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Size Effects on the Properties of High Z Scintillator Materials

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ABSTRACT

Particle size effects of nano- and polycrystalline metal tungstate MWO_4 ($M = Ca, Pb, Cd$) scintillators were examined through a comparison of commercially available powders and solution precipitation prepared nanoscaled materials. The scintillation behaviors of nanoparticles and commercial powders were examined with ion beam induced luminescence (IBIL), photoluminescence (PL), and cathodoluminescence (CL) spectroscopy techniques. For commercial microns sized MWO_4 powders, spectral emission differences between CL and PL were only observed for Cd and Pb tungstates when compared to reported single crystals. The IBIL wavelength emissions also differed from the commercial MWO_4 CL and PL data and were red shifted by 28 and 14 nm for $CaWO_4$ and $CdWO_4$; respectively, while $PbWO_4$ had no significant change. IBIL analysis on $CaWO_4$ nanoparticles produced a 40 nm blue shift from the commercial powder emission. These preliminary results suggest that both size and cation Z may affect the emission properties of the MWO_4 scintillators.

Keywords: Nanoscintillators, Metal Tungstates MWO_4 ($M = Ca, Pb, Cd$), Ion Beam Induced Luminescence (IBIL), Photoluminescence (PL), Cathodoluminescence (CL)

1. INTRODUCTION

Currently the properties of single crystal scintillators (e.g., chemical instability, cost, difficult processing, poor energy resolution, etc.) have limited their utility.[1, 2] In response to this, new compositions of polycrystalline and nanomaterials have been explored for scintillator applications. Some materials of interest include standard metal tungstates MWO_4 ($M = Pb, Ca, Cd$), lanthanide doped alkaline earth chalcogenides ($CaS:Ln^{3+}$), bismuth germanium oxides $Bi_4Ge_3O_{12}$ (BGO), and the lanthanide doped aluminum garnets $Y_3Al_5O_{12}$ (YAG:Ln) and $Lu_3Al_5O_{12}$ (LuAG:Ln). These materials are chemically stable (non-hygroscopic oxides), have high stopping power, and represent material classes that scintillate from self-activation or activated mechanisms. These materials are also good candidates for transparent nanocrystalline ceramic and nanocomposites scintillators. Critical to the successful development of improved scintillator is to understand/control radioluminescence and transport mechanisms at multiple scale lengths (nano-micro-meso). Our initial foray into developing this necessary basal knowledge has focused on probing the fundamental changes in scintillation behavior based on particle size (bulk to nano), activator concentration, surface chemistries, and morphology of tungsten and high Z based materials.

The materials studied in this effort are the chemically stable, self-activated, MWO_4 materials. These scintillators have found utility for a variety of applications ranging from X-ray imaging to high-energy physics, due their radiation hardness, non-hygroscopic nature, high density, and efficient light yield.[3, 4] The MWO_4 materials are attractive for nanoscaled investigations because their size, morphology, and surface chemistry can be synthetically tailored.[5] It was also of interest to probe the intrinsic luminescence of the WO_6^{2-} and explore how changing the cation and crystalline symmetry of these materials would also affect scintillation behavior. Here we compare poly- and nanocrystalline MWO_4 ($M = Pb, Ca, Cd$) scintillation characteristics using cathodoluminescence (CL), photoluminescence (PL), and ion beam induced luminescence (IBIL) to see how these materials differ from reported single crystal scintillator emission. IBIL using 2.5 MeV protons was selected to provide first order simulation of a neutron environment and determine the stability of luminescence properties from ceramics and nanoscale materials.

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2. EXPERIMENTAL

Commercial MWO_4 ($M = Ca, Cd, Pb$) and all reagents used for nanoparticle synthesis were purchased from Aldrich and used as received. The MWO_4 nanoparticles were prepared by following solution precipitation routes described elsewhere.[5-7] Manipulation of air sensitive reagents was performed under argon using standard glovebox and Schlenk line protocols. Scanning Electron Microscopy (SEM) images were obtained from samples 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). Transmission Electron Microscopy (TEM) images were from particles, dispersed in ethanol or toluene and placed directly onto a lacy carbon type-A, 300 mesh, copper TEM grid purchased from Ted Pella, Inc. The resultant particles were studied using a Philips CM 30 TEM at 300 keV. Cathodoluminescence (CL) spectra were collected with a Gatan MonoCL spectrometer in a FEI Nova nanoSEM200 unit. Photoluminescence (PL) was obtained on a QuantaMaster fluorometer equipped with a Xe arc lamp, from Photon Technology Internal, Inc. PL spectra were taken using a 0.25 nm step size and integrating for 0.1 second. Ion Beam Induced Luminescence (IBIL) data was collected on pressed pellet (6 mm X 1 mm) samples that were excited with 2.5 MeV H^+ ions generated from a 6 MV Tandem or 3 MV Pelletron Accelerator. The IBIL emission spectrum was collected using Andor Technology's Newton electron multiplying CCD detector.

3. RESULTS AND DISCUSSION

In an effort to establish baseline measurements, literature reports on single crystal MWO_4 properties were compared to the experimentally derived properties of commercially available polycrystalline MWO_4 . The SEM images of these powders are shown in Figure 1. The size of the $CaWO_4$ particles ranged between 2 and 15 μm . Both the Cd and Pb tungstates had agglomerated grains that were 0.2–0.5 and 0.2–0.8 μm , respectively. Powder XRD and Raman analysis (not shown) confirmed the phase purity of the samples.

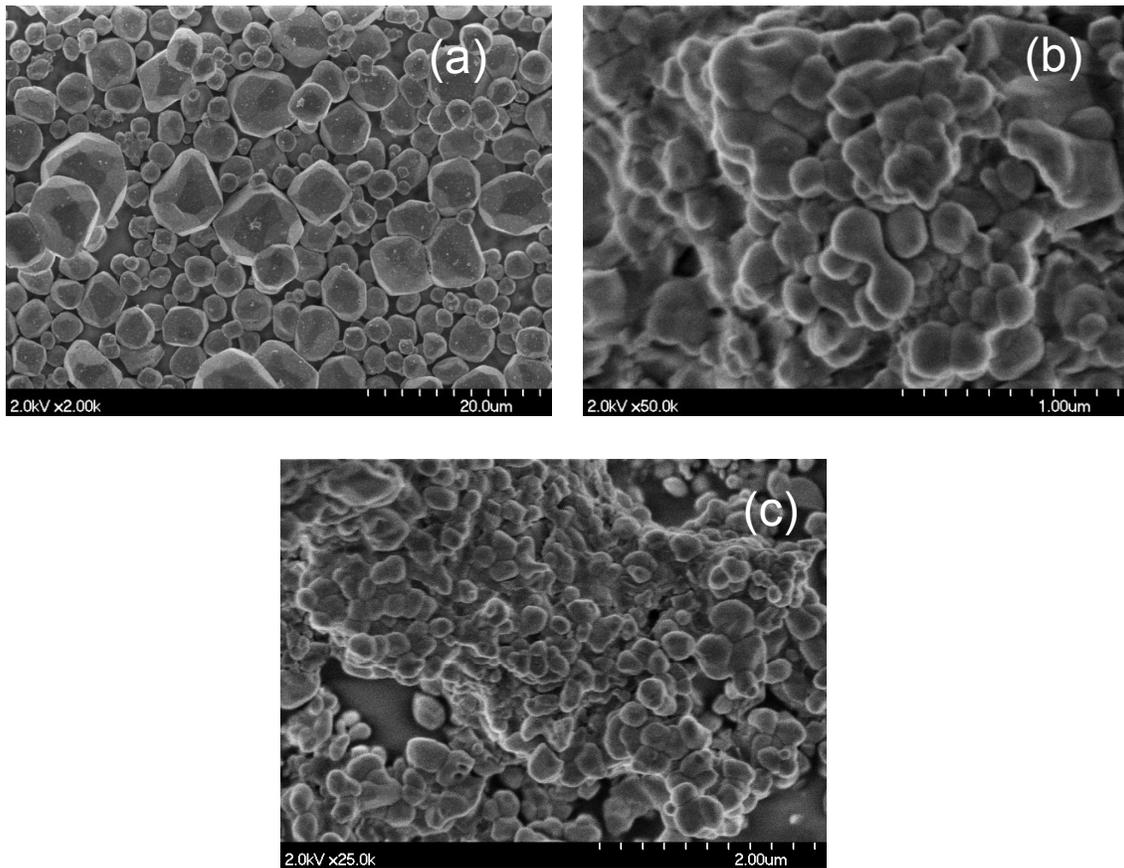


Figure 1. SEM images of commercially available: (a) $CaWO_4$, (b) $CdWO_4$ and (c) $PbWO_4$.

Following the electron microscopy study, scintillation emission wavelength was examined for the micron-sized powders using CL, PL, and IBIL. A summary of the CL, PL and IBIL results for all the MWO_4 is listed in Table 1. Figure 2 illustrates the commercial $CaWO_4$ CL behavior with varying electron beam energy. The PL vs. IBIL spectra for commercial $CaWO_4$ and $PbWO_4$ powders are presented in Figures 3 and 4, respectively.

The CL and PL emissions for the commercial polycrystalline $CaWO_4$ were comparable to the single crystal data, while spectral shifts were observed for the Cd and Pb tungstate samples. The CL spectra for commercial $CaWO_4$, Figure 2, illustrates how increasing the energy from 5–30 keV increases the light intensity and narrows the emission spectrum. A maximum emission wavelength (λ_{em}) of 419 nm was generated with 30 keV, Figure 2d, and is in agreement with reported wavelengths centered between 415–420 nm for single crystals.[3] For the commercial $CaWO_4$ sample, our PL λ_{em} was found near 420 nm ($\lambda_{ex} = 263$ nm). The emission differences between single crystals and the commercial Cd and Pb tungstates are 10 and 30 nm, respectively. For example single $CdWO_4$ crystals have an λ_{em} at 475 nm vs. commercial $CdWO_4$ powders at 485 nm, and single $PbWO_4$ crystals have a PL emission at 520 nm vs. 470 nm for commercial $PbWO_4$ powders.[4, 8]

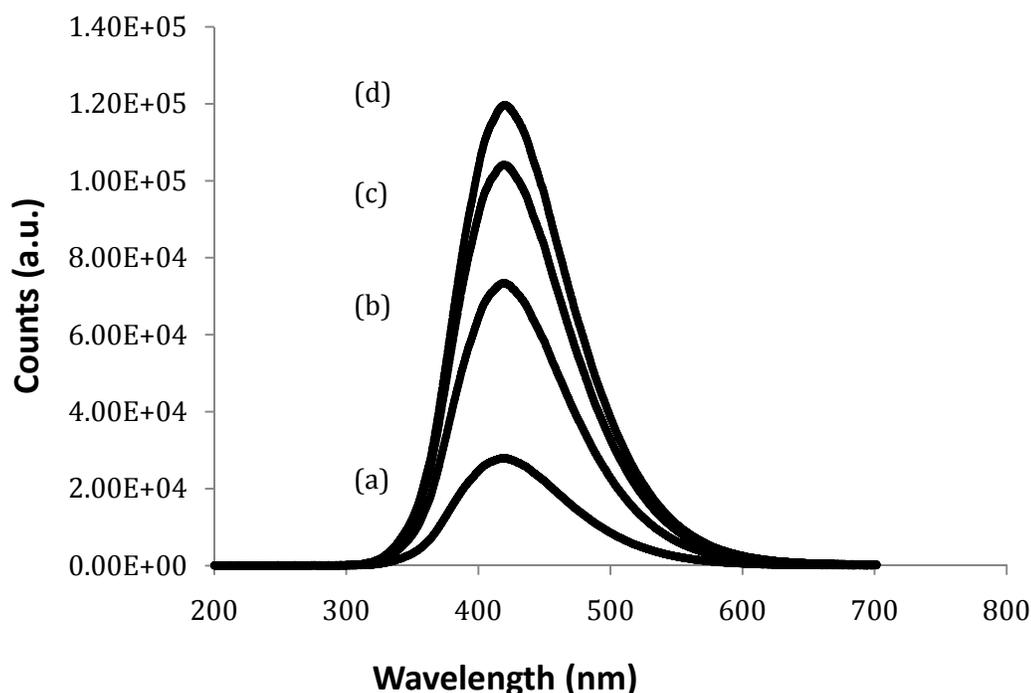


Figure 2. $CaWO_4$ CL emission spectra collected at (a) 5, (b) 15, (c) 20, and (d) 30 keV respectively.

To simulate the scintillation emission generated from neutron environments, IBIL was used to excite our samples with 2.5 MeV H^+ ions, Figures 3 and 4. Table 1 shows the comparison of IBIL to PL λ_{em} . To the best of knowledge, there is limited information concerning IBIL characteristics for polycrystalline and nanocrystalline tungstates since they have been primarily characterized with CL and PL techniques.[5, 9] Thus, it is of interest to determine how IBIL influences MWO_4 emission, since single crystal emissions are different based on the excitation energy used.

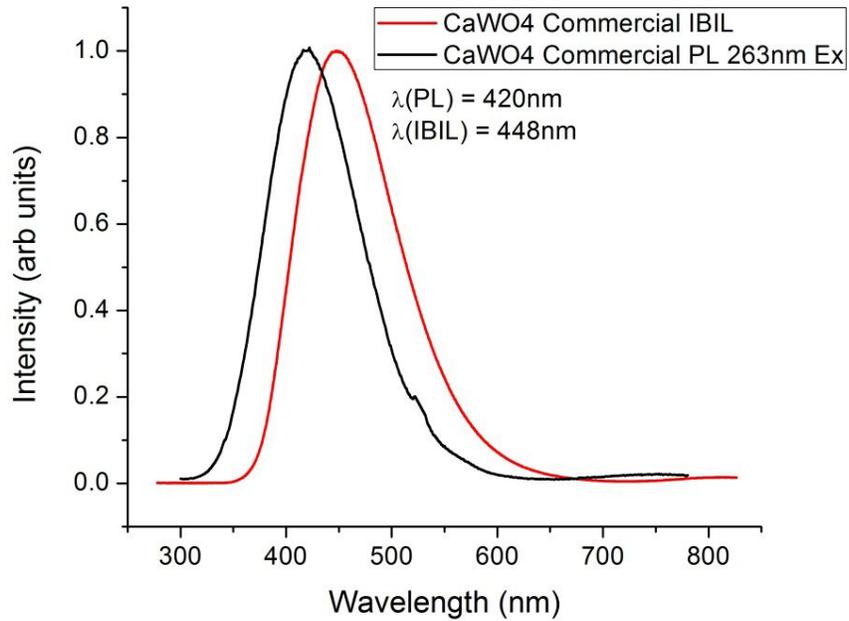


Figure 3. Commercial CaWO₄ emission spectra for: (black) PL and IBIL (red).

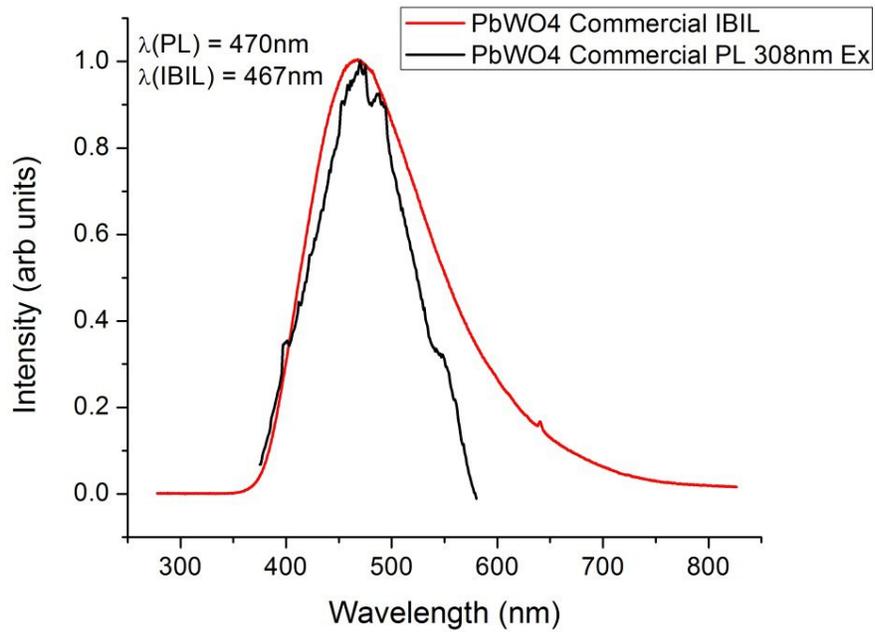


Figure 4. Commercial PbWO₄ emission spectra for: (black) PL and IBIL (red).

For example, the radioluminescence of single crystals PbWO_4 had noticeable differences in full width half maximum (FWHM) and a 20–30 nm blue shift when compared to their emission produced by photoluminescence.[4]

The commercial MWO_4 powders produced similar shaped PL and IBIL spectra, but begin to differ in their emission wavelengths, Figures 3 and 4. Spectral red shifts were only produced in IBIL emissions for both Ca and Cd, while Pb did not undergo a significant change. It appears that a chemical (cation Z) or structural variation associated with the MWO_4 may have an influence on the noted spectral differences. We observed that CaWO_4 with the lighter Z Ca ions had the largest red shift of 28 nm of the tungstates measured, whereas, the CdWO_4 produced a 14 nm red shift. Finally, PbWO_4 with the heavier Z Pb cation, produced the least change in IBIL emission shift, but had a narrower spectrum when compared to PL. The spectral shift characteristics for the MWO_4 also seem to be influenced by particle size. For example the single crystal PbWO_4 IBIL emission spectrum, from H^+ produced under different conditions, was found at 430 nm and is in contrast to our polycrystalline powders.[9] Continuation of this research will determine how grain sizes larger than those reported in this study effect the IBIL emission to help us determine if this change in behavior is related to size, cation Z, structural variation, and/or scintillation mechanism.

Table 1. Summary of emission wavelengths (λ_{em}) observed in this work and reported for single crystal MWO_4 .

Material	Density (g/cm^3)[2]	CL λ_{em} (nm)	PL λ_{ex} (nm)	PL λ_{em} (nm)	IBIL λ_{em} (nm)
CaWO₄ Single Crystal ** λ_{em} = 415–420 nm[3]	6.1				
CaWO₄ Commercial Powder 2–15 μm	6.1	419 30 keV	263	420	448
CaWO₄ Nanoparticle 50–150 nm	6.1	419 30 keV	243	423	409
CaWO₄ Calcined Powder (1000°C) 10–35 μm	6.1		250	455	478
CdWO₄ Single Crystal ** λ_{em} = 475 nm[8]	7.9				
CdWO₄ Commercial Powder 0.2–5 μm	7.9	473 30 keV	287	485	499
CdWO₄ Nanorod 7 x 100 nm	7.9				493
PbWO₄ Single Crystal	8.3			520[4]	430[9]
PbWO₄ Commercial Powder 0.2–8 μm	8.3	422 30 keV	308	470	467
PbWO₄ Nanoparticles 10 nm	8.3	422 30 keV			514
PbWO₄ Nanorods 10 nm x 1 μm	8.3				517

Nanoparticle MWO_4 were also examined and compared to the commercial powder using IBIL to determine if the IBIL emission characteristics could be tailored based on the size and shape of the nanomaterials. Preliminary investigations used CaWO_4 nanoparticles (10–150 nm).[5, 6] CdWO_4 nanorods (7 x 100 nm)[7] and PbWO_4 nanorods (10 nm x 1 μm).[5] For our CaWO_4 materials, Table 1 lists some of the spectral differences noted from the IBIL emissions, along with the grain sizes determined by electron microscopy. The nanomaterials exhibited blue spectral shifts while the larger micron sized grains of synthesized CaWO_4 were found to be red shifted in comparison to the commercial powders.

CdWO₄ nanorods show little change in IBIL emission. The PbWO₄ nanoparticle IBIL emissions are close to single crystal PL and are red shifted compared to our polycrystalline data.

4. CONCLUSION

As an effort to produce improved ceramic scintillator applications, we are investigating the size effects on scintillation behavior for a variety of high Z based materials. A fundamental study on the scintillation behavior of poly- and nanocrystalline materials was conducted on a family of metal tungstates (MWO₄, M = Ca, Cd, Pb). Initial measurements, on commercial powders, were compared to reported single crystal data to determine how the emission behavior between CL, PL, and IBIL changed. During the experiments, two effects were observed: (i) polycrystalline CaWO₄ exhibited similar CL and PL emissions behavior while both red and blue spectral shifts were noted for the Cd and Pb tungstate samples and (ii) while using IBIL to simulate some effects of a neutron environment on commercial powders, the cation Z or structural variations of the tungstate may be associated with producing spectral shifts between IBIL and PL spectra maximum. Analysis of the IBIL spectra for commercial Ca and Cd indicated red spectral shifts while Pb did not show a significant change. Preliminary IBIL studies on nanoscaled CaWO₄ and calcined micron sized particles indicate that nanomaterials will produce a blue shift in emission while the micron-sized particles (>15µm) will result in a red shift when compared to the commercial materials. Further investigation into the governing mechanisms and controlling variables for these phenomena are currently underway.

ACKNOWLEDGEMENTS

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