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Synthesis, characterisation and photoluminescence of nanocrystalline calcium tungstate

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Calcium tungstate nanocrystalline was successfully synthesised via a microwave irradiation method using $Ca(NO_3)_2$ and Na_2WO_4 in ethylene glycol, without the requirement of any calcination. The product was analysed by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and photoluminescence spectrometry. XRD, SAED and TEM revealed that the product was body-centred tetragonal $CaWO_4$ with an average particle size of 12 nm. Different oscillation modes were detected by Raman spectroscopy and FTIR. They showed the strong W–O stretching in $[WO_4]^{2-}$ tetrahedrons at 711–933 cm^{-1}. Photoluminescence (PL) of $CaWO_4$ nanocrystalline showed the maximum emission peak at 422 nm.

Keywords: calcium tungstate; scheelite structure; microwave irradiation

1. Introduction

$CaWO_4$ with scheelite structure is an important optical material. It can be used for luminescence, thermoluminescence and stimulated Raman scattering behaviour. Its superior blue phosphor (433 nm) property is used in oscilloscopes and as a scintillating material for detecting X-rays and γ-rays for medical applications [1–3]. Several physical and chemical methods including chemical bath deposition [1], a facile microemulsion-mediated hydrothermal procedure [2], pulse laser ablation [4], molten salt method [5], sonochemical method [6] and microwave-assisted synthesis [7], used for preparing nanocrystalline $CaWO_4$, were reported. Among them, microwave irradiation method has the advantage of short reaction time, simple and efficient, compared to a conventional method. The products have small particle size, narrow particle size distribution and high purity. The synthesis of nanocrystalline $CaWO_4$ and $NiWO_4$ powders via water-based citrate complex precursors using microwave irradiation were reported. The precursors were calcined at 300–500°C for 3 h. At 400°C and 3 h calcination, the average crystallite sizes of the products were 21 nm for $CaWO_4$ and 20 nm for $NiWO_4$ [7].

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For the present research, nanocrystalline $CaWO_4$ was synthesised by microwave irradiation method without any calcination. The product was intensively characterised by a variety of techniques to determine the phase, morphology, vibrations and photon emission.

2. Experiment

To synthesise nanocrystalline $CaWO_4$, each 0.005 mole of $Ca(NO_3)_2$ and Na_2WO_4 were separately dissolved in 15 mL ethylene glycol. They were mixed with 30 min stirring in a home-made autoclave for microwave heating. The reaction proceeded by 50% of 600 W microwave heating for 20 min. The microwaving was cyclic – on for 60 s every 60 s interval. Finally, white precipitates were synthesised, washed with distilled water and absolute ethanol and dried in air at 80°C for 24 h. The final products were analysed using an X-ray diffractometer (XRD) with a Cu-Kα line of SIEMENS D500. Raman spectroscopy (HORIBA JOBIN YVON T64000) was carried out using 50 mW Ar laser with 514.5 nm wavelength. Fourier transform infrared (FTIR) spectrum was recorded using a BRUKER TENSOR27 spectrometer. A transmission electron microscope (TEM) and selected area electron diffractometer (SAED) of JEOL JEM-2010 were operated at 200 kV. Photoluminescence (PL) emission was recorded using 214 nm excitation wavelength at room temperature by PERKIN-ELMER LS50B luminescence spectrometer.

3. Results and discussion

XRD pattern of calcium tungstate, shown in Figure 1(a), corresponds to the JCPDS database No. 72-1624 [8]. No impurities were detected in this product. Its lattice parameters were calculated using plane spacing equation for tetragonal structure [9] and Bragg's law for diffraction. They are $a = 5.2548$ Å and $c = 11.3785$ Å, respectively, very close to the JCPDS database values ($a = 5.2425$ Å and $c = 11.3715$ Å) [8]. The peaks at $2\theta = 26.5–31.0°$ were enlarged and normalised and fitted with two Gaussian curves
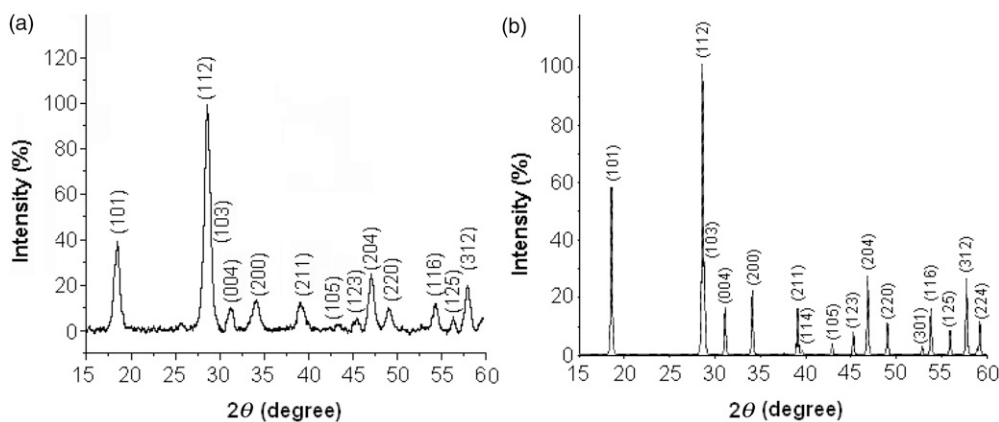

Figure 1. (a) XRD pattern of $CaWO_4$ synthesised using a microwave radiation and (b) its simulated diffraction pattern.

(Figure 2), the (1 1 2) and (1 0 3) peaks. The broadening of these diffraction peaks indicates that $CaWO_4$ particles are of the size of nanometres. The crystallite size of $CaWO_4$, calculated using the (1 1 2) XRD peak with Scherrer's equation [9–11], is 10.88 nm – supports the broadening of the (1 1 2) and (1 0 3) peaks.

Metal tungstates (metal ionic radii >0.1 nm: Ca, Sr, Ba and Pb) have scheelite structure with body-centred tetragonal system, and C_{4h}^6 space symmetry with two formula units per primitive cell. Each of W ions without d electrons is surrounded by four oxygen ions with tetrahedral arrangement, and the W–O bonds are rather rigid [3,7,10,11]. A unit cell of calcium tungstate with $I4_1/a$ space group [8] was simulated by CaRIne version 3.1 program [12] with its calculated lattice cell. The positions and sizes of Ca, W and O radii are shown in Table 1 [12,13]. For calcium tungstate unit cell (Figure 3), tungsten atoms are coordinated to four oxygen atoms in WO_4 tetrahedrons, and calcium atoms are coordinated to eight oxygen atoms in CaO_8 polyhedrons. The XRD simulation pattern [12] using the Cu-Kα line (1.542 Å) is shown in Figure 1(b). Table 2 compares the 2θ (Bragg's angles) and intensities of the diffraction planes obtained from the experiment, simulation using CaRIne version 3.1 program and JCPDS database. Low-intensity peaks of some crystallographic planes, such as (2 0 2), (1 1 4), (2 2 2), (3 0 1) and (3 0 3) were not detected in the experiment, when comparing with the JCPDS database No. 72–1624 [8], while (2 0 2) and (2 2 2) were not present in the simulation.

Metal tungstates were composed of $[WO_4]^{2-}$ anionic units with strong covalent W–O bonds inside, with which the M^{2+} (Ca, Sr, Ba and Pb) cations have a weak coupling.

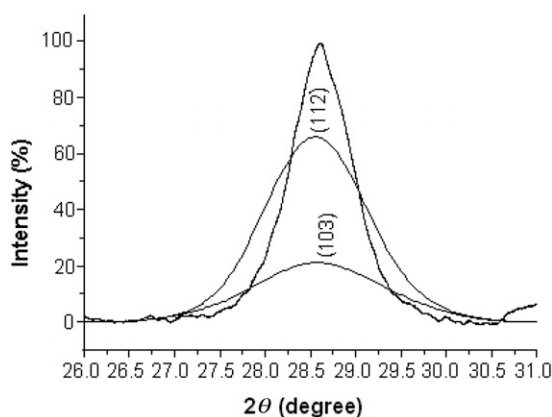Figure 2. XRD pattern for $2\theta = 26.5–31.0°$ of $CaWO_4$ synthesised using a microwave radiation.

Table 1. Atomic coordinates of $CaWO_4$ and their ionic radii.

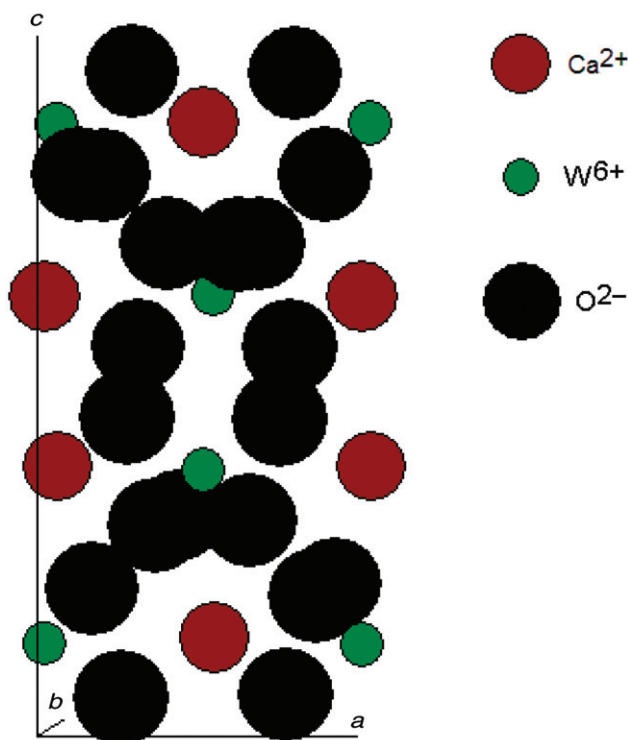| Atom	Ionic radius (Å)	Site	x	y	z
Ca	0.99	4b	0	1/4	5/8
W	0.62	4a	0	1/4	1/8
O	1.32	16f	1/4	3/25	1/20

Figure 3. Unit cell of CaWO$_4$ tetragonal structure.

Their Raman oscillations are divided into two modes: the internal and external. The first is the oscillation inside [WO$_4$]$^{2-}$, and the second, known as lattice phonons, is caused by the oscillation of M^{2+} cations relative to the rigid anionic units. For free [WO$_4$]$^{2-}$ ions with T$_d$-symmetry, the oscillations are composed of different modes: four internal, one free rotation and one translation. Group theory calculation shows 26 different oscillations: 3A$_g$, 5A$_u$, 5B$_g$, 3B$_u$, 5E$_g$ and 5E$_u$. The even oscillations (3A$_g$, 5B$_g$ and 5E$_g$) are Raman active. Only four of those of the odd (4A$_u$ and 4E$_u$) are IR active, and their remains (1A$_u$ and 1E$_u$) are acoustic. The 3B$_u$ oscillations are silent [6,10]. CaWO$_4$ has [WO$_4$]$^{2-}$ tetrahedral symmetry. Its Raman spectrum was recorded on 150–1000 cm^{-1}, as shown in Figure 4(a). The $\nu_{f.r.}$(A$_g$), ν_2(A$_g$), ν_4(B$_g$), ν_3(E$_g$), ν_3(B$_g$) and ν_1(A$_g$) oscillations were detected at 210, 332, 400, 797, 838 and 912 cm^{-1}, respectively.

Transmittance mode of CaWO$_4$, analysed by FTIR is shown in Figure 4(b). In general, scheelite structure has T$_d$-symmetry which has four oscillations: ν_1(A$_1$), ν_2(E), ν_3(F$_2$) and ν_4(F$_2$) [6,10]. The ν_3(F$_2$) oscillation is anti-symmetric stretching in [WO$_4$]$^{2-}$ tetrahedrons. The strong W–O stretching in [WO$_4$]$^{2-}$ tetrahedrons was detected at 711–933 cm^{-1}, and weak W–O bonding (ν_4(F$_2$)) at 433 cm^{-1}.

TEM image, SAED pattern and particle size distribution of nanocrystalline CaWO$_4$ are shown in Figure 5. It was composed of round nanosized particles (Figure 5(a)) with different orientations. SAED pattern (Figure 5(b)) shows several concentric rings of bright spots – corresponding with the (1 0 1), (1 1 2), (0 0 4), (2 0 0), (1 1 4), (2 0 4), (2 2 0), (1 1 6)

Table 2. The 2θ Bragg's angles and diffraction intensities (I) of $CaWO_4$ obtained from the experiment, simulation and JCPDS database.

Plane	JCPDS database		Experiment		Simulation	
	2θ (°)	I (%)	2θ (°)	I (%)	2θ (°)	I (%)
(101)	18.62	62.60	18.47	36.83	18.57	58.10
(112)	28.73	100.00	28.84	100.00	28.61	100.00
(103)	29.05	22.80	29.02	20.43	28.84	26.40
(004)	31.44	13.10	31.12	9.40	31.12	16.50
(200)	34.18	18.90	34.23	13.23	34.13	22.20
(202)	37.76	0.40	–	–	–	–
(211)	39.20	13.90	38.84	11.88	39.13	16.30
(114)	39.93	1.60	–	–	39.65	1.60
(105)	43.33	3.10	43.04	2.40	42.94	4.10
(123)	45.45	7.30	45.48	4.62	45.27	8.20
(204)	47.12	26.50	47.03	25.12	46.85	27.30
(220)	49.11	11.10	48.90	10.06	49.04	11.20
(222)	51.84	0.10	–	–	–	–
(301)	52.97	2.20	–	–	52.88	3.10
(116)	54.32	13.30	54.21	11.83	53.84	16.00
(125)	56.31	6.00	56.26	5.81	55.95	8.30
(312)	57.89	21.30	57.94	19.38	57.76	25.60
(303)	58.08	12.60	–	–	57.89	1.90
(224)	59.49	9.60	28.61	0.69	59.23	11.50
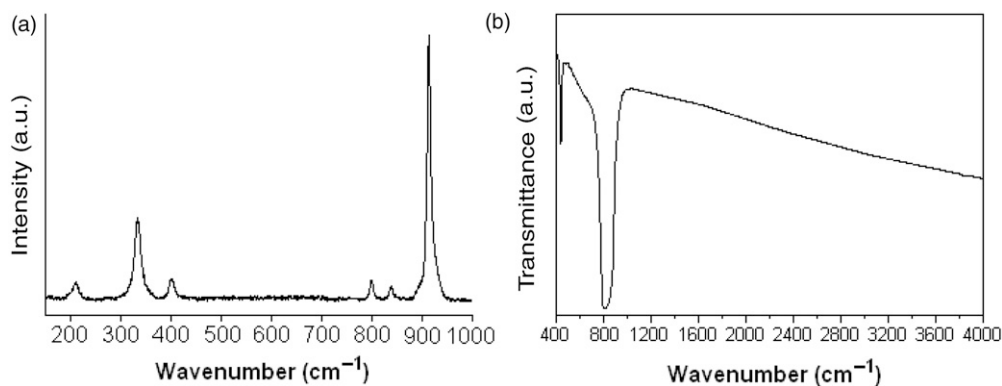
Figure 4. (a) Raman and (b) FTIR spectra of $CaWO_4$ synthesised using a microwave radiation.

and (125) planes of $CaWO_4$ [8]. The average particle size measured from TEM image is 12 nm. Its particle size distribution (Figure 5(c)) is narrow, implying that the particle sizes are rather uniform – favouring the luminescent property.

The crystal-field splitting and hybridisation of $[WO_4]^{2-}$ tetrahedrons are shown in Figure 6. The $W5d(t_2)$ and $W5d(e)$ orbitals are hybridised with the $O2p(\sigma)$ and $O2p(\pi)$ ligand orbitals to form $[WO_4]^{2-}$ tetrahedrons. The four ligand $p(\sigma)$ orbitals are compatible with the tetrahedral representation for a1 and t_2 symmetries, and the eight ligand $p(\pi)$
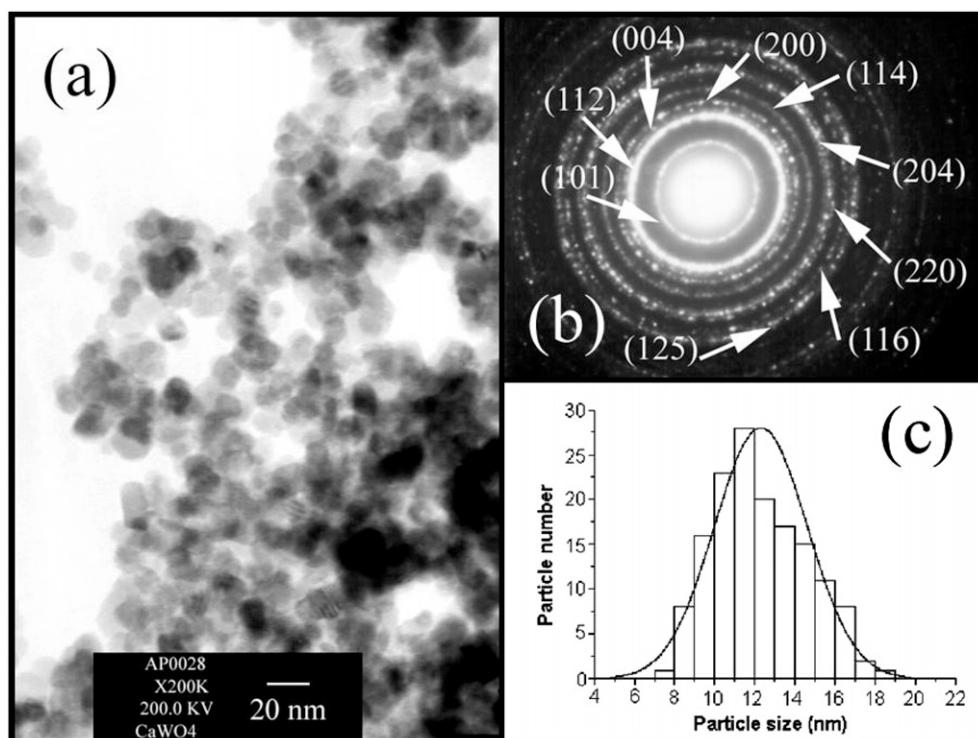
Figure 5. (a) TEM image, (b) SAED pattern and (c) particle size distribution of $CaWO_4$ synthesised using a microwave radiation.
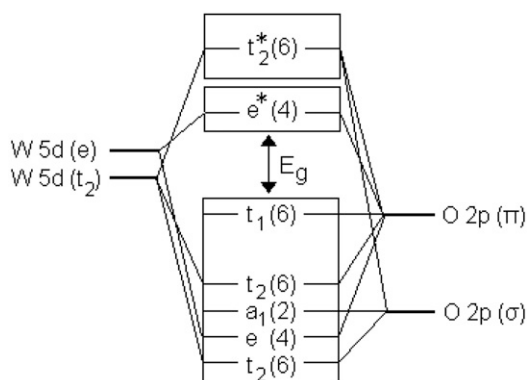

Figure 6. Schematic diagram of the crystal-field splitting and hybridisation of the $[WO_4]^{2-}$ anionic tetrahedrons.

orbitals are for t_1, t_2 and e symmetries. The top occupied state has t_1 symmetry, formed from $O2p(\pi)$ states. The lowest unoccupied state has e symmetry formed from a combination of the $W5d(e)$ and $O2p(\pi)$ orbitals to give anti-bonding (*). The hybridisation between W5d and O2p orbitals is specified as covalent bonding between the ions.
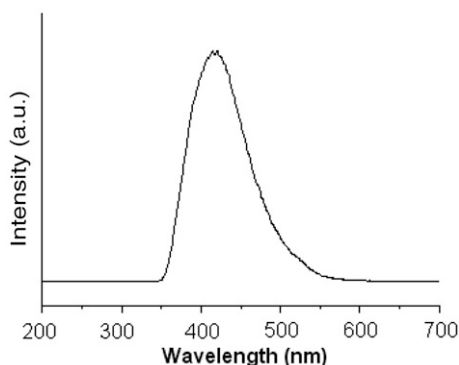
Figure 7. PL emission of $CaWO_4$ synthesised using a microwave radiation.

For ground state, all one-electron states below band gap are filled to give a many-electron $^1A_1$ state. At the lowest excited state, there is one hole in t_1 (primarily $O2p(\pi)$) state and one electron in e (primarily W5d) state, giving rise to many-electron $^1T_1$, $^3T_1$, $^1T_2$ and $^3T_2$ states. Only $^1T_2 \rightarrow \, ^1A_1$ transition is allowed [6], which caused the emission. PL emission (Figure 7) was recorded using 214 nm excitation wavelength, and shows the maximum intrinsic emission peak at 422 nm – caused by the annihilation of self-trapped excitons of the $[WO_4]^{2-}$ excited complexes.

4. Conclusions

Nanocrystalline $CaWO_4$ was successfully synthesised by microwave irradiation method. It is very simple and needs no requirement of any calcination at high temperature. The product is pure body-centred tetragonal $CaWO_4$ with the average particle size of 12 nm. PL shows the emission peak at 422 nm due to the $^1T_2 \rightarrow \, ^1A_1$ transition in the $[WO_4]^{2-}$ excited complexes.

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