Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2386-2388

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17846

Synthesis and Characterization of $CaWO_4$ Phosphor Powders in Glycerol Solvent by Solvothermal Method

J. ZHANG, S.Q. FANG, Y. TANG*, W.J. HOU and C.C. QIU

Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, P.R. China

*Corresponding author: E-mail: tangying2282@163.com, jiangzhu415@163.com

Received: 18 April 2014; *Accepted*: 23 June 2014; *Published online*: 30 March 2015; AJC-17039

A solvothermal method had been applied to synthesize $CaWO_4$ powders. We used glycerol as the solvent and designed different reaction conditions to explore the effect of different factors (such as pH, temperature, time and surfactant). All products had been characterized by X-ray diffraction, X-ray spectrometry, scanning electron microscopy and fluorescence. It is observed that the temperature played an important role in crystallinity and fluorescence. The concentration of surfactant also had an effect on its morphology. On the basis of a series of experiments, we found that the sample prepared at the condition of pH = 10, T = 160 °C, t = 12 h had well-crystalline, well-dispersed and strong fluorescence.

Keywords: $CaWO_4$, Solvothermal, Characterization, Glycerol.

INTRODUCTION

In recent years, there is an increasing interest in $CaWO_4$ due to its widely applications in the field of electrical engineering[1], laser optics and scitillators in medical devices[2-5]. It can be used as luminescent materials which have more potential advantages than traditional materials[6,7]. The chemical properties of $CaWO_4$ are stable and it can be excited blue light by UV-rays, X-rays and electron beam. It can also change the fluorescence color, fluorescence intensity and luminescence time[8] by doping with different rare elements, which makes it have a wide application in the field of photo electricity. Various methods, such as solid state reaction[9], Pechini method[10], combustion method[11,12], co-precipitation method[13], hydrothermal method[14], micro-emulsion method[15], microwave method[16] and solvothermal method[17], have been reported to prepare $CaWO_4$ crystals, powders and films. To the best of our knowledge, there is no report about the synthesis of $CaWO_4$ with glycerol as solvent. In this paper, glycerol was used as solvent to synthesize $CaWO_4$ crystals by solvothermal method. We controlled reaction conditions (such as pH, temperature, time, surfactant) to synthesize $CaWO_4$ powders with different morphologies and sizes and finally discussed the influence of different conditions on luminescence properties.

EXPERIMENTAL

$CaWO_4$ powders were prepared by the reaction of calcium chloride and hydrated sodium tungstate at different pH, temperature, time and different concentration of surfactant cetyl trimethyl ammonium bromide (CTAB) in the autoclave. In a typical procedure, 20 mL of glycerol was mixed with 10 mL $CaCl_2$ (1 mol/L) in 100 mL conical flask with vigorous stirring and then 10 mL Na_2WO_4 (1 mol/L) and certain concentration of CTAB were added into the solution, simultaneously. The pH of the solution was adjusted by 1 mol/L NaOH. After stirred for 0.5 h, the total solution was added into a Teflon-lined stainless steel autoclave with 50 mL capacity. The autoclave was maintained at a set reaction temperature in drying oven for enough time and then cooled to room temperature naturally. The resulting white precipitate was collected by centrifugation at the speed of 1500 r/s for 10 min and then washed three times with distilled water and alcohol. The final products were dried in a drying oven at 80 °C for 2 h. The reaction conditions were summarized in Table-1.

The dried samples were characterized by X-ray powder diffraction (XRD) with graphite mono-chromatized CuK_α radiation (tube voltage = 30 KV, tube current = 20 mA, λ = 1.5418 nm, TD-3500, Shimadzu Co.). The morphologies and sizes of the samples were characterized by scanning electron microscopy (SEM, Quanta 250) operated at an accelerating voltage of 200 kV. The luminescent spectra were performed on the PL spectrometer (SLM INSTRU-MENTS). All of the measurements were performed at room temperature.

RESULTS AND DISCUSSION

The Scheelite-type $CaWO_4$ had a tetragonal structure with space group ($I4_1/a$ (88)). The calcium ions were 8-fold

TABLE-1
SUMMARY OF THE REACTION CONDITIONS AND THE MORPHOLOGY OF THE PRODUCTS

Sample No.	Temp. (°C)	pH	Time (h)	CTAB (mol L^{-1})	Morphology
S1	80	10	12	-	Sphere
S2	120	10	12	-	Sphere
S3	160	10	12	-	Sphere
S4	120	10	6	-	Sphere
S5	120	10	18	-	Sphere
S6	120	10	24	-	Sphere
S7	120	5	12	-	Sphere
S8	120	7	12	-	Sphere
S9	120	10	12	0.15	Sphere and rod
S10	120	10	12	0.5	Sphere and rod
S11	120	10	12	0.85	Sphere and rod

coordinated with the oxygen atoms surrounding tungstate groups[18]. The XRD patterns of all of the $CaWO_4$ samples showed obvious diffraction peaks which were consistent with the JCPDS No. 41-1431 and could be easily indexed to a scheelite crystal structure. The lattice constants calculated from XRD patterns were a = b = 5.243 Å and c = 11.373 Å. Typically, the XRD spectra of $CaWO_4$ labeled S1, S3, S6, S7 and S11 were shown in Fig. 1. The sharpness of the diffraction peaks indicated that the products were well-crystalline.

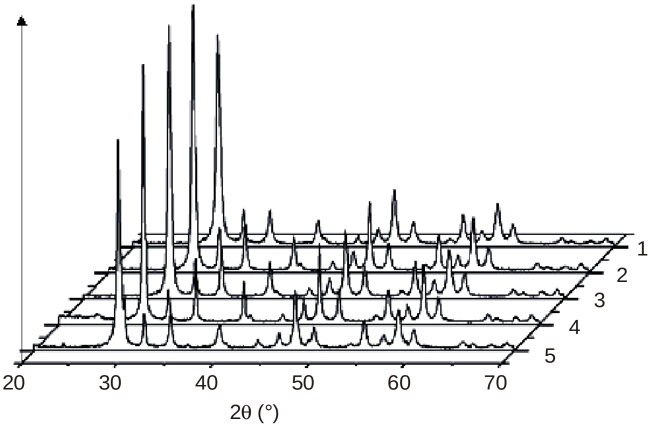

Fig. 1. XRD spectra of S1, S3, S6, S7 and S11. 1: S1 (pH = 10, T = 80 °C, t = 12 h); 2: S3 (pH = 10, T = 160 °C, t = 12 h); 3: S6 (pH = 10, T = 120 °C, t = 24 h); 4: S7 (pH = 5, T = 120 °C, t = 12 h); 5: S11 (CTAB = 0.85 mol/L, pH = 10, T = 120 °C, t = 12 h)

It was obvious that the diffraction peaks of S3 and S6 were sharper than the others in Fig. 1. Among all of the samples, the diffraction peaks of S3 were sharpest. On the basis of above experiments, it can be inferred that the pH value and the concentration of CTAB had little influence on the intensity of diffraction peaks. But the temperature and time played important roles in the crystallization of $CaWO_4$. With the increase of temperature and time, the diffraction peak became much sharper and the crystalline of $CaWO_4$ became much higher. Moreover, the effect of the temperature was dominating. Although the pH value had no obvious effect on the crystalline, we could discover that when the pH value was below 7, fewer products were obtained.

The EDS image and the atom ratio of S3 (Table-2) are showed in Figs. 2. It can be seen that only Ca, W and O singles were found in the spectrum. The atom ratio of Ca:W:O is about 1:1:4, corresponding to the chemical formula of $CaWO_4$. No other impurities were detected in the product.

TABLE-2
ATOM RATIO OF S3

Element	Wt (%)	At (%)
O	23.28	66.76
Ca	15.75	18.03
W	60.97	15.22

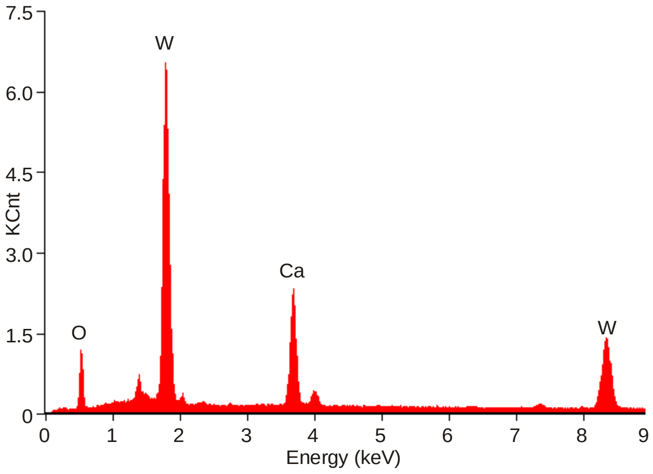

Fig. 2. EDS spectrum of S3

Without the addition of CTAB, the morphology of the products was sphere and had a little difference on size which was from 100 to 1000 nm, while some samples were non-uniform, or atom reunited. Only the sample of S3 had the uniform morphology and well-dispersed. The size of which was from 800 nm to 900 nm (Fig. 3). On the contrary, with the addition of CTAB, the morphology of the samples had a big difference (Fig. 4). Compared with those samples without CTAB, it is observed that with the increasing of CTAB, the thinner rod grew on the surface of $CaWO_4$ sphere and reunited. It can be inferred that the addition of CTAB may produce virgate or floriform $CaWO_4$.

The fluorescence spectra of the typical samples of S1, S3, S6, S7 and S11 were shown in Figs. 5 and 6. S11 was excited at 237 nm. They exhibited only peak at 421 nm. By using the light with the wavelength at 242 nm, S6 was excited and had a broad emission peaks at 417 nm. When excited at 230 nm, S7 were emitted light at 415 nm. S1 and S3 (excited at the same wavelength of 240 nm) both had emission peaks at 415 nm. Although the reaction conditions were different. It could be inferred that the emission spectra of all samples were mainly due to the intrinsic electronic transfer[19] of WO_4^{2-} or the self-trapped centers with excition energies located within the band gap[17]. Fig. 6 showed that the widely excited wavelength range from 230 to 240 nm could excite luminescence of $CaWO_4$. From the emission image (Fig. 6), it is observed that the intensity of the fluorescence emissions in S3 was much stronger than those of S1, S6, S7 and S11, which was connected with its uniform morphology and well-dispersed. Besides, it was obvious that the intensity of S7 was the weakest, which indicated that the reaction temperature made tremendous contribution to the emission intensity. Reaction time and the amount of surfactant also improved the emission intensity to some degree, while the pH value could lead to less products and decrease emission intensity.

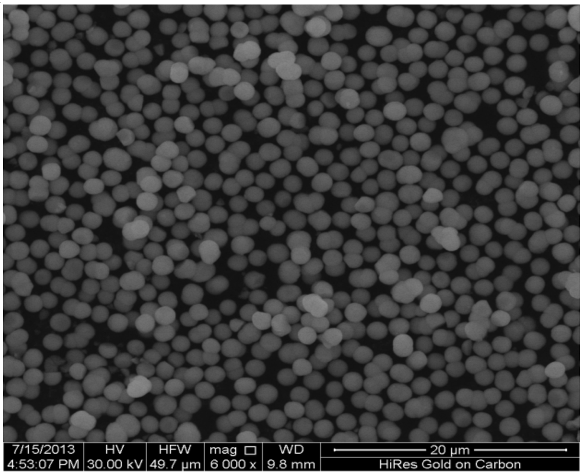

Fig. 3. SEM pattern of S3

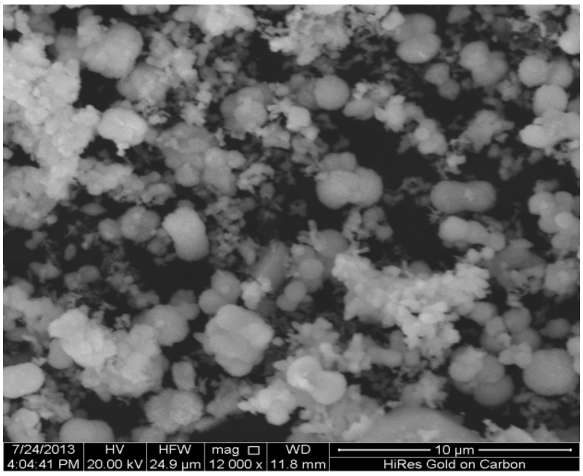

Fig. 4. SEM pattern of S11

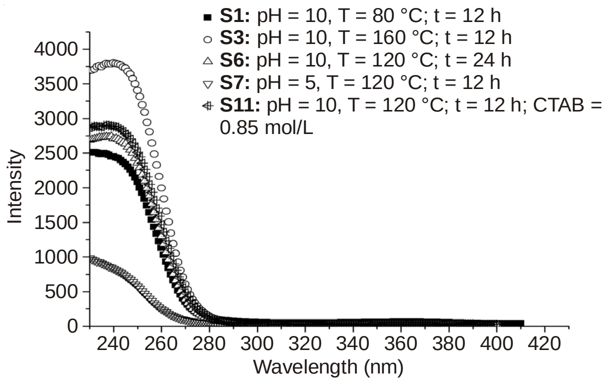

Fig. 5. Excited image of S1, S3, S6, S7 and S11

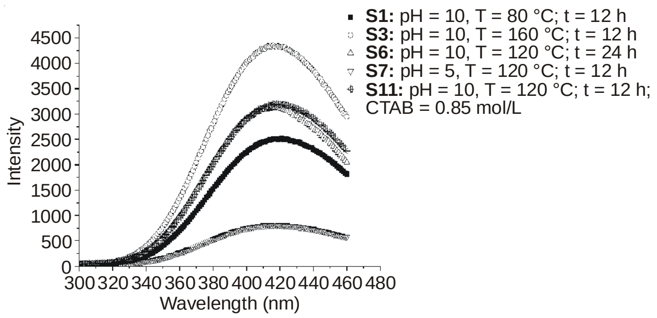

Fig. 6. Emission image of S1, S3, S6, S7 and S11

Conclusion

Spherical and rod like crystals of $CaWO_4$ were prepared by solvothermal method with the solvent of glycerol. Reaction temperature and the amount of surfactant played an important roles on the morphology, size and fluorescence of the resulting products. When the higher reaction temperature and the more surfactant was performed, the fluorescence of the product was stronger. Moreover, the temperature made the most contribution to the formation of uniform morphology and well-dispersed. The method we used to synthesize $CaWO_4$ had a great advantages, such as the simpler equipment, more convenience operation, more uniform morphology and stronger luminosity than the method reported by other literatures. Therefore, it can be expanded to the synthesis of other tungstates.

REFERENCES

1. N. Sharma, G.V. Subba Rao and B.V.R. Chowdari, *Electrochim. Acta*, **50**, 5305 (2005).
2. S. Oishi and M. Hirao, *J. Mater. Sci. Lett.*, **8**, 1397 (1989).
3. M. Moszynski, M. Balcerzyk, W. Czarnacki, A. Nassalski, T. Szczesniak, H. Kraus, V.B. Mikhailik and I.M. Solskii, *Nucl. Instrum. Methods Phys. Res. A*, **553**, 578 (2005).
4. H. Kraus, V.B. Mikhailik and D. Wahl, *Nucl. Instrum. Methods Phys. Res. A*, **553**, 522 (2005).
5. M. Nikl, P. Bohacek, E. Mihokova, M. Kobayashi, M. Ishii, Y. Usuki, V. Babin, A. Stolovich, S. Zazubovich and M. Bacci, *J. Lumin.*, **87-89**, 1136 (2000).
6. E. Cavalli, P. Boutinaud, R. Mahiou, M. Bettinelli and P. Dorenbos, *Inorg. Chem.*, **49**, 4916 (2010).
7. Y. Su, L. Li and G. Li, *Chem. Mater.*, **20**, 6060 (2008).
8. Z. Piskula, K. Staninski and S. Lis, *J. Rare Earths*, **29**, 1166 (2011).
9. M.V. Nazarov, D.Y. Jeon, J.H. Kang, E.-J. Popovici, L.-E. Muresan, M.V. Zamoryanskaya and B.S. Tsukerblat, *Solid State Commun.*, **131**, 307 (2004).
10. C.A. Kodaira, H.F. Brito and M.C.F.C. Felinto, *J. Solid State Chem.*, **171**, 401 (2003).
11. C. Zhao and D. Chen, *Mater. Lett.*, **61**, 3673 (2007).
12. S. Yin, D. Chen and W. Tang, *J. Alloys Comp.*, **441**, 327 (2007).
13. Y. Yang, S. Cao and Z. Wang, *J. Chinese Ceramic Soc.*, **36**, 1606 (2008).
14. Y. Hakuta, T. Haganuma, K. Sue, T. Adschiri and K. Arai, *Mater. Res. Bull.*, **38**, 1257 (2003).
15. T. Hirai, T. Hirano and I. Komasawa, *J. Colloid Interf. Sci.*, **253**, 62 (2002).
16. L. Wang, E. Qi, M. Li, S. Qin and J. Wang, *J. Chinese Ceramic Soc.*, **39**, 491 (2011).
17. S.-J. Chen, J. Li, X.-T. Chen, J.-M. Hong, Z. Xue and X.-Z. You, *J. Cryst. Growth*, **253**, 361 (2003).
18. V.M. Longo, L. Gracia, D.G. Stroppa, L.S. Cavalcante, M. Orlandi, A.J. Ramirez, E.R. Leite, J. Andrés, A. Beltrán, J.A. Varela and E. Longo, *J. Phys. Chem.*, **115**, 20113 (2011).
19. Y. Wang, J. Ma, J. Tao, X. Zhu, J. Zhou, Z. Zhao, L. Xie and H. Tian, *Mater. Lett.*, **60**, 291 (2006).