.0 ^a
O5	8d	0.071 (2) [0.0733 (5)]	0.464 (2) [0.47255 (36)]	0.321 (3) [0.3226 (5)]	1.0 ^a
O6	8d	0.302 (3) [0.2923 (5)]	0.330 (2) [0.33169 (35)]	0.353 (3) [0.3608 (5)]	1.0 ^a

wRp = 12%; Rp = 9%;

$\chi^2 = 1.9$

^a Isotropic thermal factors held constant during refinement

[] indicate work of Ref. ²³

TABLE IV. Interatomic Distances (Å) of $\text{In}_2(\text{WO}_4)_3$ at 310°C (583K)

Atoms	Length	In Octahedron Length		Metal	Length Metal Distance
<i>W(1) tetrahedron</i>		<i>In Octahedron</i>			
W(1) – O(2)	1.80 (3)	In – O(1)	2.12 (3)	In – W(1)	3.74 (6)
W(1) – O(2)	1.88 (2)	In – O(2)	2.08 (3)	In – W(1)	3.82 (6)
O(2) – O(2')	2.58 (6)	In – O(3)	2.16 (3)	In – W(1)	3.74 (6)
O(2) – O(4)	3.06 (5)	In – O(4)	2.23 (2)	In – W(1)	3.75 (5)
O(2) – O(4')	2.80 (5)	In – O(5)	2.21 (3)	In – W(1)	3.88 (5)
O(4) – O(4')	3.20 (5)	In – O(6)	2.01 (3)	In – W(1)	3.70 (6)
		O(1) – O(2)	2.80 (5)		
W(2) tetrahedron		O(1) – O(3)	3.08 (5)		
W(2) – O(1)	1.89 (2)	O(1) – O(5)	3.18 (5)		
W(2) – O(3)	1.89 (2)	O(1) – O(6)	3.06 (5)		
W(2) – O(5)	1.68 (2)	O(2) – O(3)	3.24 (5)		
W(2) – O(6)	1.88 (3)	O(2) – O(4)	3.23 (5)		
O(1) – O(3)	3.02 (6)	O(2) – O(5)	2.97 (5)		
O(1) – O(5)	2.98 (5)	O(3) – O(4)	2.89 (4)		
O(1) – O(6)	2.87 (5)	O(3) – O(6)	2.78 (5)		
O(3) – O(5)	2.70 (8)	O(4) – O(5)	3.24 (5)		
O(3) – O(6)	3.23 (6)	O(4) – O(6)	3.01 (5)		
O(5) – O(6)	2.94 (3)	O(5) – O(6)	3.07 (5)		

TABLE V. Selected Bond Distances(Å) of $\text{Sc}_2(\text{WO}_4)_3$ at 300K.*

Atom	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
Sc1	2.079 (5)	2.086 (5)	2.086 (5)	2.109 (5)	2.105 (5)	2.105 (5)
W1		1.749 (6)		1.763 (6)		
W2	1.765 (7)		1.757 (7)		1.760 (7)	1.740 (7)

*indicates work of Ref. ²³

TABLE VI. Bond Angles (°) of $\text{In}_2(\text{WO}_4)_3$ at 310°C (583K).

Atom	Angle	Atom	Angle
<i>W(1) tetrahedron</i>		<i>In Octahedron</i>	
O(2) – W1-O(2')	93.5 (16)	O(1) – In – O(2)	81.1 (9)
O(2) – W1-O(4)	115.8 (11)	O(1) – In – O(3)	90.9 (10)
O(2) – W1-O(4')	101.7 (10)	O(1) – In – O(4)	172.3 (10)
O(4) – W1-O(4')	124.6 (15)	O(1) – In – O(5)	93.0 (10)
		O(1) – In – O(6)	93.3 (11)
		O(2) – In – O(3)	98.1 (10)
		O(2) – In – O(4)	95.7 (10)
		O(2) – In – O(5)	86.3 (8)
W(2) tetrahedron		O(2) – In – O(6)	174.3 (11)
O(1) – W2 – O(3)	110.8 (12)	O(3) – In – O(4)	82.6 (9)
O(1) – W2 – O(5)	116.6 (12)	O(3) – In – O(5)	174.5 (9)
O(1) – W2 – O(6)	101.4 (11)	O(3) – In – O(6)	83.3 (10)
O(3) – W2 – O(5)	99.2 (11)	O(4) – In – O(5)	93.8 (9)
O(3) – W2 – O(6)	119.3 (12)	O(4) – In – O(6)	90.0 (9)
O(5) – W2 – O(6)	110.4 (11)	O(5) – In – O(6)	92.7 (10)

3.2. c $\text{In}_2(\text{WO}_4)_3$ at 225°C (498K)

Sleight and Brixner investigated the monoclinic – to – orthorhombic phase transition of many $\text{Sc}_2(\text{WO}_4)_3$ -type Pnca materials, including $\text{In}_2(\text{WO}_4)_3$. Materials transitioned from the Pnca structure to monoclinic $\text{P } 2_1/a$, which is a ferroelastic transition. The given monoclinic prototype of $\text{P } 2_1/a$ was $\text{Fe}_2(\text{MoO}_4)_3$. Sleight and Brixner also identified the phase transition temperature and measured lattice parameters of these materials. $\text{In}_2(\text{WO}_4)_3$ transitioned at 252°C.⁴³ DSC data shown in Figure 19 agrees with this data.

Data for the low temperature phase of $\text{In}_2(\text{WO}_4)_3$ were collected below the transition temperature at 225°C. A total of 5600 data points were collected. Initial lattice parameters were taken from the work of Sleight and Brixner.⁴³ Atom positions were taken from Chen's report on the refinement of $\text{Fe}_2(\text{MoO}_4)_3$.⁴⁴ A 5-variable shifted-Chebyshev polynomial of the first kind described the background. Peak profiles were described using the pseudo-Voight function described by Thompson *et al.*³⁷ The refined profile parameters were LX, LY, the transparency, the asymmetry and the zero shift. Thermal parameters of the oxygen atoms were constrained to a value of 0.01. Refinement of only the cation positions and thermal parameters resulted in residual statistics of $\chi^2 = 1.9$, $\text{wRp} = 12\%$, and $\text{Rp} = 9.5\%$. Oxygen positions were varied; however, the resulting bond angles were not realistic. Therefore, the oxygen positions were constrained to their original positions. Further refinement was carried out assuming second phases of In_2O_3 . Final refinements suggested that In_2O_3 was a minor phase at 2.5 wt. %.

A cartoon, Figure 22, is presented using Chen's refined data of $\text{Fe}_2(\text{MoO}_4)_3$ to give an overview of the space group $\text{P } 2_1/a$. Blue balls represent iron atoms, molybdenum atoms are red, and oxygen atoms are yellow. The structure of $\text{Fe}_2(\text{MoO}_4)_3$ consists of corner sharing octahedra and tetrahedra. Using the direct method, Chen determined that the average bond length of Mo – O and Fe – O as well as the O – M – O bond angles were close to those of ideal polyhedra. The average M – O bond length was $1.754 \pm 0.004 \text{ \AA}$, compared to an ideal $1.76 \text{ \AA}$. Fe – O bond distances measured $1.990 \pm 0.005 \text{ \AA}$, compared to the ideal $1.995 \text{ \AA}$ using the high spin Fe^{3+} radius. The measured tetrahedral angles of all MoO_4 polyhedra were 109° and 90° for FeO_6 octahedra.⁴⁴

Assuming similar behavior with the low temperature phase of $\text{In}_2(\text{WO}_4)_3$, the ideal bond lengths were calculated to be 1.90 Å for W – O distances and 1.995 Å for In – O distances. Bond angles should measure the same 90° for octahedral coordination and 109° for tetrahedral coordinated polyhedra. The measured lattice parameters and the average bond distances and bond angles are presented in Tables VII and VIII.

Atomic positions of the cations show minor deviations from the Fe and Mo starting positions. Note that of 34 atoms and thermal parameters, only 10 atom sites and corresponding thermal parameters were refined. The oxygen atom positions were refined. However, the resulting bond distances of W – O or In – O were less than 1 Å. This was believed to be unrealistic using the guidelines presented for $\text{Fe}_2(\text{MoO}_4)_3$. Thus the oxygen atom positions were fixed to those values reported by Chen.⁴⁴ The data is presented to show that the low temperature form of $\text{In}_2(\text{WO}_4)_3$ is best described using the $\text{Fe}_2(\text{MoO}_4)_3$ -type $P 2_1/a$ crystal group. The W – O bond lengths, on average, are slightly smaller than the ideal at 1.836 (14) Å, while the In – O bond lengths are slightly larger at an average of 2.082 (20) Å. The bond angles are close to ideal at 109.37 (7)° for the WO_4 tetrahedra and 89.96 (8) ° for the InO_6 octahedra. Lattice parameters were also in close agreement with those measured by Sleight and Brixner. Refined lattice parameters were 16.4061 (17) Å, $b = 9.6629$ (10) Å, $c = 19.0989$ (19) Å, and $\beta = 125.4105$ (4)° compared to published values of 16.359 Å, $b = 9.632$ Å, $c = 19.006$ Å, and $\beta = 125.30$ °.⁴³ Therefore, it is believed that the low temperature phase of $\text{In}_2(\text{WO}_4)_3$ crystallizes in the monoclinic $P 2_1/a$ space group. A more definitive picture of the monoclinic phase as well as definition of minor phases would be possible using neutrons as an energy source.

Lamda = 1.540562, L-S Cycle 410

Hist 1
Obsvd & Diff Data

Figure 21. Observed (+), calculated (line), and difference (lower line) of $\text{In}_2(\text{WO}_4)_3$ heated to 225°C (498K). The sample powder was synthesized via solution-method and fired to 800°C (1073K). Tick marks represent predicted peak positions of $\text{In}_2(\text{WO}_4)_3$.

Figure 22. Monoclinic P $2_1/a$ structure of $M_2(MoO_4)_3$. Figure was generated using atomic positions reported by Chen.⁴⁴ Blue (smallest) balls represent M atom, red (small) balls represent molybdenum, and yellow (larger) balls represent oxygen.

TABLE VII. Atomic Coordinates and Anisotropic Thermal Parameters of $\text{In}_2(\text{WO}_4)_3$ at 225°C (498K)

(Space Group $P 2_1/a$; $a = 16.40444$ (44) Å, $b = 9.66161$ (20) Å, $c = 19.09642$ (48) Å, $\beta = 125.4127$ (2)°)

Atom	Position	x	y	z	U*100 (Å ²)
W1	4e	-0.0079 (10) [-0.00713 (4)]	0.2492 (17) [0.24655 (8)]	0.4862 (8) [0.48740 (4)]	3.31 (37)
W2	4e	0.3556 (10) [0.36091 (4)]	0.1133 (17) [0.12818 (8)]	0.1306(8) [0.13732 (4)]	2.80 (39)
W3	4e	0.1410 (9) [0.13921 (4)]	0.1104 (15) [0.11241 (8)]	0.2559 (6) [0.24898 (4)]	2.47 (41)
W4	4e	0.1476 (11) [0.15104 (4)]	0.6162 (19) [0.61604 (8)]	0.3822 (7) [0.38521 (4)]	4.65 (53)
W5	4e	0.3526 (9) [0.35122 (4)]	0.6299 (14) [0.63085 (8)]	0.2177 (7) [0.21211 (4)]	2.87 (41)
W6	4e	-0.0004 (11) [0.00270 (4)]	0.7486 (18) [0.74458 (8)]	0.0178 (8) [0.01982 (4)]	3.14 (33)
In1	4e	0.3821 (18) [0.38066 (7)]	0.9603 (28) [0.9651 (1)]	0.3168 (14) [0.31899 (4)]	2.4 (5)
In2	4e	0.3728 (14) [0.37004 (7)]	0.4610 (21) [0.4593 (1)]	0.0527 (11) [0.04482 (6)]	3.7 (6)
In3	4e	0.1212 (17) [0.11910 (7)]	0.4797 (25) [0.4738 (1)]	0.1878 (13) [0.18524 (6)]	2.3 (5)
In4	4e	0.1102 (13) [0.10588 (7)]	0.9812 (21) [0.9830 (1)]	0.4242 (11) [0.41592 (6)]	2.6 (6)
O1 ^a	4e	0.5817 (0)	0.3872 (0)	0.-0.0001 (0)	1.0
O2 ^a	4e	0.9882 (0)	0.4875 (0)	0.1715 (0)	1.0
O3 ^a	4e	0.8280 (0)	0.1937 (0)	0.0949 (0)	1.0
O4 ^a	4e	0.7744 (0)	0.4974 (0)	0.0544 (0)	1.0
O5 ^a	4e	0.5225 (0)	0.4253 (0)	0.1443 (0)	1.0

TABLE VII continued. Atomic Coordinates and Anisotropic Thermal Parameters of $\text{In}_2(\text{WO}_4)_3$ at 225°C (498K)

(Space Group P 2₁/a; a = 16.40444 (44) Å, b = 9.66161 (20) Å, c = 19.09642 (48) Å, β = 125.4127 (2) °)

Atom	Position	x	y	z	U*100 (Å ²)
O6 ^a	4e	0.7321 (0)	0.5194 (0)	0.2728 (0)	1.0
O7 ^a	4e	0.4204 (0)	0.1099 (0)	0.4139 (0)	1.0
O8 ^a	4e	0.1843 (0)	0.2854 (0)	0.2464 (0)	1.0
O9 ^a	4e	0.5482 (0)	0.3536 (0)	0.4437 (0)	1.0
O10 ^a	4e	0.3877 (0)	0.3088 (0)	0.9753 (0)	1.0
O11 ^a	4e	0.0644 (0)	0.3818 (0)	0.0674 (0)	1.0
O12 ^a	4e	0.4115 (0)	0.3627 (0)	0.5010 (0)	1.0
O13 ^a	4e	0.8575 (0)	0.3829 (0)	0.2325 (0)	1.0
O14 ^a	4e	0.2484 (0)	0.0396 (0)	0.5128 (0)	1.0
O15 ^a	4e	0.1164 (0)	0.1065 (0)	0.3324 (0)	1.0
O16 ^a	4e	0.5327 (0)	0.9432 (0)	0.3626 (0)	1.0
O17 ^a	4e	0.7422 (0)	0.9597 (0)	0.1926 (0)	1.0
O18 ^a	4e	0.6654 (0)	0.9378 (0)	0.3007 (0)	1.0
O19 ^a	4e	0.9619 (0)	0.9339 (0)	0.3116 (0)	1.0
O20 ^a	4e	0.0945 (0)	0.3111 (0)	0.5939 (0)	1.0
O21 ^a	4e	0.1568 (0)	0.8062 (0)	0.3913 (0)	1.0
O22 ^a	4e	0.0451 (0)	0.6577 (0)	0.1210 (0)	1.0
O23 ^a	4e	0.3629 (0)	0.6027 (0)	0.1228 (0)	1.0
O24 ^a	4e	0.3438 (0)	0.8171 (0)	0.2257 (0)	1.0

wRp = 12%; Rp = 9.5%; χ^2 = 1.9

^a Isotropic thermal factors and lattice positions held constant during refinement
[] indicates data reported by Ref. ⁴⁴

TABLE VIII. Average Bond Distances (Å) of W – O and Average O – W – O Angles of Monoclinic $\text{In}_2(\text{WO}_4)_3$ at 225°C (498K)

Atoms	Length	Atom	Length
W(1) – O(7)	1.813 (15)	W(2) – O(2)	1.848 (14)
W(1) – O(7)	1.808 (13)	W(2) – O(2)	1.947 (16)
W(1) – O(7)	1.877 (15)	W(2) – O(2)	1.670 (15)
W(1) – O(7)	1.838 (14)	W(2) – O(2)	1.928 (12)
Average	1.834 (14)	Average	1.848 (14)
	[1.753 (6)]		[1.759 (8)]
Average O- W –O angle 109.45 (7.3)		Average O- W –O angle 109.16 (7.3)	
	[109.47 (1.33)]		[109.46 (1.15)]
W(3) – O(5)	1.908 (11)	W(4) – O(14)	1.875 (14)
W(3) – O(6)	1.831 (13)	W(4) – O(16)	1.790 (16)
W(3) – O(8)	1.883 (14)	W(4) – O(18)	1.819 (13)
W(3) – O(15)	1.726 (11)	W(4) – O(21)	1.842 (19)
Average	1.837 (12)	Average	1.832 (16)
	[1.754 (4)]		[1.750 (6)]
Average O- W –O angle 109.38 (6.8)		Average O- W –O angle 109.42 (7.8)	
	[109.49 (0.55)]		[109.47 (0.91)]
W(5) – O(17)	1.805 (13)	W(6) – O(1)	1.779 (16)
W(5) – O(19)	1.756 (11)	W(6) – O(10)	1.869 (15)
W(5) – O(23)	1.932 (11)	W(6) – O(11)	1.832 (15)
W(5) – O(24)	1.827 (13)	W(6) – O(22)	1.872 (13)
Average	1.830 (12)	Average	1.838 (15)
	[1.749 (7)]		[1.757 (11)]
Average O- W –O angle 109.42 (6.2)		Average O- W –O angle 109.43 (9.8)	
	[109.49 (1.39)]		[109.47 (0.91)]

TABLE VIII continued. Average Bond Distances (Å) and Average O – W – O Angles of In₂(WO₄)₃ at 225°C (498K)

Atoms	Length	Atom	Length
In(1) – O(6)	2.098 (25)	In(2) – O(1)	2.142 (19)
In(1) – O(7)	2.138 (23)	In(2) – O(3)	2.027 (19)
In(1) – O(13)	2.074 (25)	In(2) – O(4)	2.110 (18)
In(1) – O(16)	2.096 (25)	In(2) – O(5)	2.057 (18)
In(1) – O(20)	2.091 (24)	In(2) – O(10)	2.197 (18)
In(1) – O(24)	2.018 (23)	In(2) – O(23)	1.986 (18)
Average	2.085 (24)	Average	2.086 (18)
	[1.994 (26)]		[1.993(22)]
Average O- W –O angle 90.01 (9.4)		Average O- W –O angle 89.94 (7.2)	
	[90.06 (1.55)]		[90.00 (2.21)]
In(3) – O(2)	2.135 (24)	In(4) – O(9)	2.039 (18)
In(3) – O(8)	2.123 (22)	In(4) – O(12)	2.017 (18)
In(3) – O(11)	2.136 (22)	In(4) – O(14)	1.968 (18)
In(3) – O(17)	2.020 (24)	In(4) – O(15)	2.180 (18)
In(3) – O(18)	2.000 (21)	In(4) – O(19)	2.166 (18)
In(3) – O(22)	2.073 (22)	In(4) – O(21)	2.098 (18)
Average	2.081 (22)	Average	2.078 (18)
	1.988 (25)		[1.983 (20)]
Average O- W –O angle 89.94 (8.7)		Average O- W –O angle 89.94 (7.2)	
	[89.98 (1.86)]		[90.02 (2.28)]

[] indicates data reported by Ref. ⁴⁴

3.2. d. Structure Analysis of $\text{In}_6\text{WO}_{12}$

A bulk powder sample of $\text{In}_6\text{WO}_{12}$ was used to collect 6800 reflections for Rietveld refinement. The initial structure model for the powder data was the single crystal work of Michel and Kahn.⁴¹ Twelve atom positions including thermal parameters as well as the peak profile were varied. Profile variables U, V, W and the Scherrer coefficient for Gaussian broadening were constrained during refinement. The peak profiles were described using a pseudo-Voigt function with the Finger-Cox-Jephcoat asymmetry parameter. The asymmetry parameter does a better job of modeling low angle asymmetry.³⁵ A seven variable shifted Chebychev polynomial of the first kind was used to describe the background. Oxygen thermal parameters were constrained to a value of 0.01. Later refinements indicated the minor presence of an extra phase, which upon inspection was identified as In_2O_3 . Refinement of the phase fraction and respective profile parameters yielded a χ^2 -value of 2.1. The refined pattern and residual statistics are provided in Figure 23.

Tables IX, X, and XI contain the measured atom positions, bond lengths and bond angles respectively from the refinement. Included in the tables also are numerical comparisons to the reported single crystal work. In general all the data are within ten percent of the reference work. However, there are discrepancies. Bond lengths of both the oxygen to metal ion of O(1) are in close agreement with published results. The latter metal-metal ion lengths of O(1) have deviated from the reported values. Similar differences are visible in the data of O(2) both in the latter oxygen-metal bond lengths and the metal-to-metal data. Further explanation for the numerical deviations may be found by looking at the miscellaneous data presented in Table XIII. The Xe and Ye and L-terms were refined in the peak profile of $\text{In}_6\text{WO}_{12}$. These terms were used to improve the calculated fit, however, no relations to the sample were made.

In Section 3.1.d measured lattice parameters of $\text{In}_6\text{WO}_{12}$ were reported to be 6.2323 (1) Å, 99.01°. Refinement of the $\text{In}_6\text{WO}_{12}$ structure yielded lattice parameter measurements of 6.23392 (4) Å, 99.03 (2)°. Both measurements are close to the reported literature values.

The report on single crystal $\text{In}_6\text{WO}_{12}$ did not report bond angles; however, deformation tensors with respect to the ideal fluorite were derived. Structural

development of the rhombhedral symmetry is also given using the periodic bond chain concept. Using this concept, isolated $\text{WO}(1)_6$ octahedral units are surrounded by In and O(2). These units traverse in the $\langle 001 \rangle$ and $\langle 011 \rangle$ directions. These directions form the natural faces $\{100\}$ $\{01-1\}$ $\{11-1\}$ that defines the habit of $\text{In}_6\text{WO}_{12}$.⁴¹

Figure 23. Observed (+), calculated (line), and difference (lower line) of $\text{In}_6\text{WO}_{12}$ synthesized via solution-method and fired to 800°C (1073K). Lower tick marks represent predicted peak positions of $\text{In}_6\text{WO}_{12}$ (higher) and In_2O_3 (lower).

TABLE IX. Atomic Positions of In₆WO₁₂[Space Group R $\bar{3}r$; a= 6.23392 (4) Å, 99.0339 (2)]

Atom	Position	x	y	z	U*100 (Å ²)
W	1a	0.0 [0.0]	0.0 [0.0]	0.0 [0.0]	0.03 (3)
In	6f	0.1394 (1) [0.1397 (1)]	0.3224 (1) [0.3214 (1)]	0.6046 (1) 0.6044 (1)]	0.26 (2)
O1	6f	-0.048 (1) [-0.0426 (15)]	0.089 (2) [0.0974 (13)]	0.289 (1) [0.2969 (12)]	1.0 ^a
O2	6f	0.413 (1) [0.4057 (12)]	0.589 (1) [0.5838 (12)]	0.835 (1) [0.8214 (12)]	1.0 ^a

wRp = 9%; Rp = 7%; $\chi^2=2.1$ ^a Isotropic thermal factors held constant during refinement[] indicates work of Ref. ⁴¹

TABLE X. Bond Distances (Å) of In₆WO₁₂

Bond	Length	In ₆ WO ₁₂ *	Bond	Length	In ₆ WO ₁₂ *
O(1)			O(2)		
O(1) - W	1.894 (7)	1.930	O(2) - In	2.308 (6)	2.070
O(1) - In	2.277 (6)	2.210	O(2) - In	2.057 (8)	2.120
O(1) - In	2.264 (8)	2.280	O(2) - In	2.098 (7)	2.210
O(1) - In	2.743 (8)	2.770	O(2) - In	2.187 (8)	2.240
In - In	3.44 (6)	3.443	In - In	3.44 (5)	3.328
W - In	3.55 (4)	3.536	In - In	3.41 (5)	3.410
W - In	3.54 (4)	3.536	In - In	3.41 (5)	3.410
In - In	3.81 (7)	3.552	In - In	3.56 (2)	3.443
W - In	3.97 (5)	3.873	In - In	3.32 (5)	3.552
In - In	3.80 (7)	4.028	In - In	3.84 (2)	3.842

* work of Ref. ⁴¹TABLE XI. Bond Angles (°) of In₆WO₁₂

Bond Angle	Angle (deg)	In ₆ WO ₁₂ *	Bond Angle	Angle (deg)	In ₆ WO ₁₂ *
W - O(1) - In	136.65 (34)	-na-	In - O(2) - In	103.99 (30)	-na-
W - O(1) - In	116.61 (30)	-na-	In - O(2) - In	101.26 (26)	-na-
In - O(1) - In	98.58 (34)	-na-	In - O(2) - In	98.59 (28)	-na-
			In - O(2) - In	117.90 (4)	-na-
			In - O(2) - In	102.97 (30)	-na-
			In - O(2) - In	127.80 (4)	-na-

* work of Ref. ⁴¹

4. Summary and Conclusion

Bulk powders in the $\text{In}_2\text{O}_3 - \text{WO}_3$ pseudo-binary phase system were analyzed via x-ray diffraction for phase stability within the temperature region of 800°C to 1400°C. Within this temperature regime, two stable binary oxide materials were found: $\text{In}_2(\text{WO}_4)_3$ and $\text{In}_6\text{WO}_{12}$. Unexpectedly, processing technique of the initial powders influenced the purity of the final powders. $\text{In}_2(\text{WO}_4)_3$ was quite sensitive to processing techniques. The Dabney solution method yielded a highly contaminated product. Whereas mixing 1M solutions of H_2WO_4 and $\text{In}(\text{NO}_3)_3$ yielded a highly pure $\text{In}_2(\text{WO}_4)_3$ powder at lower firing temperature as compared to solid state mixing. The purity of $\text{In}_6\text{WO}_{12}$ was not affected by either solution synthesis or solid state synthesis.

Differential scanning calorimetry data was used to determine that $\text{In}_2(\text{WO}_4)_3$ underwent a first order phase transition between 260°C and 250°C. The material changed symmetry from orthorhombic to monoclinic upon cooling. The phase change was identifiable in the collected bulk phase diffractograms by the presence of a minor peak at $\sim 25.4^\circ 2\theta$. Rietveld refinement was undertaken to understand the structure of the materials. All three phases were adequately refined. The high temperature phase of $\text{In}_2(\text{WO}_4)_3$ adopted the $\text{Sc}_2(\text{WO}_4)_3$ -type Pnca structure. Pnca is a non-standard setting of the space group Pbcn. The low temperature phase of $\text{In}_2(\text{WO}_4)_3$, below 250°C is believed to crystallize in the $\text{Fe}_2(\text{MoO}_4)_3$ -P $2_1/a$ monoclinic structure. Bulk powders of $\text{In}_6\text{WO}_{12}$ were successfully refined using the $R\bar{3}r$ space group.

5. Future Work

- Neutron scattering or diffraction of $\text{In}_2(\text{WO}_4)_3$: It would be interesting to refine both the orthorhombic and the monoclinic forms of $\text{In}_2(\text{WO}_4)_3$. The monoclinic form appears to be the most intriguing with 24 oxygen positions and thermal parameters to refine.
- Computer simulations of ion insertion: Ion storage is one of the possible applications of these materials. Computer simulation offers the ability to pre-determine the resulting structural changes due to ion insertion and whether (or not) the flexibility of said structural changes without the necessity of costly caustic chemicals.
- Electrochromic studies on thin films: Thin films are the ideal form for electrochromic studies because of their real world application. Thin films of $\text{In}_6\text{WO}_{12}$ have already been fabricated. New methods may be needed to form $\text{In}_2(\text{WO}_4)_3$ and stabilize the high temperature orthorhombic form. Electrochromic studies of the surviving materials from the computer simulation will quantify the amount of ion uptake as well as give information on the efficiency of the material as an ion storage device.

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