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ORIGINAL ARTICLE

Luminescent Property of $CaWO_4$ Powders Prepared with Aqueous Reactions

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ABSTRACT

$CaWO_4$ powders have been synthesized by reaction between $Ca(NO_3)_2$ and Na_2WO_4 aqueous solutions. The reaction product was calcined at temperature of 400-700ºC for 1-2h in air. XRD analysis indicated that single-phase $CaWO_4$ powder with a monoclinic scheelite structure was formed for all samples. The powders appear white color. SEM micrograph indicated that powders had uniform morphology and grain size about 130-860nm which increased with increasing calcining temperature and calcining time. Luminescence measurements indicated that the powders showed a broad blue-green emission band. The luminescence intensity obviously increased with increasing the calcining temperature. The emission intensity do not increased with increasing calcining time as increase in the grain size. The largest intensity of luminescence peak was up to 926 counts for the powders calcined at 700ºC. The air atmospheres should inhibited increase of the emission intensity with calcining time.

Key words: $CaWO_4$; powders; synthesis; grain size; crystallinity; atmosphere; luminescence

Introduction

Scheelite calcium tungstate is well known for their interesting luminescence and structural particularities and therefore has been extensively studied during the past century. For example, Kröger wrote a monograph presenting a complete summary of the luminescence properties of these and related materials(Kröger, F.A., 1948). It was also used for 75 years in X-ray photography as screen intensifies due to its capability of absorbing X-rays and converting their energy into radiation enabling the blackening of the photographic film(Blasse, G. and B.C. Grabmaier, 1994). Nowadays the challenge is to use $CaWO_4$ as solid-state optoelectronic devices like lasers, optical fibers components or scintillators (Nikl, M., P. Bohacek, 2002; Nikl, M., P. Bohacek, 2000; Kobayashi, M., M. Ishii, 1993; Nikl, M., 2000). $CaWO_4$ is also the object of interesting structural studies because it presents a great variety of phases depending on the preparation conditions (Errandonea, D., M. Somayazulu, 2003; Errandonea, D., F.J. Manjón, 2004; Eung Soo Kim, Soon Ho Kim, 2006) D. Errandonea, F.J. Manjón, M. Somayazulu and D. Haüsermann, *J. Solid State Chem.* 177 (2004), p. 1087. **Article** | PDF (507 K) | View Record in Scopus | Cited By in Scopus (30).

The nanomaterials and nanostructures are of a great interest for the modern science and technology. The properties and phenomena of these materials and structures are mainly due to the quantum confinement (QC), which is determined by the sizes of 10 – 20 interatomic distances, and to the surface/interface effects, which are amplified by the enormous surface/volume ratio(10^8-$10^8 m^{-1}$). Luminescent property of $CaWO_4$ nanocrystal may be dependent on the character of the powders. The character is found to depend on the synthesis process and processing parameters, such as, reaction temperature, and pH, *et al*.

The scheelite $CaWO_4$ nano-crystalline has been synthesized with various techniques, including combustion process(Xiaoming Lou and Donghua Chen, 2008), the hydrothermal process(Fang Leia and Bing Yan, 2008), sonochemical method(Titipun Thongtem, Anukorn Phuruangrat), pulsed laser induced synthesis(Jeong Ho Ryu,

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Sin Young Bang, 2007), solids reaction method(Eung Soo Kim, Soon, 2006), a molten salt method(Yonggang Wang, Junfeng Ma, 2006). In this work, we reported (i) low cost synthesis of $CaWO_4$ nanocrystal with aqueous reaction-calcination processes and (ii) the excellent luminescent properties of the synthesized $CaWO_4$ nanocrystals and (iii) the discussion on air atmosphere effect of the luminescence property.

2. Experimental Procedure

The $CaWO_4$ powders were prepared by a method based on an approach previously used for fabrication of 3D metal tungstates (MWO_4, M=Mn, Co, Ni and Cu). Equimolecular $Ca(NO_3)_2$ and Na_2WO_4 were respectively dissolved in distilled water. The two solutions are of concentration of 0.01M respectively. Two solutions were then slowly mixed with a constant stirring. In the process of the mixing, a white precipitation was fast formed in the precursor. By filtering and washing with distilled water, the precipitation was then dried at 100°C for 4h and calcined at different temperatures of 400-700°C for 1h and 2h respectively.

The phase indentification of the $CaWO_4$ powders was conducted at room temperature using X-Ray diffractometer (XRD, $CuK_{\alpha 1}$, λ=0.15406nm, Model No. D/Max-2200PC, Rigaku, Japan). Scanning electron microscopy (SEM, Model No: JXM–6700F, Japan) was used to analyze the particle morphology and the agglomeration of the powders. The luminescent properties of the $CaWO_4$ nanocrystals were measured on the luminescent spectrophotometer (Modal No: LS-55, PE, US).

3. Results and discussion

The $CaWO_4$ powders calcined at 400-500°C for 1h show grey color. With increasing calcining temperature and calcining time, all other powders appear white color. The XRD patterns of the $CaWO_4$ powders are shown in Fig. 1 and Fig. 2, which indicated that monoclinic scheelite structure was an only XRD-detactable phase for all powders prepared in this experiment. The intensities of the XRDe peaks of the powders calcined at 600°C and 700°C for 1h were respectively about 3000 counts. The intensity increased to 3500 counts with increasing calcining temperature to 700°C for 2h. The large intensity of The XRD peak corresponds to a large increase in crystallinity of the powders. The average crystalline sizes calculated by Scherrer's equation were 28.5-44.7nm, as summarized in table 1. The lattice constant *a* and *c* of the $CaWO_4$ powders were calculated from XRD data analyses, and are summarized in table 1. The $CaWO_4$ powders possess of a larger constant *a* and a less *c* for calcining time of 1h than for 2h.

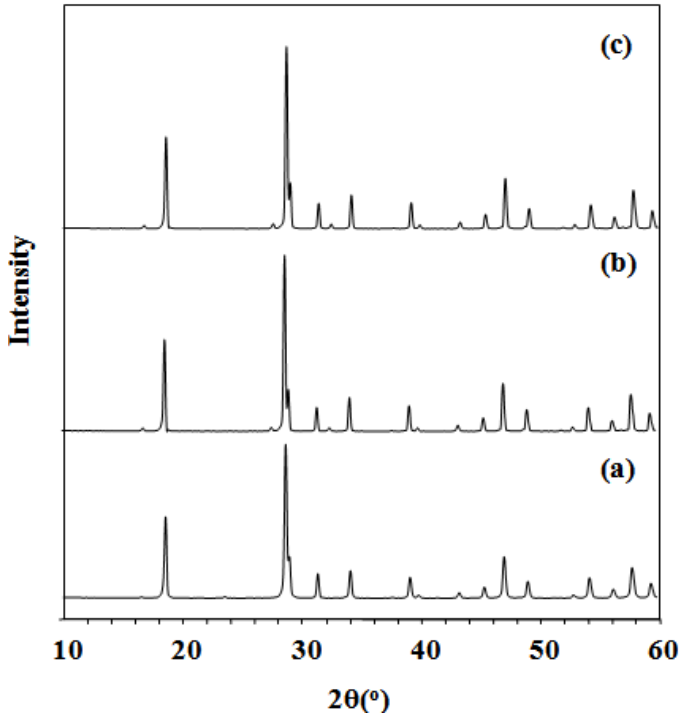

Fig. 1: XRD patterns of $CaWO_4$ powders calcined at (a) 500°C, (b) 600°C, and (c) 700°C for 1h, respectively

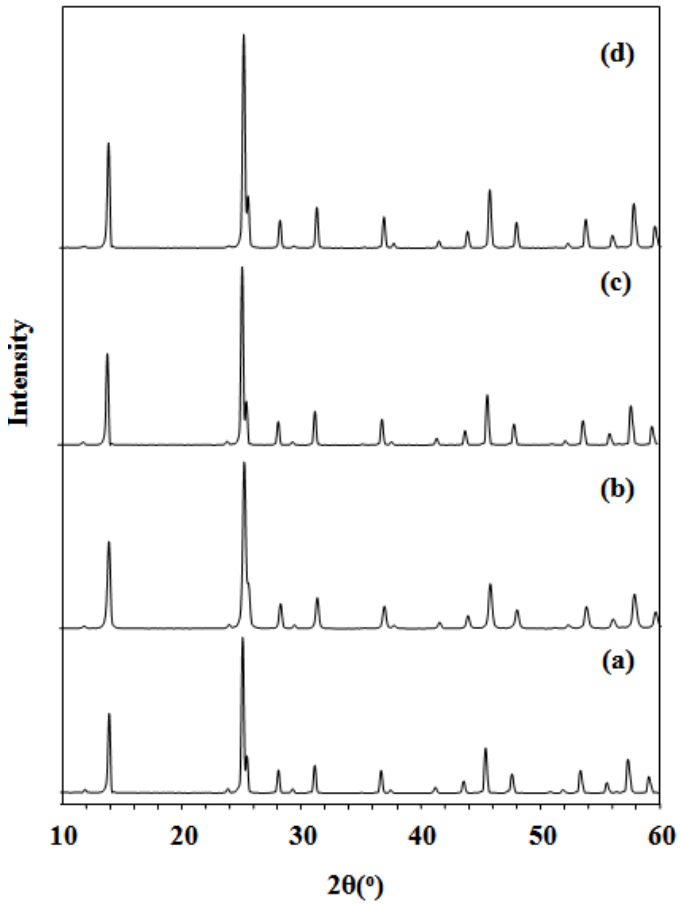

Fig. 2: XRD patterns of the $CaWO_4$ powders calcined at (a) 400ºC, (b) 500ºC, (c) 600ºC, and (c) 700ºC for 2h, respectively.

Table 1: The lattice parameter of the $CaWO_3$ powders determined with the XRD data analysis, and grain size determined with SEM micrographs

calcining schedule	lattice parameter			particle size
	a(A)	c(A)	c/a	(nm)
500 ºC1h	5.244	11.323	2.159	
600 ºC1h	5.244	11.348	2.164	310
700 ºC1h	5.244	11.345	2.163	790
400 ºC2h	5.239	11.333	2.163	130
500 ºC2h	5.236	11.357	2.167	380
600 ºC2h	5.232	11.359	2.171	770
700 ºC2h	5.219	11.366	2.178	860

The SEM micrographs of the $CaWO_4$ powders are shown in Fig. 3, which indicated that the $CaWO_4$ powders were of particle size about 100-1000nm, which increased remarkably with calcining temperature and calcining time. The particle calcined at 600-700ºC for 1h and calcined at 400-500ºC for 2h appear nearly spherical morphology, but become quasi-tetragonal at 600-700ºC for 2h.

Scherrer's equation is only available in crystalline size range of 1-100 nm, the result calculated by Scherrer's equation is also affected by widening of diffraction peak resulted from micro-strain and dislocation in crystalline particle. So that, the sizes determined from XRD should only be approximate data, the real sizes of the synthesized powder grains should be the results determined by SEM analysis.

The luminescence properties of the $CaWO_4$ nanocrystals were determined on the luminescent spectrophotometer and shown in Fig. 4 and Fig. 5. The wavelengths of monitor and excitation are at 425nm (2.92eV) and 247nm (5.02) respectively. The powders showed a broad excitation band and a broad deep blue-green emission band. Two main emissions are near 406nm (~3.05eV) and 424nm (~2.92eV). Table 2 summarizes the positions and intensities of excitation and emission bands of the $CaWO_4$ powders. The intensities of excitation peaks and emission peaks increased with increasing calcining temperature for either time of 1h and 2h, which can be attributed to increase in the grain size of the CaWO4 powders. The peak

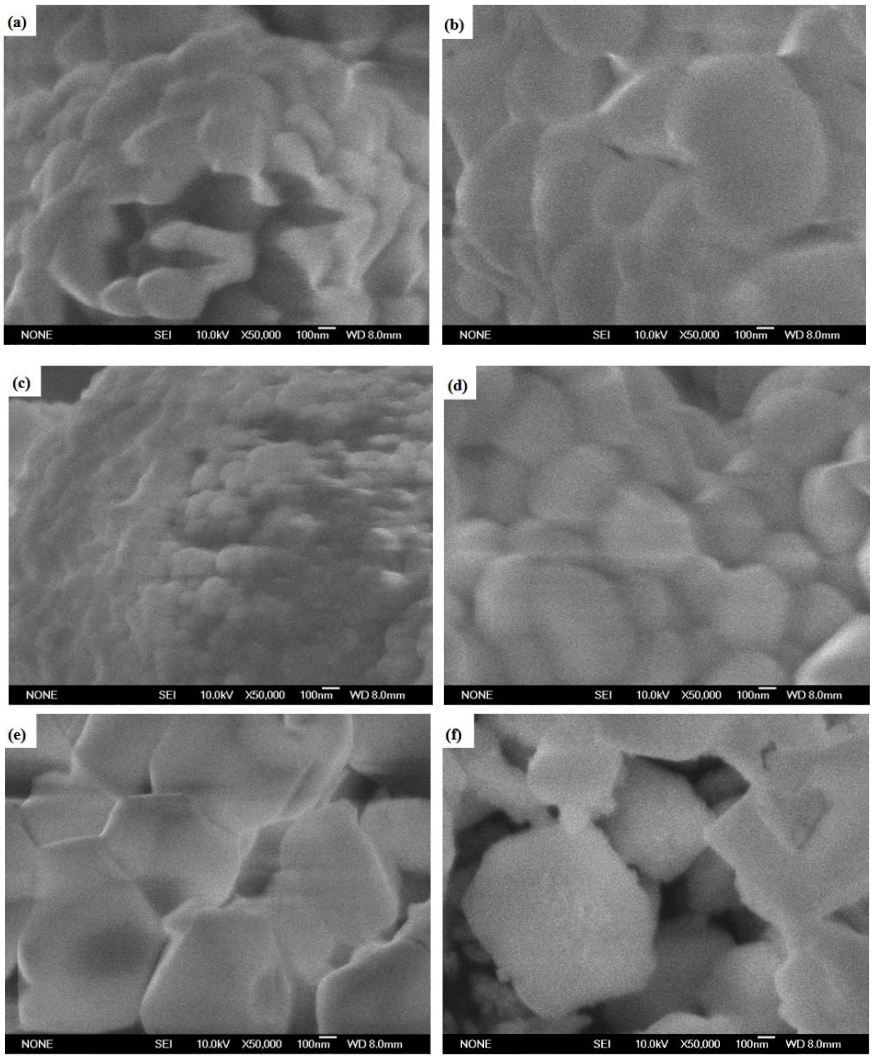

Fig. 3: SEM micrographs of the $CaWO_4$ powders (a) calcined at 600ºC for 1h (b) calcined at 700ºC for 1h (c), (d), (e) and (f) calcined at 400ºC, 500ºC, 600ºC and 700ºC for 2h respectively

Table 2: Characters of the excitation and emission peaks of the $CaWO_4$ powders (λ_{em}=425nm, λ_{ex}=247nm)

Calcining Schedules	Excitation		Emisssion	
	Position (nm)	Intensity (counts)	Position (nm)	Intensity (counts)
600ºC 1h	231.0	801.08	405.5	875.82
	248.5	850.70	425.0	869.24
700ºC 1h	231.0	845.88	404.5	910.13
	248.5	859.35	423.5	926.24
400ºC 2h	231.0	762.08	406.0	780.03
	247.5	771.00	426.0	769.06
500ºC 2h	231.5	745.12	408.0	727.49
	248.0	742.20	422.0	778.94
600ºC 2h	232.0	860.51	408.5	893.19
	248.0	899.57	424.5	905.15
700ºC 2h	231.5	883.65	403.5	875.35
	247.5	871.16	425.0	892.20

intensities also increased with calcining time, except for emission peaks of the powders calcined at 700ºC for 2h are lower than that for 1h, however these increases were not matched with the increases of grain sizes and crystallinity as that with the calcining temperature. This phenomenon can be explained as follow. The air atmosphere changed the defect subsystem of the particle surface in longer period of the higher temperature calcination. Yakovyna *et al* (2008) reported that thermal treatment in different atmospheres causes change of

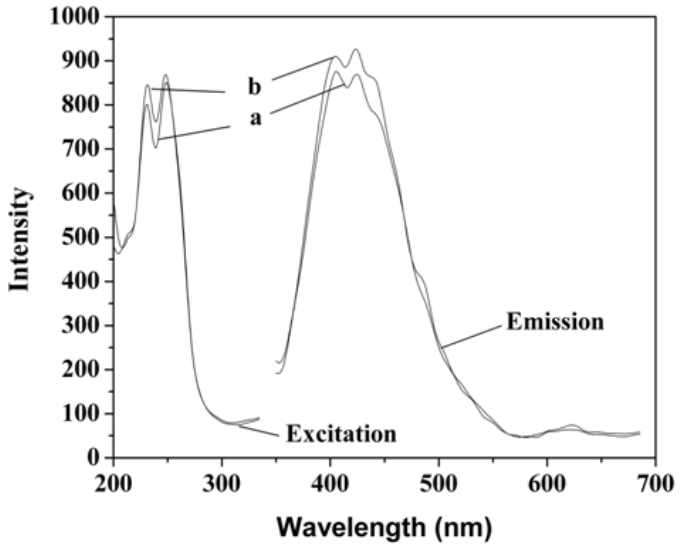

Fig. 4: The luminescence spectra of the $CaWO_4$ powders (a) calcined at 600ºC and (b) 700ºC for 1h respectively, Excited at 247nm, monitored at 425nm

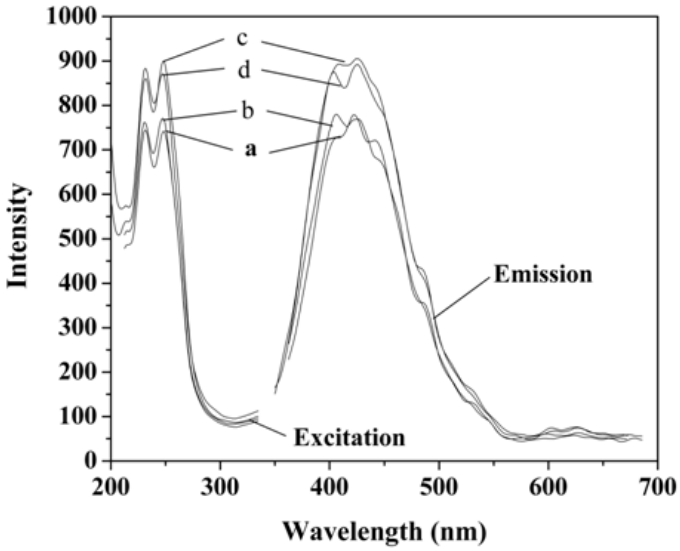

Fig. 5: The luminescence spectra of the $CaWO_4$ powders (a) calcined at 400ºC, (b) 500ºC, (c) 600ºC, and (d) 700ºC for 2h, respectively, Excited at 247nm, monitored at 425nm

the defect subsystem of the $CaWO_4$ crystal, resulting in the alteration of the spectral dependences. Thermal treatment in oxygen atmospheres at 900-1200ºC resulted in a relative decrease in the intensity of the emission band (~2.9eV) which is excited at 230nm (~5.4eV). However the intensity of the emission band (~2.3eV) obviously increased when excited below the fundamental absorption edge 4.7eV (4.4eV, λ=280nm) but decreased abruptly with increasing thermal treatment temperature to 1200ºC. It is generally accepted that emission of tungstate with scheelite structure excited at high energy is due to radiative decay of self-trapped excitations localized at regular WO_4^{2-} complexes while emission excited at low energy is associated with anion defective WO_3 complexes(Mikhailik, V.B., H. Kraus, 2004; Mikhailik, V.B., H. Kraus, 2005). The air atmosphere would similarly resulted in decreases of anion defective WO_3 complexes in the long calcining period of 2h. The excitation (5.02eV, 247nm) was also near the low energy (4.7eV). Thus, the powders prepared in this work do not shown emission intensities that matched with their grain sizes at calcining time of 2h. In addition, the calcining time of 2h resulted in larger anisotropy in atomic arrangements and larger crystallinity of the crystal than that of 1h. Orhan *et al* (2005) reported that the luminescence intensity of the $CaWO_4$ is much higher in the disordered films than in the crystalline one. Their experimental results strongly indicate that the luminescence of the $CaWO_4$ excited at 488nm is very sensitive to its structure and that

relatively weak variations in the atomic arrangements can induce significant changes in the emission spectra. Their result also could be associated with the anion defective WO_3 complexes due to the films were calcined in air and oxygen atmospheres (Orhan *et al* 2005).

The stronger light diffusion of the powder with a less size generally resulted in less intensity of luminescence, and so larger grain size is required for higher luminescence property. However, effect of specific surface area used for the absorption and emission of the light could becomes superior with increasing grain size to enough large. This also may be a reason of the change in luminescence intensity with the grain size of the powder.

4. Conclusion

Ultrafine $CaWO_4$ powders have been successfully synthesized with aqueous reaction process. The powder characters and luminescence property of powders calcined at 400-700°C for 1-2h were studied. The synthesized powders show excellent luminescence.

The crystallinity and grain size of the powders increased with increasing calcining temperature and calcining time. The powders showed a broad excitation band and broad deep blue-green emission band. The emission intensity obviously increased with increasing calcining temperature. The emission intensity do not matched with the grain size with increasing calcining time. The calcining atmosphere of air should be responsible for the luminescence change with calcining time. The $CaWO_4$ powder calcined at 700°C for 1h shown a largest luminescence intensity of 926 counts at excitation wavelength of 425nm (2.92eV). The excellent luminescence property, low cost and convenient synthesis technique, make the $CaWO_4$ powder able for many potential luminescent applications. It will be of interest to investigate the synthesis and luminescence property of the $CaWO_4$ powder at various calcining atmospheres under different excitation energy to improve the luminescence intensity.

References

Blasse, G. and B.C. Grabmaier, 1994. Luminescent Materials, Springer, Berlin, Heildelberg.

Errandonea, D., M. Somayazulu and D. Haüsermann, 2003. Phase Transitions and Amorphization of $CaWO_4$ $_{at}$ High Pressure, Phys. Stat. Sol. (B), 235(1): 162-169.

Errandonea, D., F.J. Manjón, M. Somayazulu and D. Haüsermann, 2004. Effects of Pressure on the Local Atomic Structure of $CaWO_4$ and $YLiF_4$: Mechanism of the Scheelite-to-Wolframite and Scheelite-to-Fergusonite Transitions, J. Solid State Chem., 177: 1087-1097.

Eung Soo Kim, Soon Ho Kim and Burtrand I. Lee, 2006. Low-Temperature Sintering and Microwave Dielectric Properties of $CaWO_4$ Ceramics for LTCC Applications, J. Europ. Ceram. Soc., 26(10-11): 2101-2104.

Fang Leia and Bing Yan, 2008. Hydrothermal Synthesis and Luminescence of $CaMO_4$: RE^{3+} (M=W, Mo; RE=Eu, Tb) Submicro-Phosphors, J. Solid State Chem., 181(4): 855-862.

Jeong Ho Ryu, Sin Young Bang, Jong-Won Yoon, Chang Sung Lim and Kwang Bo Shim, 2007. Pulsed Laser Induced Synthesis of Scheelite-Type Ccolloidal Nanoparticles in Liquid and the Size Distribution by Nanoparticle Tracking Analysis, Appl. Surf. Sci., 253(20): 8408-8414.

Kröger, F.A., 1948. Some Aspects of the Luminescence of Solids, Elsevier, Amsterdam.

Kobayashi, M., M. Ishii, Y. Usuki and H. Yahagi, 1993. Scintillation Characteristics of $PbWO_4$ Single Crystals at Room Temperature, Nucl. Instrum. Methods Phys. Res. A., 333(2-3): 429-433.

Mikhailik, V.B., H. Kraus, D. Wahl, *et al*., 2004. One- and Two-Photon Excited Luminescence and Band-Gap Assignment in $CaWO_4$, Phys.Rev. B., 69(20): 205110.

Mikhailik, V.B., H. Kraus, G.Miller, *et al*., 2005. Luminescence of $CaWO_4$, $CaMoO_4$, and $ZnWO_4$ Scintillating Crystals under Different Excitations, J. Appl. Phys., 97: 083523.

Nikl, M., P. Bohacek, N. Mihokova, N. Solovieva, A. Vedda, M. Martini, G.P. Pazzi, P. Fabeni, M. Kobayashi and M. Ishii, 2002. Enhanced Efficiency of $PbWO_4$:Mo,Nb Scintillator, J. Appl. Phys., 91: 5041-5049.

Nikl, M., P. Bohacek, E. Mihokova, M. Kobayashi, M. Ishii, Y. Usuki, V. Babin, A. Stolovich, S. Zazubovich and M. Bacci, 2000. Excitonic Emission of Scheelite Tungstates AWO_4 (A=Pb, Ca, Ba, Sr), J. Lumin., 87(9): 1136-1139.

Nikl, M., 2000. Wide Band Gap Scintillation Materials: Progress in the Technology and Material Understanding, Phys. Stat. Sol. (A,), 178: 595-620.

Orhan, E., M.A. Santos, M.A.M.A Maurera, F.M. Pontes, A.G. Souza, J. Andrès, A. Beltràn, J.A. Varela, P.S. Pizani, C.A. Taft and E. Longo, 2005. Towards an Insight on the Photoluminescence of Disordered $CaWO_4$ from a Joint Experimental and Theoretical Analysis, J. Solid State Chem., 178(4): 1284-1291.

Sagrario M. Montemayor, and Antonio F. Fuentes, 2004. Electrochemical Characteristics of Lithium Insertion in Several 3D Metal Tungstates (MWO_4, M=Mn, Co, Ni and Cu) Prepared by Aqueous Reactions, Ceram. Inter., 30(3): 393-400.

Titipun Thongtem, Anukorn Phuruangrat and Somchai Thongtem, Characterization of $MeWO_4$ (Me = Ba, Sr and Ca) Nanocrystallines Prepared by Sonochemical method, *Appl. Surf. Sci.,* Article in Press,

Xiaoming Lou and Donghua Chen, 2008. Synthesis of $CaWO_4:Eu^{3+}$ Phosphor Powders via a Combustion Process and Its Optical Properties, Mater. Letters, 62(10-11): 1681-1684.

Yonggang Wang, Junfeng Ma, Jiantao Tao, Xiaoyi Zhu, Jun Zhou, Zhongqiang Zhao, Lijin Xie and Hua Tian, 2006. Synthesis of $CaWO_4$ Nanoparticles by a Molten Salt Method, Mater. Letters, 60(2): 291-293.

Yakovyna, V., Y. Zhydachevskii, V.B. Mikhailik, I. Solskii, D. Sugak, M. Vakiv, 2008. Effect of the Thermo-Chemical Treatments on the Luminescence and Scintillation Properties of $CaWO_4$, Opt. Mater., 30: 1630-1634.