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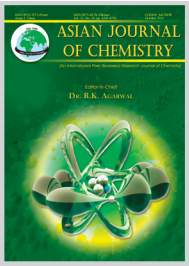

Solid-State Metathetic Synthesis and Photoluminescence of Calcium Tungstate Particles Assisted by Cyclic Microwave Irradiation

WON-CHUN OH, CHONG YEON PARK, JEONG WON JEON and CHANG SUNG LIM*

Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 356-706, South Korea

*Corresponding author: Tel/Fax: +82 41 660 1445; E-mail: cslim@hanseo.ac.kr

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A solid-state metathetic (SSM) route assisted by cyclic microwave irradiation was used to synthesize calcium tungstate ($CaWO_4$) particles. Well crystallized $CaWO_4$ particles were formed at 600 ºC for 3 h, showing a fine and homogeneous morphology with sizes of 1-2 µm. The characteristics of the solid-state metathetic reaction of the $CaWO_4$ particles were examined in detail based on the exothermic reaction. The obtained $CaWO_4$ particles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. The optical properties were examined by photoluminescence emission and Raman spectroscopy.

Key Words: Calcium tungstate, Solid-state metathetic reaction, Cyclic microwave irradiation, Photoluminescence, Raman spectroscopy.

INTRODUCTION

Calcium tungstate ($CaWO_4$) particles from a Scheelite type matal tungstate family are intensively investigated by crystal growers, radilologists, materials scientists and physicist due to their luminescence, thermo-luminescence and stimulated Raman scattering behaviour[1] and have potential application in the field of photonics, electronics and green energy. Calcium tungstate is one of the most widely used phosphors in industrial radiology and medical diagnosis[2], as well as it can be employed for a variety of applications such as tunable fluorescence and sensor for dark matter search[3,4].

Calcium tungstate has a Scheelite-type crystal structure with lattice parameters of a = b = 5.243 Å and c = 11.374[1]. Recently, several processes have been developed over the past decade to enhance the applications of $CaWO_4$ prepared by a range of processes, such as co-precipitation[5], a solvothermal method[5-8], spray pyrolysis[9], a reverse micelle system[10,11], a solution synthesis[12], sol-gel[13], a mechano-chemical method[14], a molten salt method[15,16], a hydrothermal method[17-19], a microwave-assisted synthesis[20-24] and a solid-state metathetic reaction[25,26]. For practical applications of $CaWO_4$ particles, well-defined particle features with homogeneous particle size distribution and morphology of the $CaWO_4$ particles are required. Cyclic microwave-assisted solid-state metathetic (SSM) synthesis of the $CaWO_4$ provide a convenient route for the synthesis of $CaWO_4$, which were obtained in the form of loosely connected submicrometer sized particles at considerably lower temperatures than those normally employed for their synthesis[23,24]. The well-defined crystallization depends on the heat-treatment temperatures of the $CaWO_4$ particles. Post heat-treatment plays an important role in the well-defined crystallized morphology.

In this study, we synthesized $CaWO_4$ particles using a solid-state metathetic method with cyclic microwave irradiation. The characteristics of the solid-state metathetic reaction of $CaWO_4$ particles are discussed in detail based on the exothermic reaction accompanying the formation of a high lattice energy by-product of NaCl. The synthesized $CaWO_4$ particles were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The optical properties were examined by photoluminescence (PL) emission and Raman spectroscopy.

EXPERIMENTAL

Calcium chloride and $Na_2WO_4 \cdot 2H_2O$ of analytic reagent grade were used to prepare the $CaWO_4$ compound. The preparation of $CaWO_4$ was carried out by reacting well-ground mixtures of $CaCl_2$ and $Na_2WO_4 \cdot 2H_2O$ at a molar ratio of 1:1. The sample mixtures were dried at 100 ºC for 12 h, placed into crucibles and exposed to domestic microwaves (Samsung Electronics Corp. Korea) operating at a frequency of 2.45 GHz and a maximum out-put power of 1250 W for 15 min. The cyclic microwave operation was set between 60 s on and 30 s off. The samples were treated with ultrasonic radiation and washed many times with distilled water and ethanol to remove the sodium chloride reaction by-product. The samples were dried at 100 ºC in an oven and heat-treated at 600 ºC for 3 h.

The phase existings in the particles after the solid-state metathetic reactions and heat-treatment were identified by XRD (D/MAX 2200, Rigaku, Japan). FTIR (Nicolet IR200, Thermo Electron corporation, USA) was used to examine the thermal-decomposition behaviour of the solid-state metathetic reaction and the obtained particles over the frequency range, 4000 to 400 cm^{-1}. The microstructure and surface morphology of the $CaWO_4$ particles were observed by SEM (JSM-5600, JEOL, Japan). The photoluminescence spectra were recorded using a spectrophotometer (Perkin-Elmer LS55, UK) at room temperature. Raman spectroscopy measurements were performed using a LabRam HR (Jobin-Yvon, France). The 514.5 nm line of an Ar-ion laser was used as excitation source, the power was kept at 0.5 mW on the sample.

RESULTS AND DISCUSSION

Fig. 1 shows an XRD pattern of the synthesized $CaWO_4$ particles after solid-state metathetic reaction followed by heat-treatment at 600 ºC for 3 h. All XRD peaks could be assigned to a tetragonal phase $CaWO_4$ with a Scheelite-type structure, which is in good agreement with the crystallographic data of $CaWO_4$ (JCPDS: 41-1431). This means that the tetragonal phase $CaWO_4$ can be prepared using this solid-state metathetic reaction assisted by cyclic microwave irradiation. The formation of $CaWO_4$ crystalline phases requires heat treatment at 600 ºC for 3 h. The $CaWO_4$ formed had a scheelite-type crystal structure with lattice parameters of a = b = 5.243 Å and c = 11.374[1]. This suggests that solid-state metathetic synthesis is suitable for the growth of $CaWO_4$ crystallites and development of the strongest intensity peaks at (112), (200) and (312) planes, which were the major peaks of the $CaWO_4$, with some preferred orientation[12,14].

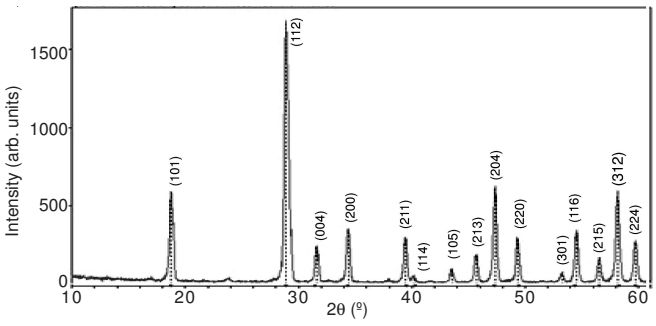

Fig. 1. XRD patterns of the $CaWO_4$ particles after solid-state metathetic reaction followed by heat-treatment at 600 ºC for 3 h

Fig. 2 shows a SEM image of the $CaWO_4$ particles after solid-state metathetic reaction followed by heat-treatment at 600 º for 3 h. The SEM image shows a fine and homogeneous morphology with sizes of 1-2 μm. The microwave metathetic synthesis resulted in fine particles with a controlled morphology and the formation of the product in a green manner without the generation of solvent waste, because the microwave radiation provided the energy required to overcome the energy barrier that precludes a spontaneous reaction and helped heat the bulk of the material uniformly. The solid state metathesis reactions, such as $CaCl_2 + Na_2WO_4 \rightarrow CaWO_4 + 2NaCl$, involves the exchange of atomic/ionic species, where the driving force is the exothermic reaction and formation of NaCl with a high lattice energy[23,26]. Solid-state metathetic reactions occur so rapidly that all the enthalpy released is essentially used to heat up the solid products. The solid-state metathesis reactions provide convenient route for the synthesis of metal tungstates, which were obtained in the form of loosely connected submicron sized particles at considerably lower temperatures than those usually employed for their synthesis. For tungstate materials to be used for practical applications, control of the particle size distribution and morphology of the particles is needed. The well-defined particle features of the $CaWO_4$ particles synthesized by solid-state metathetic reactions have control over the morphology of the final particles and can be used for such technological applications.

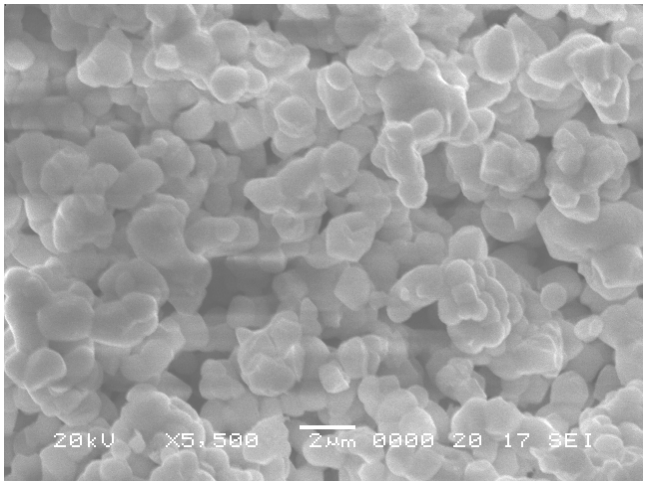

Fig. 2. SEM image of the $CaWO_4$ particles after solid-state metathetic reaction followed by heat-treatment at 600 ºC for 3 h

Fig. 3 shows FTIR spectrum of the obtained $CaWO_4$ particles at the wavenumber range of 4000-480 cm^{-1}. The stretching vibration was detected as a strong W-O stretch in the $[WO_4]^{2-}$ tetrahedrons at 816 cm^{-1}. Similar characteristics absorption bands of MWO_4 (M = Ba, Ca, Sr) for the Scheelite oxides having S_4 site symmetry in this region were reported in the literature[10]. The $[WO_4]^{2-}$ is constituted by four internal modes ($\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$) specified as an anti-symmetric stretching vibration[22]. All modes are Raman active, but $\nu_3(F_2)$ and $\nu_4(F_2)$ are IR active.

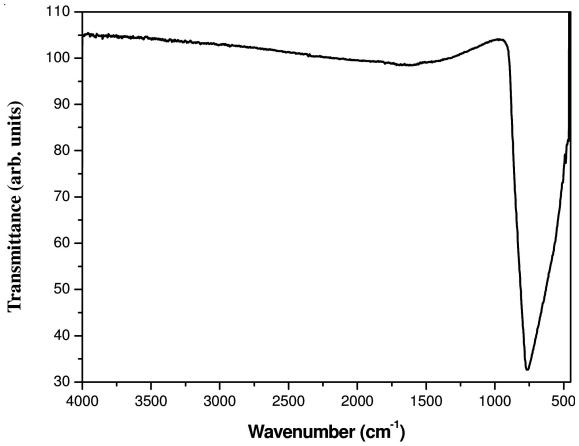

Fig. 3. FT-IR spectra of the $CaWO_4$ particles after solid-state metathetic reaction followed by heat-treatment

Fig. 4 presents a room-temperature photoluminescence emission spectrum of the $CaWO_4$ particles after solid-state metathetic reaction followed heat-treatment at 600 ºC for 3 h. With excitation at 250 nm, the $CaWO_4$ particles exhibit a strong photoluminescence emission in the green wavelength range of 470-480 nm. It is generally assumed that the measured emission spectrum of metal tungstates are mainly attributed to the charge-transfer transitions within the $[WO_4]^{2-}$ complex[27,28]. The photoluminescence intensity of phosphors depends strongly on the particle shape and distribution. Generally, for the similar morphological samples, the homogenized particle must be favourable to luminescent characteristics because of less contamination or fewer dead layers on the phosphor surface. This is similar to the photoluminescence emission spectra of the $CaMoO_4$ nanocrystalline synthesized by microwave-assisted citrate complex method[29]. The strong photoluminescence intensity is attributed to the well-defined and homogeneous particle morphology with sizes of 1-2 μm (Fig. 4).

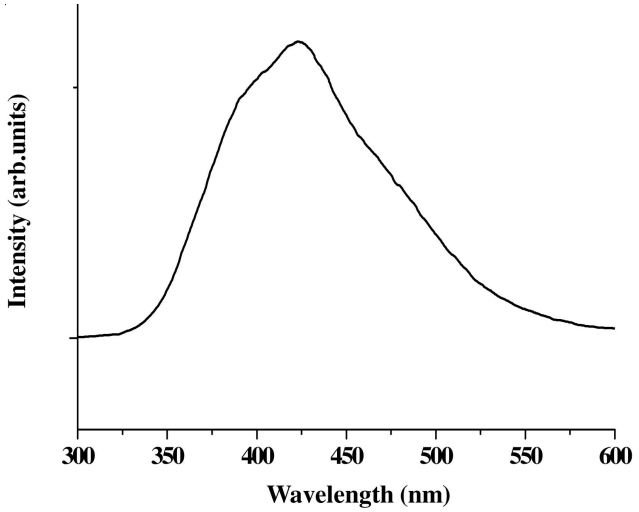

Fig. 4. Photoluminescence emission spectra of the $CaWO_4$ particles exited at 240 nm at room temperature

Fig. 5 shows a Raman spectrum of the $CaWO_4$ particle excited 514.5 nm line of an Ar-ion laser kept at a power of 0.5 mW on sample. The vibration modes in the Raman spectrum of molybdates are classified into two groups, internal and external[30,31]. The internal vibrations are related to the $[WO_4]^{2-}$ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Ca^{2+} cation and rigid molecular units. In the free space, $[WO_4]^{2-}$ tetrahedrons show T_d-symmetry. In this case, the vibrations of the $[WO_4]^{2-}$ ions are constituted by four internal modes ($\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$), one free rotation mode ($\nu_{fr}(F_1)$) and one transition mode (F_2), When $[WO_4]^{2-}$ ions are present in a scheelite-type structure, its point symmetry reduces to S_4. Therefore, all degenerative vibrations are split due to the crystal field effect. For a tetragonal Scheelite primitive cell with a k = 0 wave vector[22,31], there are 26 different vibrations ($\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$), as determined by group-theory calculations. Among them, the $3A_g$, $5B_g$ and $5E_g$ vibrations are Raman-active. Only $4A_u$ and $4E_u$ of the $5A_u$ and $5E_u$ vibrations are active in the IR frequencies and the remaining ($1A_u$ and $1E_u$) are acoustic vibrations. The $3B_u$ vibration is a silent mode. The Raman modes for the $CaWO_4$ particles in Fig. 5 were detected as $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(E_g)$, $\nu_4(B_g)$ and $\nu_2(B_g)$ vibrations at 912, 838, 796, 399, 332 and 274 cm^{-1}, respectively, which provide evidence of a Scheelite structure. The well-resolved sharp peaks for the $CaWO_4$ particles indicate that the synthesized particles are highly crystallized. The external modes were localized at 211-115 cm^{-1}. This result is in agreement with that reported in the literature[14]. The internal vibration mode frequencies exhibited dependence on lattice parameters and the degree of the partially covalent bond between the cation and molecular ionic group $[WO_4]^{2-}$. The type of cations (Ca^{2+}, Sr^{2+}, Ba^{2+}) can influence on the Raman modes by changing the size of the crystal unit cell and by covalent cation effect[31]. The essential dependence of the bandwidth of $\nu_1(A_g)$ Raman mode on the peculiarities of crystal lattice and the type of Me^{2+} cation in the series of MWO_4 (M = Ca, Sr, Ba, Pb) crystals with scheelite structure. The moving in the series of tungstates $Ca^2 \rightarrow Sr^{2+} \rightarrow Ba^{2+}$ increases the unit cell and interionic distance inside the molecular group. The degree of covalent bond between the cation and molecular group usually decreases within the series $Ca^2 \rightarrow Sr^{2+} \rightarrow Ba^{2+}$. This anomalous phenomenon can be explained by decreasing of interaction between internal and external Raman modes in the Scheelite structure in metal tungstates.

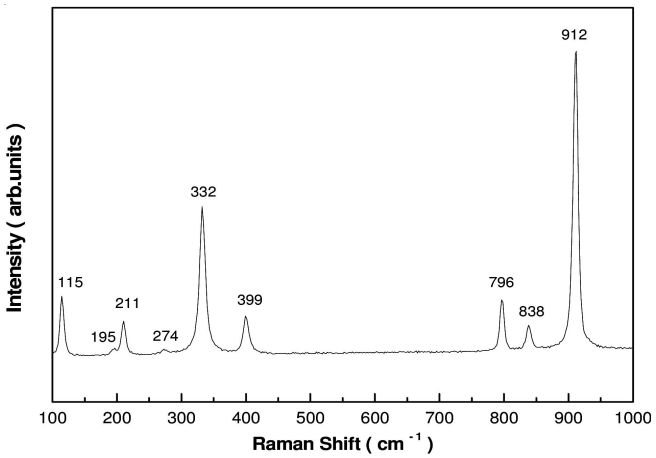

Fig. 5. Raman spectra of the $CaWO_4$ particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the sample

Conclusion

Calcium tungstate ($CaWO_4$) particles were well crystallized by the solid-state metathetic method with cyclic microwave irradiation, showing the fine and homogeneous morphology with sizes of 1-2 μm. With excitation at 250 nm, the $CaWO_4$ particles exhibit a strong photoluminescence emission in the green wavelength range of 470-480 nm. The strong photoluminescence intensity is attributed to the well-defined and homogeneous particle morphology of the $CaWO_4$ particles. The stretching vibration in FTIR was detected as a strong W-O stretch in the $[WO_4]^{2-}$ tetrahedrons at 816 cm^{-1}. With excitation at 250 nm, $CaWO_4$ particles exhibit photoluminescence emission in the blue wavelength range of 470-480 nm. The internal Raman mode for the $CaWO_4$ particles was detected at

912, 838, 796, 399, 332 and 274 cm^{-1}. The external modes were localized at 211-115 cm^{-1}. The well-resolved Raman spectrum for the $CaWO_4$ particles provide that the synthesized particles are highly crystallized.

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