Research Article

Fast Microwave-Assisted Synthesis and Photoluminescence of CaWO₄ Nanocrystals

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Received 30 May 2013; Accepted 20 September 2013

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In this work, CaWO₄ nanoparticles have been synthesized by microwave-assisted method at a low temperature of 120°C. The as-prepared powders were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR). It is found that the reaction time played an important role in the morphology controlling and crystallinity level of CaWO₄ crystals. The effects of photoluminescent properties have a great relationship with crystallinity.

1. Introduction

In recent years, with the advance of nanoscale materials science and technology, the synthesis of nanoscale materials with unique properties is becoming more and more important for studying the variation of materials’ properties with size and morphology [1–5]. Nanomaterials based on the scheelite-type have attracted considerable interest because of their luminescent property approved use in electrooptic applications [6–8]. SrWO₄, CaWO₄, PbWO₄, and BaWO₄ were considered to be typical oxides structure of scheelite-type. Locating within tetrahedral O-ion cages, W ions are isolated from each other in the scheelite structure, while Ca, Ba, Sr, and Pb ions are surrounded by eight oxygen ions [9].

CaWO₄ with a scheelite structure is an important optical material, which has attracted particular interest because of its applications in quantum electronics or scintillators as laser host material [11, 12]. CaWO₄ powders are usually prepared by traditional solid-state reactions which require high temperature and harsh reaction conditions [13]. Recently, CaWO₄ nanoparticles have been prepared by various wet chemical methods [14–18], which needs long reaction time, or nonaqueous solvents, such as hydrothermal method, citrate complex method, combustion process, coprecipitation, microwave-hydrothermal methods, polymeric precursor method, and microwave-solvothermal methods [19–22].

Therefore, to synthesize CaWO₄ nanoparticles with a mild method (e.g., low temperature and/or quick reaction time) is of significance in both fundamental and applied studies [23].

In this paper, we report the synthesis, crystal structure, and fluorescence property of CaWO₄ nanocrystals, which is prepared from the reaction of CaCl₂ and Na₂WO₄·2H₂O in the presence of PEG1000 by fast microwave-assisted method. By controlling the different reaction time, the degree of crystallinity of CaWO₄ can be controlled. It means that we can obtain CaWO₄ with higher crystallinity target structure by adjusting the reaction time, which is important for the preparation of aimed productions in the system of Ca–W–O.

2. Experimental Section

2.1. Synthesis. CaCl₂ (AR), Na₂WO₄·2H₂O (AR), and PEG1000 (AR) were used as the starting materials, and all of them were of analytical grade without any further purification. CaWO₄ nanocrystals were prepared by microwave-assisted method in the absence of any organic additives. In a typical procedure, 0.1093 g CaCl₂, 0.1003 g Na₂WO₄·2H₂O, and 0.1409 g PEG1000 were put into quartz tube and dissolved in 10 mL distilled water, and the mixture was vigorously stirred for 10 min to ensure that all reagents were dispersed homogeneously. And then put the sealed quartz
tube into the microwave reactor. Reaction temperature and
time, pressure, and microwave power output were adjusted
according to the parameters of the reactor. After cooling to
room temperature naturally, the precipitates were collected,
washed with distilled water and absolute ethanol for several
times, and then dried in a vacuum oven at about 60°C for 24 h.

2.2. Characterization. The morphologies of CaWO₄ samples
were examined by transmission electron microscopy (TEM)
(JEM-2010, JEOL, Japan). The FT-IR spectra (Nicolet-380,
Nicolet Instrument Co., USA) were recorded in the region
of 4000–400 cm⁻¹. X-ray diffraction (XRD) patterns were
measured on a MiniFlex2 goniometer. Employing a scanning
rate of 0.02° s⁻¹ in the 2θ range from 5° to 70°, the operating
voltage and current were maintained at 30 kV and 15 mA,
respectively. Photoluminescence (PL) spectra were recorded
by a Hitachi 850 fluorescence spectrometer with a Xe lamp at
room temperature. Fourier transform infrared spectroscopic
(FT-IR) analysis was carried out using pressed KBr disks in
the region of 4000–400 cm⁻¹ by using a Perkin Elmer
spectrometer instrument.

3. Results and Discussion

3.1. Structural Analysis. The phase identification of all the
products was performed by XRD. To investigate the effect
of reaction time on the crystallinity, CaWO₄ products was
performed by XRD. To investigate the effect of reaction
time, pressure, and microwave power output were adjusted
according to the parameters of the reactor. After cooling to
room temperature naturally, the precipitates were collected,
washed with distilled water and absolute ethanol for several
times, and then dried in a vacuum oven at about 60°C for 24 h.

Figure 1 shows the XRD patterns of the products obtained
via microwave-assisted method. When reaction time is 5 min,
the crystallinity of as-prepared product is considerably low,
and there are few peaks that cannot be observed. Therefore,
a longer time supports the formation of the thermodynamically
stable, well-crystallized, and uniform products. It is very
 clear that the crystallinity of obtained products increase with
the increasing of reaction time for 15 min (Figure 1(a)). In a
word, the reaction time of the reaction systems was found to
play an important role in determining the crystallinity of the
CaWO₄ nanocrystals.

To further confirm the formation of the CaWO₄ crystal
structure, Fourier transform infrared (FT-IR) spectroscopy
was performed on the as-prepared CaWO₄ nanocrystals
(Figure 2). The bands at 1383 cm⁻¹, 1576 cm⁻¹, 1636 cm⁻¹, and
3441 cm⁻¹ are assigned to O–H stretching vibration and H–
O–H bending vibration [24], respectively. The two bands are
the characteristic vibrations of water from air absorbed on
the sample surface physically which is completely different
from coordinated water in compounds. The 111 cm⁻¹ band
is the characteristic vibrations of CO₂ in the air. A strong
absorption band around 800 cm⁻¹ is related to O–W–O
stretches of the WO₄ tetrahedron, because the AWO₄-type
sheelite oxides, having S4 site symmetry for the WO₄ groups,
which show the main absorption bands in the region of 400–
1000 cm⁻¹, centered around 911, 405, and 833 cm⁻¹ based on
the v1, v2, and v3 modes of the WO4 groups, respectively [25].
The 453 cm⁻¹ band is attributed to the v2 stretching vibration
of W–O on the same grounds.

3.2. Morphology Control. Figure 3 shows the typical TEM
images of CaWO₄ samples synthesized via microwave-
assisted method at 120°C with different reaction time. It
is very remarkable that CaWO₄ nanocrystals are 63 nm in
diameter, when reaction time is 15 min (Figure 3(c)). But the
diameter of as-prepared CaWO₄ is 46 nm and 62 nm, when
reaction time is 5 min and 10 min (Figures 3(a) and 3(b)),
respectively, which are in good agreement with the XRD
results. This result further confirms that longer heating time
would promote the crystallization of CaWO₄ nanocrystals.
Figure 3(c) shows that the spacing of the lattice fringe is
0.4835 nm and in consonance with the (101) face. Thus, it indicates that CaWO₄ nanocrystals were synthesized by directional connection and self-assembly.

At room temperature, PL property of the CaWO₄ nanoparticles was initially studied. Figure 4 shows the representative PL spectrum of the CaWO₄ nanoparticles synthesized at 120°C for 5 min (a), 10 min (b), and 15 min (c), respectively. With the excited wavelength at 250 nm, the corresponding broad emission peak at 420 nm was observed. Further studies on PL property of the as-prepared CaWO₄ nanoparticles were in progress. With the increasing of the reaction time, the emission peak value increases constantly, which has the same change with morphology and crystallinity. These results strongly indicate that the PL properties of CaWO₄ are sensitive to the degree of structural order-disorder (crystallinity) and the relatively weak variations in the atomic arrangements which was basically in agreement with the analysis of Orhan et al. [21]. In general, the possible reasons are associated with the charge-transfer transitions within the [WO₄]²⁻ complexes [26–29] or due to the vacancies as [WO₃ ⋅ VO] [30] and [CaO₂ ⋅ VO] [31].

4. Conclusions

CaWO₄ nanocrystals have been successfully prepared by microwave-assisted method at a low reaction temperature of 120°C with different time. Experimental results indicated that the crystallinity of as-synthesized CaWO₄ was affected by the reaction time. With the prolonging of the reaction time, the crystallinity of the sample got higher, and the average diameter of particles got bigger. The CaWO₄ nanocrystal obtained by this preparation method has favourable luminescence, which receives emissive wavelength at 420 nm with the excitation wavelength at 250 nm. It indicated that the kernel became bigger, the crystallinity was higher, and the intensity of fluorescence changed to become stronger as time went on.

Acknowledgments

The authors acknowledge with thanks the financial support of Provincial Natural Science Foundation of Hunan, China, (13JJ6041) and the National Natural Science Foundation of China (21343008).
Conflict of Interests

The authors declared that they have no conflict of interests to this work.

References


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