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# Effect of solvents on the microstructure of $CaWO_4$ prepared by a solvothermal synthesis

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**Different sizes of nanostructured $CaWO_4$ have been prepared by a simple solvothermal synthesis at a low temperature of 160 °C for 6 h through the reaction between $Ca(NO_3)_2{\cdot}4H_2O$ and $Na_2WO_4{\cdot}2H_2O$ using various solvents as the reaction medium. The products, characterized by X-ray diffraction (XRD), were specified as pure $CaWO_4$ with the scheelite structure. Scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis showed that the particle sizes are mainly related to the physical and chemical properties of the solvents used in the solvothermal synthesis. Photoluminescence properties were also investigated.**

**Key words: Nanocrystalline materials, Solvothermal synthesis, $CaWO_4$.**

## Introduction

$CaWO_4$ compound is an important inorganic material that has been a subject of numerous investigations on its luminescent properties. It is attractive for application in lasers, and fluorescent lamps [1-4]. It is well known that the physical properties of nanomaterials are strongly related to their crystallite size and their morphology. Hence, controlling the size and morphology of nanostructures is still a major challenge. Thus far, several methods have been developed for the preparation of $CaWO_4$ phosphors. In solid state reactions, a high reaction temperature and a long heating time are required to obtain a pure phase. Therefore, producing agglomerated particles of irregular shape by solid state reactions is unavoidable. Furthermore, inhomogeneous compounds of metal tungstates might be formed easily because $WO_3$ has a tendency to vaporize at high temperatures [5-7]. Thus far, a number of attempts have been made to develop the preparation of $CaWO_4$ by applying soft solution methods such as a polymerized complex method [7], spray pyrolysis [8], and a metathetic reaction [9]. In this study, nanoparticles have been prepared by solvothermal synthesis using water, glycerol-water, and propylene glycol-water as the solvents. The microstructures and photoluminescence properties of the synthesized powders have been characterized and the relationship with the solvent has been investigated in detail.

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## Experimental procedure

In a typical synthesis, 0.003 mole $Ca(NO_3)_2{\cdot}4H_2O$ and $Na_2WO_4{\cdot}2H_2O$ was dissolved in 30 ml pure water or mixed solvents of glycerol-water (or propylene glycol-water) with the volume ratio 25/5. Then the resulting solution was loaded into a Teflon-lined stainless-steel autoclave. The autoclave was then sealed and maintained at 160 °C for 6 h for the reaction. After the system was cooled down to room temperature, the white powders in the autoclave were filtered and washed with distilled water and ethanol several times, and finally dried at 80 °C for 12 h.

The crystallinity and phase purity of the prepared samples were analyzed by an X-ray diffractometer with CuKα radiation (wavelength: 0.15406 nm) operating at 20 kV-15 mA in the 2θ range of 10°-60°. The morphology and particle sizes of samples were determined by a field emission-scanning electron microscope (FE-SEM, JSM-6335F) operated at 15 kV accelerating voltage and a transmission electron microscope (TEM, JEOL JEM-2010) operating at 20 kV. Fourier transform infrared spectra (FT-IR, 510 Nicolet) were acquired in the range of 400-4000 $cm^{-1}$. The emission spectra was measured by Perkin Elmer Luminescence spectrometer LS50B.

## Results and Discussion

Fig. 1 gives the representative XRD patterns of all samples. All the diffraction peaks could be indexed to the tetragonal cell of $CaWO_4$, which are consistent with reported values [10] (JCPDS file no. 77-2234). No impurity phases were detected. The sharp peaks indicated good

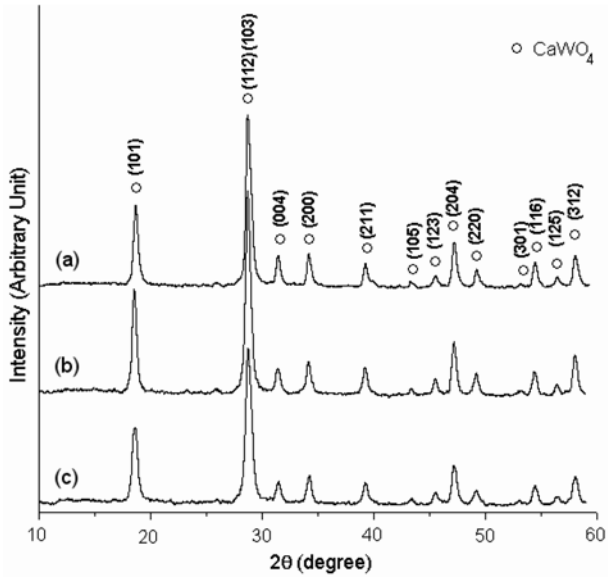


**Fig. 1.** XRD patterns of the $CaWO_4$ powders prepared in different solvents: (a) pure water, (b) glycerol-water and (c) propylene glycol-water.

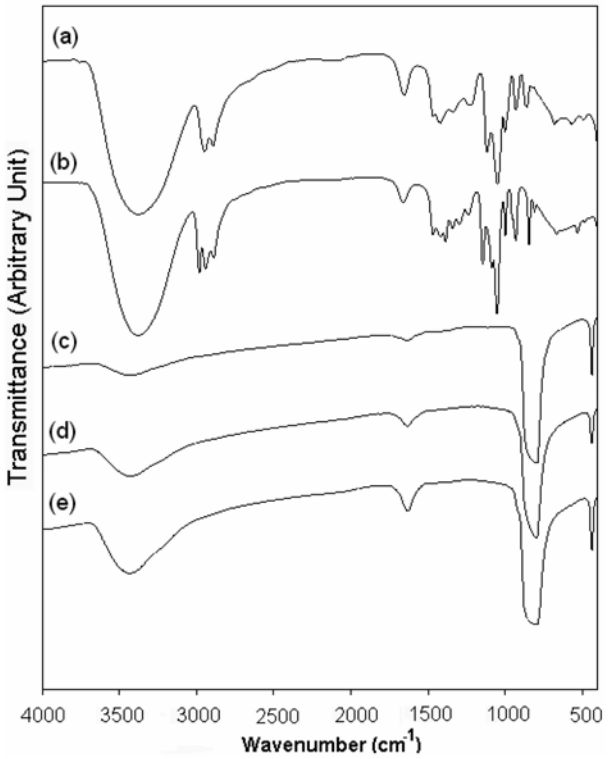


**Fig. 2.** FT-IR spectra of pure solvents (a) propylene glycol, (b) glycerol and those of the $CaWO_4$ powders prepared in different solvents (c) pure water, (d) glycerol-water and (e) propylene glycol-water.

crystallization of the $CaWO_4$. For the $CaWO_4$ structure, $Ca^{2+}$ and $[WO_4]^{2-}$ are loosely bound together and arranged as a cubic close-packed array. W ions are within tetrahedral O-ion cages and are isolated from each other, while Ca ions are surrounded by eight oxygen ions [8]. The FT-IR spectra of the $CaWO_4$ powders obtained in different solvents (Fig. 2(c)-(e)) revealed the presence of O-H stretching and O-H bending of residual water at 3,070-3,690 $cm^{-1}$ and 1,620 $cm^{-1}$ [11], respectively. The strong peak at 705-875 $cm^{-1}$ is associated with the stretching vibration of the W-O bond in $[WO_4]^{2-}$ tetrahedra [12, 13], which is in accord with the detection of tungstates analyzed by XRD. Another weak W-O stretching band was detected at 409-443 $cm^{-1}$ [13, 14] as well. For comparison reasons, the IR spectra of pure glycerol and propylene glycol (Fig. 2(a)-(b)) were also measured, showing absorption bands in the region 2875-2975 $cm^1$ characteristic of the C-H stretching vibration of hydrocarbons, the bands at 1450-1500 $cm^1$ attributed to the bending vibration of the C-H in the methylene group [14], and the strong band at 1044 $cm^1$ corresponding to the stretching vibration of the C-O group in the polyol molecule [15]. There are no bands specific to pure propylene glycol or glycerol in the FT-IR spectra of the $CaWO_4$ powders, clearly indicating that the final products have no organic impurities.

Fig. 3 shows SEM micrographs of $CaWO_4$ powders prepared in different solvents. The powders prepared in pure water compose of rather round nano-sized particles in irregular micro-sized clusters as shown in Fig. 3(a). The nano-sized particles formed and subsequently in clusteres together in small groups. Fig. 3(b) and (c) show the SEM micrographs of the powders prepared in mixed solvents of glycerol-water and propylene glycol-water. These powders are nano-sized particles. The particle sizes and particle size distributions of the $CaWO_4$ powders were also investigated by TEM images as shown in Fig. 4 and particle size distributions shown in Fig. 5. The average sizes are $44.2 \pm 13.9$, $23.3 \pm 6.7$, $14.3 \pm 3.7$ nm for the powders prepared in pure water, glycerol-water and propylene glycol-water, respectively. The main reasons for these phenomena can be expressed by considering some physical properties of different solvents used in the present research [16] as shown in Table 1. It is obvious that each solvent possessed a different boiling point, dielectric constant and thermal conductivity. For the present research, the resulting powders treated in water prefer to form with a large particle size and as high quality crystals because the higher dielectric constant and thermal conductivity correspond to the higher solubility of the inorganic solute and high diffusion rate of ions in the solution. On the other hand, in the case of using glycol solvents, because of the low diffusion rate of ions in the solvent, crystalline growth was suppressed, and led to the formation of fine nano-particles. The dielectric constant of the solvent has an important influence on the growth rate of $CaWO_4$ powders during solvothermal synthesis since small particles will be more stable in a solvent with a low dielectric constant than in a solvent with a high dielectric constant. The possibility of a complex between the ions and the organic solvent will also hinder the growth of $CaWO_4$ particles during solvo-thermal synthesis [17-19]. Therefore, we believe that the properties of the solvent lead to a change of the crystallite

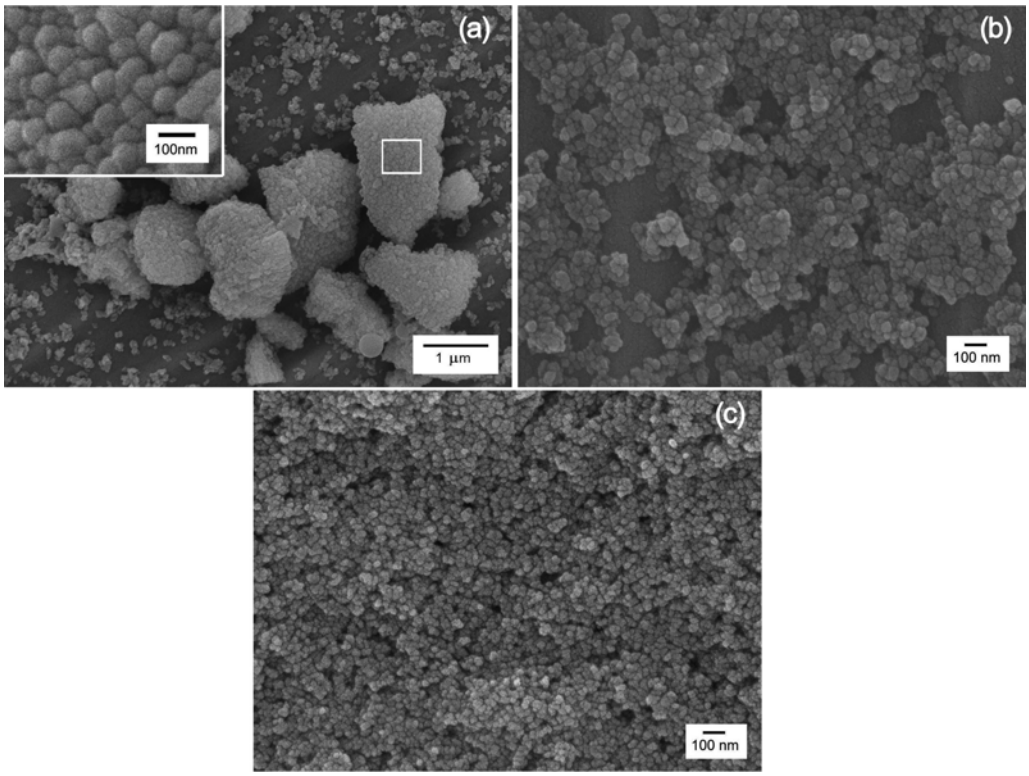


**Fig. 3.** SEM micrographs of the $CaWO_4$ powders prepared in different solvents: (a) pure water, (b) glycerol-water and (c) propylene glycol-water. (Insets are shown at higher magnification.)

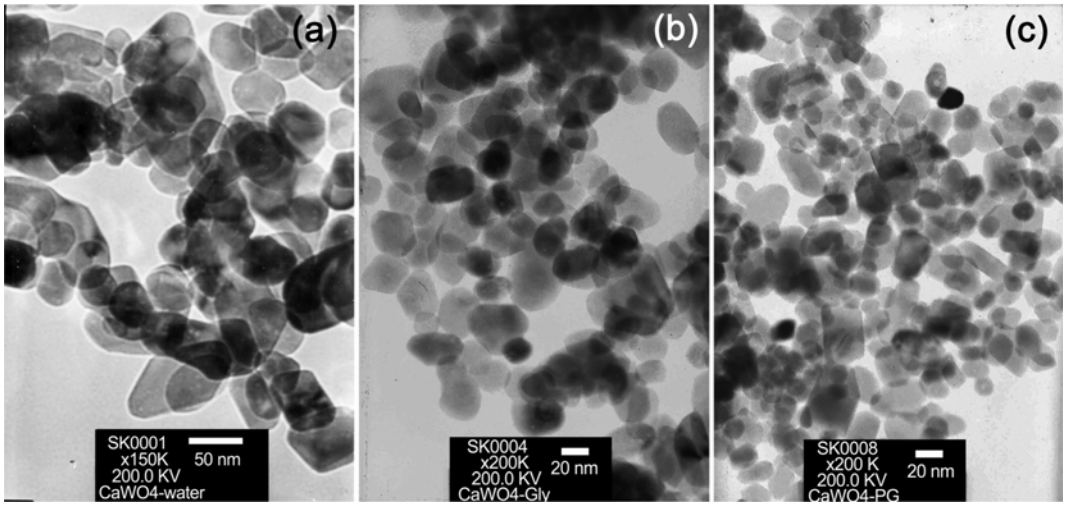


**Fig. 4.** TEM micrographs of $CaWO_4$ powders prepared in different solvents: (a) pure water, (b) glycerol-water and (c) propylene glycol-water.

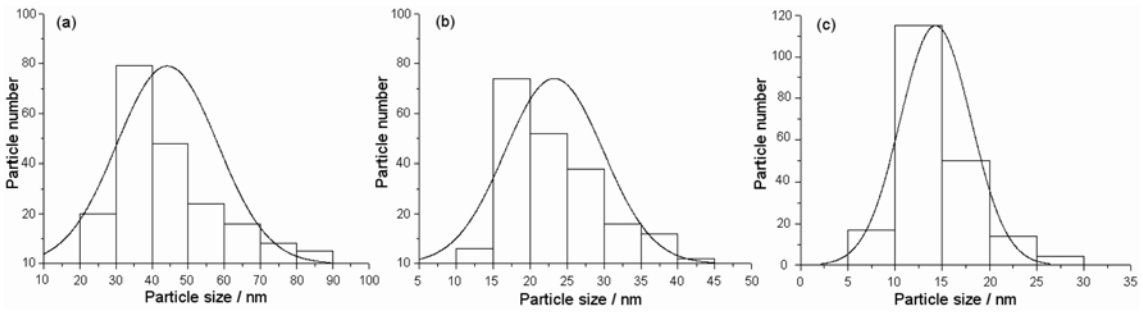


**Fig. 5.** Particle size distributions of $CaWO_4$ prepared in different solvents: (a) pure water, (b) glycerol-water and (c) propylene glycol-water.

**Table 1.** Physical and chemical data of solvents utilized in the present research [16]

| Solvent | Water | Glycerol | Propylene glycol |
|---|---|---|---|
| Molecular formula | $H_2O$ | $C_3H_8O_3$ | $C_3H_8O_2$ |
| Molecular weight | 18.02 | 92.09 | 76.10 |
| Boiling point (°C) | 100 | 290 | 187.6 |
| Density (g $cm^{-3}$, 20 °C) | 0.997 | 1.2613 | 1.0361 |
| Dielectric constant (20 °C) | 80.1 | 46.53 | 27.5 |
| Thermal conductivity (W/m K, 25 °C) | 0.607 | 0.292 | 0.200 |

size of $CaWO_4$.

Metal tungstate crystallizes in the scheelite structure with tightly bound $(WO_4)^2$ molecular ions loosely bound to $M^{2+}$ cations. It is generally thought that in materials such as tungstate and molybdates the observed absorption and fluorescence spectra are associated with transitions within the molecular anion groups. The absorption transitions are attributed to charge transfer transitions in which an oxygen 2p electron goes into one of the empty tungsten 5d orbitals [20]. The crystal-field splitting and hybridization of the molecular orbitals of $(WO_4)^2$ tetrahedra [22] are shown in Fig. 6. The W 5d($t_2$) and W 5d(e) orbitals are hybridized with the O 2p(σ) and O 2p(π) ligand orbitals to form $(WO_4)^2$ tetrahedra. The four ligand p(σ) orbitals are compatible with the tetrahedral representation for $a_1$ and $t_2$ symmetries and the eight ligand p(π) orbitals are for $t_1$, $t_2$ and e symmetries. The top occupied state has $t_1$ symmetry formed from O 2p(π) states. The lowest unoccupied state has e symmetry formed from a combination of the W 5d(e) and O 2p(π) orbitals to give antibonding (*). The hybridization between the W 5d and O 2p orbitals is specified as covalent bonding between the ions. For the ground state system, all one-electron states below the band gap are filled, resulting in a many-electron $^1A_1$ state. At the lowest excited state, there is one hole in the $t_1$ (primarily O 2p(π)) state and one electron in the e (primarily W 5d) state which give rise to many-electron $^1T_1$, $^3T_1$, $^1T_2$ and $^3T_2$ states. Among them, only the $^1T_2 \rightarrow {}^1A_1$ transition is an electric dipole-allowed transition [20-22].

For the present research, the photoluminescent (PL) spectra of $CaWO_4$ have a similar shape due to the similarity in the morphologies. Fig. 7 shows the emission spectra of the $CaWO_4$ powders ($\lambda_{ex}$ = 283 nm). The PL emission at 444 nm wavelength is due to the $^1T_2 \rightarrow {}^1A_1$ transition of electrons within $(WO_4)^2$ anions [21-23]. The broad shoulders are from some defect centers with respect to oxygen, and interpreted as extrinsic transitions. The PL intensity for the powders prepared in pure water, which shows a large particle size, is the highest and controlled by the number of charge transfers. The strong luminescence intensity indicates the good crystallinity. It is obvious that PL intensities are decreased with a decrease of the particle sizes. These show that the solvents play a role in the product formations, morphologies, particle sizes and PL intensities. It is well known that the luminescent properties of solids greatly depend on their particle size and morphology. This relationship is of current interest, and may lead to new fabrication processes to yield high quality luminescent materials.

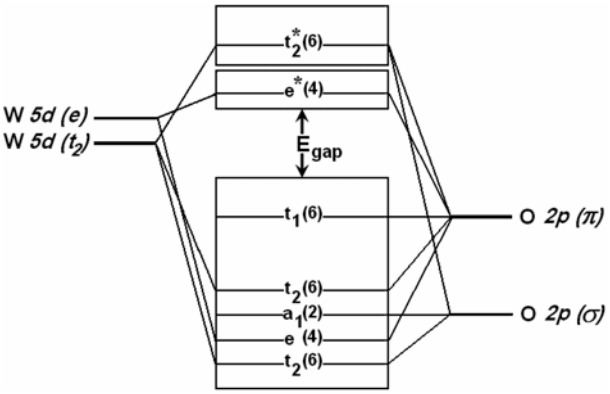


**Fig. 6.** A schematic diagram of the crystal-field splitting and hybridization of the molecular orbitals of a tetrahedral $WO_4^{2-}$ tetrahedron. $E_{gap}$ indicates the energy band gap. "*" indicates antibonding (unoccupied) states. The boxes are included to emphasize the fact that the discrete states are broadened by neighboring cluster interactions in the solid material. The number in parentheses indicates the degeneracy of the $(WO_4)^{2-}$ complex.

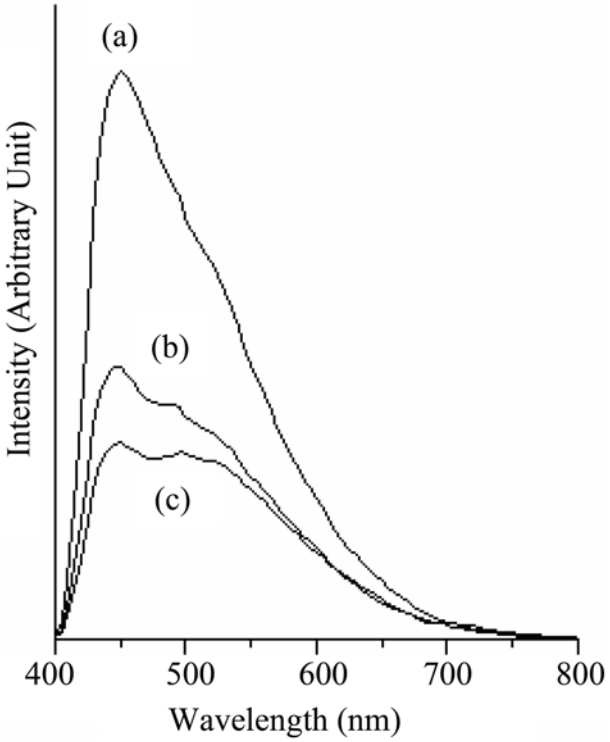


**Fig. 7.** PL spectra of $CaWO_4$ powders prepared in different solvents: (a) pure water, (b) glycerol-water and (c) propylene glycol-water.

## Conclusions

$CaWO_4$ nanoparticles with different sizes were produced at 160 °C for 6 h by solvothermal reactions in different solvents. They provided the evidence of the scheelite

structure with W-O stretching vibration in $[WO_4]^{2-}$ tetrahedra at 705-875 $cm^{-1}$. Photoluminescence (PL) emissions were detected at 444 nm due to the $^1T_2 \rightarrow {}^1A_1$ transition of $(WO_4)^2$ tetrahedra.

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