Synthesis and characterization of metal tungstates by novel solid-state metathetic approach

Purnendu Parhi, T.N. Karthik, V. Manivannan

Department of Mechanical Engineering, Campus Delivery 1374, Colorado State University, Fort Collins, CO 80523, USA

Received 8 August 2007; received in revised form 16 October 2007; accepted 20 October 2007
Available online 26 October 2007

Abstract

Novel solid state metathetic approach (SSM) (ACl₂ + Na₂WO₄ → AWO₄ + 2NaCl, A = Ca, Sr, Ba, Zn, Mn, Ni) assisted by microwave energy has been successfully applied to the synthesis of tungstates of scheelite- and wolframite-type that are of technological importance. Well crystalline phases of scheelite-type tungstates, MWO₄ (M = Ca, Sr, Ba) have been synthesized where the characteristics of SSM reaction and the formation of high lattice energy by-product NaCl drives the reaction toward completion. Among wolframite-type tungstates, single-phase ZnWO₄ is synthesized by SSM reactions at ambient conditions and MWO₄ (M = Ni, Mn) are synthesized after subjecting the amorphous product to moderate temperature of heating (around 500°C for 6 h). This alternative method of synthesis where the metathesis reactions proceed in solid state has features like: simple method of synthesis, cost-effectiveness, high yield, easy scale up, and thus has advantages over already known methods of synthesis.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Solid-state reaction; Scanning electron microscopy; X-ray diffraction

1. Introduction

AWO₄ type of compounds (A = bi-valent element) are well known. The most common are the minerals scheelite (CaWO₄) used for optical properties (scintillation counters, lasers, optical fibers) and wolframite (FeWO₄, MnWO₄) which is the most common raw material for producing tungsten metal. In the AWO₄ type of compounds, if A²⁺ has a small ionic radius, <0.77 Å (Mg, Zn) it will form the monoclinic wolframite structure, but larger A²⁺ cations >0.77 Å (Ca, Ba) form the tetragonal scheelite structure. Monoclinic ZnWO₄ is also a known material named sanmartinite.

AWO₄-type have attracted a great deal of interest in the recent years due to their use as laser host materials [1,2], as scintillator [3,4], oxide ion conductors [5], microwave applications [6] and magnetic materials [7]. These tungstate materials doped with rare-earth ions have optical and laser properties.

AWO₄ powders have been prepared by a traditional solid-state reaction [8] and by various wet methods such as co-precipitation [9], solvo-thermal process [10–12], sol–gel reaction [13], reverse micellar reaction [14], microwave irradiation [15], and mechanochemical method [16]. Ryu et al. have synthesized MWO₄ (M = Ca, Ni) using citrate combustion method [17]. The citrate complex route assisted by microwave has been used by the same group for synthesis of MWO₄ (M = Ca, Sr, Ba, Pb) [18]. Nanocrystalline particle synthesis of MWO₄ (M = Ca, Sr, Ba, Cd, Zn, Pb) has been carried out by Chen et al. using ethylene glycol [19]. Polymethacrylic acid as a template reagent has been used by Zhao et al. for synthesis of SrWO₄ hollow sphere [20]. Among these different methods the solution based chemical synthetic methods play a crucial role in the design and production of fine ceramics and have been successful in overcoming many of the limitations of the traditional solid state, high-temperature methods. The use of solution chemistry can eliminate major problems such as long diffusion paths, impurities and agglomeration which will result in products with improved homogeneity.

However, wet methods have disadvantages such as complicated synthetic steps, use of expensive equipment, high synthetic temperature and long sintering time. On the other hand, due to excessive energy consumption, complex apparatus and techniques the solid-state reaction becomes gradually unpopular and unsatisfied. However, solid-state synthesis of materials by
metathetic route is emerging as a viable alternative approach to synthesize high-quality novel inorganic materials in a short amount of time.

Solid-state metathetic approach has been successfully applied for the synthesis of many oxide materials. For example, Gopalakrishnan et al. have synthesized oxides of K2La2Ti3O10, Ca3La2CuTi2O10 belonging to Ruddlesden-Popper type of materials, ABO5 perovskite type of materials like LaMO3 (M = Co, Mn), ATiO3 (A = Ca, Sr and Ba) and double perovskites like Ba3MM′2O9 (M = Mg, Ni, Zn; M′ = Nb, Ta) by this approach [21–24]. In addition, Kaner et al. have synthesized oxides of Zr, Hf and Cu using this approach [25,26]. Recently we have synthesized Zn3(PO4)2 at room-temperature using this procedure [27].

Synthesis of scheelite-type ABO4 (A = Ca, Sr, Pb; B = Mo, W) has been reported by solution-based metathetic approach where the desired product was precipitated after dissolving high purity alkaline earth and lead chloride in distilled water, and adding this solution to the solution of appropriate amounts of sodium molybdate and tungstate [28]. Synthesis of wolframite-type MnWO4 was reported by solution-based metathesis reactions, when the precipitate obtained from mixing equimolar solutions of corresponding hydrated metal nitrates and hydrated sodium tungstates was heated to 800°C for 15 h [29].

Here we report the synthesis of scheelite-type ABO4 (A = Ca, Sr, Ba) by novel solid-state metathetic approach assisted by microwave energy radiation and extended the same approach to the successful synthesis of tungstates of wolframite-type MWO4, (M = Zn). To the best of our knowledge such an approach towards the synthesis of metal tungstates has not been reported thus far.

2. Experimental

Na2WO4, CaCl2, SrCl2, BaCl2, ZnCl2, MnCl2, NiCl2 obtained from Alfa Aesar, USA, were used as precursors for the preparation of the metal tungstate compounds. Preparation of calcium tungstate was carried out by reacting a well-ground mixture of CaCl2 and Na2WO4 in a molar ratio of 1:1. Sample mixtures were put into crucibles and then exposed to domestic microwave operating at a frequency of 2.45 GHz and a power of 1100 W for 10 min duration. The samples were washed with distilled water to remove the sodium chloride reaction by-product and dried at 80°C. Preparation of strontium, barium and zinc tungstate powders were carried out in a similar manner by reacting to a well-ground mixture of AC12 (A = Sr, Ba, Zn) and Na2WO4 as mentioned above. For the synthesis of MnWO4 and NiWO4, the microwave synthesized product after washing was heated at 500°C for 6 h.

Powder X-ray diffraction (XRD) measurements were carried out using Scintag X2 diffractometer with Cu Kα radiation and Peltier detector. A scan rate of 1°/min with a step size of 0.02° was employed to obtain the XRD spectra. Scanning electron microscope (SEM) characterization was performed on the JSM-6500F, a field emission system with the In-Lens Thermal Field Emission Electron Gun (TFEG). Diffuse reflectance (DR) spectra were recorded in the wavelength range 250–2500 nm using Varian Associates Cary 500 double beam spectrophotometer equipped with Praying mantis. X-ray photoelectron spectroscopy (XPS) experiments were performed on a Physical Electronics 5800 spectrometer. This system has a monochromatic Al Kα X-ray source (hα = 1486.6 eV), hemispherical analyzer, and multichannel detector. A low energy (30 eV) electron gun was used for charge neutralization on the non-conducting samples. The binding energy (BE) scales for the samples were referenced to the C 1s peak at 284.8 eV. To determine the SSM reaction final adiabatic temperatures Pyro manufactured calibrated Micro Optical Pyrometer was used. The as-prepared sample is thoroughly washed with distilled water and dried with acetone to dissolve NaCl and get the desired product CaWO4. XRD (Fig. 2a) showed a well crystalline, single-phase nature for the product with yield >80%. Calcium tungstate crystallizes in tetragonal crystal structure. Scheelite structures of strontium and barium tungstates were synthesized in the method described above and their single-phase nature of.

3. Results and discussion

Fig. 1a shows the powder XRD of scheelite-type calcium tungstate product as a result of solid-state metathesis reaction between calcium chloride and anhydrous sodium tungstate. The XRD pattern contains peaks corresponding to two phases, NaCl (marked with *) and that of metal tungstate (marked with #). The formation of NaCl as a by-product confirms the reaction is characteristic of solid-state metathesis reactions: fast, energetic involving exchange of reacting partners and driven by high lattice energy of the co-produced salt (NaCl), as established in the literature [21–27,29]. Microwave radiation has provided the required energy to overcome the energy barrier which precludes spontaneous reaction and helped to heat the bulk of the material uniformly resulting in fine particles of controlled morphology and forming the product in a “green” manner without generation of any solvent wastes. The as-prepared sample is thoroughly washed with distilled water and dried with acetone to dissolve NaCl and get the desired product CaWO4. XRD (Fig. 2a) showed a well crystalline, single-phase nature for the product with yield >80%. Calcium tungstate crystallizes in tetragonal crystal structure. Scheelite structures of strontium and barium tungstates were synthesized in the method described above and their single-phase nature of.
material is confirmed by XRD (Fig. 2b and c). Crystal structure details about the scheelite-type of tungstates synthesized by solid-state metathesis approach are summarized in Table 1. All the peaks of the XRD are indexed and well matched with the reported phases of JCPDS [38].

SSM approach has been extended to the synthesis of tungstates of wolframite-type as well. Fig. 1b shows the XRD of as-prepared material that contains both NaCl and the desired zinc tungstate phases. Presence of sodium chloride once again confirms the reaction has proceeded in solid-state metathesis way. The desired product is obtained after dissolving sodium chloride and the XRD showed well crystalline single-phase nature with yield >80%. Intensities of the peaks (Fig. 3c) and the cell parameters clearly confirmed the phases belong to wolframite ZnWO₄ (Table 1). For NiWO₄ and MnWO₄, XRD showed amorphous nature for the as-washed products which were subjected to moderate temperature of heating, i.e. around 500 °C for 6 h in air to obtain single-phase crystalline phases (Fig. 3a and b). All the peaks of the XRD are indexed and well matched with the reported phase of JCPDS [39]. The lattice parameters for these compounds are also given in Table 1. It is possible that the formation of amorphous products for Ni and Mn could be due to insufficient and inhomogeneous transfer of microwave energy to form the product. Varying the microwave conditions (power and duration of the reaction), within the limitations of the microwave equipment yielded only amorphous products. It is interesting to note that the previous report of synthesis of such compounds, including that of low temperature methods (except hydrothermal method) [15,28] obtained crystalline product only after subjecting the as-prepared product to high-temperature sintering.

3.1. Thermodynamics behind metathesis

Solid state metathesis reactions, an example of which is shown in this study (ACl₂ + Na₂WO₄ → AWO₄ + 2NaCl, A = M²⁺) involves exchange of atomic/ionic species, where the driving force being the formation of thermodynamically stable alkali or alkaline earth halides with high lattice energy. Thermodynamic basis for such metathetic reactions are reported in the literature [23,40–42]. SSM reactions are characterized by a large enthalpy change (ΔHₘ) and high adiabatic temperature (Tₘ). The final adiabatic temperature measured was 1623 K for ZnWO₄. Using thermodynamic data available in the literature [43], we have calculated the enthalpy (ΔH) and free energy changes (ΔG) associated with the formation of tungstates, and presented the result in Table 2. The result show, (ΔH − 36.17 KJ/mol for ZnWO₄) that both enthalpy and free energy favors the metathesis reaction and the enthalpy change is indeed the driving force for the metathesis involving the formation of NaCl. We believe the final adiabatic temperature for scheelite tungstates to be below 650 °C. Due to restricted wavelength response of the device to the red region of the visible, optical pyrometers can only be used to measure objects that are hot enough to be incandescent or glowing, which limited the lower end of the temperature measurement range of the devices to be about 650 °C. SSM

<table>
<thead>
<tr>
<th>Composition</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α</th>
<th>β</th>
<th>γ</th>
<th>Volume (Å³)</th>
<th>Z</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaWO₄</td>
<td>5.216(0)</td>
<td>5.216(0)</td>
<td>11.313(0)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>307.79</td>
<td>4</td>
<td>I 4/a</td>
</tr>
<tr>
<td>SrWO₄</td>
<td>5.376(0)</td>
<td>5.376(0)</td>
<td>11.876(0)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>350.66</td>
<td>4</td>
<td>I 4/a</td>
</tr>
<tr>
<td>BaWO₄</td>
<td>5.570(2)</td>
<td>5.570(2)</td>
<td>12.637(0)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>400.86</td>
<td>4</td>
<td>I 4/a</td>
</tr>
<tr>
<td>ZnWO₄</td>
<td>4.720(0)</td>
<td>5.700(0)</td>
<td>4.950(0)</td>
<td>90</td>
<td>91.22</td>
<td>90</td>
<td>133.17</td>
<td>2</td>
<td>P 2/c</td>
</tr>
<tr>
<td>MnWO₄</td>
<td>4.798(0)</td>
<td>5.710(6)</td>
<td>4.973(8)</td>
<td>90</td>
<td>91.22</td>
<td>90</td>
<td>136.26</td>
<td>2</td>
<td>P 2/c</td>
</tr>
<tr>
<td>NiWO₄</td>
<td>4.599(2)</td>
<td>5.660(6)</td>
<td>4.906(8)</td>
<td>90</td>
<td>90.03</td>
<td>90</td>
<td>127.74</td>
<td>2</td>
<td>P 2/c</td>
</tr>
</tbody>
</table>
Table 2
Thermodynamic data for CaWO₄ and ZnWO₄ synthesized by metathesis reactions. \( \Delta H^\circ_T \) and \( S^\circ_T \) were calculated using the expression, \( \Delta H^\circ_T = \Delta H^\circ_{298} + 298 \int_T^{298} (C_p/T)\,dT \) and \( S^\circ_T = S^\circ_{298} + 298 \int_T^{298} (C_p/T)\,dT \), together with the expression of \( C_p \) as a function of \( T \). \( \Delta G^\circ_T \) values were calculated by using the expression \( \Delta G^\circ_T = \Delta H^\circ_T - T \Delta S^\circ_T \). \( C_p \) values were taken from reference [43].

<table>
<thead>
<tr>
<th>Composition</th>
<th>( \Delta H^\circ_{298} ) (KJ mol(^{-1}))</th>
<th>( \Delta S^\circ_{298} ) (KJ mol(^{-1}))</th>
<th>( \Delta G^\circ_{298} ) (KJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnWO₄</td>
<td>-97.8</td>
<td>0.0167</td>
<td>-102.77</td>
</tr>
<tr>
<td>CaWO₄</td>
<td>-36.17</td>
<td>0.095</td>
<td>-190.35</td>
</tr>
</tbody>
</table>

3.2. Characterization of MWO₄ materials

Among scheelite tungstates, SEM showed spherical shape particles for Ca, Sr compounds Fig. 4a and b and rod-like features for Ba materials (Fig. 4c). Zn compounds have well defined prism-type morphology and the particles are sub-micron in size (Fig. 4d). For other wolframite tungstates Ni and Mn, SEM showed the particles were agglomerated in nature as shown in Fig. 4e and f.

For tungstate materials to be used as practical phosphor as one of the potential technological applications, a dense pinhole free coating of the same has to be produced on the desired substrate. The quality of coating is determined mainly by the particle size distribution and morphology of the particles. For example, in case of a fluorescent lamp phosphor, the optimum coating thickness is roughly proportional to its mean particle size: that is, the smaller the particle size, the thinner the coating can be. Fine-particle phosphors also yield denser coatings. The well-defined particle features of the tungstates synthesized by SSM reactions showed that these reactions have control over morphol-

![Fig. 4. SEM pictures of (a) CaWO₄, (b) SrWO₄, (c) BaWO₄, (d) ZnWO₄, (e) MnWO₄ and (f) NiWO₄ showing particle features.](image-url)
ogy of the final particles and could be used for such technological applications.

Fig. 5a shows the XPS of CaWO$_4$ (scheelite) and Fig. 5b shows the XPS of ZnWO$_4$ (wolframite). XPS provides valuable information concerning the elements in the near surface region. Examination of the binding energies of the core-level electronic states of the elements in the surface region provides qualitative, semi-quantitative and chemical-state information. Since the electron binding energy of elements differs from each other, a full-scan spectrum was given for an overall understanding on surface elemental constituents of the tested sample. In the spectra we can see peaks corresponding to Ca$2s$ (442.0 eV), Ca$2p$ (351.6 eV), W4s (598.2 eV), O1s (534.8 eV), W4d (250.8 eV), W4f (39.6 eV). Similarly in the spectra of ZnWO$_4$ we can see peaks corresponding to Zn$2p_{1/2}$ (1047.6 eV), Zn$2p_{3/2}$ (1024.4 eV), Zn3s (142.0 eV), Zn3p (91.6 eV), W4s (587.6 eV), W4p$_3/2$ (429.2 eV), W4p$_1/2$ (477.2 eV), W4d (252.0 eV), W4f (37.6 eV), O1s (533.2 eV). The C1s peak at 284.8 eV is due to adventitious carbon present in the surface.

### 3.3. Physical property measurement of MWO$_4$ compounds

In order to determine the optical band gap for the technologically important tungstate materials, DR measurements were carried out. Fig. 6a shows the diffuse reflectance spectra of the CaWO$_4$, SrWO$_4$, BaWO$_4$ samples in the UV–vis–NIR range whereas Fig. 7a shows the diffuse reflectance spectra of the MnWO$_4$, NiWO$_4$, and ZnWO$_4$. The diffuse reflectance data was

![Fig. 5](image1.png)

Fig. 5. XPS of (a) scheelite-type (a) CaWO$_4$ and (b) wolframite-type MnWO$_4$.

![Fig. 6](image2.png)

Fig. 6. (a) Diffuse reflectance spectra of (1) CaWO$_4$, (2) SrWO$_4$, and (3) BaWO$_4$ in the wavelength range 250–2500 nm. (b) Plot of $F(R_\infty)$ vs. $E$ (eV) for the estimation of the optical absorption edge energy.

![Fig. 7](image3.png)

Fig. 7. (a) Diffuse reflectance spectra of (1) ZnWO$_4$, (2) NiWO$_4$, and (3) MnWO$_4$ in the wavelength range 250–2500 nm. (b) Plot of $F(R_\infty)$ vs. $E$ (eV) for the estimation of the optical absorption edge energy.
used to calculate the absorption coefficient from the Kubelka-Munk \([44]\) function defined as

\[
F(R_\infty) = \frac{\alpha}{S} = \left(1 - R_\infty \right)^2 / 2R
\]

here \(\alpha\) is the absorption coefficient and \(S\) the scattering coefficient, and \(F(R_\infty)\) is the KM function. For the diffuse reflectance spectra, KM function can be used instead of \(\alpha\) for estimation of the optical absorption edge energy \([45]\). It was observed that a plot of \(F(R_\infty)E\) versus \(E\) was linear near the edge for direct allowed transition \((n = 1/2)\). The intercept of the line on abscissa \((F(R_\infty)E = 0)\) gave the value of optical absorption edge energy. The values are determined to be \(-4.8\) eV for the scheelite tungstates and around \(3\) eV for wolframite tungstates. Figs. 6b and 7b shows the plot of the same. Table 3 summarizes the optical absorption edge energies for all the tungstates studied under this study. The diffuse reflectance spectra for direct band gap orthorhombic \((\beta)\ [46]\) \(\text{Ta}_2\text{O}_5\) prepared by heating Ta metal in air is also studied for comparison. The value of optical absorption edge energy for indirect allowed transition for \(\text{Ta}_2\text{O}_5\) was found to be \(4.0 \pm 0.2\) eV, which is consistent with the value reported in the literature \([47]\).

4. Conclusions

Novel solid-state metathesis approach has been employed to synthesize technologically important tungstate materials. SEM showed well-defined morphology for most of the tungstates prepared by this method, which have distinct advantages in terms of simplicity, easy scale up, and are relatively inexpensive with high yield. Optical absorption edge energies for the tungstates synthesized in this study have been determined. The thermodynamic factors, which are the fundamental force behind the design of SSM reactions are considered, and the overall enthalpy released in the reaction is calculated.

Acknowledgement

The authors would like to acknowledge Prof. Allan Kirkpatrick, Head of Department, Mechanical Engineering for his continued help, encouragement and support.

References

[38] JCPDS Card No. 77-2234, 08-0490, 72-0746, ICDD, PCPDFWIN v.2.1, JCPDS-International Centre for Diffraction Data, 2000.


