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Sonochemical synthesis of $MMoO_4$ (M = Ca, Sr and Ba) nanocrystals

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MMoO₄ (M = Ca, Sr and Ba) were successfully produced using M(NO₃)₂·2H₂O and Na₂MoO₄·2H₂O in ethylene glycol by a 5 h sonochemical process. A tetragonal crystal system with a scheelite structure was detected using an X-ray diffractometer (XRD) and a selected area electron diffraction (SAED) technique. The calculated lattice parameters (a nm, c nm) are (0.5232, 1.1430), (0.5402, 1.2027) and (0.5560, 1.2766) for M = Ca, Sr and Ba, respectively. They are in accord with those of the corresponding JCPDS software. A transmission electron microscope (TEM) revealed the presence of nanocrystals in the products. Their sizes were 11.5 ± 3.1 nm, 15.9 ± 4.8 nm and 18.1 ± 4.8 nm for M = Ca, Sr and Ba, respectively. Their crystallographic planes were aligned in systematic arrays characterized using a high resolution transmission electron microscope (HRTEM). Six different vibration wavenumbers were detected using a Raman spectrometer and are specified as v₁(A_g), v₃(B_g), v₄(B_g), v₂(A_g) and v_{f.r.}(A_g). A Fourier transform infrared (FTIR) spectrometer provided evidence of the scheelite structure with a Mo-O stretching vibration in MoO₄²⁻ tetrahedrons at 740-950 cm⁻¹.

Key words: Sonochemical synthesis, Nanocrystals, CaMoO₄, SrMoO₄, BaMoO₄.

Introduction

 $MMoO_4$ (M = Ca, Sr and Ba) are scheelite-structured materials with two formula units per primitive cell [1-3], and have I41/a or $C_{4\,h}^{\,6}\,$ space-group symmetry [1-4]. They show a band emitted by intrinsic vibration inside $[MoO_4]^{2-}$ tetrahedrons [5]. They have attracted much interest due to their applications as scintillating media and in other electro-optical devices [3]. There are a variety of methods used to produce scheelite structured materials, such as the Czochralski technique [3, 6], a mechanochemical process [7], a solvothermal synthesis [8], a metathetic reaction [9] and microwave-assisted synthesis [6]. The purpose of this research is to produce MMoO₄ (M = Ca, Sr and Ba) nanocrystals using a sonochemical process in an open system at atmospheric pressure. The process proceeded without the assistance of other additives.

Experiment

 $MMoO_4$ (M = Ca, Sr and Ba) nanocrystals were sonochemically synthesized using 0.005 mol each of $M(NO_3)_2 \cdot 2H_2O$ (M = Ca, Sr and Ba) and Na₂MoO₄ · 2H₂O dissolved in 30 ml ethylene glycol. The reactions proceeded for 5 h. The final products were washed with de-ionized water and absolute ethanol, dried at 70°C for 12 h, and intensively characterized.

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Results and Discussion

XRD spectra (Fig. 1) were compared with those of the JCPDS software (reference codes : 07-0212, 08-0482 and 08-0455) [2], and specified as $MMoO_4$ (M = Ca, Sr



Fig. 1. XRD spectra of the products.

and Ba). No other characteristic peaks of impurities were detected showing that the products are pure phase. Their strongest intensity peaks are at $2\theta = 28.8$, 27.7 and 26.5 degrees for CaMoO₄, SrMoO₄ and BaMoO₄, respectively. They diffracted from the same plane specified as (112). They have the scheelite structure with a tetragonal crystal system and have I4₁/a or C⁶_{4h} space-group symmetry [1-4]. Calculated lattice parameters [10] for CaMoO₄ (a = b = 0.5232 and c = 1.1430 nm), SrMoO₄ (a = b = 0.5402 and c = 1.2027 nm) and BaMoO₄ (a = b = 0.5560 and c = 1.2766 nm) are very close to those of the corresponding JCPDS software [2], and have an influence on their interplanar spaces.

To produce $MMoO_4$, $M(NO_3)_2 \cdot 2H_2O$ reacted with $Na_2MoO_4 \cdot 2H_2O$ in ethylene glycol using a sonochemical process :

$$M(NO_3)_2 \cdot 2H_2O + Na_2MoO_4 \cdot 2H_2O$$

$$\xrightarrow{ethylene glycol}{} MMoO_4 + 2NaNO_3 + 4H_2O \quad (1)$$

During the sonochemical process, particles vibrated and completely mixed. The reactions proceeded efficiently. Finally, pure products were produced.

Vibrations of MMoO₄ are classified into the internal and external modes [11]. The first belongs to the vibration inside $[MoO_4]^{2-}$ units. Their centers of masses are stationary. The second is called lattice phonon mode which corresponds to the motion of M^{2+} cations and the rigid molecular units [3, 11]. In free space, $[MoO_4]^{2-}$ have T_d-symmetry [1, 11]. Their vibrations are composed of four internal modes (v₁(A₁), v₂(E), v₃(F₂) and v₄(F₂)), one free rotation (f.r.) mode (v_{f.r.}(F₁)), and one translation mode (F₂) [11]. In lattice space, the symmetry is reduced to S₄. All degenerative vibrations are split [1, 11] due to the crystal field effect and Davydov splitting [11]. For the tetragonal scheelite primitive cell (wavevector, **k** = **0**) [11, 12], there are 26 different vibrations ($\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$) determined by group-theory calculation [1, 11]. Among them, 3Ag, 5Bg and 5Eg vibrations are Raman-active. Only $4A_u$ and $4E_u$ of the $5A_u$ and $5E_u$ vibrations are active in IR frequencies, and the remains $(1A_u \text{ and } 1E_u)$ are acoustic vibrations. The $3B_{\mu}$ vibrations are silent modes [11, 12]. For the present analysis, six different vibrations were detected in the Raman spectra (Fig. 2a). Among them, $v_1(A_g)$, $v_3(B_g)$, $v_3(E_g)$, $v_4(B_g)$, $v_2(A_g)$ and $v_{fr}(A_g)$ are at 881, 849, 795, 391, 323 and 204 cm⁻¹ for CaMoO₄, 892, 838, 790, 357, 323 and 189 cm⁻¹ for SrMoO₄, and 892, 849, 800, 362, 327 and 178 cm⁻¹ for BaMoO₄, respectively. Each vibration mode is in accord with Raman vibrations analyzed by other researchers [1, 11]. The spectra provide evidence of the scheelite structure for the three products [1, 11].

The molybdates were also analyzed using FTIR. Their spectra are shown in Fig. 2b. For T_d -symmetry, $v_3(F_2)$ and $v_4(F_2)$ are IR active, and correspond to stretching and bending modes, respectively [3]. The spectra show a band of Mo-O stretching vibration in MoO₄²⁻ tetrahedrons [3] at 740-950 cm⁻¹. It is one of the internal modes specified as $v_3(F_2)$ antisymmetric stretching vibrations [3] of the three products. Weak Mo-O bending vibrations [13] were also detected at about 425 cm⁻¹ for CaMoO₄ and SrMoO₄.

TEM images, SAED patterns, HRTEM images and Particle-sized distributions of the products are shown in Figs. 3-5. TEM images show that different products are nanocrystals 8-30 nm in size. Their SAED patterns are composed of a number of bright spots arranged into concentric rings. The electrons have been reflected and diffracted from crystallographic planes of the unit cells belonging to the products to produce bright spots. The rings are diffuse and hollow showing that the products are composed of nanocrystals with different orientations. Interplanar spaces were calculated [14, 15] using diameters



Fig. 2. (a) Raman and (b) FTIR spectra of the products.



Fig. 3. (a) TEM image and SAED pattern, (b) HRTEM image and (c) Particle-size distribution of CaMoO₄.



Fig. 4. (a) TEM image and SAED pattern, (b) HRTEM image and (c) Particle-size distribution of SrMoO₄.



Fig. 5. (a) TEM image and SAED pattern, (b) HRTEM image and (c) Particle-size distribution of BaMoO₄.

of the diffraction rings, and compared with those of the JCPDS software [2]. They correspond to (101), (112), (004), (200), (211), (204), (220), (116) and (312) planes for CaMoO₄, (101), (112), (004), (200), (114), (204), (220), (116) and (312) planes for SrMoO₄, and (112), (200), (211), (105), (204), (220), (116) and (312) planes for BaMoO₄. The products belong to the tetragonal crystal system $(a = b \neq c)$ [2]. HRTEM images of lattice planes were characterized. The images show that their crystallographic planes are aligned in systematic arrays although the products are composed of a number of nanocrystals with different orientations. Among the different products, the (112), (004) and (112) planes were respectively detected on CaMoO₄, SrMoO₄ and BaMoO₄. Their sizes were measured from 500 particles on TEM images. The size distributions are very similar to a normal curve. The analysis shows that the particles have different sizes ranging from the smallest to biggest. Averaged sizes are 11.5±3.1 nm, 15.9±4.8 nm and 18.1±4.8 nm for CaMoO₄, SrMoO₄ and BaMoO₄, respectively. They increased with an increase in the atomic masses and radii of the M^{2+} cations (Ca²⁺ = 0.112 nm, Sr²⁺ = 0.125 nm, Ba²⁺ = 0.142 nm) [11].

Conclusions

MMoO₄ (M = Ca, Sr and Ba) nanocrystals were successfully produced from $M(NO_3)_2 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ in ethylene glycol using a sonochemical process. XRD, SAED and TEM analyses revealed the presence of MMoO₄ nanocrystals 8-30 nm in size. Their size distributions are 11.5 ± 3.1 nm, 15.9 ± 4.8 nm and 18.1 ± 4.8 nm for CaMoO₄, SrMoO₄ and BaMoO₄, respectively. Lattice atoms are aligned in systematic arrays characterized using HRTEM. Six different vibrations were detected using Raman spectroscopy. They provide evidence of the scheelite structure. By using FTIR, very strong Mo-O stretching vibrations in $[MoO_4]^{2-}$ tetrahedrons were detected at 740-950 cm⁻¹.

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