

Synthesis of CaWO_4 , SrWO_4 and BaWO_4 with nanosized particles using cyclic microwave radiation

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Scheelite tungstates (MWO_4 , M = Ca, Sr and Ba) were successfully synthesized by the reactions of $\text{M}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in propylene glycol and NaOH using cyclic microwave radiation. The tungstates were detected using SAED. TEM and SEM analyses revealed the presence of dispersed nanosized particles for CaWO_4 , nanosized particles in irregular clusters for SrWO_4 , and nanosized particles in clusters shaped like dumb-bells for BaWO_4 . Raman spectra provide evidence of the scheelite structure with six different vibration modes. Arrays of crystallographic planes were detected using HRTEM. PL emission of the products is caused by the ${}^1\text{T}_2 \rightarrow {}^1\text{A}_1$ transition of electrons within $[\text{WO}_4]^{2-}$ tetrahedrons in the blue spectral region at 407-419 nm.

Key words: Cyclic microwave radiation, Dispersed nanosized CaWO_4 , Nanosized SrWO_4 in irregular clusters, Nanosized BaWO_4 in dumb-bell shaped clusters.

Introduction

CaWO_4 , SrWO_4 and BaWO_4 are typical scheelite tungstates [1-6] specified as having cubic close-packed arrays of M^{2+} cations and $[\text{WO}_4]^{2-}$ anions. They have the $\text{I4}_1/\text{a}$ or C_{4h} space group [2] with two formula units per primitive cell [5], and have attracted interest for a wide variety of applications. Among them are laser host materials in quantum electronics and scintillators [1, 4], a stimulated Raman scattering technique [3] and catalysts [7]. Their luminescent property is caused by the electronic transition between oxygen and tungsten within tetrahedral $[\text{WO}_4]^{2-}$ units [8]. Tungstates with different shapes and sizes have been prepared by different methods, such as spray pyrolysis [1], a template-free precipitation technique [3], a chemical solution method [6], a solvothermal-mediated microemulsion method [9], pulse-laser deposition [10] and microwave-assisted synthesis with further calcination [11]. Sometimes, templates, surfactants and other additives were used to control the product morphologies. For the present research, CaWO_4 , SrWO_4 and BaWO_4 with different morphologies were synthesized in basic solutions using cyclic microwave radiation without the requirement of any further calcination. The reaction proceeded in an open system at atmospheric pressure. No other additives were used. The process is very simple, attractive and novel for synthesizing pure products.

Experiment

Each of 0.005 mol $\text{M}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (M = Ca, Sr and Ba) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 20 ml propylene glycol containing 10 ml 3 M NaOH. The reactions cyclically proceeded using 600 W microwave for 10 cycles. One cycle was 2 minutes long and was composed of radiation and non-radiation for 1 minute each. The final products were washed with water and 95% ethanol, dried at 80°C for 24 h, and intensively characterized using a selected area electron diffraction (SAED) as well as a transmission electron microscope (TEM) and a high resolution transmission electron microscope (HRTEM) operated at 200 kV, a scanning electron microscope (SEM) operated at 15 kV, a Raman spectrometer using a 50 mW Ar laser with $\lambda = 514.5$ nm, and a photoluminescence (PL) spectrometer using 214, 270 and 344 nm exciting wavelengths for CaWO_4 , SrWO_4 and BaWO_4 at room temperature, respectively.

Results and Discussion

Phases of the products were analyzed using SAED. The patterns (Fig. 1) were interpreted [12, 13]. They correspond to (101), (112), (004), (200), (114), (204), (220), (116) and (215) planes for CaWO_4 , (101), (112), (004), (200), (211), (204), (220), (116) and (312) planes for SrWO_4 , and (112), (200), (114), (204), (220), (116) and (224) planes for BaWO_4 (reference codes : 41-1431 for CaWO_4 , 85-0587 for SrWO_4 and 43-0646 for BaWO_4) [14]. The products have the scheelite structure, belong to the tetragonal crystal system [1-6, 14], and

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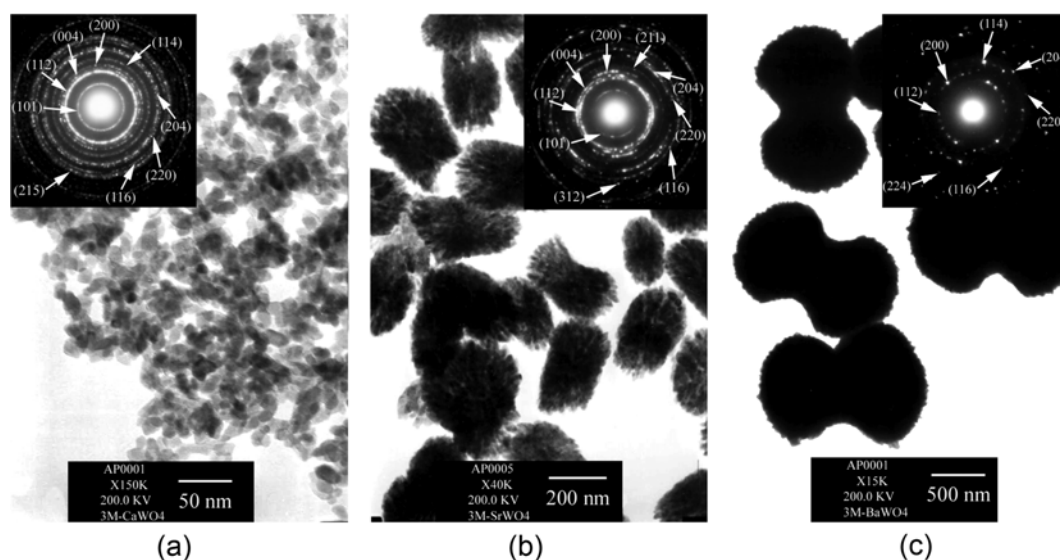
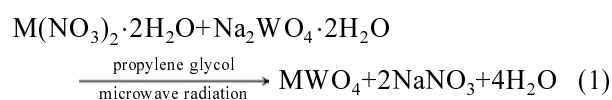


Fig. 1. SAED patterns and TEM images of (a) CaWO_4 , (b) SrWO_4 and (c) BaWO_4 .

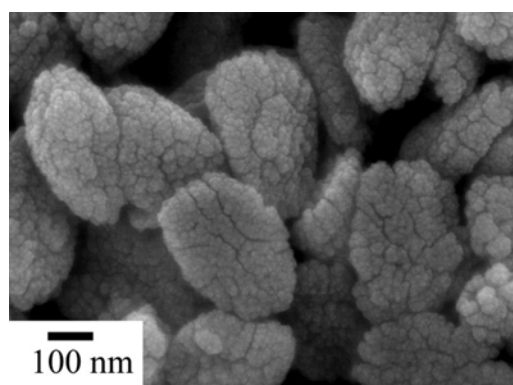
have $I4_1/a$ or C_{4h}^6 space-group symmetry [1, 2, 14]. The patterns appear as concentric rings characterized as polycrystals, due to the diffraction of electrons through the products. They are diffuse showing that the products are composed of a number of nanosized crystals.

TEM images show that the products consist of dispersed nanosized particles for CaWO_4 (Fig. 1a), nanosized particles in irregular clusters for SrWO_4 (Fig. 1b), and nanosized particles in clusters shaped like dumb-bells for BaWO_4 (Fig. 1c). Lattice planes (Fig. 2) of CaWO_4 are uniformly arranged in a systematic array and specified as (101). The (101) plane corresponds to the innermost ring of the SAED pattern for CaWO_4 . SEM images (Fig. 3) show that the products are composed of a number of nanosized particles. They are in irregular clusters for SrWO_4 (Fig. 3a), and clusters shaped like dumb-bells for BaWO_4 (Fig. 3b). It is believed that some stress developed in the dumb-bells as well. For the present research, SEM and TEM results are in good accord.

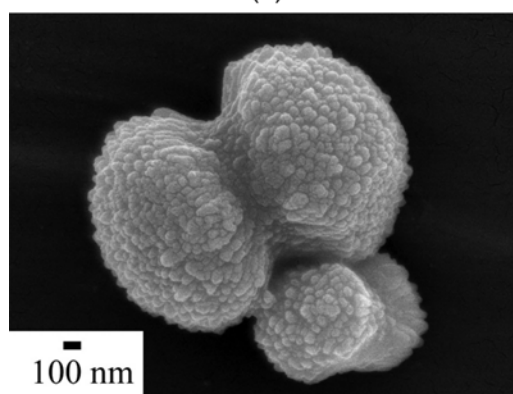
To produce MWO_4 , $\text{M}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ reacted with $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in propylene glycol under basic condition using cyclic microwave radiation.



Microwave radiation has attracted attention for producing materials. It is able to reduce the reaction time, and can rapidly lead to very high temperatures which have the influence of accelerating the reaction process. When



(a)



(b)

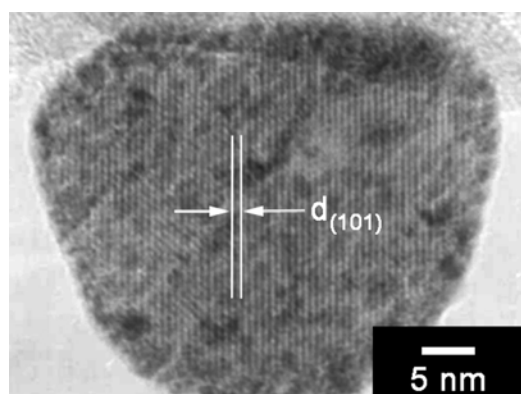


Fig. 2. HRTEM image of CaWO_4 .

Fig. 3. SEM images of (a) SrWO_4 and (b) BaWO_4 .

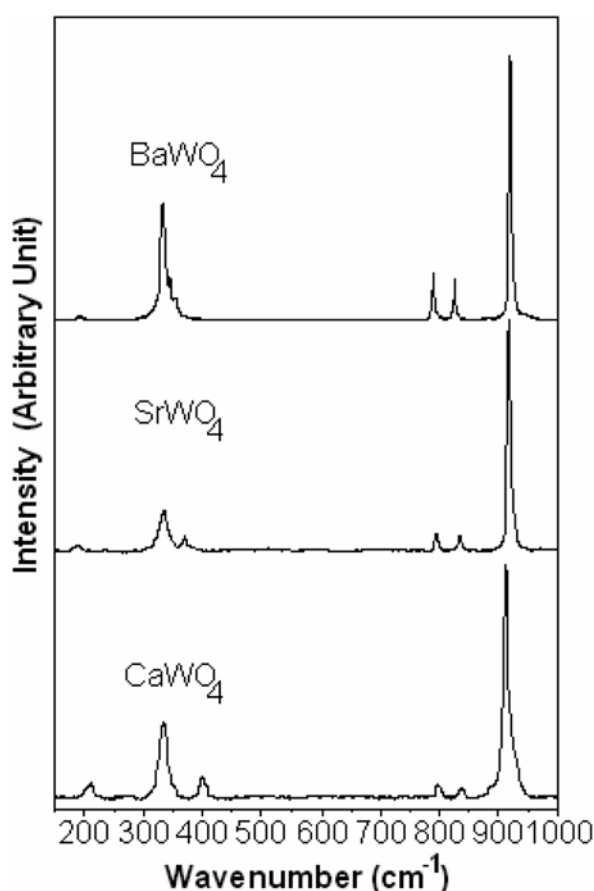


Fig. 4. Raman spectra of CaWO_4 , SrWO_4 and BaWO_4 .

microwave radiation is supplied to chemical solutions, one or more components dissolving in the solutions is capable of coupling with the radiation. This leads to a higher heating rate than that achieved by a conventional method. It can solve the problems of temperature and concentration gradients by focusing large amounts of microwave radiation into solutions. The vibrating electric field applies a force on charged particles which accordingly vibrate. This has an influence on the reaction to proceed with a shorter time and lower power. Subsequently, a pure product is produced [15].

The products were stimulated using 514.5 nm Ar laser. Raman spectra (Fig. 4) show six different modes of $\nu_1(\text{A}_g)$, $\nu_3(\text{B}_g)$, $\nu_3(\text{E}_g)$, $\nu_4(\text{B}_g)$, $\nu_2(\text{A}_g)$ and free rotation at 913, 838, 798, 401, 337 and 211 cm^{-1} for CaWO_4 , 922, 838, 799, 372, 337 and 190 cm^{-1} for SrWO_4 , and 921, 826, 791, 345, 332 and 191 cm^{-1} for BaWO_4 , respectively. Each of the modes is in accord with Raman vibrations analyzed by other researchers [5, 16]. The spectra of the three products provide evidence of the scheelite structure [5, 16]. Compare to the Ar laser, a great deal of energy was lost during the inelastic scattering process.

The crystal-field splitting and hybridization of the molecular orbitals of $[\text{WO}_4]^{2-}$ tetrahedrons [2] are shown in Fig. 5. The $\text{W } 5d(t_2)$ and $\text{W } 5d(e)$ orbitals are hybridized with the $\text{O } 2p(\sigma)$ and $\text{O } 2p(\pi)$ ligand orbitals to form

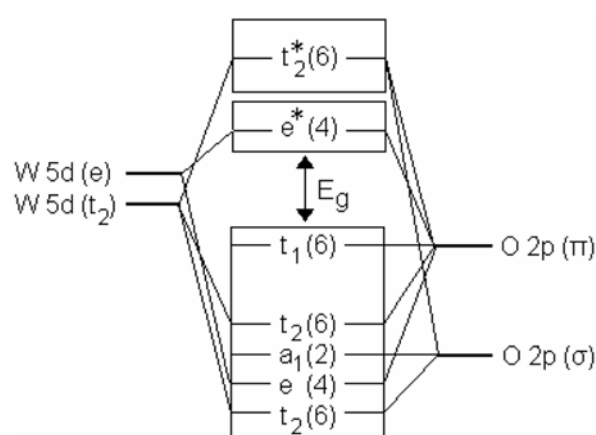


Fig. 5. Schematic diagram of the crystal-field splitting and hybridization of the molecular orbitals of $[\text{WO}_4]^{2-}$ tetrahedrons [E_g = Energy band gap, * = Antibonding (Unoccupied) states, Degeneracy of each cluster state is specified as the figures in brackets.].

$[\text{WO}_4]^{2-}$ tetrahedrons. The four ligand $p(\sigma)$ orbitals are compatible with the tetrahedral representation for a_1 and t_2 symmetries and the eight ligand $p(\pi)$ orbitals are for t_1 , t_2 and e symmetries. The top occupied state has t_1 symmetry formed from $\text{O } 2p(\pi)$ states. The lowest unoccupied state has e symmetry formed from a combination of the $\text{W } 5d(e)$ and $\text{O } 2p(\pi)$ orbitals to give antibonding (*). The hybridization between the $\text{W } 5d$ and $\text{O } 2p$ orbitals is specified as covalent bonding between the ions. For a ground state system, all one-electron states below the band gap are filled to give a many-electron $^1\text{A}_1$ state. At the lowest excited state, there is one hole in the t_1 (primarily $\text{O } 2p(\pi)$) state and one electron in the e (primarily $\text{W } 5d$) state which give rise to many-electron $^1\text{T}_1$, $^3\text{T}_1$, $^1\text{T}_2$ and $^3\text{T}_2$ states. Among them, only $^1\text{T}_2 \rightarrow ^1\text{A}_1$ transition is electric dipole allow [2, 17].

Photoluminescent (PL) spectra (Fig. 6) show the narrow central peaks with their surrounding shoulders. The central (intrinsic) peaks are considered to be from the $^1\text{T}_2 \rightarrow ^1\text{A}_1$ transition of electrons within $[\text{WO}_4]^{2-}$

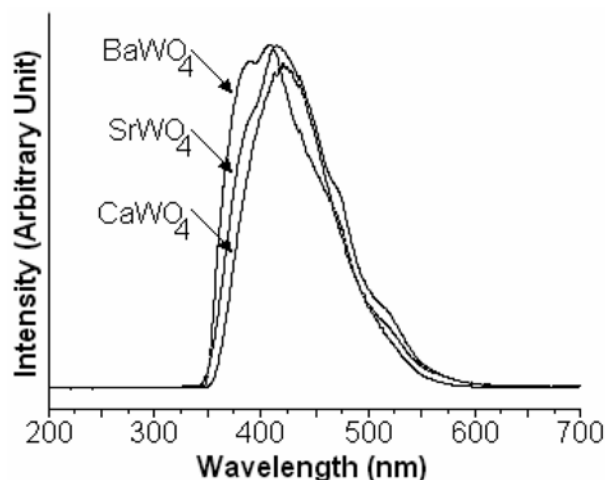


Fig. 6. PL spectra of CaWO_4 , SrWO_4 and BaWO_4 .

anions [2, 17, 18]. The transition can be treated as an exciton [18]. The shoulders are from some defects and impurities, and are specified as extrinsic transitions [18]. The PL intensity is controlled by the number of charged transfers. For the present analysis, the emission peaks are in the blue spectral region at 407-419 nm. The results are in the same range as others [18-20]. Shapes, sizes, degree of crystallinity, exciting wavelength and other factors can play a role in their emission as well.

Conclusions

CaWO_4 , SrWO_4 and BaWO_4 were successfully synthesized using a cyclic microwave radiation. Each of them is a pure phase, and is composed of dispersed nanosized particles for CaWO_4 , nanosized particles in irregular clusters for SrWO_4 , and nanosized particles in clusters shaped like dumb-bells for BaWO_4 . The products provide evidence of the scheelite structure with six different vibration modes. Their emission peaks are due to the $^1\text{T}_2 \rightarrow ^1\text{A}_1$ electronic transition in $[\text{WO}_4]^{2-}$ tetrahedrons in the blue spectral region.

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