Materials Science-Poland, *Vol. 28*, *No. 2*, *2010*

Synthesis of nanocrystalline metal molybdates using cyclic microwave radiation

A. PHURUANGRAT[1], T. THONGTEM[2*], S. THONGTEM[1]

[1]Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

[2]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Nanocrystalline compounds $MMoO_4$ (M = Ca, Sr and Ba) were synthesized in propylene glycol using cyclic microwave radiation. XRD, TEM, SAED and EDX analyses revealed the presence of nanocrystallites of the phases containing the corresponding alkaline earth metals, Mo and O. The calculated lattice parameters and the crystallite sizes both increased with the increase in the atomic masses and the ionic radii of the divalent metals. Six different vibrations were detected using Raman spectroscopy, and very strong Mo–O stretching mode of $[MoO_4]^{2-}$ tetrahedrons was observed using FTIR.

Keywords: *alkaline earth metal molybdate; cyclic microwave-assisted synthesis; scheelite structure*

1. Introduction

Nanomaterials have very unusual physical and chemical properties, different from their bulks [1, 2]. Metal molybdates $MMoO_4$ (M = Ca, Sr and Ba, ionic radii of divalent metals > 0.1 nm) with scheelite structure [3] are very suitable for use as luminescent materials, optical fibres, scintillators and catalysts [4, 5].

A variety of methods are used to synthesize nanosized metal molybdates such as hydrothermal processing [5], reverse microemulsion [6], reverse micelles with solvothermal method [7], the molten salt method [8] and solid state reactions [9]. Recently, the microwave-assisted route has been applied as a novel way to synthesize nanomaterials. The process requires a short reaction time. The products have a narrow particle size distribution and high purity compared with those synthesized by the conventional method [2]. Previously, metal molybdates were synthesized via a citrate complex route assisted by microwave radiation, followed by high temperature calcination [4]. For the present research, purified nanocrystalline $MMoO_4$ (M = Ca, Sr and Ba) were synthesized using cyclic microwave radiation without any further calcination at high temperatures.

*Corresponding author, e-mail: ttpthongtem@yahoo.com

2. Experimental

0.005 mol of each $M(NO_3)_2$ (M = Ca, Sr and Ba) and Na_2MoO_4 was separately dissolved in 15 cm^3 propylene glycol (PG). The corresponding solutions were mixed and stirred for 30 min. The mixtures were heated at 600 W cyclic microwave radiation. Every 100 s, the microwave was switched on for 15 s and switched off for 85 s. The cyclic process was terminated after 30 min had elapsed. Finally, white precipitates were produced. They were washed with distilled water and absolute ethanol, and dried in air at 80 °C for 24 h.

The final products were characterized using an X-ray diffractometer (D-500 Siemens) with CuK_α radiation, a graphite monochrome and Ni filter with 2θ scanning angle ranging from 15° to 60°, Fourier transform infrared spectrometer (Bruker Tensor 27) with the spectral resolution of 4 cm^{-1} with KBr as a diluting agent, Raman spectrometer (Horiba Jobin Yvon T64000) using 50 mW Ar laser (λ = 514.5 nm) with the spectral resolution of 5 cm^{-1}, and a transmission electron microscope (Jeol, Jem-2010) operating at 200 kV with an energy dispersive X-ray analyzer (Oxford Instruments, INCA).

3. Results and discussion

XRD spectra of $MMoO_4$ (M = Ca, Sr and Ba) are shown in Fig 1. The phases were identified by comparing their spectra with those of the JCPDS standard, PDF numbers: 85-0585 ($CaMoO_4$), 86-0586 ($SrMoO_4$) and 29-0193 ($BaMoO_4$) [10].

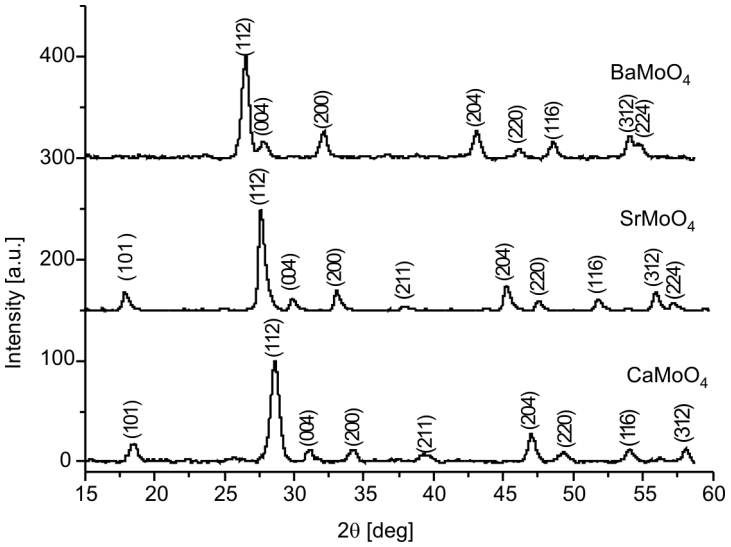

Fig. 1. XRD spectra of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$

No characteristic peaks of impurities were detected. The molybdates have tetragonal scheelite structure ($a = b \neq c$ and $\alpha = \beta = \gamma = 90°$) with $I4_1/a$ space group [6, 10]. Their lattice parameters were calculated from the equation of plane spacing for the tetragonal structure and Bragg's law for diffraction [11]. They are a = 0.5221 nm, c = 1.1417 nm for $CaMoO_4$, a = 0.5417 nm, c = 1.2004 nm for $SrMoO_4$, and a = 0.5610 nm, c = 1.2766 nm for $BaMoO_4$. The calculated parameters are very close to those of the JCPDS standard [10]. Increase in the lattice parameters was related to the atomic masses and ionic radii of alkaline earth metals (Ca^{2+} – 0.112 nm, Sr^{2+} – 0.125 nm, Ba^{2+} – 0.142 nm) [3], which imply the difference of charge densities in MO_8 polyhedral environment of the scheelite structure [12].

The crystallite sizes of $MMoO_4$ (M = Ca, Sr and Ba) were calculated from the (112) peaks of XRD spectra and by applying Scherrer's formula, $B = \lambda k/L\cos\theta$, where λ, θ, L, k and B are the wavelength of CuK_α radiation, the Bragg angle, the average crystallite size, a constant (0.89), and the full width at half maximum of (112) peak in radians, respectively [11]. The calculated crystallite sizes of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ are 14.48, 15.83 and 18.00 nm, respectively. They all increased with the increase in the ionic radii and the atomic masses of the alkaline earth metals.

It is proposed that the most likely reaction occurring in the synthesis of the nanocrystalline molybdates via the cyclic microwave radiation process is:

$$M(NO_3)_2 + Na_2MoO_4 \rightarrow MMoO_4 + 2NaNO_3$$

PG and microwave radiation influence the fabrication of uniform nanosized particles, which can be explained as follows. PG has a high boiling point (187 °C) [13], thus the problem of overheating by microwave radiation can be overcome. At 25 °C, PG has a high permanent dipole moment (2.50 D) and a high electric permittivity (30.2) [14] which enables coupling with the electric field leading to the molecular vibration of PG. The solution may be rapidly heated to a high temperature and due to the microwave vibration (2.45 GHz) [15], nucleation and growth proceed in uniform environment. Finally, nanosized particles are synthesized.

Alkaline earth metal molybdates contain $[MoO_4]^{2-}$ tetrahedrons. 26 various vibrations in the lattice space ($3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$) were determined by the group theory calculations [3,16]. $3A_g$, $5B_g$ and $5E_g$ vibrations are Raman active. Only $4A_u$ and $4E_u$ of the $5A_u$ and $5E_u$ vibrations are infrared active, and the remaining ones ($1A_u$ and $1E_u$) are acoustic vibrations. $3B_u$ vibrations are silent modes [3, 17]. Raman spectra (Fig. 2) show six vibrations at 875, 845, 792, 392, 322 and 204 cm^{-1} for $CaMoO_4$, 883, 842, 794, 368, 327 and 181 cm^{-1} for $SrMoO_4$, and 887, 834, 788, 359, 327 and 192 cm^{-1} for $BaMoO_4$. They correspond to $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(B_g)$, $\nu_2(A_g)$ and $\nu_{\text{free rotation}}(A_g)$ modes, respectively [18].

FTIR spectra of the molybdates are shown in Fig 3. For T_d symmetry, $\nu_3(F_2)$ and $\nu_4(F_2)$ modes are infrared active. They correspond to stretching and bending modes, respectively [19, 20]. Very strong Mo–O stretching vibration in $[MoO_4]^{2-}$ tetrahedrons was detected at 783–955 cm^{-1} and weak Mo–O bending vibration was evident at 422 cm^{-1}.

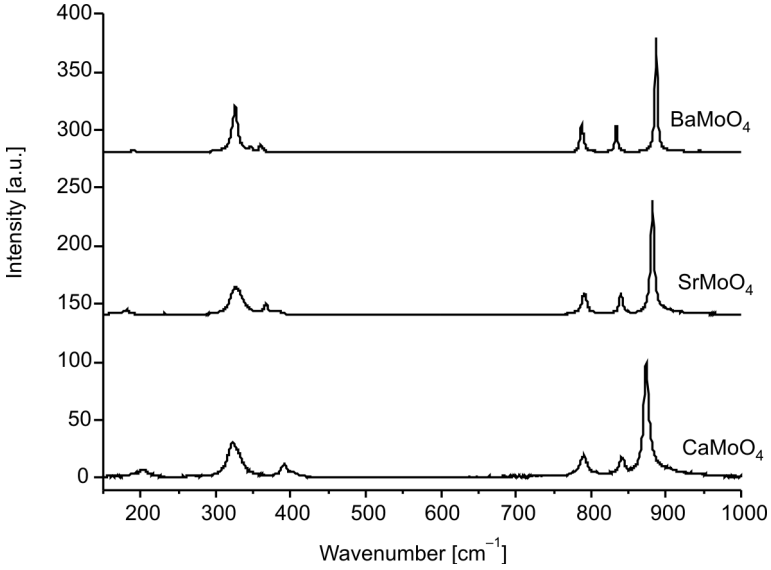

Fig. 2. Raman spectra of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$

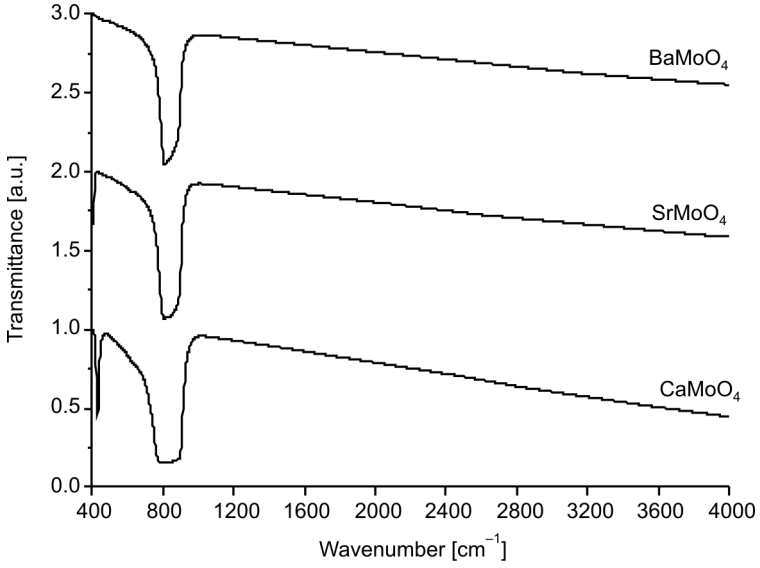

Fig. 3. FTIR spectra of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$

TEM images and SAED patterns of metal molybdates are shown in Fig 4. The products were composed of a number of round nanosized particles. Their average sizes were estimated from 500 particles seen on TEM images. Their distribution curves (Fig. 5) are narrow. The particle sizes are 20 ± 5 nm for $CaMoO_4$, 21 ± 5 nm for $SrMoO_4$, and 22 ± 5 nm for $BaMoO_4$.

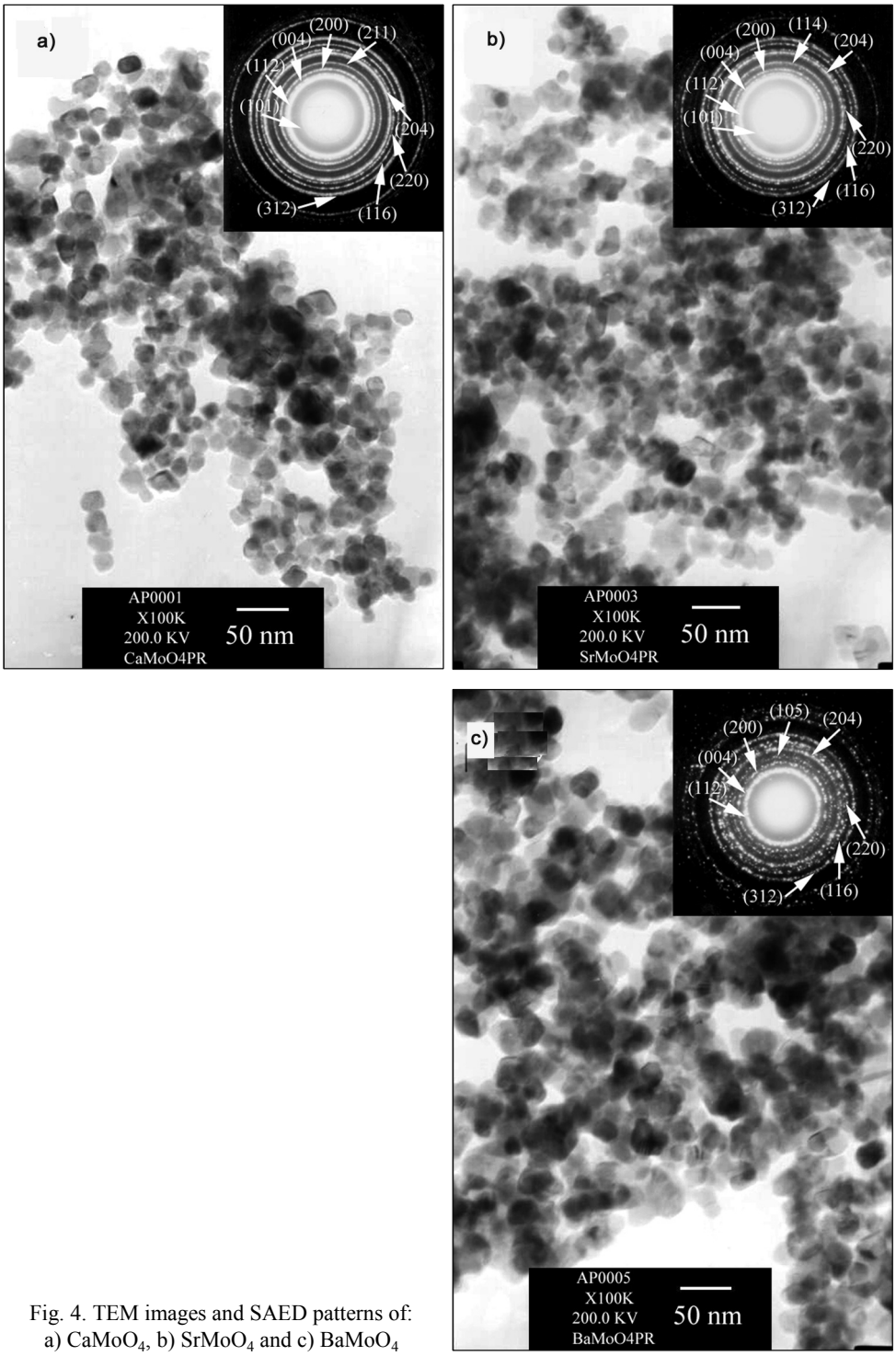

Fig. 4. TEM images and SAED patterns of: a) $CaMoO_4$, b) $SrMoO_4$ and c) $BaMoO_4$

Narrow particle size distributions and homogeneous particles favour good luminescent properties [21]. The products contain less contaminations, or fewer dead layers on the phosphor surface [21]. SAED patterns show a number of bright spots: the brightness of some of them is continuous, whereas for others they are at random. The spots are so close that they form fully concentric rings. These indicate that the molybdates consist of nanosized polycrystals with different orientations. Interplanar spaces were calculated from the diameters of the rings [22, 23], and compared with those of the JCPDS standard [10]. Crystallographic planes were indexed on the patterns. The products are specified as $MMoO_4$ (M = Ca, Sr and Ba).

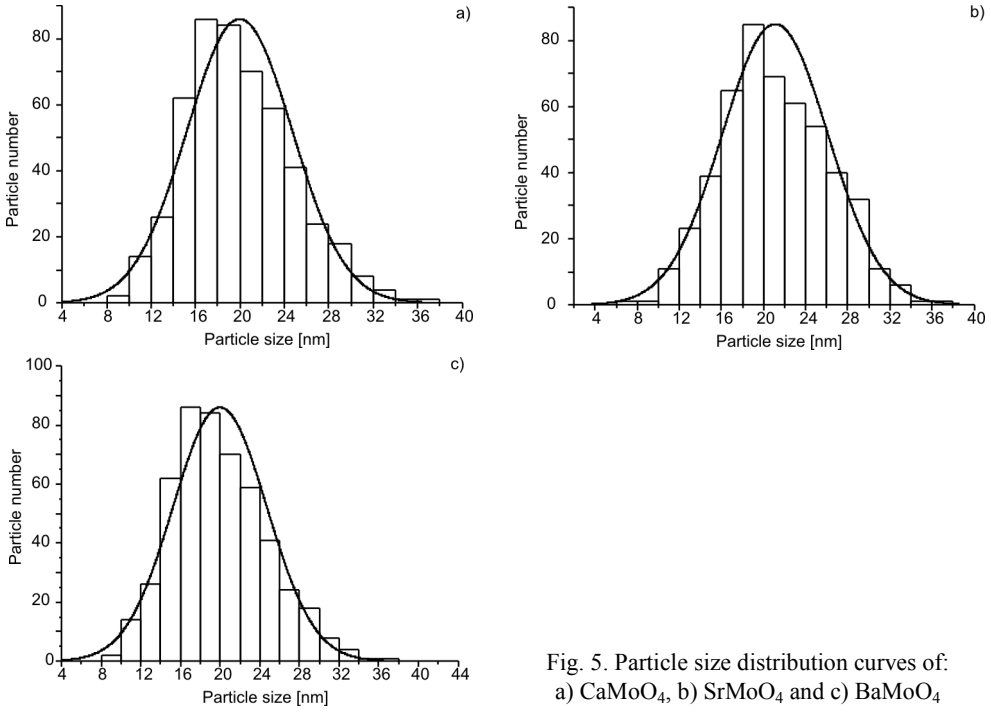

Fig. 5. Particle size distribution curves of: a) $CaMoO_4$, b) $SrMoO_4$ and c) $BaMoO_4$

EDX analyses of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ (results not shown) revealed Ca peaks at 3.69 keV (K_α) and 4.01 keV (K_β), Sr peaks at 1.81 keV (L_α), 14.14 keV (K_α) and 15.84 keV (K_β), and Ba peaks at 4.47 keV (L_α), 4.83 keV ($L_{\beta1}$), and 5.16 keV ($L_{\beta2}$). O peaks of the three molybdates were detected at 0.53 keV (K_α), and Mo peaks were detected at 2.29 keV (L_α), 17.45 keV (K_α) and 19.61 keV (K_β) [24]. Elemental analysis shows that the M:Mo:O atomic ratios are very close to those of the corresponding stoichiometric molybdates. Cu of copper grids and C layers were also detected.

4. Conclusions

Nanocrystalline compounds $MMoO_4$ (M = Ca, Sr and Ba) were successfully synthesized from $M(NO_3)_2$ and Na_2MoO_4 in propylene glycol, by applying cyclic micro-

wave radiation. XRD, SAED and EDX analyses revealed the presence of nanocrystalline $MMoO_4$ containing the corresponding alkaline earth metals, Mo and O. The products were composed of a number of round nanosized particles, according to TEM analysis. Their size distributions are very narrow. Six vibrations were detected using Raman spectroscopy. FTIR data revealed very strong Mo–O stretching vibrations in $[MoO_4]^{2-}$ tetrahedrons, which were detected in the 783–955 cm^{-1} range. FTIR data also confirmed weak Mo–O bending at 422 cm^{-1}.

Acknowledgements

The authors are extremely grateful to the Thailand Research Fund and the National Research Council of Thailand for supporting the research, and the Graduate School of Chiang Mai University for general funding.

References

[1] ZHAO Y., LIAO X.H., HONG J.M., ZHU J.J., Mater. Chem. Phys., 87 (2004), 149.
[2] LIAO X.H., CHEN N.Y., XU S., YANG S.B., ZHU J.J., J. Cryst. Growth, 252 (2003), 593.
[3] BASIEV T.T., SOBOL A.A., VORONKO Y.K., ZVEREV P.G., Opt. Mater., 15 (2000), 205.
[4] RYU J.H., YOON J.W., SHIM K.B., J. Alloy. Comp., 413 (2006), 144.
[5] ZHANG Y., YANG F., YANG J., TANG Y., YUAN P., Solid State Commun., 133 (2005), 759.
[6] LI Z., DU J., ZHANG J., MU T., GAO Y., HAN B., CHEN J., CHEN J., Mater. Lett., 59 (2005), 64.
[7] ZHANG C., SHEN E., WANG E., KANG Z., GAO L., HU C., XU L., Mater. Chem. Phys., 96 (2006), 240.
[8] WANG Y., MA J., TAO J., ZHU X., ZHOU J., ZHAO Z., XIE L., TIAN H., Ceram. Int., 33 (2007), 693.
[9] PARHI P., SINGH S.S., RAY A.R., RAMANAN A., Bull. Mater. Sci., 29 (2006), 115.
[10] Powder Diffract. File, JCPDS Int. Centre Diffr. Data, U.S.A. (2001).
[11] SURYANARAYANA C., NORTON M.G., *X-ray Diffraction. A Practical Approach*, Plenum Press, New York, (1998).
[12] ERRANDONEA D., PELLICER-PORRES J., MANJON F.J., SEGURA A., FERRER-ROCA CH., KUMAR R.S., TSCHAUNER O., RODRÍGUEZ-HERNÁNDEZ P., LÓPEZ-SOLANO J., RADESCU S., MUJICA A., MUÑOZ A., AQUILANTI G., Phys. Rev. B, 72 (2005), 174106.
[13] ANDREESCU D., MATIJEVIĆ E., GOIA D.V., Colloid. Surf. A, 291 (2006), 93.
[14] SENGWA R.J., J. Mol. Liq., 108 (2003), 47.
[15] CHEN D., TANG K., SHEN G., SHENG J., FANG Z., LIU X., ZHENG H., QIAN Y., Mater. Chem. Phys., 82 (2003), 206.
[16] PORTO S.P.S., SCOTT J.F., Phys. Rev. 157 (1967), 716.
[17] GOLUBOVIĆ A., GAJIĆ R., DOHČEVIĆ-MITROVIĆ Z., NIKOLIĆ S., J. Alloys Comp., 415 (2006), 16.
[18] CHEN D., TANG K., LI F., ZHENG H., Cryst. Growth Design, 6 (2006), 247.
[19] DE AZEVEDO MARQUES A.P., DE MELO D.M.A., PASKOCIMAS C.A., PIZANI P.S., JOYA M.R., LEITE E.R., LONGO E., J. Solid State Chem., 179 (2006), 671.
[20] CLARK G.M., DOYLE W.P., Spectrochim. Acta, 22 (1966), 1441.
[21] RYU J.H., YOON J.W., LIM C.S., OH W.C., SHIM K.B., J. Alloy. Comp., 390 (2005), 245.
[22] THONGTEM T., PHURUANGRAT A., THONGTEM S., J. Mater. Sci., 42 (2007), 9316.
[23] THONGTEM T., KAOWPHONG S.AND THONGTEM S., J. Mater. Sci., 42 (2007), 3923.
[24] *X-ray Absorption and Emission Energy*, Oxford Instrum. Analyt., Halifax Rd., High Wycombe Bucks HP12 3SE, U.K.

Received 7 October 2007
Revised 2 December 2007