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Morphological and Phase Controlled Tungsten Based Nanoparticles: Synthesis and Characterization of Scheelite, Wolframite, and Oxide Nanomaterials

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For the first time tungsten based nanoparticles (WNPs) of scheelite (MWO_4: M = Ca, Sr, Ba, Pb), wolframite (MWO_4: M = Mn, Fe, Zn and $(Mg_{0.60}Mn_{0.17}Fe_{0.26})WO_4$), and the oxide ($WO_3$ and $W_{18}O_{49}$) were synthesized from solution precipitation (i.e., trioctylamine or oleic acid) and solvothermal (i.e., benzyl alcohol) routes. The resultant WNPs were prepared directly from tungsten(VI) ethoxide ($W(OCH_2CH_3)_6$, **1**) and stoichiometeric mixtures of the following precursors: $[Ca(N(SiMe_3)_2)_2]_2$ (**2**), $Pb(N(SiMe_3)_2)_2$ (**3**), $Mn[(\mu\text{-}Mes)_2Mn(Mes)]_2$ (**4**), $[Fe(\mu\text{-}Mes)(Mes)]_2$ (**5**), $Fe(CO)_5$ (**6**), $[Ba_2(\mu_3\text{-}ONep)(\mu\text{-}ONep)_2(ONep)(HONep)_3(py)]_2$ (**7**), $Sr_5(\mu_4\text{-}O)(\mu_3\text{-}ONep)_4(\mu\text{-}ONep)_4(HONep)(py)_4$ (**8**), and $[Zn(Et)(ONep)(py)]_2$ (**9**) where Mes = $C_6H_2(CH_3)_3$-2,4,6, ONep = $OCH_2C(CH_3)_3$, Et = CH_2CH_3, and py = pyridine. Through these routes, the WNP morphologies were found to be manipulated by the processing conditions, while precursor selection influenced the final phase observed. For the solution precipitation route, **1** yielded (5 × 100 nm) $W_{18}O_{49}$ rods while stoichiometric reactions between **1** and **2**−**9** generated homogeneous sub-30 nm nanodots, -diamonds, -rods, and -wires for the MWO_4 systems. For the solvothermal route, **1** was found to produce wires of WO_3 with aspect ratios of 20 while (**1** and **2**) formed 10−60 nm $CaWO_4$ nanodots. Room temperature photoluminescent (PL) emission properties of select WNPs were also examined with fluorescence spectroscopy (λ_{ex} = 320 nm). Broad PL emissions = 430, 420, 395, 420 nm were noted for 5 × 100 nm $W_{18}O_{49}$ rods, 5 × 15 nm, $CaWO_4$ rods, 10−30 nm $CaWO_4$ dots, and 10 nm $BaWO_4$ diamonds, respectively.

Introduction

There is little precedent for the use of solution route strategies that yield controlled morphologies of tungsten based nanoparticles (WNP), such as the metal tungstates (MWO_4) [i.e., scheelite ($CaWO_4$), wolframite ($(Mn,Fe)WO_4$)], or the simple tungsten oxides (WO_x). Solvothermal (SOLVO) and hydrothermal routes to MWO_4 that react commercially available $Na_2WO_4 \cdot H_2O$ with metal halides,[1−11] acetates,[12−16] nitrates,[8,9,17,18] and sulfates[11] have provided a glimpse of the possible controlled WNPs that can be produced through judicious choice of processing and precursor selection. As for the WO_x, only a handful of solution precipitation (SPPT) routes have been developed based on tungsten hexacarbonyl ($W(CO)_6$)[19,20] and tungsten(IV) chloride (WCl_4).[21,22] These reports indicated that the final WNP properties were influenced by the crystallization temperature and solvents used during the SPPT process. Nonetheless, the fundamental development of synthetic pathways that allow

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for the generation of tailored WNPs is still being sought. This is because control over the WNP morphology and phase is critical for their use in a number of diverse energy and sensor applications, such as, solid state lightning, bioimaging, scintillators, humidity sensors, batteries, and catalysts.[6,11,19,23]

We are interested in using WNP for bioimaging and sensing applications, which necessitates the development of controlled morphological 10−30 nm MWO_4 materials. To realize this goal, a general SPPT route that employed metal alkoxides ($M(OR)_x$) was sought. The continued interest in $M(OR)_x$ precursors stems from the fact that they possess an easily manipulated ligand set which offers greater control over the final nanomaterials than other systems. The ease of manipulation of this family of compounds has allowed us to formulate the "precursor structure affect" for controlled nanomorphology in a number of nanoceramic systems[23−25] as well as the "precursor decomposition pathway" for influencing the final crystalline phase.[24,25] Previous reports that employ $M(OR)_x$ for the preparation of even the simple WO_x nanomaterials were surprisingly limited but promising in terms of morphological control.[26,27] WO_x nanorods were successfully synthesized from tungsten alkoxide ($W(OR)_6$) precursors (tungsten(VI) *iso*-propoxide ($W(OPr^i)_6$)[27] and tungsten(VI) oxo methoxide ($WO(OMe)_4$)[26]), in a benzyl alcohol SPPT route and in a study of "reactions under autogenic pressure at elevated temperature", respectively. Unfortunately, these methods required high temperatures (700 °C) or needed additional calcination procedures to form WO_3. In addition to the limited references concerning the use of $W(OR)_x$, reports of WNP synthesized from metal amides $M(NR_2)_x$ or metal alkyls (MR_x) which have also shown great efficacy in both SPPT and SOLVO routes to ceramic nanomaterials have not been reported.[23,24,28]

For this investigation, we focused on exploiting the precursor structure decomposition phenomena associated with these neglected $M(OR)_x$ precursors to decipher the key variables for the production of tailored WNP nanomaterials. We also compared the reactivity and decomposition of $M(NR_2)_x$, MR_x, and $M(CO)_x$ in a newly developed SPPT routes that offer control over the final WNPs. These precursors have several advantages over the more commonly employed halides and nitrates including high solubility, high volatility, low decomposition temperatures, and condensation control that can be invoked through judicious manipulation of the ligand set. These tailored precursors allow for specific properties in the final materials to be fine-tuned. Following this approach enabled the development of a SPPT route to high yields of scheelite and wolframite nanomaterials, which to our knowledge has not been previously reported. In addition, a selection of $M(OR)_x$ and $M(NR_2)_x$ precursors have been studied using a SOLVO route. Both MWO_4 and WO_x nanomaterials were prepared using the commercially available tungsten(VI) ethoxide ($W(OEt)_6$, **1**) and stoichiometric mixtures of the following precursors in both SPPT and SOLVO routes: $[Ca(N(SiMe_3)_2)_2]_2$ (**2**), $Pb(N(SiMe_3)_2)_2$ (**3**), $Mn[(\mu\text{-}Mes)_2Mn(Mes)]_2$ (**4**), $[Fe(\mu\text{-}Mes)(Mes)]_2$ (**5**), $Fe(CO)_5$ (**6**), $[Ba_2(\mu_3\text{-}ONep)(\mu\text{-}ONep)_2(ONep)(HONep)_3(py)]_2$ (**7**), and $[Sr_5(\mu_4\text{-}O)(\mu_3\text{-}ONep)_4(\mu\text{-}ONep)_4(HONep)(py)_4]$ (**8**), and $[Zn(ONep)(Et)(py)]_2$ (**9**), where Mes = $C_6H_2(CH_3)_3$-2,4,6, ONep = $OCH_2C(CH_3)_3$, Et = CH_2CH_3, and py = pyridine. These precursors were easily introduced into both routes and produced WNPs with controlled properties. The details of their synthesis and characterization are discussed below.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glovebox techniques. The following chemicals were used as received and were stored under argon: Alfa Aesar, **1**; Aldrich, iron pentacarbonyl ($Fe(CO)_5$) (**6**), *neo*-pentanol (HONep), Sr^0, Ba^0, CaI_2, $PbBr_2$, $MnBr_2$, $FeBr_2$, $KN(Si(CH_3)_3)_2$, MgBrMes (1.0 M in THF), diethyl zinc ($ZnEt_2$) (1.0 M in hexanes), benzyl alcohol (BzOH), trioctylamine (TOA), oleic acid (OA), chloroform ($CHCl_3$), toluene (tol), pyridine (py), tetrahydrofuran (THF), and ethanol (EtOH). Solvents used to synthesize the precursors were obtained in Sure/Seal bottles and stored under an argon atmosphere. The following compounds were synthesized according to published procedures: **2**,[24,29,30] **3**,[31] **4**,[32] **5**,[33] **7**,[28,34] **8**,[35] and **9**.[25]

General Synthesis of WNPs. A general description of both synthetic routes is first presented, followed by the complete experimental details and observations noted for each WNP synthesized. Two synthetic routes (a) SPPT and (b) SOLVO were used to synthesize WO_x, MWO_4 (M = Ca, Sr, Ba, Pb, Mn, Fe, Zn), and (Fe,Mn)WO_4 ceramic nanoparticles from stoichiometric mixtures of commercially available **1** with **2**−**9**, respectively.

(a) SPPT. A mixture of TOA/OA[36] (4.9 g, 13 mmol/1.8 g, 6.3 mmol) was placed in a three-neck round-bottom flask equipped with a reflux condenser, septum, and thermocouple. Stoichiometric mixtures of **1** with **2**−**9**, respectively, were added to the TOA/OA solution at room temperature under flowing argon. The solution was heated (∼100 °C), and a clear orange or brown solution formed before undergoing a final color change and the formation of a precipitate (245−380 °C). After reaching the desired temperatures, the heating source was removed and the solutions were allowed to cool to room temperature. The WNPs were isolated by extraction with $CHCl_3$ followed by precipitation through the addition of

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ethanol (EtOH). The WNP precipitate was collected by centrifugation and rinsed with EtOH a second time before being dispersed again with $CHCl_3$ or toluene. *Note: over time, wire-like morphologies were observed to settle out of the dispersing solutions.*

(b) SOLVO. In the glovebox, stoichiometric mixtures of **1** and **2** were dissolved in ∼15 mL of BzOH, and the clear solutions were transferred to the Teflon lined 45 mL Parr acid digestion bomb. The bomb was taken out of the glovebox, placed in a furnace, and heated to 200 °C for 48 h at a rate of 10 °C/min. After this time, the bomb was cooled back to 24 at 10 °C/min. After cooling to room temperature, the WNP precipitate was collected by centrifugation and rinsed twice with EtOH.

SPPT Experimental Details. *$W_{18}O_{49}$.* **1** (1.6 g, 3.6 mmol) was used. Heating the solution to 100 °C formed a clear brown solution that changed to clear blue-green as the temperature increased. A dark blue precipitate occurred at 310 °C. The reaction was held at this temperature for 10 min before cooling to room temperature. Percent yield: 0.48 g (58.5%).

$CaWO_4$. Heating a mixture of **2** (0.54 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear brown solution that turned clear blue-green as the temperature increased (∼200 °C). A blue-green precipitate occurred at 276 °C. The reaction was held at 276 °C for 1 min before cooling to room temperature. Percent yield: 0.18 g (41.9%).

$SrWO_4$. Heating a mixture of **8** (0.46 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear orange solution that turned clear blue-green as the temperature increased (∼200 °C). A blue-green precipitate occurred at 367 °C. The reaction was held at 367 °C for 2 min before cooling to room temperature. Percent yield: 0.39 g (77.3%).

$BaWO_4$. Heating a mixture of **7** (0.72 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear orange solution that turned clear yellow as the temperature increased (∼200 °C). A white precipitate occurred at 356 °C. The reaction was heated to 362 °C and held for 1 min before cooling to room temperature. Percent yield: 0.24 g (41.5%).

$PbWO_4$. Heating a mixture of **3** (0.79 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear brown solution that turned clear blue as the temperature increased (∼250 °C). A light blue precipitate occurred at 356 °C. The reaction was heated to 362 °C and held for 15 min before cooling to room temperature. Percent yield: not calculated, mixed phase product.

$(Fe_{0.25}Mn_{0.75})WO_4$. Heating a mixture of **4** (0.18 g, 0.55 mmol), **5** (0.052 g, 0.18 mmol), and **1** (0.33 g, 0.73 mmol) to 100 °C formed a clear orange solution that turned dark blue as the temperature increased (∼270 °C). A brown precipitate occurred at 386 °C, and the reaction was held at 386 °C for 10 min before cooling to room temperature. Percent yield: Mg impurity prevented accurate calculation.

$MnWO_4$. Heating a mixture of **4** (0.49 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear orange solution that turned dark green as the temperature increased (∼200 °C). A light blue precipitate occurred at 375 °C. The reaction was held at 375 °C for 10 min before cooling to room temperature. Percent yield: not calculated, mixed phase product.

$FeWO_4$. Heating a mixture of **5** (0.75 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear orange solution that turned dark blue as the temperature increased (∼270 °C) and then to brown at 351 °C. A light brown precipitation occurred at 380 °C. The reaction was held at 380 °C for 10 min before cooling to room temperature. Percent yield: not calculated, mixed phase product.

$FeWO_4$. Heating a mixture **6** (0.29 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear orange solution that turned black as the temperature increased (∼180 °C) and then dark blue at 230 °C. A dark brown precipitation occurred at 330 °C. The reaction was held at 330 °C for 10 min before cooling to room temperature. Percent yield: 0.29 (63.0%).

$ZnWO_4$. Heating the mixture of **9** (0.39 g, 1.5 mmol) and **1** (0.68 g, 1.5 mmol) to 100 °C formed a clear orange solution that turned dark green as the temperature increased (∼200 °C) and then to blue at 250 °C. A light blue precipitation occurred at 340 °C. The reaction was held at 340 °C for 10 min before cooling to room temperature. Percent yield: not calculated, mixed phase product.

SOLVO Experimental Details. *WO_3.* **1** (0.20 g, 0.44 mmol) was dissolved in BzOH (15 mL) to form a clear orange solution. A blue precipitate and clear orange mother liquor were collected after cooling to room temperature. Percent yield: not calculated, mixed phase.

$CaWO_4$. **1** (0.20 g, 0.44 mmol) and **2** (0.16 g, 0.44 mmol) were dissolved in BzOH (15 mL) to form a clear orange solution. A white precipitate and clear yellow mother liquor were collected after cooling to room temperature. Percent yield: not calculated, mixed phase product.

Powder X-ray Diffraction (PXRD). Dried and washed WNP powders were mounted directly onto a Si zero background holder purchased from the Gem Dugout. Phase identification for the nanoscale materials was determined PXRD patterns collected on a PANalytical powder diffractometer employing Cu Kα radiation (1.5406 Å) and a RTMS X'Celerator detector. Samples were scanned at a rate of 0.02°/2 s in the 2θ range of 10−100°.

Photoluminescence. The photoluminescence (PL) emission of select scheelites and WO_x were examined at room temperature using a Fluorolog-3 Model FL3-21 from Horiba Jobin Yvon. Solutions of washed WNP particles prepared from SOLVO were dispersed in EtOH. WNPs prepared by SPPT were dispersed in $CHCl_3$, tol, or THF. An excitation wavelength (λ_{ex} = 320 nm) was used to obtain the emission spectra detected in the 350−600 nm range. The emission spectra were corrected for nonuniform responses of the photomultiplier tube and the grating inside the emission monochromator.

Transmission Electron Microscopy (TEM). An aliquot of the particles dispersed in EtOH (SOLVO) or $CHCl_3$ (SPPT) was placed directly onto a lacy carbon type-A, 300 mesh, copper TEM grid purchased from Ted Pella, Inc. The aliquot was then allowed to dry overnight. The resultant particles were studied using two instruments: the Philips CM 30 TEM with the Thermo Noran System Six Energy Dispersive X-ray (EDX) System and FEI Tecnai TF30 TEM/STEM with the EDAX EDX System, both operating at 300 kV accelerating voltage.

Scanning Electron Microscopy (SEM). The samples were dispersed onto carbon tape and coated with gold palladium using an Edwards sputter coater. Samples were imaged using a Zeiss Supra 55VP field emitter gun scanning electron microscope (FEGSEM). A Noran EDS detector and Noran System Six software was used for the acquisition of EDS spectra.

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Molar ratios of the solid solution $(Fe_{0.60}Mn_{0.17}Mg_{0.26})WO_4$ were determined by digesting 0.10 g of the nanoparticles in 5 mL of high purity hydrochloric acid and 5 mL of deionized water (DI H_2O) at 70 °C. The solution was cooled to room temperature, diluted with DI H_2O, and then analyzed with a Perkin-Elmer Elan 6100 ICP-MS to determine the elemental molar ratios.

Results and Discussion

As mentioned previously, the properties of W-based systems depend critically on the phase and composition of the various components. For example, the simple WO_x species are a main component of catalyst systems, lithium

Table 1. Summary of Reaction Products Formed from SPPT and SOLVO Routes

precursor(s)	reaction	route	products	morphology	size (nm)	phase
1 and **2**	$W(OEt)_6 + M(NR_2)_x$	SPPT[a]	$CaWO_4$	rods	5 × 15	scheelite
1 and **2**	$W(OEt)_6 + M(NR_2)_x$	SOLVO[b]	$CaWO_4 + WO_x$	dots	15−40	scheelite mixed
1 and **8**	$W(OEt)_6 + M(OR)_x$	SPPT	$SrWO_4$	diamonds and rods	20	scheelite
1 and **7**	$W(OEt)_6 + M(OR)_x$	SPPT	$BaWO_4$	dots	10	scheelite
1 and **3**	$W(OEt)_6 + M(NR_2)_x$	SPPT	$PbWO_4 + WO_x$	diamonds and rods	10−50 50 × 1.8 μm	scheelite mixed
1 and **4**	$W(OEt)_6 + M(R)_x$	SPPT	$(Mg_{0.60}Mn_{0.17}Fe_{0.26})WO_4$	rods	5 × 80−100	wolframite HT-phase
1 and **4**	$W(OEt)_6 + M(R)_x$	SPPT	$(Mg,Mn)WO_4 + MgWO_4$	irregular	10−30	wolframite mixed
1 and **5**	$W(OEt)_6 + M(R)_x$	SPPT	$FeWO_4 + Fe_2O_3 + W_{18}O_{49}$ + HT $MgWO_4$	rods	10 × 80	wolframite mixed
1 and **6**	$W(OEt)_6 + M(CO)_x$	SPPT	$FeWO_4$	rods	10 × 50	wolframite
1 and **9**	$W(OEt)_6 + M(OR)(R)_x$	SPPT	$ZnWO_4 + WO_x$	rods	15 × 150	wolframite mixed
1	$W(OEt)_6$	SPPT	$W_{18}O_{49}$	rods	5 × 100	oxide
1	$W(OEt)_6$	SOLVO	$WO_3 + WO_3{\cdot}0.33H_2O$	wires	10−100 × 10 μm	oxide mixed

[a] SPPT: trioctylamine and oleic acid. [b] SOLVO: benzyl alcohol.

batteries, photo- and electrochromics, and gas sensors.[19,22] Their desirable bulk optic and electronic properties used for these applications arise from WO_6 octahedra packing arrangements and stoichiometery.[37,38] For bulk MWO_4, the W coordination chemistry has also been shown to dictate the fluorescent, magnetic, catalytic, and electronic properties.[11,39,40] The MWO_4 are categorized by the W−O coordination that is influenced by the divalent ionic (M^{2+}) radii size, where the scheelites (large M^{2+}) have tetrahedral coordination and the wolframites (small M^{2+} radii) adopt octahedral coordination. Because the crystal chemistry is so influential on the final bulk materials properties, it is important to investigate how the selection of precursor (i.e., $M(OR)_x$, $M(NR_2)_x$, and MR_x) will effect the final WNP phase.

Current WNP synthetic methods (i.e., SOLVO, hydrothermal) have had varied success in producing controlled morphologies.[1−3,5−11,13−15,18,41−44] Although a number of unique morphologies have been synthesized, there are few examples of <30 nm WNP and little is known about the fluorescent and electronic behavior in this size regime. To understand the WNP nanocrystal-structure property relationships of sub-30 nm particles, we have chosen to investigate a SPPT strategy to synthesize these nanomaterials. Recently, SPPT routes, with various amine and carboxylic acid solvents, were used to synthesize transition metal oxides ($W_{18}O_{49}$, MnO, FeO)[19,36,45] and perovskites (A^ETiO_3, A^E = Sr, Ba),[46] through the thermal decomposition of metal acetates, carbonyls, and noncrystallographically characterized $A^ETi(OR)_6$ alkoxides. Here, we investigated the combination of trioctylamine and oleic acid (TOA/OA) for our SPPT route to synthesize WNPs. It was determined that commercially available **1** produced WO_x while stoichiometeric ratios of **1** and the precursors $M(NR_2)_x$ **2**−**3**, MR_x **4**−**6**, and ONep derivatives **7**−**9** produced MWO_4. Discussion of the synthetic process follows for (i) solution precipitation (scheelite, wolframite, oxide) and (ii) solvothermal routes (scheelite, oxide). Table 1 summarizes the reaction products isolated as well as the effect of precursor and processing conditions on the final WNP properties.

SPPT Synthesis of Scheelite WNPs. Using the SPPT route (TOA/OA), we undertook the synthesis of MWO_4 (M = Ca, Sr, Ba, Pb) nanoparticles using stoichiometric amounts of **1** and **2**, **1** and **8**, **1** and **7**, or **1** and **3**, respectively. The PXRD patterns for these WNPs are presented in Figure 1a−d. Phase pure tetragonal patterns, Figures 1a−c, were observed and indexed to scheelites: $CaWO_4$ (PDF no. 41-1431),[47] $SrWO_4$ (PDF no. 08-0490),[47] and $BaWO_4$ (PDF no. 43-0646),[47] respectively. However, under the conditions used, the reaction between (**1** and **3**) formed a precipitate containing two phases that were indexed to the tetragonal phase of $PbWO_4$ stolzite (Figure 1d), (PDF no. 190708)[47] and a secondary phase centered at 24.5 ° (2θ) assigned to a tungsten suboxide $W_{24}O_{68}$. This assignment is tenuous because the secondary phase's reflections are weak and broad, and remaining $W_{24}O_{68}$ peaks are coincidental with the stronger $PbWO_4$ reflections. Formation of $W_{24}O_{68}$ under the reaction conditions used for $PbWO_4$ may have resulted from Pb's volatility. Future synthetic reactions that utilize **3** will have a 5−10% augmentation (based on sol−gel template generated $PbTiO_3$ nanotubes) to account for this characteristic Pb loss.[48] The resulting PXRD data for all the reaction products obtained confirmed that the precursors and conditions used in the SPPT route to synthesize the scheelites were successful in producing crystalline WNPs.

Bright field TEM images of the isolated scheelite MWO_4 (M = Ca, Sr, Ba, Pb) WNPs prepared from the SPPT route

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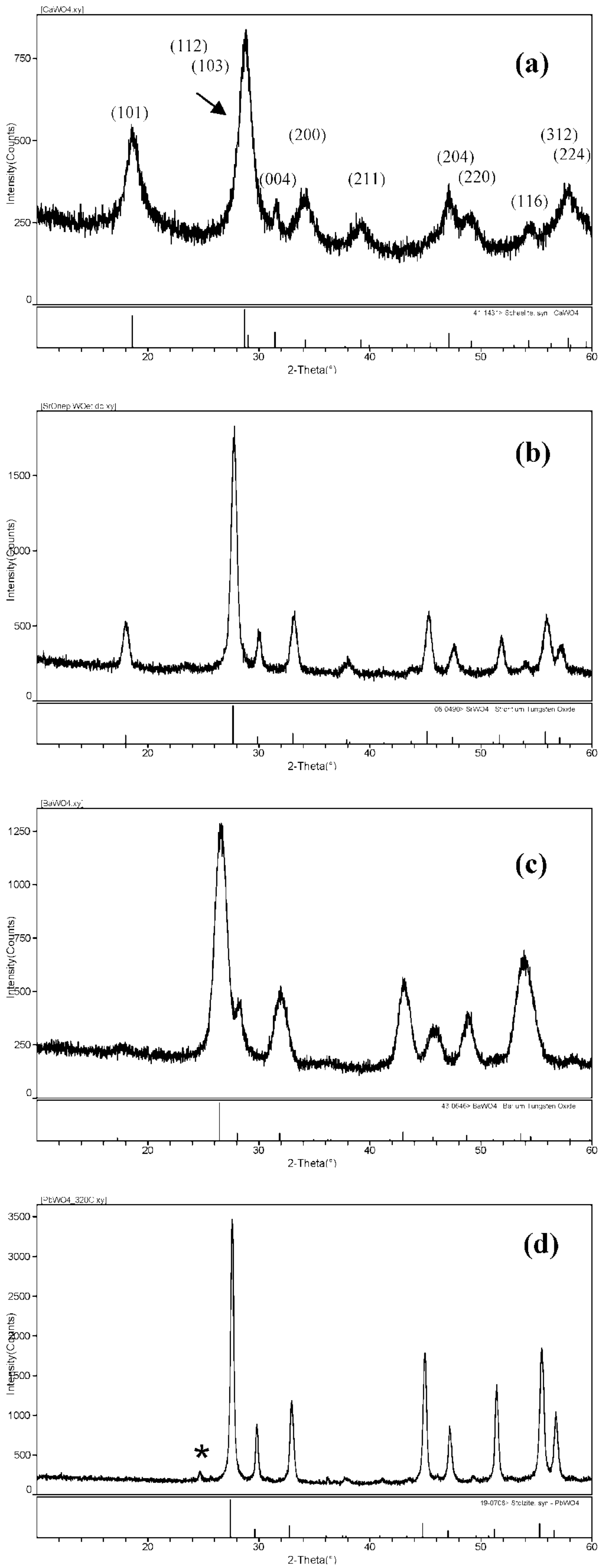

Figure 1. PXRD patterns of scheelite WNPs synthesized from SPPT: (a) **1** and **2** made $CaWO_4$, (b) **1** and **8** made $SrWO_4$, (c) **1** and **7** made $BaWO_4$, and (d) **1** and **3** made $PbWO_4$ and $^*W_{24}O_{68}$.

are shown in Figure 2a−d, respectively. These images reveal that the scheelites formed in TOA/OA vary in size and shape depending on the crystallization temperature and time used. The composition of each scheelite was examined by EDS and confirmed that W was present for each sample along with Ca for (**1** and **2**); Sr (**1** and **8**); Ba (**1** and **7**); and Pb (**1** and **3**). Dark field imaging (see the Supporting Information section) confirmed that the individual scheelite particles were single crystallites.

The bright field TEM image, Figure 2a, shows that **1** and **2** reacted to synthesize 5 × 15 nm $CaWO_4$ nanorods within 1 min after reaching the crystallization temperature of 276 °C. The dimensions and uniformity of these rods are in considerable contrast to the reported $CaWO_4$ rods prepared by hydrothermal synthesis using citric acid[49] (3−10 × 31 nm) or CTAB[3] (20−30 × 600−1000 nm) and SOLVO using PEG-200 (20 × 100−250 nm). By switching to **1** and **8** to generate $SrWO_4$, Figure 2b, ~20 nm diamond shaped particles and 5 × 150 nm rods were formed after 2 min at 367 °C. The inset TEM image in Figure 2b has a 20 nm scale bar and details the edges of the diamonds formed. The reaction between **1** and **7** to synthesize $BaWO_4$ at 362 °C for 1 min formed ~10 nm irregular shaped particles that consist mainly of dots, but rough diamond-like structures are also observed, Figure 2c. Using the SPPT route overcomes the limitation of generating these morphologies, within the 20 nm size regime, that have not been reported for SOLVO routes. The dimensions observed for Ba and Sr WNPs prepared by SPPT are of considerable contrast to the micrometer sized diamond or bipyramidal morphologies isolated for $BaWO_4$ and $SrWO_4$ using eggshell membrane templates[5,43] and the block copolymer PEG-*b*-PMMA in cationic reverse micells.[7]

Finally, $PbWO_4$ produced from **1** and **3** contained two morphologies, diamonds and rods, of varying sizes. Figure 2d reveals rods (50−100 nm × 1.0−1.8 μm) while the inset shows an island of diamonds particles (10−50 nm). The differences in shape and size may result from the 15 min dwell time spent at the crystallization temperature. For example, the middle narrow and crooked wire appears to have been produced by separate diamonds that have oriented themselves and sintered together. A similar oriented attachment process of has been observed for hydrothermally grown TiO_2[50] wires and for a wet chemical preparation of (500−800 nm × 3.0−3.5 μm) $PbWO_4$[8] spindles using cetyltrimethylammonium bromine (CTAB). On the basis of EDS analysis, both rods and diamonds were assigned to $PbWO_4$.

Overall, the characterization results for the final scheelite nanomaterials indicate that the precursors used in the SPPT route produced WNPs that are fairly uniform, can have narrow size distributions, and possess distinct morphologies that are half to three-quarters smaller than scheelites synthesized from other routes.[4,5,7,8,43] Our synthetic route can produce < 30 nm size particles with distinct shapes because (i) $M(OR)_x$ and $M(NR_2)_x$ precursors are soluble and can

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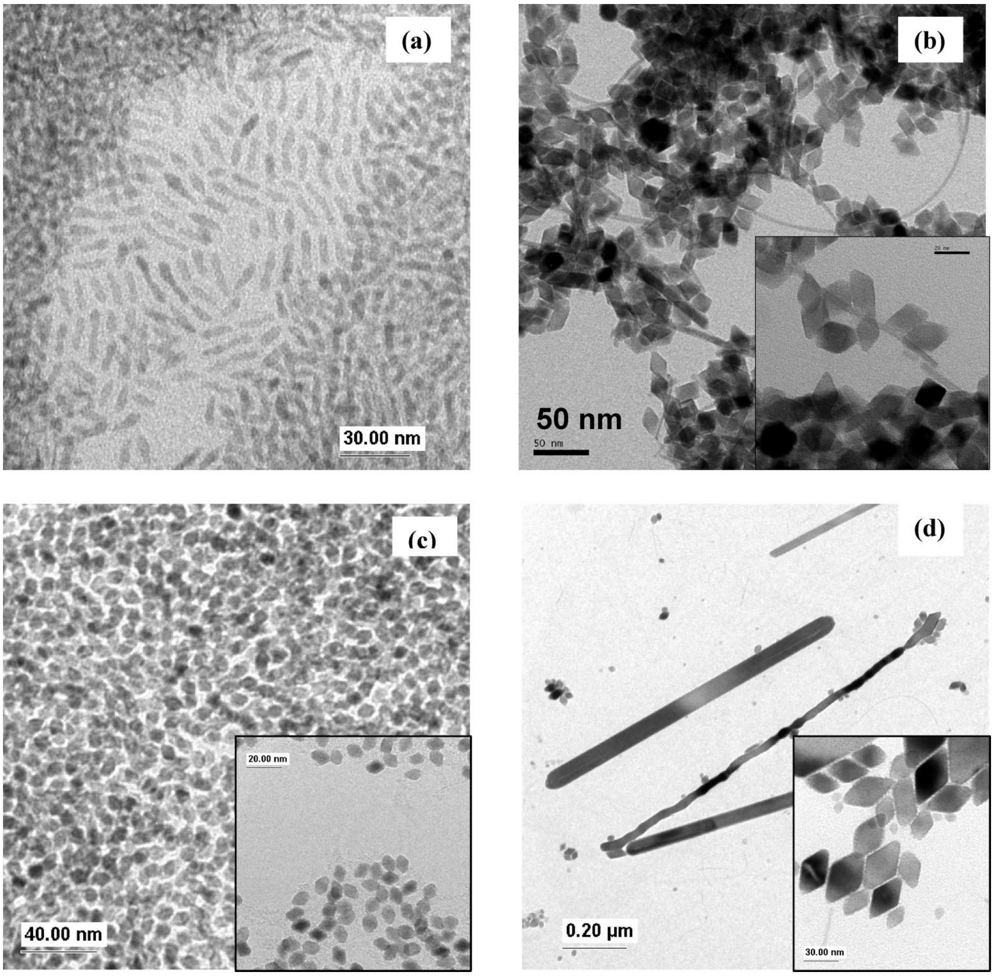

Figure 2. TEM images of scheelite WNPs synthesized from SPPT: (a) $CaWO_4$ (276 °C, 1 min), (b) $SrWO_4$ (367 °C, 2 min), inset 20 nm, (c) $BaWO_4$ (362 °C, 1 min), inset 20 nm, and (d) $PbWO_4$ (356 °C, 15 min), inset 30 nm.

easily decompose within the TOA/OA system at relatively low temperatures and (ii) the SSPT route provides ease of monitoring and adjusting crystallization growth. Over time, the mixture of $M(OR)_x$ and $M(NR_2)_x$ precursors in the TOA/OA produces rods from attached and oriented diamonds through the Ostwald ripening process.

SPPT Synthesis of Wolframite WNPs. The SPPT route also was extended to garner a series of wolframite nanorods, $(Mn,Fe)WO_4$ and MWO_4 (M = Mn, Fe, Zn), using **1**, **4**, and **5**; **1** and **4**; **1** and **5**; **1** and **6**; and **1** and **9**, respectively. All wolframite reactions were held for 10 min at specific crystallization temperatures to form 1-D MWO_4 materials. Figure 3 shows the characterization results for the synthesis of two simple wolframites, $FeWO_4$ and $ZnWO_4$. Using **1** and **6** at 330 °C, we were successful in the synthesis of phase pure $FeWO_4$ or ferberite (PDF no. 46-1146)[47] 10 × 50 nm rods, Figure 3a. From the reaction between **1** and **9** at 340 °C, $ZnWO_4$ or sanmartinite (PDF no. 15-0774) nanorods with 10−15 nm diameters and lengths of 60−150 nm were crystallized, Figure 3b. A secondary suboxide $W_{24}O_{68}$ (PDF no. 36-0103)[47] phase was also noted in the $ZnWO_4$ diffraction pattern. Through the SPPT route, the aspect ratio of our rods (5−10) are easily formed in 10 min as compared to 1-D MWO_4 prepared from a hydrothermal route that required pH adjustments and 12 h reaction times.[11] The solubility and decomposition of the precursors used also permit isolation of these WNPs in the TOA/OA system.

Next, the synthesis of the solid solution $(Mn_{0.75}Fe_{0.25})WO_4$ and its end members were investigated. Figures 4 and 5 show the TEM, EDS, and PXRD, respectively, for these reaction products. The observed C signal in the EDS spectra is due to a number of sources not directly related to the nanomaterial's C content (e.g.,TEM substrate, contamination buildup, differential absorption of the soft carbon X-rays). Figure 4a shows the bright field TEM image and EDS spectra of nanorods produced from **1**, **4**, and **5**. The rods produced have ∼25 nm diameters, variable lengths of 80−100 nm, and to our surprise, were found to contain Mg, Mn, Fe, and W. This serendipitous addition of Mg was a result of the incomplete removal of $MgBr_2$ formed during the synthesis of the mesityl precursors. ICP-MS was used to determined the molar ratios of the cations present in the nanorods and found Mg:Mn:Fe:W = 0.60:0.17:0.26:1.0. Due to the high Mg concentration and precursor volatility, the PXRD pattern (Figure 5a) for these rods was best identified as a high-temperature (HT) metastable phase of $MgWO_4$ (PDF no. 19-0776)[47] known to exist above ∼1200 °C.[51−54] Of the alkaline earth tungstates $MgWO_4$ crystallizes in the wolframite

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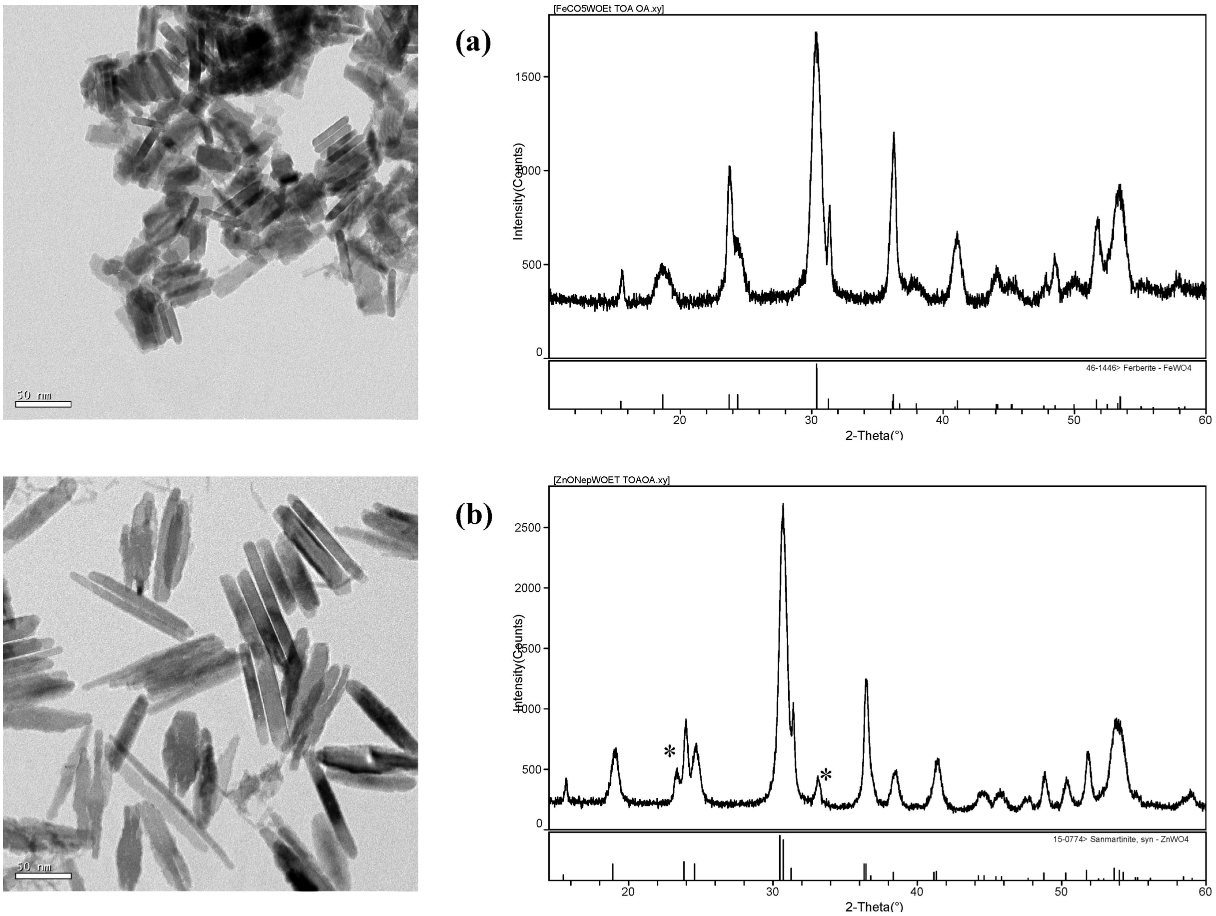

Figure 3. TEM images and respective PXRD patterns for wolframite WNPs synthesized from SPPT: (a) **1** and **6** made $FeWO_4$ (330 °C, 10 min) and (b) **1** and **9** made $ZnWO_4$ and *WO_x (340 °C, 10 min).

structure because of its smaller cationic radii and can form two polymorphs such as the tetragonal and HT triclinic phases.[53] Our nanorod's diffraction pattern was similar to the pattern for a HT triclinic $MgWO_4$ powder prepared from hydrothermal methods at 210 °C.[51,54] However, the PXRD pattern collected displayed shifted *d*-spacing along with additional allowed reflections. These observations are consistent with the formation of a solid solution due to the substitution of Mn^{2+} and Fe^{2+} for Mg^{2+}. A solid solution containing these cations is not unlikely because the ionic radii are within range (i.e., Mg^{2+} (0.72Å), Fe^{2+} (0.78Å), and Mn^{2+} (0.67Å))[55] to allow for substitution. From our data, we indexed a possible unit cell for the $(Mg_{0.60}Mn_{0.17}Fe_{0.26})WO_4$ nanorods as orthorhombic, *Cmcm*, where $a = 4.07(1)$ Å, $b = 23.60(1)$ Å, $c = 7.71(1)$ Å, and $V = 741$ Å^3.

Attempts to synthesize the two end members of the targeted binary phase were also performed with separate reactions between **1** and **4** or **1** and **5**. TEM images and EDS spectra for WNPs are shown in Figure 4b,c. EDS detected no differences in elemental composition for the mixture of rod-like (10 × 25 nm) and dot-like (10−30 nm) particles formed by **1** and **4** which had Mg, Mn, and W (Figure 4b). The primary phase for these WNPs was initially identified as $(Fe,Mn)WO_4$ (PDF no. 12-0727)[47] by PXRD. However, the absence of Fe presence in the EDS data and confirmation of Mn content suggested the formation of a $(Mg,Mn)WO_4$ solid solution, with a secondary phase due to the HT $MgWO_4$ phase (PDF no. 19-0776),[47] Figure 5b. The reaction between (**1** and **5**) formed uniform 10 × 80 nm rods with only Fe and W detected, Figure 4c. PXRD indicated multiple phases composed of $FeWO_4$ or ferberite (PDF no. 46-1446)[47] along with Fe_2O_3 (PDF no. 52-1449),[47] $W_{18}O_{49}$ (PDF no. 05-0392)[47] and HT $MgWO_4$ (PDF no. 19-0776),[47] Figure 5c. For clarity, a detailed index of the products formed is presented in the Supporting Information.

The formation of $(Mg_{0.60}Mn_{0.17}Fe_{0.26})WO_4$ and the mixed phases observed for $FeWO_4$ and $MnWO_4$ produced from the mestityl derivatives **4** and **5** suggest that these precursors are highly reactive and capable of forming multiple phases including a metastable HT phase under the conditions used. Further investigations on synthesizing wolframite solid solutions are currently underway to probe the precursor decomposition pathways[24] and to determine the reaction conditions necessary for isolating the various phases associated with $MgWO_4$. Understanding how to control phase formation of complex solid solutions and simple systems through the precursor chemistry used is necessary since it is not well understood how all nanostructure−property relationships will deviate from their bulk references. Also as previously discussed, the presence of Mg indicates that Br

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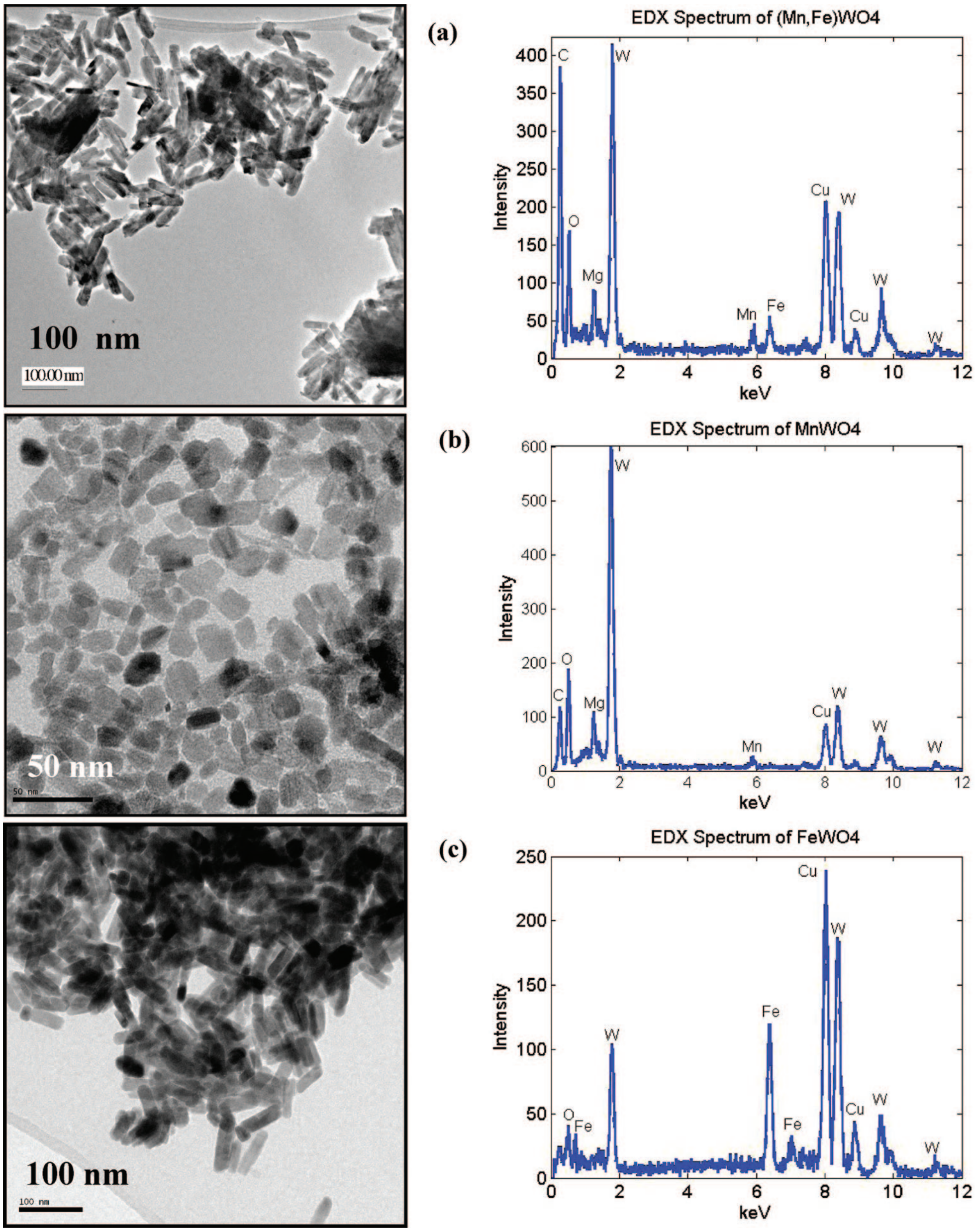

Figure 4. TEM images and respective EDS spectra of wolframite WNPs synthesized from SPPT: (a) $(Mg_{0.60}Mn_{0.17}Fe_{0.26})WO_4$ made from **1**, **4**, and **5** (386 °C, 10 min), (b) (Mg,Mn)WO_4,and $MgWO_4$ made from **1** and **4** (375 °C, 10 min) and (b) $FeWO_4$ and FeO_x/WO_x from **1** and **5** (351 °C, 10 min).

should be present as the counteranion.[32,33] Because Br was not detected by EDS, it may have reacted in the SPPT system in two different manners. In the first instance, free H^+ released either after the coordination of the OA to the nanocrystalline surface or from the reaction of OA with the precursors could lead to the formation of HBr gas. Or Br may have remained in solution and coordinated with a protonated TOA to form TOA^+Br^-, which could have been rinsed away with solvents used during the washing process.

SPPT Synthesis of $W_{18}O_{49}$ Rods. Finally, **1** was was used to explore the precursor influence on the final WO_x phase and morphology produced in the TOA/OA SPPT route. The TEM images, Figure 6a, reveal that the decomposition reaction of **1** formed single-crystalline nanorods with ~5 nm diameters and lengths of ~100 nm. Two strong reflections (010) and (020) observed in the PXRD pattern, Figure 6b, were indexed to $W_{18}O_{49}$ (PDF no. 05-0392),[47] an oxygen deficient $WO_{2.72}$, and intermediate reduction product of WO_3.[56] The broadest peaks identified in the pattern were associated with the nonuniform *hkl* line broadening where the 0*k*0 reflections have sharp peak intensity and the *h* and *l* reflections are broadened. The nanowire's large aspect ratio produces these significant differences in the fwhm values of the peak profiles, as noted for other $W_{18}O_{49}$ nanorods.[19,20] The broadness was not found to be associated with the zero-background sample holder.

The phase and morphology produced from **1** in the TOA/OA system has been reported for other solution[19−21,42] and synthetic routes[56] used to produce nano- and micrometer sized $W_{18}O_{49}$ materials from various tungsten precursors. It can be inferred that any excess $W(OEt)_6$ in the MWO_4 reactions could easily form the secondary suboxides phases found in the scheelite and wolframite diffraction patterns.

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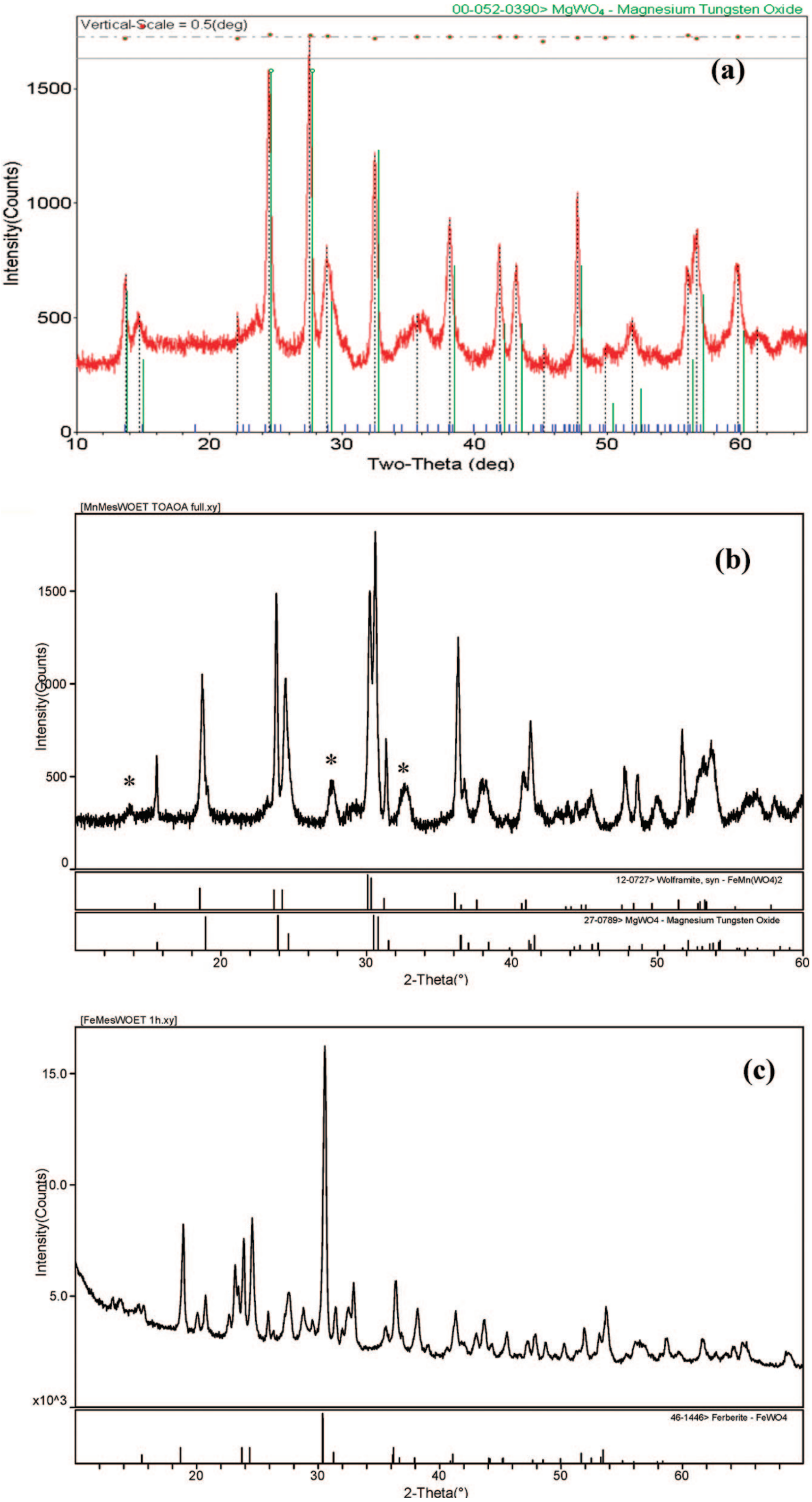

Figure 5. PXRD patterns of wolframite WNPs synthesized from SPPT: (a) **1**, **4**, and **5** made ($(Mg_{0.60}Mn_{0.17}Fe_{0.26})WO_4$), (b) **1** and **4** made $(Mg,Mn)WO_4$ and *HT $MgWO_4$, and (c) **1** and **5** made $FeWO_4$ and FeO_x/WO_x phases.

A preliminary investigation of the reaction mechanism for the SPPT route, by FTIR spectroscopy, suggests that $M(OR)_x$ reacts with the OA in the TOA/OA system to produce metal alkoxy acetate species before decomposing into the WNPs (**1** reacted with OA, C═O 1561 cm^{-1}; neat OA, C═O 1710 cm^{-1}).[57−61] The formation of a $W(OR)_x(OA)_y$ species in the TOA/OA solvent system is expected, since $M(OR)_x$ readily forms complex structures in the presence of carboxylic acids;[57−63] however, due to esterification more complex oxo structures may form as well.[57−63]

SOLVO Synthesis of WNPs. To demonstrate the versatility of the precursors used to synthesize WNPs, we extended their use to produce WO_x and MWO_4 in a SOLVO route using BzOH. Recently, A^ETiO_3 nanoparticles were prepared

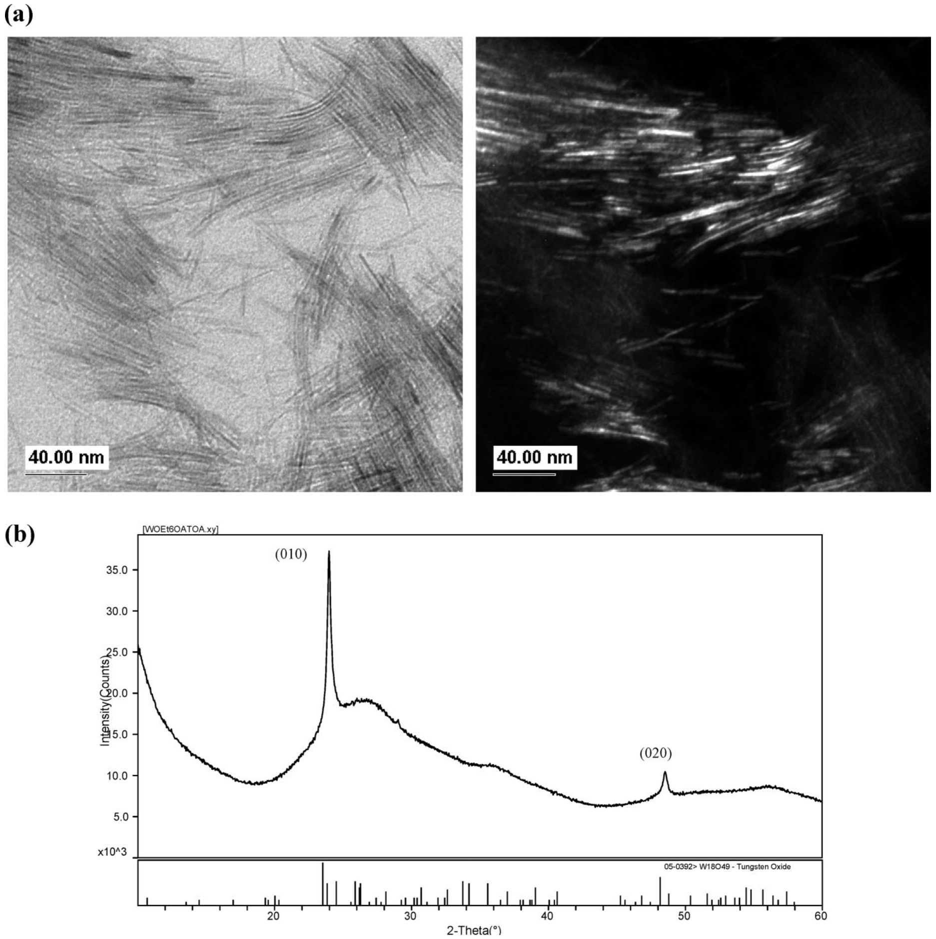

Figure 6. Characterization of $W_{18}O_{49}$ synthesized from **1** using SPPT (310 °C, 10 min): (a) bright- and dark-field TEM images and (b) PXRD pattern.

in a BzOH SOLVO route from $A^E(ONep)_2$, $A^ETi_2(ONep)_{10}$, $Ti(ONep)_4$, and in situ generated "$A^ETi(OCH_2C_6H_5)_6$".[28,64] This nonaqueous system has proven to be an excellent SOLVO route for the general synthesis of metal oxides prepared from $M(OR)_x$ and $M(NR)_x$.

WO_3. The reaction of **1** in BzOH formed light-blue precipitate that crystallized as a mixture of tungsten oxide WO_3 (PDF no. 04-005-4487)[47] and tungsten oxide hydrate $*WO_3 \cdot 0.33H_2O$ (PDF no. 01-087-1203), Figure 7a. Although anhydrous BzOH was used and the reaction was prepared in a glovebox, a secondary hydrated tungsten oxide formed. SEM and TEM images of the precipitate (Figure 7b,c, respectively) reveal that WO_3 wires with various aspect ratios were produced with lengths up to 10 μm long. This is in contrast to (20−100 × 300−1000 nm) $W_{18}O_{49}$ rods and (30−100 nm) $WO_3 \cdot H_2O$ platelets, respectively synthesized from $W(OPr^i)_6$ and WCl_6 in BzOH at low temperatures and ambient pressure.[27]

$CaWO_4$. The reaction between **1** and **2** generated 15−40 nm scheelite and WO_x dots, Figure 8. These $CaWO_4$ dots are similar to those prepared from other SOLVO routes using $Na_2WO_4 \cdot H_2O$ in ethylene glycol or poly(ethylene glycol).[1,2] Under the conditions evaluated, the BzOH system does not appear to aid in directing crystalline growth of $CaWO_4$.

Comparison of the SOLVO and SPPT routes show that the two are amenable to $M(OR)_x$ and $M(NR_2)_x$ precursors to yield WO_x and MWO_4 particles. However, the SPPT route has an advantage over SOLVO because uniform and shaped particles below 30 nm can easily be garnered in the TOA/OA system. Through SPPT, these previously unattained characteristics of MWO_4 can be produced.

Luminescent Properties of WNPs. Through our synthesis routes, we were able to produce unique WNP models for an investigation of size and morphology effects on the luminescence behavior.[3,18,20,49] Since previous synthetic routes to MWO_4 have been limited in producing uniform < 30 nm diamonds and rods and have not used TOA/OA or BZOH solvent systems, we used this opportunity to measure the photoluminescent (PL) emission of our 15 nm $CaWO_4$ rods and 10 nm $BaWO_4$ diamonds. These particular MWO_4 samples have ideal shapes and sizes necessary for alternative bioimaging applications and are being further investigated

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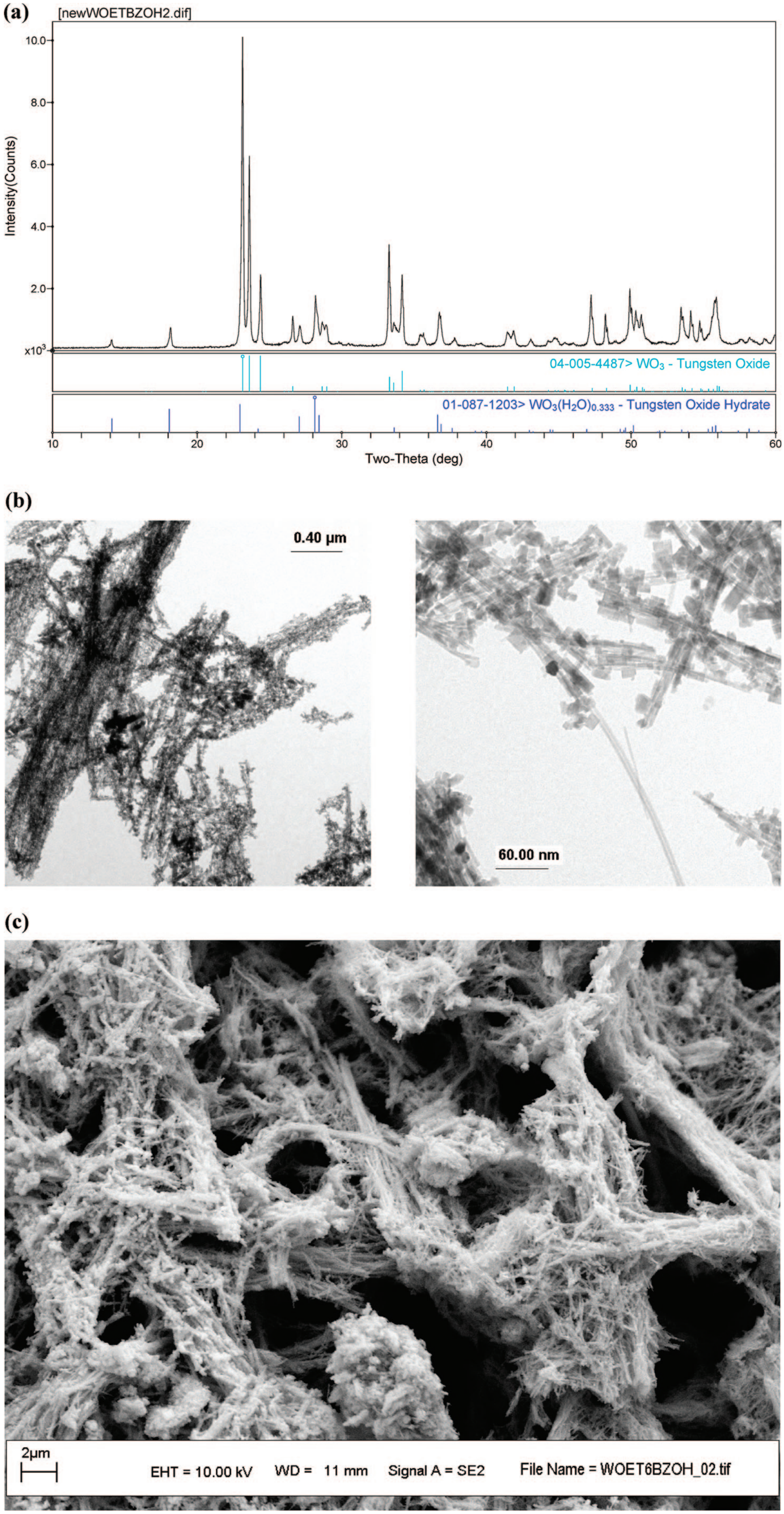

Figure 7. Characterization of WO_3 and *$WO_3 \cdot 0.33H_2O$ synthesized from **1** using SOLVO (200 °C, 48 h): (a) PXRD, (b) TEM, and (c) SEM image.

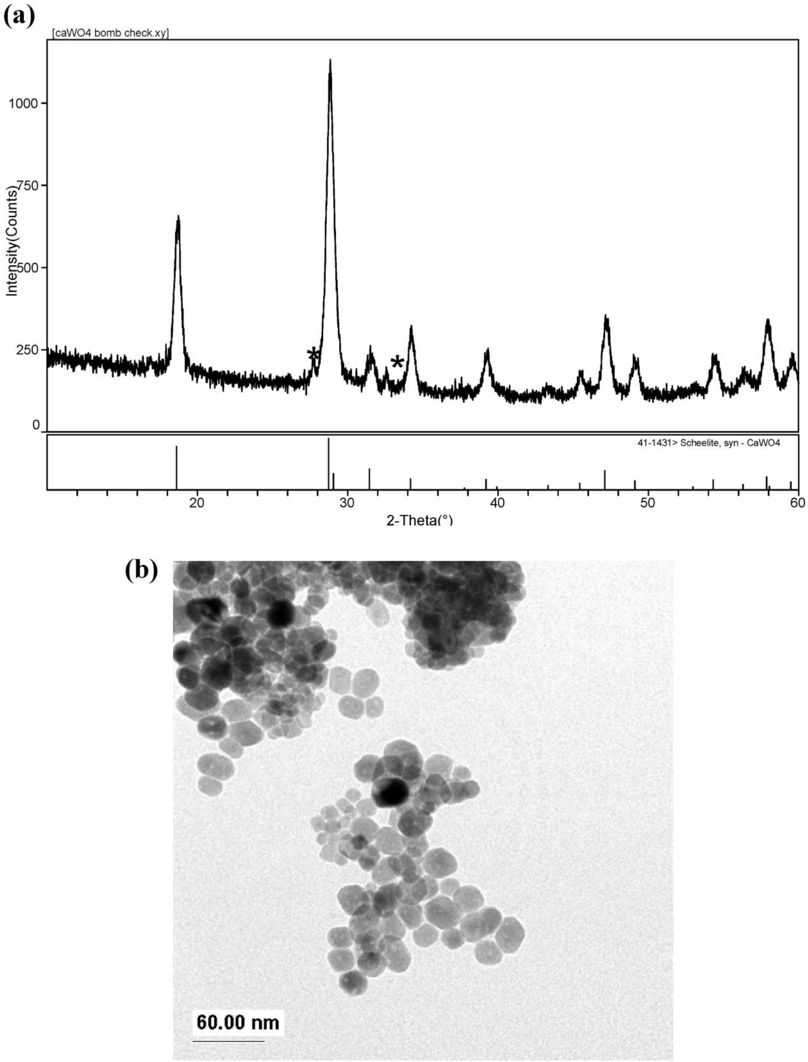

Figure 8. Characterization of $CaWO_4$ and $*WO_x$ synthesized from **1** and **2** using SOLVO (200 °C, 48 h): (a) PXRD and (b) TEM.

with lanthanide activators. Measurements of the PL behavior of $W_{18}O_{49}$ rods and 10−30 nm $CaWO_4$ dots were also performed. All particles were washed 3 times prior to PL characterization. The room temperature PL emission spectra produced for these materials, using $\lambda_{ex} = 320$ nm, are shown in Figure 9. A vial containing 5 × 15 nm $CaWO_4$ rods dispersed in $CHCl_3$ is shown in Figure 10. Under white light the solution is colorless, and under a UV light from a hand-held emitter it fluoresces blue. PL investigations on the remaining MWO_4 are underway.

The exact mechanism for the optical behavior of $W_{18}O_{49}$ is not well understood since there are few examples of room temperature PL data for $W_{18}O_{49}$ nanomaterials from which to derive information. Multiple emission maxima ($\lambda_{ex} = 275$ nm) have been previously observed;[20] however, we found that our $W_{18}O_{49}$ nanorods produced only a single broad emission spectrum centered at 430 nm, Figure 9a. Our data was in close agreement with the broad PL emission reported for $WO_3 \cdot H_2O$ particles centered at 425 nm ($\lambda_{ex} = 365$ nm).[22] One similarity to the multiple maximum spectrum reported for other $W_{18}O_{49}$ rods is that our λ_{em} is close to the reported length dependent blue $\lambda_{em} = 437$ nm ($\lambda_{ex} = 275$ nm)[20] that increases relative to rod length. The PL behavior of WO_x nanoparticles and rods, in general, has been attributed to result from band-to-band transitions and oxygen defects found at the particle surface. Differences noted may result from the surface moieties and oxygen defects as opposed to the morphology since they are based on particles produced in oleylamine[20] and benzyl alcohol,[22] respectively.

The intrinsic luminescence behavior of the WO_4^- for the 15 nm $CaWO_4$ rods, 10−30 nm $CaWO_4$ dots, and 10 nm $BaWO_4$ diamonds was also probed at room temperature using $\lambda_{ex} = 320$ nm, Figure 9. Similar to WO_x nanomaterials, the effects of size, morphology, and surface chemistry can change the emission behavior of MWO_4 nanomaterials. Results for our MWO_4 indicate that surface chemistry and particle size have a role in PL intensity and emission behavior. For example, Figure 9b,c shows the emission spectra for $CaWO_4$ rods and dots, respectively. The broad blue PL emission observed for these $CaWO_4$ rods (from TOA/OA) was centered at 425 nm while the $CaWO_4$ dots (from BzOH) had an emission at 395 nm. The $BaWO_4$ diamonds had an emission at 420 nm, Figure 9d. Despite the morphology and particle size, the PL emission of the 15 nm $CaWO_4$ rods and 10 nm $BaWO_4$ diamonds are within reported ranges for both bulk powders[65] and nanoparticles[2,49] found at 421 and 417 nm ($\lambda_{ex} = 290$ and 247), respectively. The PL emission maximum, for our 10−30 nm $CaWO_4$ dots,

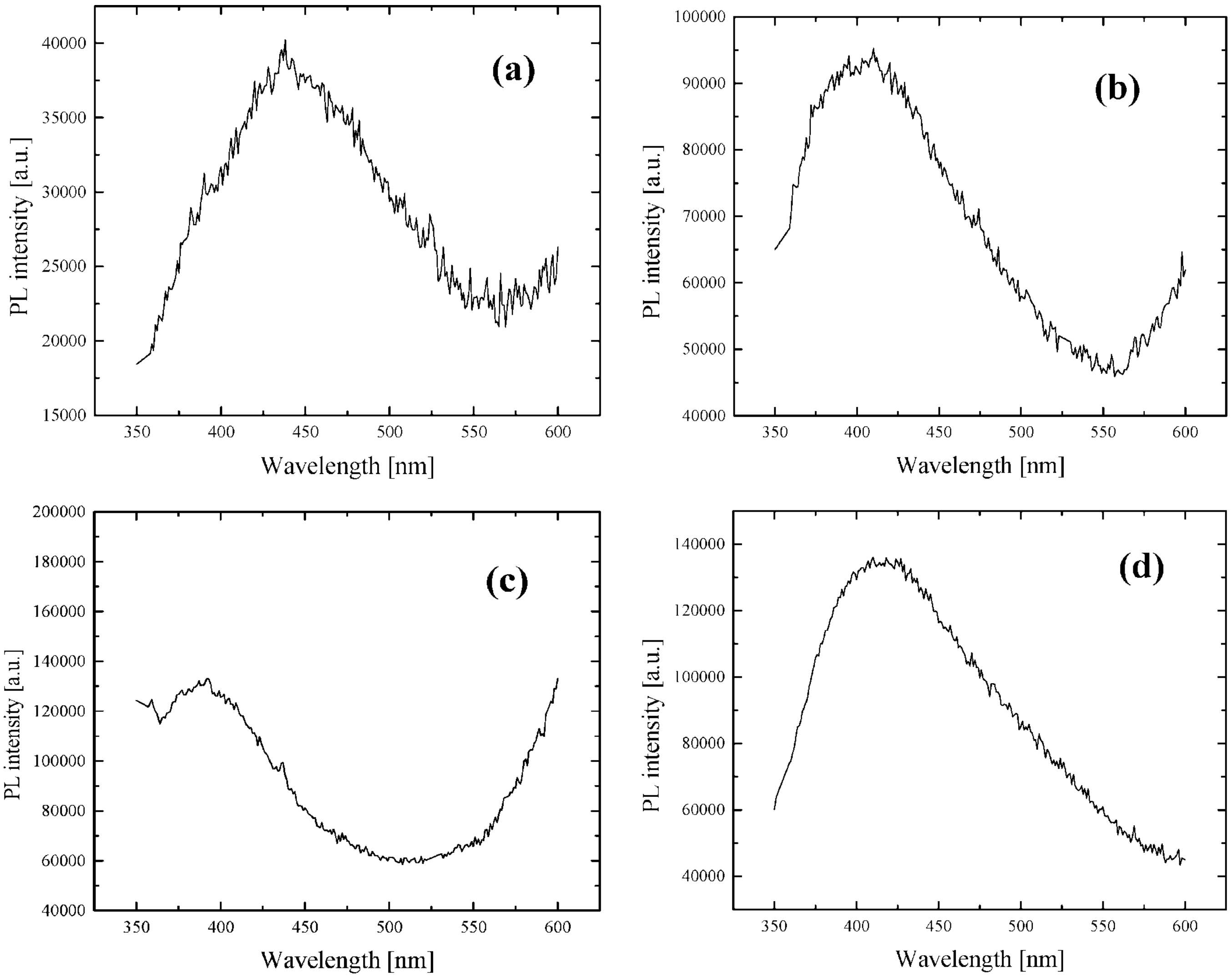

Figure 9. Room temperature PL emission spectra of (a) 5 × 100 nm $W_{18}O_{49}$ rods, (b) 5 × 15 nm $CaWO_4$ rods, (c) 10 − 30 nm $CaWO_4$ dots, and (d) 10 nm $BaWO_4$ diamonds, $\lambda_{ex} = 320$ nm.

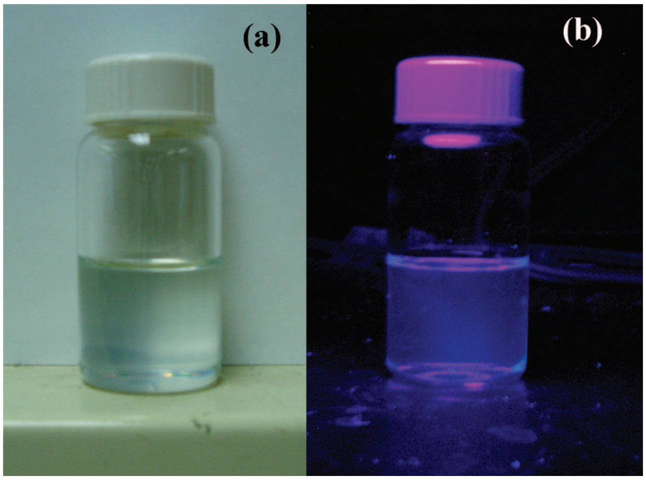

Figure 10. Picture of $CaWO_4$ rods dispersed in $CHCl_3$ under (a) white light and (b) UV light from a hand-held emitter.

were also within close agreement with films made from $CaWO_4$ dots prepared from reverse micelles ($\lambda_{em} = 401$ nm, $\lambda_{ex} = 240$ nm).[65] Other reports on $CaWO_4$ nanoparticle fluorescence also indicate that particle size and surface chemistry tend to change the intensity and emission maxima.[3,4,49] For example, PL emissions such as 430 nm ($\lambda_{ex} = 283$ nm),[1] 435 nm ($\lambda_{ex} = 238$ nm), and 521 nm ($\lambda_{ex} = 360$ nm)[4] have all been reported for various particle sizes and surface chemistries of $CaWO_4$. In addition, the PL intensity is considered tunable by morphology. Recently, two reports concerning the effects of a critical size and morphology of PL emission behavior of $CaWO_4$ particles have suggested that rods can enhance PL intensity, whereas intensity can decrease as a particle size diminishes.[2,49] Overall, broad and weak PL emission demonstrates that our $CaWO_4$ rods and $BaWO_4$ diamonds have low quantum efficiencies but continue to fluoresce for morphologies in this size regime.

Summary and Conclusions

For the first time, a general SPPT route to scheelite, wolframite, and tungsten oxide WNPs was developed using $M(OR)_x$, $M(NR_2)_x$, $M(CO)_x$, and MR_x precursors. Medium-to-high yields of the as-prepared crystalline products were isolated from either SPPT (trioctylamine/oleic acid) and

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(65) Zhang, G.; Jia, R.; Wu, Q. *Mater. Sci. Eng. B* **2006**, *128*, 254.

SOLVO (benzyl alcohol) routes at moderate temperatures. A reduction in crystallization time (minutes) was achieved by precursor selection and the SPPT route, which is in considerable contrast to solvo- or hydrothermal routes which require hours or days. Since the final WNP morphology and size produced by these routes could not be explained by the PSA, the processing conditions for the routes and oriented attachment mechanisms were determined to be the influencing factors. Our experiments did indicate that the SPPT route was successful in generating phase pure, homogeneous WNPs with distinct morphologies below 30 nm in size. The final phases of the SPPT derived materials were found to vary based on precursor selection. Phase pure MWO_4 particles were produced from an all $M(OR)_x$ route or from the combination of an $M(OR)_x$ with $M(NR_2)_x$ and $M(CO)_x$. For the wolframites, the reactivity and precursor decomposition for the mesityl derivatives allowed the formation of a high-temperature metastable phase of $(Mg_{0.60}Mn_{0.17}Fe_{0.26})WO_4$. Examination of the mesityl derivatives for the synthesis of wolframite end members indicated that their reactivity and decomposition led to mixed phase products. Further evidence for how the reactivity and precursor decomposition influences the phase of the materials produced was also observed for the zinc akyl *neo*-pentoxide precursor (**9**) which formed a mixed phase product versus the alkaline earth *neo*-pentoxides (**7** and **8**) which formed phase pure nanomaterials. Finally, the room temperature photoluminescence was observed using $\lambda_{ex} = 320$ nm and produced $\lambda_{em} = 430$, 420, 395, and 420 nm for $W_{18}O_{49}$ rods, 15 nm $CaWO_4$ rods, 10−30 nm particles, and 10 nm diamonds $BaWO_4$, respectively, demonstrating that luminescence of WNPs persists in <30 nm particles with various morphologies.

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Supporting Information Available: TEM images, detailed indexing of products, and FTIR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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