SAND2014-18501C

Growth Mechanisms and Luminescent Properties of Metal Tungstate Nanomaterials

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Sandia National Laboratories — Advanced Materials Laboratory

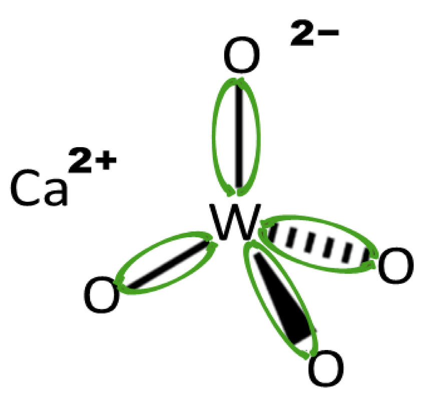
Abstract

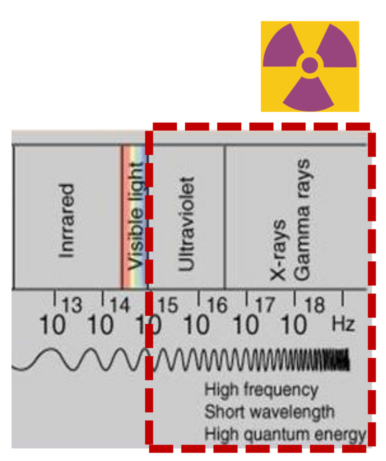
Controlling metal tungstate (MWO_4; where M = Ca, Pb, Cd) nanocrystal growth is necessary to fine-tune luminescence, size, and morphology. These final nanocrystal characteristics are being examined for scintillator, solid-state lighting, bioimaging, and tagging agent applications. This poster illustrates the materials chemistry used to unravel MWO_4 growth mechanisms and control the properties of $CaWO_4$ nanomaterials produced by solution precipitation. The effects of several variables were studied on the formation, shape, physical appearance, size, surface chemistry and luminescence behavior of the final product. The processing variables examined included the metal precursors, coordinating solvents, time, and temperature. In all reactions numerous color changes were observed. Through temporal investigations, some of the temperature stages were characterized to determine the process of scheelite formation over time. The nanomaterials isolated were characterized by PXRD, FTIR, and TEM. Finally Ion Beam Induced Luminescence was performed on other MWO_4 samples to characterize nanoscale effects. Analysis demonstrated MWO_4 nanocrystals can withstand simulated neutron environments and that their luminescence is impacted by crystal size.

Attributes of Metal Tungstates

High Energy Radiation Scintillators

Electron charge transfer occurs within the W–O bonds of the tungstate anion. These are the sites where high energy radiation absorption leads to electron excitation and return to ground state causing visible light emission. It is this phenomena, also known as photoinduced luminescence, that lends metal tungstates their optical properties.

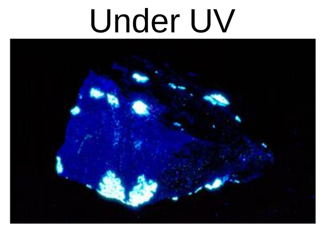




Mineral $CaWO_4$

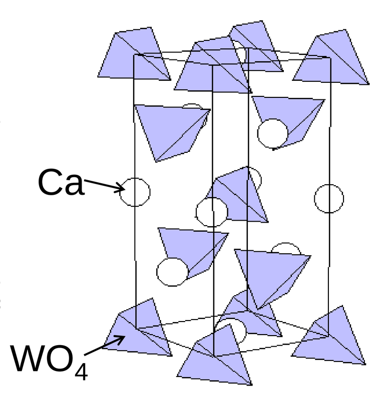
Under Visible

Under UV



Scheelite Crystal Structure

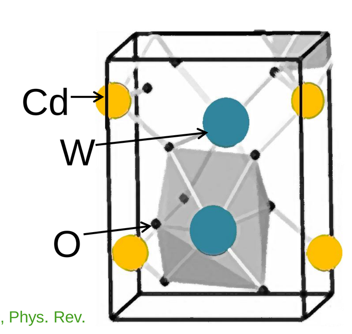
When crystalline, some metal tungstates with larger counter cations (incl. Pb, Ca) adopt a scheelite unit cell named for the mineral calcium tungstate. It is a body and corner centered tetragonal unit cell with pairs of ions occupying the interstitial sites. The tungstate ion assumes a tetrahedral shape and is found at the vertices of the unit cell.



Lacomba-Perales, R.; Ruiz-Fuertes, J.; Errandonea, D.; Martinez-Garcia, D.; Segura, A., Europhys. Lett. 2008, 83, 37002–37007.

Wolframite Crystal Structure

Metal tungstates with smaller counter cations (e.g., Cd) adopt a wolframite unit cell. It is monoclinic and the tungstate ion assumes a roughly octahedral coordination with the vertices occupied by oxygen atoms. Two of these oxygen reside outside the unit cell.

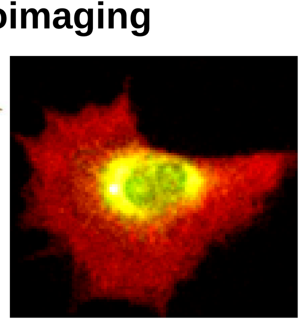


D. Errandonea, F. J. Manjon, N. G., P. Rodriguez-Hernandez, S. Radescu, A. Mujica, A. Muñoz, and C. Y. Tu, Phys. Rev. B 78, 054116 2008.
Williams, R.T., Zhang, Y.C., Abraham, Y., and Holzwarth, N.A.W.,, Proc. V Int. Conf. on Inorganic Scintillators and Their Applications, SCINT'99, Moscow: Mosk. Gos. Univ., 2000, pp. 118–127.

Applications

Due to their luminescent properties metal tungstates have many possible applications. As nanocrystals dispersed in solution they can be delivered into cells for bioimaging or embedded into polymers for scintillator and radiation detection applications. An additional benefit of using metal tungstates for radiation detection is their relatively high tolerances for ionizing radiation; they can withstand significant dosage before any substantial breakdown occurs. Finally, the relative ease of nanomaterial synthesis makes them of interest as a replacement for single crystal scintillators that are hard to grow.

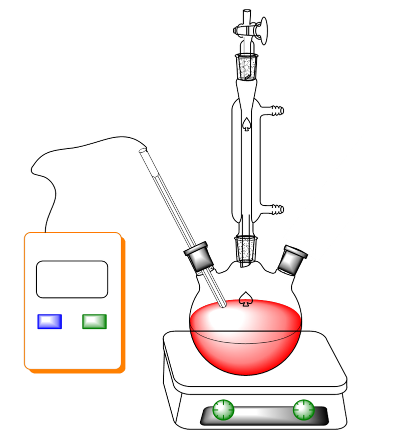
Bioimaging

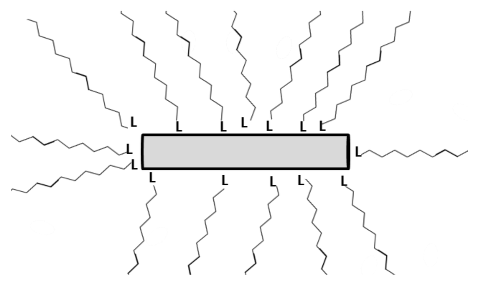


Radiation Detection & Scintillators

Solution Precipitation Routes Generate MWO_4 Nanomaterials With Various Morphologies

Solution Precipitation (SPPT) Route to Nanocrystals

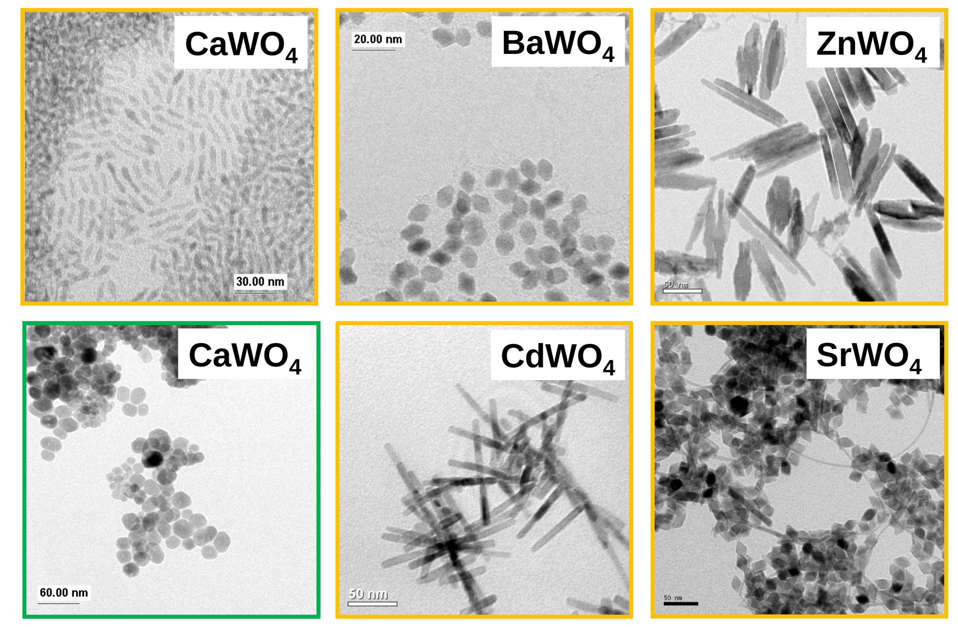




The MWO_4 nanocrystals were synthesized using the solution precipitation (SPPT) route. The apparatus shown above allows for uniform heating, without solvent loss, of the reaction under an argon atmosphere. Once the necessary temperature is reached, MWO_4 molecules begin to precipitate out of solution, nucleating to form nanoscale crystals. These crystals grow by Ostwald Ripening as smaller groups coalesce over time. The coordinating solvents (ligands) in solution weakly bind to the surface of the crystals and prevents aggregation.

Variation of Counter Cation and Synthetic Route Allow for Diverse Morphologies

Examples of MWO_4 morphologies produced from SPPT using trioctylamine and oleic acid as coordinating solvents are shown in the TEM images below. Switching to solvothermal processing with benzyl alcohol generates spherical $CaWO_4$.

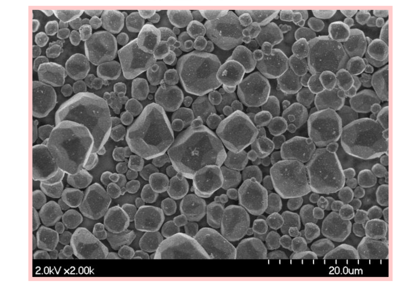


Hernandez-Sanchez, B. A.; Boyle, T. J.; Pratt III, H. P.; Dunphy, D.; Brewer, L. N. Rodriguez, M.A. Chem. Mater., 2008, 20, 6643–6656.

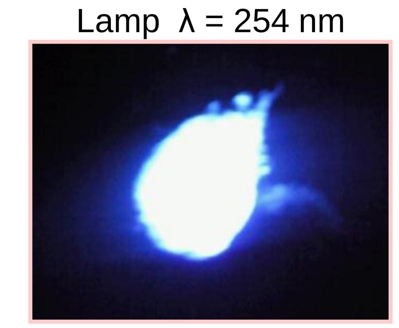
Understanding Solution Route Chemistry is Important to Control Nanocrystal Luminescent Properties.

Commercial $CaWO_4$ Powder (Sigma Aldrich)

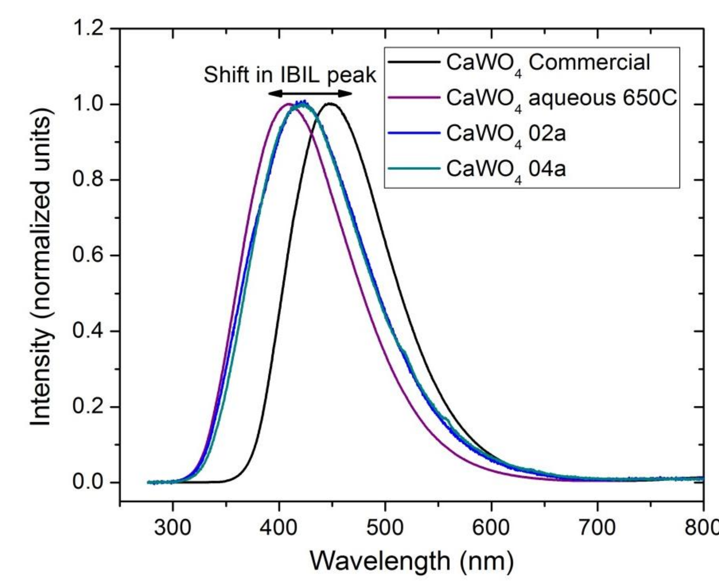
SEM



Excited Using Handheld UV Lamp λ = 254 nm



IBIL Comparison of Nano to Micro $CaWO_4$



Crystal size and surface chemistry can be controlled by processing. As crystal size decreases, emission wavelength undergoes a blue-shift when compared to micron sized $CaWO_4$.

Sample (Particle Size)	Aqueous/650°C (150 nm)	L. S. SPPT O2a (10 nm)	Commercial (2-15 µm)
IBIL λ_{em}	409 nm	421 nm	448 nm

Hernandez-Sanchez , B. A.; Boyle, T. J.; Villone, J.; Yang, P.; M.; Hoppe, S.; Thoma, S.; Hattar, K. M.; Doty, F. P.; Proc. SPIE 8509, Penetrating Radiation Systems and Applications XIII, 85090G (October 19, 2012)

Exploring SPPT Variables to Understand $CaWO_4$ Nanocrystal Growth Behavior

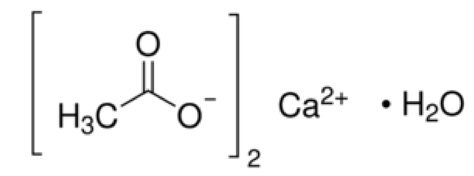
Expansion of Previous Research and Reaction Parameters

$$Ca(O_2CCH_3)_2 + W(OCH_2CH_3)_n \xrightarrow[\text{X min.}]{\text{Sol. }\Delta} CaWO_4$$

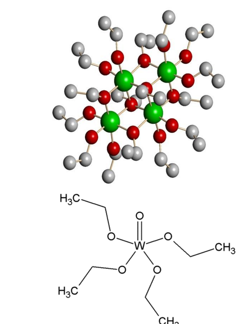
Calcium tungstate ($CaWO_4$) nanocrystals were previously synthesized by heating tungsten(VI) ethoxide and calcium *bis*(trimethylsilyl)amide in a ~2:1 molar ratio of trioctylamine (TOA) to oleic acid (OA). For commercial applications, this synthetic route needed to be modified. The first step for this work was to identify if the commercially available calcium acetate monohydrate could replace calcium amide to produce $CaWO_4$. Next the tungsten precursor was explored since tungsten(VI) ethoxide is impure and could impact nanocrystalline phase behavior. Solvents were also tested to determine their effects on $CaWO_4$ morphology. Reactions shown below were conducted using the 2:1 ratio of TOA/OA and with each individual solvent. TEM images and PXRD for reactions containing tungsten(V) ethoxide are presented.

Metal Precursors & Solvents Used in SPPT

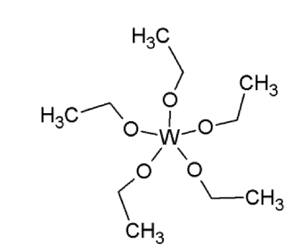
Metal Precursors



Calcium Acetate Monohydrate



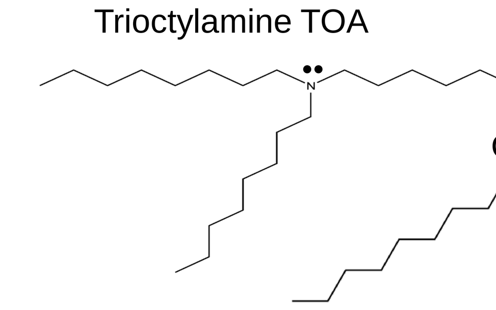
Tungsten(VI) Ethoxide W6



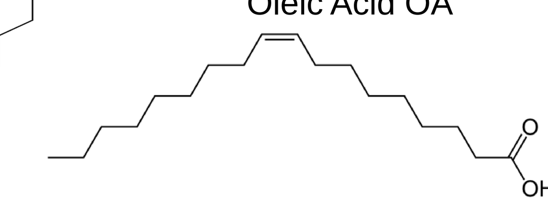
Tungsten(V) Ethoxide W5

Coordinating Solvents

Trioctylamine TOA



Oleic Acid OA

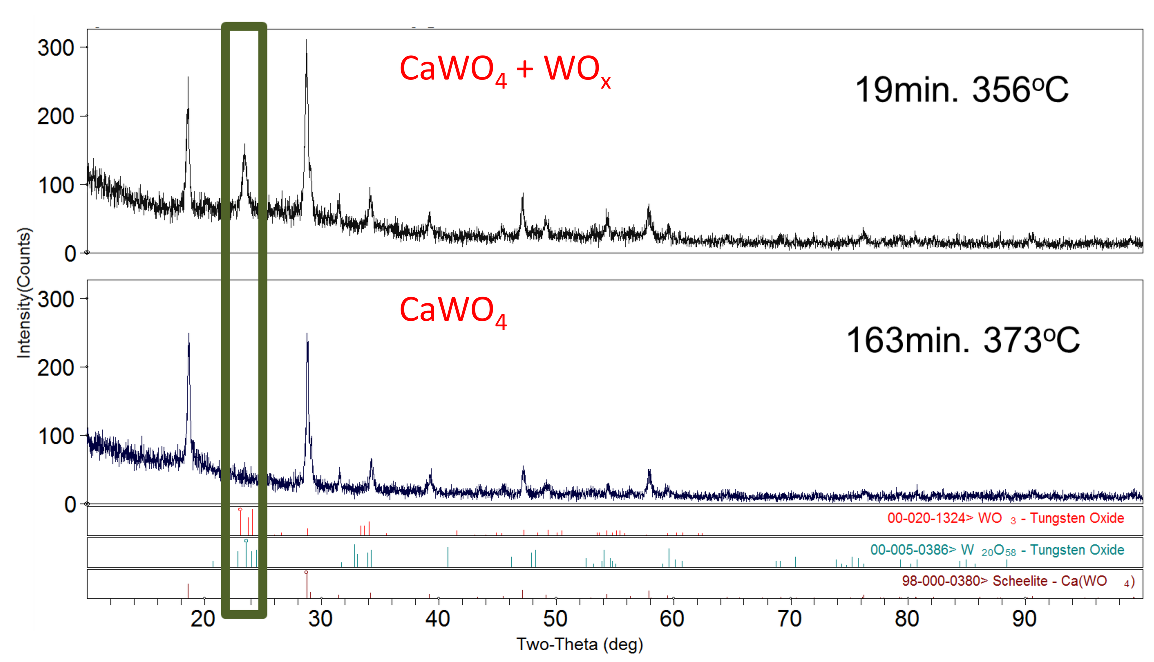


Variable Effects on Product Formation & Appearance

Tungsten Precursor	Solvent	Max Temp (°C)	Time (min.)	Final Color
$W(OCH_2CH_3)_5$	2:1 TOA/OA	280	18	White
$W(OCH_2CH_3)_6$	2:1 TOA/OA	266	31	White
$W(OCH_2CH_3)_5$	TOA	367	101	Blue-white
$W(OCH_2CH_3)_6$	TOA	363	171	Blue-white
$W(OCH_2CH_3)_5$	OA	369	163	Brown
$W(OCH_2CH_3)_6$	OA	384	186	Brown

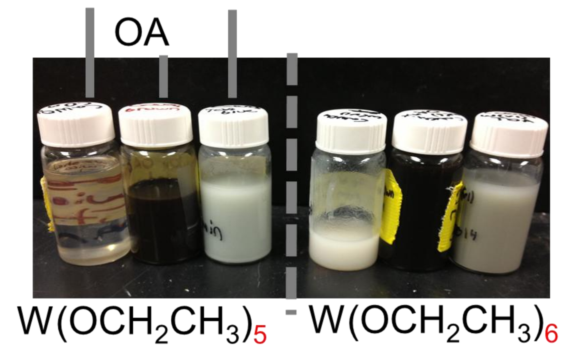
The $CaWO_4$ reactions were heated at their respective maximum temperatures until no further color changes were observed and the product was confirmed to be phase pure Scheelite by Powder X-ray Diffraction (PXRD).

Phase Behavior Over Time of $CaWO_4$ Using W5 & OA

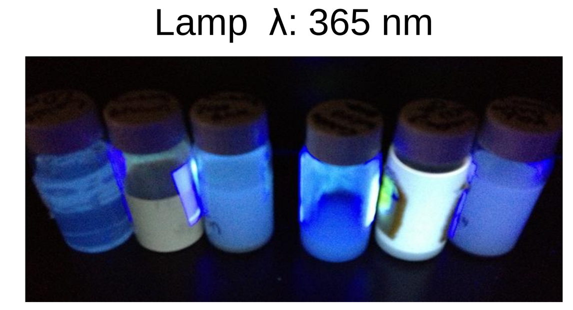


All reactions underwent a blue color change at one point during the heating process. For the highlighted reaction in the table, that may be representative of others, samples were characterized by PXRD and TEM when the blue was present (19 min.) and after it had long disappeared (163 min.). The presence of the boxed area in the diffraction pattern after 19 minutes suggests that the blue precipitate was a type of tungsten oxide that formed prior or in addition to the calcium tungstate during the reaction. After further heating only $CaWO_4$ remained. meaning the WO_x could be driving the rod shape. Further EDS analysis is needed to help confirm.

Solvent and Tungsten Precursor Effects on Calcium Tungstate Observed Luminescence

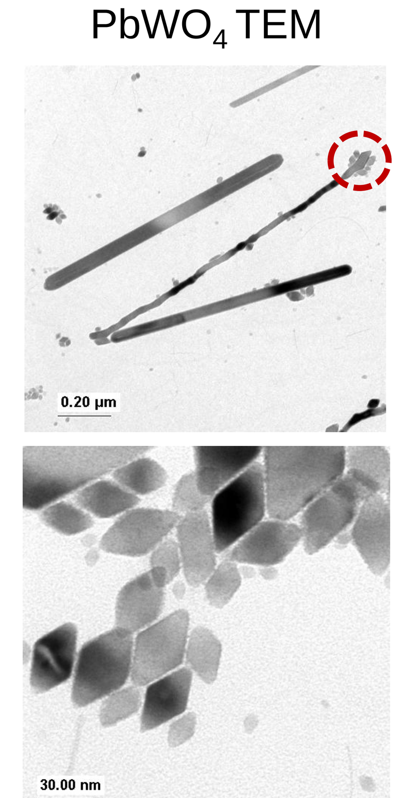


Excited Using Handheld UV Lamp λ: 365 nm



Rod Formation Through Preferred Orientation

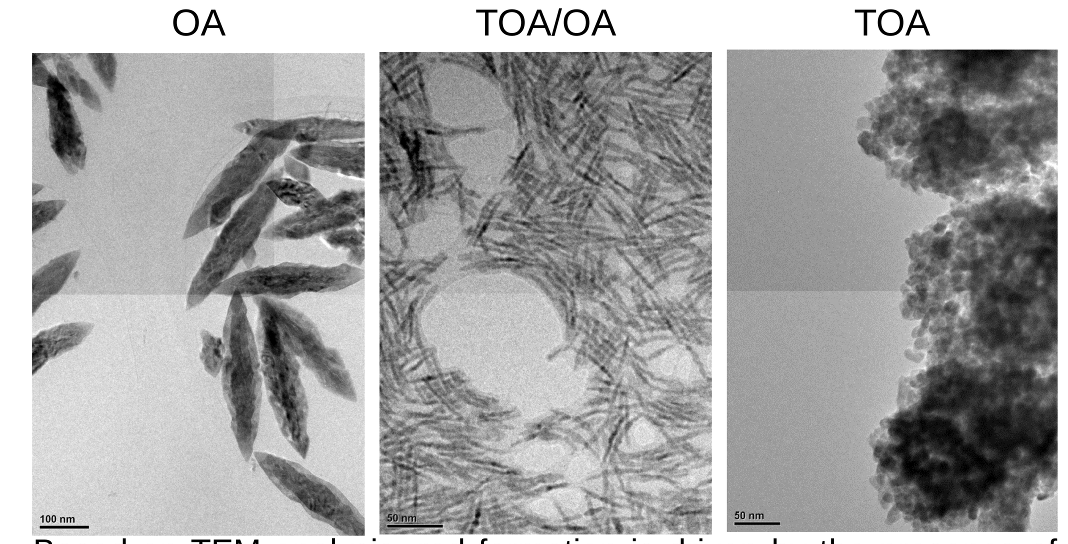
$PbWO_4$ TEM



$CaWO_4$ (W5/OA) AC STEM

During heating, some scheelite nanocrystals may first grow parallelograms, which coalesce over time to form polycrystalline rods

Solvent Effects on $CaWO_4$ Morphology Using W5 Precursor



Based on TEM analysis, rod formation is driven by the presence of oleic acid (OA). Characterization on several reactions using OA contained some quantity of rod structures. Reactions containing only trioctylamine (TOA) formed spheres instead.

Summary

- Oleic acid drives rod production while trioctylamine generates dots. The 2:1 ratio forms rods.
- With tungsten(V) ethoxide and oleic acid, the reaction forms a mixed phases of tungsten oxide and scheelite before phase pure scheelite is obtained.
- Luminescence and color of dispersed crystals may be influenced by ligand selection.
- Polycrystalline rods are formed by preferred orientation of parallelograms over time.

Acknowledgements

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.