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Low-temperature synthesis of metal tungstates nanocrystallites in ethylene glycol

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Abstract

In this paper, we report the low-temperature synthesis of metal tungstate, MWO_4 (M = Ca, Sr, Ba, Cd, Zn, Pb) nanocrystallites. By reaction between metal chloride and sodium tungstate in ethylene glycol at 180 °C for 10 h, well-crystallized tungstate particles were successfully obtained. Characterization by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) shows that the product powders consist of nanosize particles. Photoluminescence measurement reveals that the as-obtained $CaWO_4$, $CdWO_4$, and $PbWO_4$ show excitonic peaks at about 430, 500 and 500 nm, respectively. The solvent and reaction conditions are important in the formation of the products.

Keywords: A. Nanostructures; B. Chemical synthesis; C. X-ray diffraction

1. Introduction

Powders with particles of uniform shape and narrow size distribution lying in the nanometer range have been shown to possess interesting properties. Nanoscale oxide particles or mixed oxides particles are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, or ceramic materials [1,2]. Metal oxide nanoparticles are also widely used in industrial applications as catalysts, ceramic, pigments and so on. With regard to all of the applications, numerous approaches have been explored for the preparation of spherical nanosized particles ranging from lithographic technologies to chemical methods [3–5]. Compared with the conventional solid-state reaction methods, solution-based synthesis results in higher levels

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of chemical homogeneity. Also, mixing of the starting materials at the molecular level is achieved in solution-based systems, this is especially important when multi-component oxides are being prepared.

In this paper, we report the preparation of several nanosized metal tungstate powders [such as: $CaWO_4$, $SrWO_4$, $BaWO_4$, $CdWO_4$, $ZnWO_4$ and $PbWO_4$] from the reaction between metal chloride and sodium tungstate in the ethylene glycol system at low temperature. Previous investigation had shown that ethylene glycol can efficiently complex and stabilize the surface of the nanoparticles, accordingly, the particles exist almost non-agglomerated in polyol media [1]. By using ethylene glycol as the solvent, a lot of inorganic materials, such as chalcogenides, metal oxides, have been successfully prepared. But the report on the synthesis of metal tungstate has seldom been found.

Calcium tungstates ($CaWO_4$) scheelite structural family, for example are of commercial interest for applications in lasers, and fluorescent lamps because of their attractive photoluminescence properties [6–8]. Cadmium tungstate ($CdWO_4$) crystals with a monoclinic wolframite structure [9] considered to be highly functional materials because of their high average refractive index [10], low radiation damage, low aftergrow to luminescence and high X-ray absorption coefficient [11]. And some of the other transition metal tungstates (TMT) are of especial importance because of their electrical conductivity [12,13] and magnetic properties [14]. These materials also find application as catalysts [15] and humidity sensors [16].

Although many methods have been reported on the preparation and characterization of metal tungstate [17–21], our present route is relatively simple, efficient and can be applied to synthesis of a host of metal tungstates nanocrystalline at low temperature.

2. Experimental

Metal tungstates were synthesized in ethylene glycol (EG, bp = 198 °C) with the reaction of $MCl_2{\cdot}nH_2O$ (M = Ca, Sr, Ba, Cd, Zn, Pb) and Na_2WO_4 powders in an autoclave at 180 °C under self-generated pressure.

In a typical procedure, 0.001 mol $MCl_2{\cdot}nH_2O$ and slightly excessive sodium tungstate were put into a Teflon-lined stainless steel autoclave of 50 ml capacity, then the autoclave was filled with ethylene glycol to 80% of the total volume. After being sealed, the autoclave was maintained at 180 °C for 10 h without shaking or stirring during the heating period and then allowed to cool to room temperature. The precipitates were collected then washed with absolute alcohol and distilled water to remove the residue of ethylene glycol. The final product was dried in a vacuum at 50 °C for about 4 h.

The obtained samples were characterized by the X-ray powder diffraction (XRD) method. The XRD was carried out with Japan Rigaku D/-max-γA diffractometer equipped with a graphite monochromatized Cu Kα radiation ($\lambda = 1.5418$Å). A scan rate of 0.05°/s was applied to record the patterns in the 2θ range 10–70°. The morphology and particle sizes of as-obtained samples were determined by transmission electron microscopy (TEM). The images were taken with Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The luminescence and excitation spectra of the samples were determined by a Hitachi 850 fluorescence spectrometer with a Xe lamp at room temperature.

3. Results and discussion

$CaWO_4$, $PbWO_4$, etc. with the formula MWO_4 are characterized by the tetragonal space group $I4_1/a$ or C_{4h}^6 (Fig. 1). In this structure, the primitive unit cell has been described to have two MWO_4 units [22], each of which has an inversion center. The M and W sites have S_4 point symmetry. There have three crystal parameters $\{x, y, z\}$ to describe the location of the O sites, which have only a little symmetry, and are arranged in nearly tetrahedral coordination about each W site. Some literature [23] has described the crystal structure as highly ionic with $M^{+\alpha}$ cations and tetrahedral $WO_4^{-\alpha}$ anions, where $\alpha \approx 2$. The W and O with formal changes of $-\beta$ and $-\gamma$, respectively, where $4\gamma - \beta \equiv \alpha$, consist of highly ionic $WO_4^{-\alpha}$ anions. β and γ would be 6 or 2 if there were no covalent bonding.

XRD patterns of the as-obtained nanocrystalline tungstates are shown in Fig. 2. The product phases, which were obtained from the diffraction peaks in the XRD patterns, and the cell constants derived from the XRD patterns are given in Table 1. The cell constants are consistent with the reported values. The broadening of the peaks indicates small grain sizes, according to the Scherrer equation. By means of XRD, no peaks of impurities could be detected.

Fig. 3 shows typical TEM microphotographs of the as-obtained nanocrystalline samples. Nearly all the products obtained were spherical particles. The grain sizes were directly observed and it is clearly seen that almost all the samples are non-aggregated and the sizes of these samples are in the nanoscale range. And the average sizes from the TEM observation are also listed in Table 1. The results agree well with those obtained from the XRD patterns.

The PL spectra of the as-obtained tungstates are shown in Fig. 4. Fig. 4a is the PL spectrum of as-obtained $CaWO_4$, which were measured using a 283.4 nm excitation line. It exhibited only green peak at 430 nm, which was similar to the result reported in literature [24]. The PL spectra of as-obtained $CdWO_4$ (Fig. 4b) and $PbWO_4$ (Fig. 4c) also exhibited a peak at 500 and 500 nm, respectively. The corresponding excitation line is 290 nm for $CdWO_4$ and 300 nm for $PbWO_4$, respectively. The results are also in agreement with the literatures [21,25].

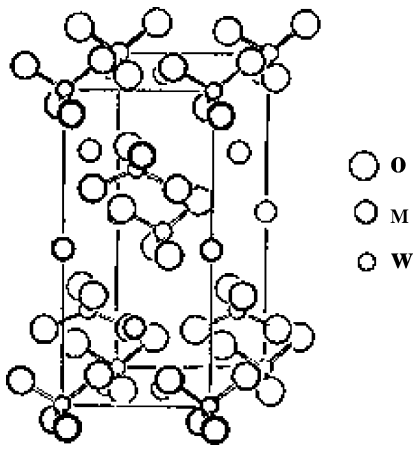

Fig. 1. The structure of MWO_4.

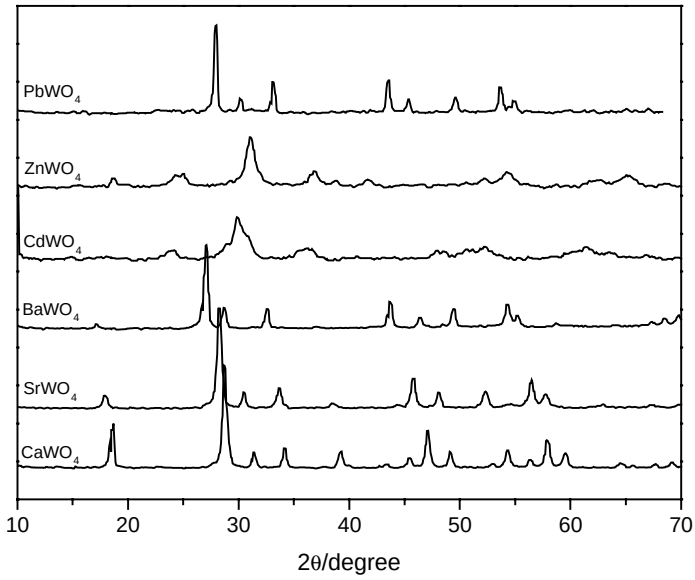

Fig. 2. XRD patterns of as-obtained nanocrystalline tungstates: $CaWO_4$, $SrWO_4$, $BaWO_4$, $CdWO_4$, $ZnWO_4$, and $PbWO_4$.

In the present experiments, ethylene glycol was selected as the solvent because it can effectively complex and stabilize the surface of the nanoparticles. Accordingly, the nanoparticles exist almost non-agglomerated in ethylene glycol media [1], which were benefit for the preparation of stable and uniform tungstates. To make a comparison, the synthesis of nanocrystalline metal tungstates was also carried out

Table 1
Characterization of as-obtained products

Products	Phase	Cell constants		TEM observed grain size (nm)	JCPDS Card
		Observed	Reported		
$CaWO_4$	Tetragonal	$a = 5.30$ $c = 11.213$	$a = 5.174$ $c = 11.19$	40	77-2236
$SrWO_4$	Tetragonal	$a = 5.434$ $c = 11.970$	$a = 5.416$ $c = 11.95$	30	85-0587
$BaWO_4$	Tetragonal	$a = 5.627$ $c = 12.731$	$a = 5.613$ $c = 12.72$	140	85-0588
$CdWO_4$	Monoclinic	$a = 5.031$ $b = 5.871$ $c = 5.079$	$a = 5.029$ $b = 5.859$ $c = 5.074$	10	14-0676
$ZnWO_4$	Monoclinic	$a = 4.729$ $b = 5.714$ $c = 4.965$	$a = 4.720$ $b = 5.700$ $c = 4.950$	70	73-0554
$PbWO_4$	Tetragonal	$a = 5.452$ $c = 12.04$	$a = 5.461$ $c = 12.04$	60	19-0708

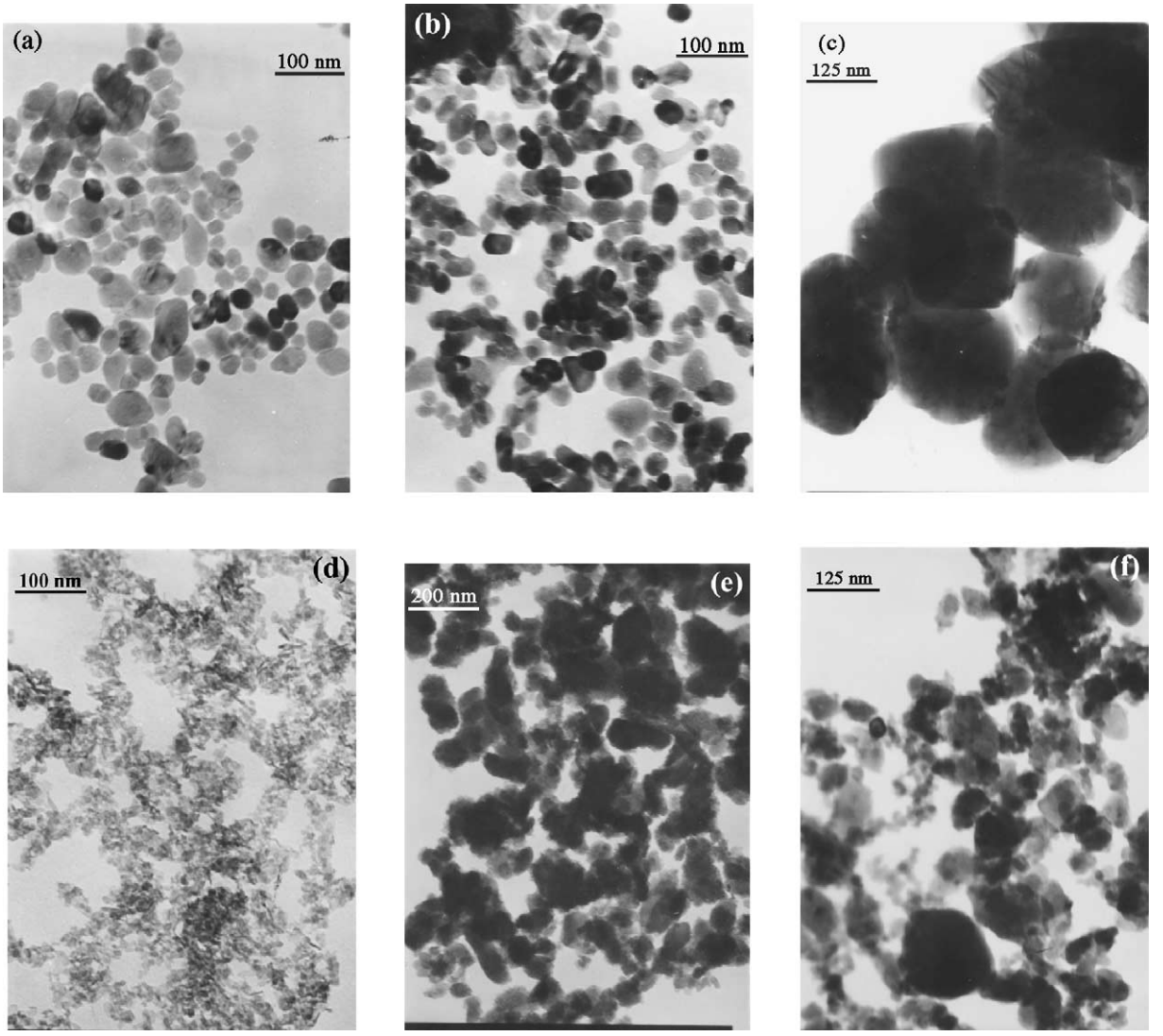

Fig. 3. TEM images of typical samples of nanocrystalline tungstates: (a) $CaWO_4$, (b) $SrWO_4$, (c) $BaWO_4$, (d) $CdWO_4$, (e) $ZnWO_4$, (f) $PbWO_4$.

in ethanol, distilled water or their mixtures with different ratio at 180 °C for 10 h, respectively. The XRD patterns show that there were many characteristic peaks of other impurity phases besides the samples of tungstates.

The influences of reaction temperature and reaction time were also studied. In our experiments, we changed the synthetic temperature in the ethylene glycol system from 10 to 200 °C keeping the other reaction condition constant. The XRD results show that no tungstates were formed below 100 °C. And temperature higher than 200 °C or time longer than 10 h, the grain sizes will grow bigger. The optimum conditions for synthesizing pure phase of metal tungstates were at 180 °C for 10 h.

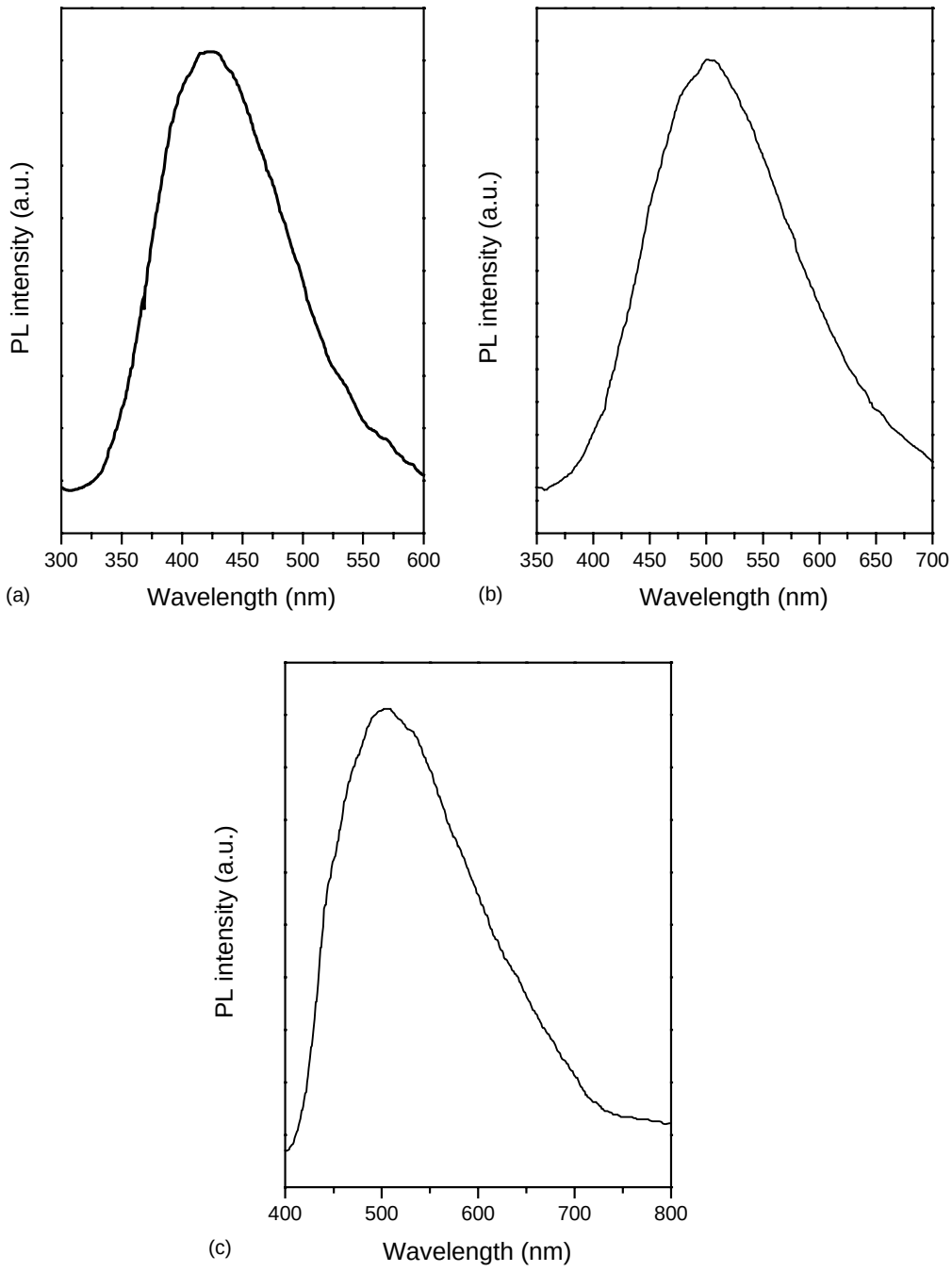

Fig. 4. Photoluminescence (PL) spectrum of as-prepared nanocrystalline tungstates: (a) $CaWO_4$, (b) $CdWO_4$, (c) $PbWO_4$.

4. Conclusion

Nanocrystalline tungstates ($CaWO_4$, $SrWO_4$, $BaWO_4$, $CdWO_4$, $ZnWO_4$, and $PbWO_4$) were successfully synthesized in ethylene glycol at 180 °C. The solvent ethylene glycol played a key role and the reaction temperature also affected the crystallization and purity of the final products. With optimum reaction conditions selected, these nanocrystalline tungstates with high qualities were successfully prepared. The simplicity of the process and high yield make it possible for industrial application.

Acknowledgements

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