

Research Article

Short Time and Low Temperature Reaction between Metal Oxides through Microwave-Assisted Hydrothermal Method

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This work demonstrates the possibility of synthesis of cadmium tungstate at low temperatures using oxide precursors. Cadmium tungstate (CdWO_4) scintillator was produced via microwave-assisted hydrothermal reaction using the precursors CdO and WO_3 . The methodology was based on microwave radiation for heating, which is remarkably faster than the solid-state route or conventional hydrothermal procedure. CdWO_4 monoclinic (wolframite) structure was successfully obtained at 120°C for synthesis times as short as 20 min. This route does not require the use of templates or surfactants and yields self-assembled nanorods with size of around 24 ± 9 nm width and 260 ± 47 nm length. The growth mechanism for the formation of CdWO_4 involves microwave-induced dissociation of the reagents and solvation of Cd^{2+} and WO_4^{2-} ions, which are free to move and start the nucleation process. The luminescence properties of the produced nanoparticles were investigated, presenting a broad emission band at around 500 nm, which is comparable to that observed for samples produced using other chemical routes. This result highlights the great potential of the proposed method as a low-cost and time saving process to fabricate luminescent oxide nanoparticles.

1. Introduction

Recent advances in synthesis technologies demonstrate that the use of microwave radiation is convenient as heating method to obtain nanomaterials in a short reaction time. Further advantages of microwave-based methodology are low cost and low environmental damage [1, 2]. The fundamental requirement is that solvent and/or reagents employed have the ability to absorb microwave energy in order to convert it into heat [3]. The thermal effects provided by microwaves are consequence of the particle interactions with the electromagnetic field, involving processes of dipolar polarization and ionic conduction [3, 4]. Such unique feature cannot be achieved using conventional heating, and it provides uniform heating that improves the yield and reproducibility of the route [3, 5].

Microwave-assisted hydrothermal method combines the advantages of fast heating and high-pressure reaction. Hydrothermal processes can promote the formation of crystalline products at temperatures much lower than those required in conventional synthesis [6–8]. The combination of microwave heating and hydrothermal environment typically

enhances the kinetics of reactions by 1-2 orders of magnitude, saving time and energy [9–11].

Tungstate materials are studied due to their potential application in different areas including catalysis, magnetic devices, humidity sensors, photonics, and scintillators [12, 13]. Conventional solid-state synthesis of CdWO_4 departs from metal oxides, which are grinded and heated up to 1000°C for several hours [5, 14]. Alternatively, sol-gel, sonochemical, solvothermal, and conventional hydrothermal syntheses are reported to produce CdWO_4 nanoparticles [15–22] but it is important to say that in all these works the precursors were either alcoxides or metal salts. Few reports can be found in literature about the microwave-assisted hydrothermal synthesis of CdWO_4 [23–25], but they make use of metal salts and organic solvents or surfactants such as toluene and PEG-1000. To our knowledge, microwave-hydrothermal method using precursor oxides in aqueous solution was not reported up to the moment to produce nanostructured CdWO_4 . In the present work, this route was successfully used, satisfying the demand for simplification and improvement of the methodology. The proposed method is also advantageous since it does not require the use of

surfactants or pH modifiers, consequently avoiding waste generation. In this work, the mechanism of nucleation and crystal growth, as well as the structural and optical characterization of the produced samples, is presented and discussed.

2. Materials and Methods

CdWO_4 polycrystalline samples were produced via microwave-assisted hydrothermal method using cadmium oxide and tungsten oxide as precursors. In a typical experiment, 2 mmol of CdO (Vetec, 99.5%) and 2 mmol of WO_3 (Fluka, 99.9%) were homogenized in an agate mortar and placed into a Teflon autoclave filled with 50 ml of distilled water. Then, the autoclave was sealed and placed in the microwave system (Brazilian patent 2008-PI0801233-4) with frequency of 2.45 GHz and maximum power of 800 W. Reactions were conducted at 120°C under autogenous pressure ($\sim 1.5 \text{ kgf/cm}^2$) for 20 min and 60 min. After cooling down to room temperature, the resulting product was collected by centrifugation and dried at 60°C in air. Due to CdO losses during heating, synthesis was also performed varying the amount of this reagent to 2.2 mmol, 2.4 mmol, and 2.6 mmol, keeping the amount of 2 mmol WO_3 .

Crystalline phases obtained were characterized by X-ray diffraction (XRD) in a Rigaku Ultima+ 2000/PC using $\text{K}\alpha$ radiation from Co. The data were acquired in step-scan mode, in the 2θ range from 10° to 80° with steps of 0.02° and acquisition time of 10 s. The composition of the samples was determined from energy dispersive X-ray (EDX) spectroscopy measured with Shimadzu EDX-7000 equipment, in semi-quantitative mode. Transmission electron microscopy (TEM) images were acquired with Jeol JEM-1400Plus microscope (accelerating voltage of 120 kV) to evaluate the size and morphology of the powders. Photoluminescence (PL) measurements were performed in an ISS PCITM spectrofluorimeter that uses a 300 W Xenon lamp as excitation source, with fixed excitation wavelength at 292 nm. X-ray excited optical luminescence (XEOL) was measured while the samples were under excitation of X-rays emitted by a Co target tube operating at 40 kV/40 mA. Both PL and XEOL were collected using an Ocean Optics HR2000 spectrometer (resolution of 0.5 nm) and all measurements were performed at room temperature.

3. Results and Discussion

XRD patterns of polycrystalline samples prepared using metal oxides in stoichiometric proportion are presented in Figure 1. One can observe that the products obtained by the proposed route are predominantly CdWO_4 with monoclinic structure (PDF #00-088-0181). The temperature of 120°C is significantly lower than that used for solid-state synthesis of this scintillator [14, 27]. Furthermore, Figure 1(a) shows that CdWO_4 is successfully formed for reaction times as short as 20 min, due to the efficiency of microwave radiation in promoting rapid reactions. Small amount of WO_3 (PDF #00-083-0950) was detected as secondary phase, indicating that Cd losses can occur during synthesis, possibly by

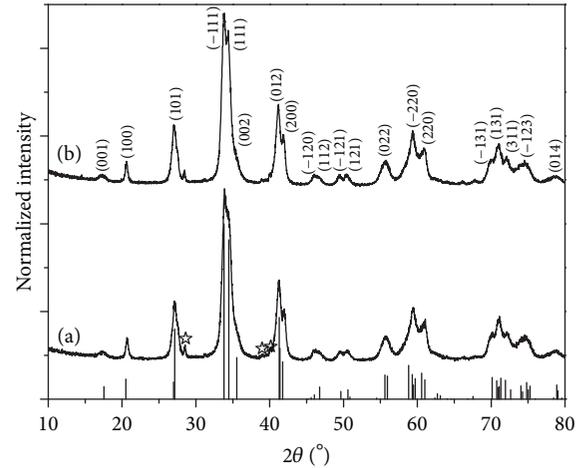


FIGURE 1: XRD patterns of the samples prepared with reagents in stoichiometric proportion, varying the time of synthesis: (a) 20 min and (b) 60 min. Bars represent the wolframite structure of CdWO_4 (some crystalline planes are indexed according to [26]) and symbols correspond to WO_3 .

volatilization or by dispersion into the water as $\text{Cd}(\text{OH})_2$ [28, 29]. Figure 1(b) corresponds to the nominally stoichiometric sample synthesized during 60 min, indicating that no noticeable change in crystalline structure was detected for longer synthesis times. From the full width at half maximum (FWHM) of the (100) diffraction peak and using Scherrer formula [30], it was possible to estimate the crystallite size D :

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta_B}, \quad (1)$$

where K is the shape coefficient (in this work, $K = 0.9$), λ is the X-ray wavelength (0.179 nm for Co target), β is the line broadening, and θ_B is the Bragg angle, in radians. The average crystalline sizes were about $23 \pm 1 \text{ nm}$ and $24 \pm 1 \text{ nm}$ for the sample produced with reaction time of 20 and 60 min, respectively.

In order to compensate the Cd loss, samples were produced departing from precursors homogenized with excess CdO. Figure 2 presents XRD patterns for the samples synthesized during 60 min using 10% (2.2 mmol), 20% (2.4 mmol), and 30% (2.6 mmol) of CdO excess. The results point to the presence of monoclinic CdWO_4 and lower proportions of WO_3 phase. The amount of WO_3 was 8% for the sample prepared with reagents in stoichiometric proportion, as estimated from the XRD data using Match! software [31]. When CdO excess of 10, 20, or 30% was used, the amount of WO_3 phase decreased to 7%, 6.5%, and 6%, respectively. Nevertheless, one must notice that the diffraction peaks of CdWO_4 become broader with increasing the amount of cadmium precursor (see Figure 2) and such behavior can be related to modifications in the microstructure of these samples, as it will be discussed later in this paper. From the evaluation using (1), a slight decrease was found of the crystalline sizes in relation to that of samples produced without excess of CdO. The results were $21 \pm 1 \text{ nm}$, $19 \pm 1 \text{ nm}$,

TABLE I: EDX results for atomic composition of the samples.

| Samples | Amount of CdO | Time of synthesis | Cd | W |
|----------------------------|---------------|-------------------|-----|-----|
| Without using excess of Cd | 2 mmol | 20 min | 40% | 60% |
| | 2 mmol | 60 min | 40% | 60% |
| Using excess of Cd | 2.2 mmol | 60 min | 42% | 58% |
| | 2.4 mmol | 60 min | 44% | 56% |
| | 2.6 mmol | 60 min | 46% | 54% |

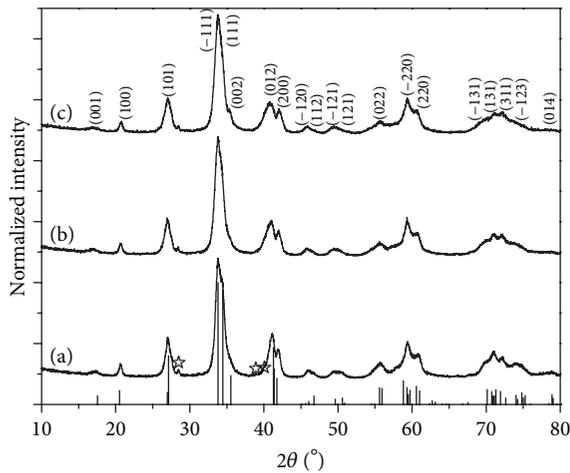


FIGURE 2: XRD patterns of the samples prepared with reagents out of stoichiometric proportion: (a) 10% excess of CdO, (b) 20% excess of CdO, and (c) 30% excess of CdO. Bars represent the wolframite structure of CdWO_4 (some crystalline planes are indexed according to [26]) and symbols correspond to WO_3 .

and 19 ± 1 nm when the excess amount of this precursor was 10, 20, and 30%, respectively.

Further investigations about composition of these products were performed through EDX. Results are presented in Table 1. Only Cd and W elements were found in the composition of the samples. Therefore, the level of impurities can be considered negligible. The percentage of O atoms could not be measured due to experimental limitations of the equipment. This means that, considering only Cd and W, CdWO_4 stoichiometric samples should contain 50% of each of these elements. However, for all samples synthesized using CdO and WO_3 precursors in stoichiometric proportion, a deficiency of Cd atoms was found. The composition of 60% W and 40% Cd is the same for synthesis times of 20 and 60 min, indicating a nondependence of the reaction time on stoichiometry, at least for the time intervals used in the present work. One can notice that the amount of Cd deficiency (10%) is in agreement with the XRD results, which pointed out approximately 8% of secondary phase WO_3 . Accordingly, for the samples prepared using CdO excess, the deviation from stoichiometry decreased to 8%, 6%, and 4% (see Table 1). These values are also consistent with those obtained from XRD and corroborate that secondary phase of WO_3 formed during the hydrothermal reaction can be controlled.

Particle morphology was investigated using TEM, and some of the images obtained are presented in Figure 3. The micrographs show that CdWO_4 powders prepared with reagents in stoichiometric proportion at 120°C for 20 min exhibit nanorods with widths of 24 ± 9 nm and lengths of 260 ± 47 nm, whereas, for reaction time of 60 min, particles with widths of 11 ± 3 nm and lengths of 98 ± 33 nm were observed. Therefore, Figures 3(a) and 3(b) indicate that the aspect ratio (or length-to-diameter ratio) is very similar despite increasing the time of synthesis. The nanorod formation is attributed to a preferred growth along the (100) direction at the expense of individual crystallites [32, 33], and it is an interesting result of this work, considering that no template or surface passivation was used in the production, as related in previous reports. The morphology obtained in this work is consistent with those reported for the synthesis of CdWO_4 departing from metal salts combined to PEG-1000 surfactant [24], indicating that CdWO_4 preferably grows into the nanorod morphology, regardless of the nature of the chemical reagents. Also, from Figures 3(a) and 3(b), it can be observed that samples prepared with reaction time of 60 min present smoother particle surface. This effect is probably due to Ostwald ripening or better crystallization of the particles hydrothermalized for longer times, although negligible influence of reaction time on the phase formation was detected from XRD data. Figures 3(c) and 3(d) correspond to samples produced with Cd excess of 20% and 30%, respectively (synthesis times of 60 min in both cases). In these micrographs, the formation of thinner particles, which tend to agglomerate into bundles, can be noticed. Respectively, their sizes were found to be of 10 ± 2 nm width and 161 ± 27 nm length or 10 ± 2 nm width and 146 ± 50 nm length, which point to higher aspect ratios in comparison to that of samples produced without excess of Cd. Such microstructure is less common but can be related to small changes in the experimental procedure that originally produced nanorods [20, 34].

About the growth mechanism of CdWO_4 using oxide precursors under microwave-hydrothermal conditions, some assumptions can be made. Initially, the microwave radiation promotes a superheating of the water as well as of the CdO and WO_3 particles. These reagents undergo a dissociation so that Cd^{2+} and WO_4^{2-} are produced and solvated by H_2O molecules. This means that the partial negative charges of H_2O electrostatically attract Cd^{2+} ions whereas the positive charges attract WO_4^{2-} . Then, free ions are able to move by the action of the radiation, and collisions occur. In such conditions, nucleation takes place in a very short time

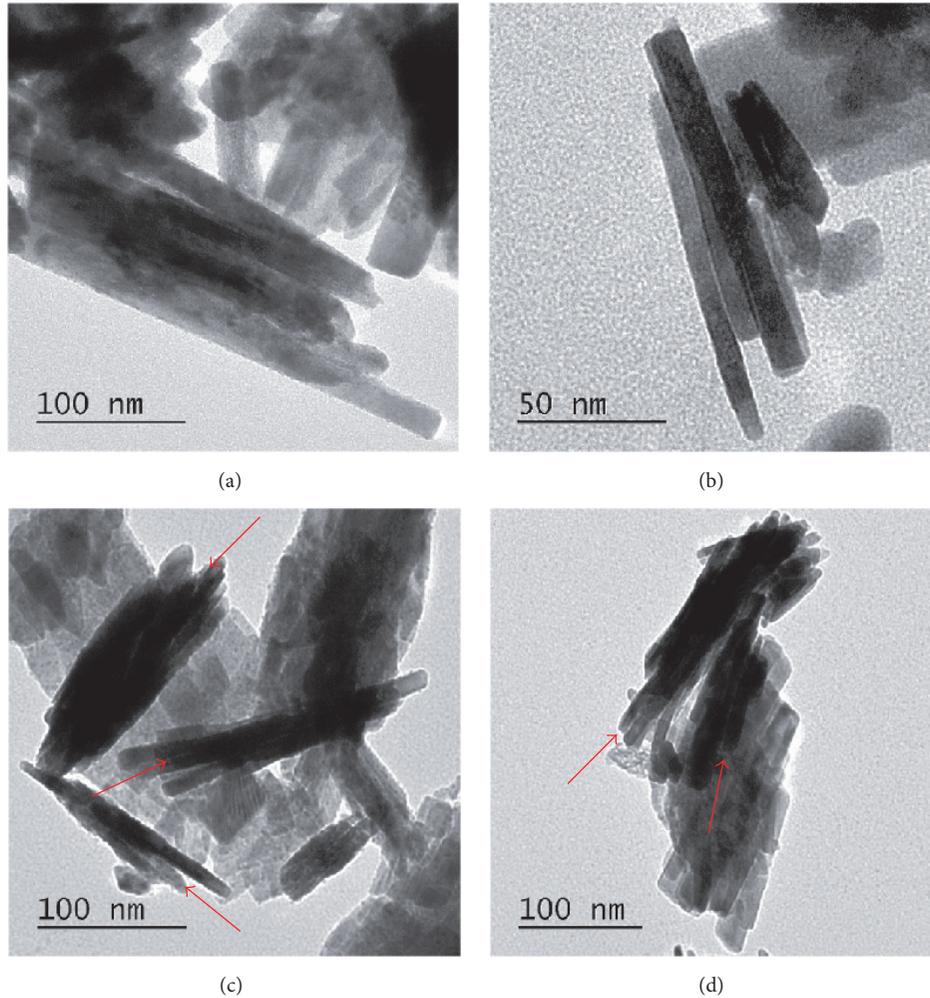


FIGURE 3: TEM images of CdWO₄ nanorods produced with varied conditions: using reagents in stoichiometric proportion, soaking time of (a) 20 min and (b) 60 min, or using Cd excess of (c) 20% and (d) 30%. Some nanofiber bundles are indicated by red arrows.

and thus leads to the production of particles in nanoscale regime [35, 36]. In the present case, CdWO₄ crystals are crystallographic oriented and self-assembled into nanorod or nanofiber morphologies.

PL and XEOL emission spectra are presented in Figures 4 and 5, respectively. Upon excitation of either UV or X-ray, the samples presented a broad band emission with maximum at 500 nm, characteristic of CdWO₄ and attributed to charge transfer transitions between W⁶⁺ and O²⁻ ions within the tungstate molecular units WO₆ [37, 38]. The luminescence profile was basically the same for reaction times of 60 min (presented in Figures 4 and 5) or 20 min (not presented). The total light output was obtained from the area under each curve, with the highest light output set as 100. These results are presented in the inset of Figures 4 and 5, as function of Cd/W ratio (as determined by EDX) and reaction times. For both excitation sources, it was observed that the light yield increases for longer reaction times, for all stoichiometric proportions used. This is probably due to the higher crystallinity achieved with longer hydrothermal

treatments. Similar results were reported for CdWO₄ samples produced by conventional hydrothermal synthesis at different conditions [39, 40]. On the other hand, works in [23, 24], about the microwave-assisted method, point to an opposite dependence of PL intensity with the reaction time, demonstrating that in these cases other factors such as particles size and the surface modification by surfactants can influence the luminescence emission.

Figures 4 and 5 show that the most intense emission corresponds to that of nominally stoichiometric samples, where the actual proportion of Cd/W is 40/60. This result suggests that the different morphologic features of the samples produced with or without Cd excess have a strong influence on the light output of the samples. This is probably due to the different effective areas of the particles with rod or fiber morphologies. Despite the fact that WO₃ as secondary phase tends to influence negatively the recombination rate of photogenerated charge carriers [41], the role played by microstructure seems to be more crucial for the light output efficiency in this case. In future works, an in-depth study of

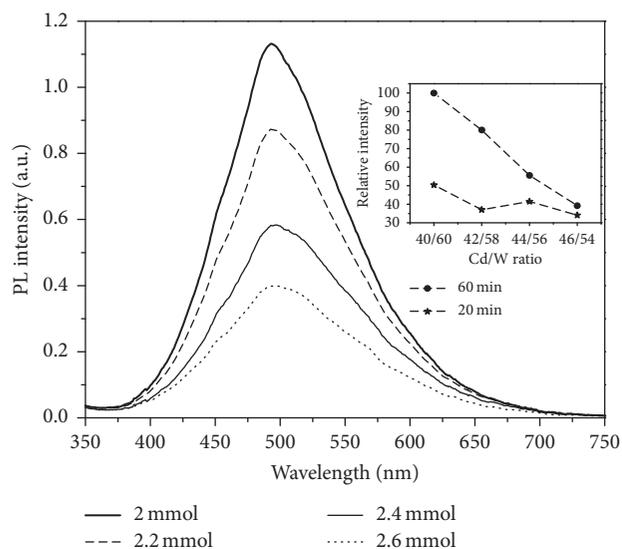


FIGURE 4: PL emission spectra of samples prepared with different cadmium precursor (CdO) amounts and reaction time of 60 min. The inset shows the total light output, for reaction times of 20 min and 60 min, obtained from the area under the luminescence curves, as function of Cd/W atomic ratio, as determined by EDX.

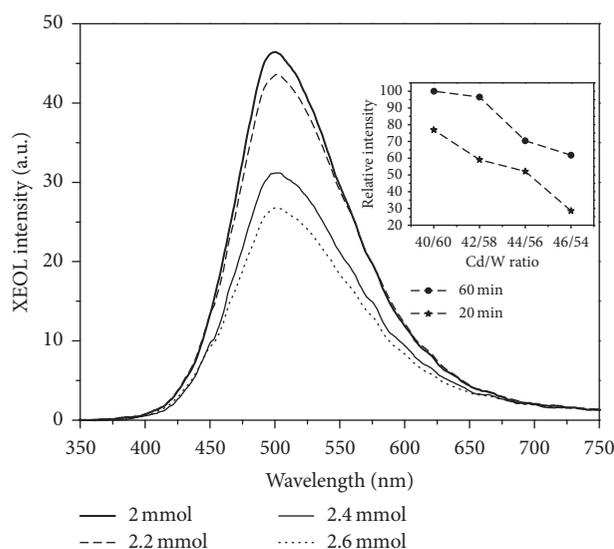


FIGURE 5: XEOL emission spectra of samples prepared with different cadmium precursor (CdO) amounts and reaction time of 60 min. The inset shows the total light output, for reaction times of 20 min and 60 min, obtained from the area under the luminescence curves, as function of Cd/W atomic ratio, as determined by EDX.

surface area and light output should be carried on to establish a quantitative relationship between these two parameters.

4. Conclusions

The results presented in this work show the feasibility of using oxide precursors for synthesizing CdWO_4 under microwave-assisted hydrothermal conditions. Methodology is conducted

at short times and low temperature, being environmentally safe and also saving time and energy. Monoclinic structure and nanorod or bundle morphologies of CdWO_4 were obtained, depending on Cd excess used in the synthesis. From the luminescence measurements, it was observed that the microstructure plays an important role in the light output of these scintillators. Samples prepared with excess of CdO precursor in relation to the stoichiometric proportion provided some reduction of the WO_3 content in the final product, but they have presented lower luminescence. Nevertheless, increasing the reaction time from 20 to 60 min favored the crystallization process and such samples have an overall higher efficiency. Different methods to avoid the loss of cadmium and formation of single crystalline phase are under investigation and will be presented in future works.

Competing Interests

The authors declare that they have no competing interests.

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References

- [1] X. Hu and J. C. Yu, "Continuous aspect-ratio tuning and fine shape control of monodisperse $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals by a programmed microwave-hydrothermal method," *Advanced Functional Materials*, vol. 18, no. 6, pp. 880–887, 2008.
- [2] C. S. Lim, "Microwave-assisted synthesis and photoluminescence of CdWO_4 by a solid-state metathetic route," *Asian Journal of Chemistry*, vol. 24, no. 9, pp. 4166–4170, 2012.
- [3] I. Bilecka and M. Niederberger, "Microwave chemistry for inorganic nanomaterials synthesis," *Nanoscale*, vol. 2, no. 8, pp. 1358–1374, 2010.
- [4] S. Das, A. K. Mukhopadhyay, S. Datta, and D. Basu, "Prospects of microwave processing: an overview," *Bulletin of Materials Science*, vol. 32, no. 1, pp. 1–13, 2009.
- [5] D. S. Sofronov, E. M. Sofronova, V. V. Starikov et al., "Microwave synthesis of cadmium and zinc tungstates," *Journal of Materials Engineering and Performance*, vol. 21, no. 11, pp. 2323–2327, 2012.
- [6] S. Komarneni, R. Roy, and Q. H. Li, "Microwave-hydrothermal synthesis of ceramic powders," *Materials Research Bulletin*, vol. 27, no. 12, pp. 1393–1405, 1992.
- [7] D. Yue, W. Luo, W. Lu et al., "A facile synthesis and optical properties of bundle-shaped $\text{TbPO}_4\cdot\text{H}_2\text{O}$ nanorods," *Advances in Condensed Matter Physics*, vol. 2013, Article ID 673945, 5 pages, 2013.
- [8] K. Byrappa, "Hydrothermal growth of polyscale crystals," in *Springer Handbook of Crystal Growth*, G. Dhanaraj, K. Byrappa, V. Prasad, and M. Dudley, Eds., pp. 599–653, Springer, Berlin, Germany, 2010.
- [9] L. S. Cavalcante, J. C. Sczancoski, L. F. Lima Jr. et al., "Synthesis, characterization, anisotropic growth and photoluminescence of BaWO_4 ," *Crystal Growth and Design*, vol. 9, no. 2, pp. 1002–1012, 2009.

- [10] G. Biasotto, A. Z. Simões, C. R. Foschini, M. A. Zaghete, J. A. Varela, and E. Longo, "Microwave-hydrothermal synthesis of perovskite bismuth ferrite nanoparticles," *Materials Research Bulletin*, vol. 46, no. 12, pp. 2543–2547, 2011.
- [11] M. L. Moreira, G. P. Mambrini, D. P. Volanti et al., "Hydrothermal microwave: a new route to obtain photoluminescent crystalline BaTiO₃ nanoparticles," *Chemistry of Materials*, vol. 20, no. 16, pp. 5381–5387, 2008.
- [12] X. C. Song, X. Cui, W. Z. Huang, Y. Zhang, H. Y. Yin, and Y. F. Zheng, "Photoactivity enhancement of Zn-doped CdWO₄ prepared with a hydrothermal method," *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, vol. 197, pp. 31–35, 2015.
- [13] L. L. Nagornaya, F. A. Danevich, A. M. Dubovik et al., "Tungstate and molybdate scintillators to search for dark matter and double beta decay," *IEEE Transactions on Nuclear Science*, vol. 56, no. 4, pp. 2513–2518, 2009.
- [14] W. Ran, L. Wang, H. Li et al., "Luminescence properties and energy transfer of CdWO₄:Sm³⁺,Bi³⁺,M⁺ (M=Li, Na, K) phosphors for white LEDs," *Ceramics International*, vol. 41, no. 3, pp. 4301–4307, 2015.
- [15] L. Nadaraia, N. Jalabadze, R. Chedia, M. Antadze, and L. Khundadze, "Preparation of Tungstate nanopowders by Sol-Gel method," *IEEE Transactions on Nuclear Science*, vol. 57, no. 3, pp. 1370–1376, 2010.
- [16] H. Shang, Y. Wang, B. Milbrath, M. Bliss, and G. Cao, "Doping effects in nanostructured cadmium tungstate scintillation films," *Journal of Luminescence*, vol. 121, no. 2, pp. 527–534, 2006.
- [17] S. M. Hosseinpour-Mashkani and A. Sobhani-Nasab, "A simple sonochemical synthesis and characterization of CdWO₄ nanoparticles and its photocatalytic application," *Journal of Materials Science: Materials in Electronics*, vol. 27, no. 4, pp. 3240–3244, 2016.
- [18] A. J. Rondinone, M. Pawel, D. Travaglini, S. Mahurin, and S. Dai, "Metastable tetragonal phase CdWO₄ nanoparticles synthesized with a solvothermal method," *Journal of Colloid and Interface Science*, vol. 306, no. 2, pp. 281–284, 2007.
- [19] Y. Wang, X. Guan, L. Li, H. Lin, X. Wang, and G. Li, "Solvent-driven polymorphic control of CdWO₄ nanocrystals for photocatalytic performances," *New Journal of Chemistry*, vol. 36, no. 9, pp. 1852–1858, 2012.
- [20] Y. Wang, J. Ma, J. Tao et al., "Hydrothermal synthesis and characterization of CdWO₄ nanorods," *Journal of the American Ceramic Society*, vol. 89, no. 9, pp. 2980–2982, 2006.
- [21] Y. Wang, J. Ma, J. Tao et al., "Low-temperature synthesis of CdWO₄ nanorods via a hydrothermal method," *Ceramics International*, vol. 33, no. 6, pp. 1125–1128, 2007.
- [22] Q. Dai, H. Song, G. Pan et al., "Surface defects and their influence on structural and photoluminescence properties of CdWO₄:Eu³⁺ nanocrystals," *Journal of Applied Physics*, vol. 102, no. 5, Article ID 054311, 2007.
- [23] L. Hou, L. Lian, L. Zhang, T. Wu, and C. Yuan, "Microwave-assisted interfacial hydrothermal fabrication of hydrophobic CdWO₄ microspheres as a high-performance photocatalyst," *RSC Advances*, vol. 4, no. 5, pp. 2374–2381, 2014.
- [24] J. Yan, Y. Shen, R. Cao, and T. Li, "CdWO₄ nanorods: ultrafast synthesis via a PEG-1000 polymer-assisted enhanced microwave synthesis route and their photoluminescence property," *Ceramics International*, vol. 40, no. 6, pp. 8081–8085, 2014.
- [25] A. S. Vanetsev, Y. V. Orlovskii, V. Nagirnyi et al., "Testing nanocrystalline CdWO₄ doped with Yb³⁺ as a possible down-conversion phosphor," *Radiation Measurements*, vol. 9, pp. 329–333, 2016.
- [26] M. Daturi, G. Busca, M. M. Borel, A. Leclaire, and P. Piaggio, "Vibrational and XRD study of the system CdWO₄-CdMoO₄," *Journal of Physical Chemistry B*, vol. 101, no. 22, pp. 4358–4369, 1997.
- [27] S. M. V. Novais, R. S. Da Silva, and Z. S. MacEdo, "Thermally stimulated luminescence of polycrystalline CdWO₄ at low temperatures," *Journal of Luminescence*, vol. 131, no. 7, pp. 1283–1287, 2011.
- [28] J. Yang, Y. Li, S. Liu et al., "Theoretical calculations of Cd isotope fractionation in hydrothermal fluids," *Chemical Geology*, vol. 391, pp. 74–82, 2015.
- [29] Z.-X. Yang, W. Zhong, Y.-X. Yin et al., "Controllable synthesis of single-crystalline CdO and Cd(OH)₂ nanowires by a simple hydrothermal approach," *Nanoscale Research Letters*, vol. 5, no. 6, pp. 961–965, 2010.
- [30] B. D. Cullity, "Diffraction I: directions of diffracted beams," in *Elements of X-Ray Diffraction*, pp. 81–106, Addison-Wesley, Philippines, 1978.
- [31] H. Putz and K. Brandenburg, *Match! Phase Identification From Powder Diffraction Data, Version 3.2.1*, 2016.
- [32] D. Ye, D. Li, W. Zhang et al., "A new photocatalyst CdWO₄ prepared with a hydrothermal method," *Journal of Physical Chemistry C*, vol. 112, no. 44, pp. 17351–17356, 2008.
- [33] Y. Wang, L. Yang, Y. Wang, X. Xu, and X. Wang, "Controllable synthesis of CdWO₄ nanorods and nanowires via a surfactant-free hydrothermal method," *Journal of the Ceramic Society of Japan*, vol. 120, no. 1402, pp. 259–261, 2012.
- [34] H.-L. Wang, X.-D. Ma, X.-F. Qian, J. Yin, and Z.-K. Zhu, "Selective synthesis of CdWO₄ short nanorods and nanofibers and their self-assembly," *Journal of Solid State Chemistry*, vol. 177, no. 12, pp. 4588–4596, 2004.
- [35] K. P. F. Siqueira, R. L. Moreira, M. Valadares, and A. Dias, "Microwave-hydrothermal preparation of alkaline-earth-metal tungstates," *Journal of Materials Science*, vol. 45, no. 22, pp. 6083–6093, 2010.
- [36] L. S. Cavalcante, V. M. Longo, J. C. Sczancoski et al., "Electronic structure, growth mechanism and photoluminescence of CaWO₄ crystals," *CrystEngComm*, vol. 14, no. 3, pp. 853–868, 2012.
- [37] M. M. Chirila, K. T. Stevens, H. J. Murphy, and N. C. Giles, "Photoluminescence study of cadmium tungstate crystals," *Journal of Physics and Chemistry of Solids*, vol. 61, no. 5, pp. 675–681, 2000.
- [38] V. Nagirnyi, M. Kirm, A. Kotlov, A. Lushchik, and L. Jönsson, "Separation of excitonic and electron-hole processes in metal tungstates," *Journal of Luminescence*, vol. 102–103, pp. 597–603, 2003.
- [39] M. Hojamberdiev, R. Kanakala, O. Ruzimuradov, Y. Yan, G. Zhu, and Y. Xu, "Besom-like CdWO₄ structures composed of single-crystalline nanorods grown under a simple hydrothermal process in ultra-wide pH range," *Optical Materials*, vol. 34, no. 11, pp. 1954–1957, 2012.
- [40] W. Tong, L. Li, W. Hu, T. Yan, and G. Li, "Systematic control of monoclinic CdWO₄ nanophase for optimum photocatalytic activity," *Journal of Physical Chemistry C*, vol. 114, no. 3, pp. 1512–1519, 2010.

- [41] I. Aslam, C. Cao, M. Tanveer et al., "A novel Z-scheme $\text{WO}_3/\text{CdWO}_4$ photocatalyst with enhanced visible-light photocatalytic activity for the degradation of organic pollutants," *RSC Advances*, vol. 5, no. 8, pp. 6019–6026, 2015.



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