

Effect of lead salts on phase, morphologies and photoluminescence of nanocrystalline PbMoO_4 and PbWO_4 synthesized by microwave radiation

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PbMoO_4 and PbWO_4 were successfully synthesized by microwave radiation using different lead salts (acetate, chloride, nitrate and sulfate) and Na_2MO_4 ($\text{M} = \text{Mo}, \text{W}$) in propylene glycol. The products were characterized by X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM, TEM), Fourier transform infrared (FT-IR), Raman spectroscopy and photoluminescence (PL) spectroscopy. In this research, morphologies, crystallization and photoluminescence of the products were influenced by the kinetics of anions, including the detection of $\text{M}-\text{O}$ ($\text{M} = \text{Mo}, \text{W}$) stretching modes in the $(\text{MO}_4)^{2-}$ tetrahedrons. Photoluminescence of PbMoO_4 synthesized from $\text{Pb}(\text{NO}_3)_2$ and of PbWO_4 synthesized from PbCl_2 showed the strongest blue emission due to the electronic diffusion in tetrahedrons at room temperature.

Keywords: *PbMoO_4 ; PbWO_4 ; microwave radiation; photoluminescence*

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1. Introduction

Molybdate and tungstate are inorganic compounds which have very interesting properties for applications such as luminescent materials, electro-optic materials, scintillators and catalysts [1, 2]. PbMoO_4 and PbWO_4 are classified in these groups and have application in high-energy physics. They are characterized by high density, short decay time and high-irradiation damage [3–5]. Photonic emission of PbMoO_4 has only blue color but PbWO_4 has two types of colors: blue (2.8 eV to 2.9 eV) and green (2.3 eV to 2.5 eV) [6].

There are different methods used to synthesize nanoscale metal molybdate and metal tungstate, such as chemical solution [2], microemulsion-based solvothermal method [3] and hydrothermal reaction [4]. Microwave-assisted route is a novel method used to synthesize nanomaterials such as metal oxide and metal sulfide [7–10]. This method has more advantages than the conventional one, including short reaction time and possibility to synthesize products with high purity and narrow particle size distribution. Ryu et al. [11, 12] succeeded in synthesizing metal molybdate and metal tungstate via a citrate complex route assisted by microwave radiation. Crystalline products were obtained by calcination at high temperature. In this research, nanocrystalline PbMoO_4 and PbWO_4 were

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synthesized by microwave radiation without calcination at high temperature.

2. Experimental

All chemicals ($\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ ACS reagent $\geq 99\%$, PbCl_2 98 %, $\text{Pb}(\text{NO}_3)_2$ ACS reagent $\geq 99\%$, PbSO_4 98 %, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ACS reagent $\geq 99\%$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ACS reagent $\geq 99\%$) were purchased from Sigma-Aldrich Chemical Co., and used without further purification.

In this research, each of 0.005 mol of lead salts (acetate, chloride, nitrate and sulfate) and Na_2MO_4 ($\text{M} = \text{Mo}, \text{W}$) was separately dissolved in 50 mL propylene glycol to form a solution. The Pb^{2+} and $(\text{MO}_4)^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) solutions were mixed and stirred for 30 min. Then the systems were processed under 600 W microwave radiation at 50 % microwave heating (duration of the heating cycle was 1 min with 1 min interval) for 10 min. Finally, white precipitates were synthesized, washed with distilled water and absolute ethanol for several times, and dried at 80 °C for 24 h.

The products were characterized by X-ray diffraction (XRD, Siemens D500) in the range of 2θ scanning angle of 15° to 60°, using $\text{CuK}\alpha$ radiation with graphite monochrome and a Ni filter, Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27, better than 1 cm^{-1}) operating in the range of 4000 cm^{-1} to 400 cm^{-1} with KBr as a diluting agent, Raman spectroscopy (T64000 HORIBA Jobin Yvon with high spectral resolution) using a 50 mW and 514.5 nm wavelength Ar green laser, scanning electron microscopy (SEM, JEOL JSM-6335F) equipped with energy dispersive X-ray spectroscopy (EDX) operating at 20 kV, transmission electron microscopy (TEM, JEOL JEM-2010) operating at 200 kV, and photoluminescence (PL) spectroscopy (Perkin Elmer LS 50B) operating at room temperature.

3. Results and discussion

XRD patterns of lead molybdate and lead tungstate (Fig. 1) synthesized from different lead

salts were indexed to tetragonal phase of PbMoO_4 (JCPDS# 08-0475) and PbWO_4 (JCPDS# 08-0476) [13]. No PbMoO_4 has been detected in the XRD pattern when lead chloride was used as a starting lead source whereas PbWO_4 , could be synthesized from the four lead salts and no impurities have been detected in the XRD patterns. Comparing the products obtained from different lead salts, PbMoO_4 synthesized from $\text{Pb}(\text{NO}_3)_2$ and PbWO_4 synthesized from PbCl_2 have the highest diffraction peaks and degree of crystallinity. These findings show that the degree of crystallinity is influenced by the kinetics of anions belonging to lead salts. The smallest anions play the crucial role in promoting atomic diffusion at the fastest rate and atomic arrangement at the highest order.

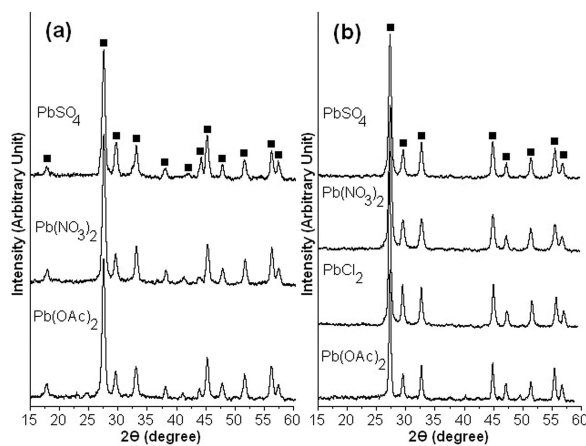


Fig. 1. XRD spectra of (a) PbMoO_4 and (b) PbWO_4 synthesized from different lead sources by microwave radiation.

Raman spectroscopy is an inelastic scattering phenomenon by a monochromatic laser beam, in the visible, near IR, or near UV range. It measures relative frequencies at which a sample scatters the radiation. FT-IR is a form of vibrational modes caused by absorbance, transmittance or reflectance of a monochromatic beam in the IR region. This spectroscopy measures absolute frequencies at which a sample absorbs the IR radiation. The vibration is Raman active if there is a change in polarizability. The vibration is IR active if there is change in dipole moment. FT-IR spectroscopy is sensitive to hetero-nuclear functional

group vibrations and polar bonds, especially OH stretching in water. Raman is sensitive to homonuclear molecular bonds. No matter whether Raman spectroscopy or FT-IR spectroscopy is used: both methods have their advantages and limitations. These combined methods are powerful tool used for materials characterization.

FT-IR spectra of PbMoO_4 and PbWO_4 (Fig. 2) show the Mo–O stretching band of $(\text{MoO}_4)^{2-}$ tetrahedrons at 750 cm^{-1} to 920 cm^{-1} and the W–O stretching band of $(\text{WO}_4)^{2-}$ tetrahedrons at 720 cm^{-1} to 981 cm^{-1} [14–16]. PbMoO_4 and PbWO_4 are composed of $(\text{MoO}_4)^{2-}$ and $(\text{WO}_4)^{2-}$ of tetrahedrons symmetry with $\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$. The even vibrations (A_g , B_g and E_g) are Raman active, the odd modes ($4A_u$ and $4E_u$) are IR active with the remains as acoustic modes, and the $3B_u$ vibration modes that are silent [17]. Raman spectra (Fig. 3) of PbMoO_4 and PbWO_4 were recorded over the range of 150 cm^{-1} to 1200 cm^{-1} . Raman peaks of PbMoO_4 were detected at 871 cm^{-1} , 768 cm^{-1} , 744 cm^{-1} , 351 cm^{-1} , 319 cm^{-1} and 167 cm^{-1} , corresponding to the $\nu_1(A_g)$, $\nu_3(B_g)$, $\nu_3(E_g)$, $\nu_4(B_g)$, $\nu_2(A_g)$ and free rotation modes, respectively. Those of PbWO_4 were detected at 906 cm^{-1} , 770 cm^{-1} , 752 cm^{-1} , 358 cm^{-1} , 327 cm^{-1} and 178 cm^{-1} , corresponding to the same Raman vibration modes of PbMoO_4 [17]. The Raman wavenumbers were blue shifted from PbMoO_4 to PbWO_4 as a result of the change of covalent bond between Pb^{2+} cations and O^{2-} anions in the tetrahedral complexes and the efficient mass of vibrating groups.

The morphology and phase of PbMoO_4 were characterized by TEM (Fig. 4). The PbMoO_4 products synthesized using lead acetate and lead nitrate as the starting lead sources are composed of 15 nm to 25 nm and $<50\text{ nm}$ nanoparticles oriented in different directions. The nanoparticle sizes of PbMoO_4 synthesized from $\text{Pb}(\text{SO}_4)_2$ are the biggest. The SAED pattern appears as distributed light spots arranged as concentric rings, due to electron diffraction through polycrystalline PbMoO_4 with different orientations. The space between adjacent planes was calculated and indexed to the crystallographic planes of PbMoO_4

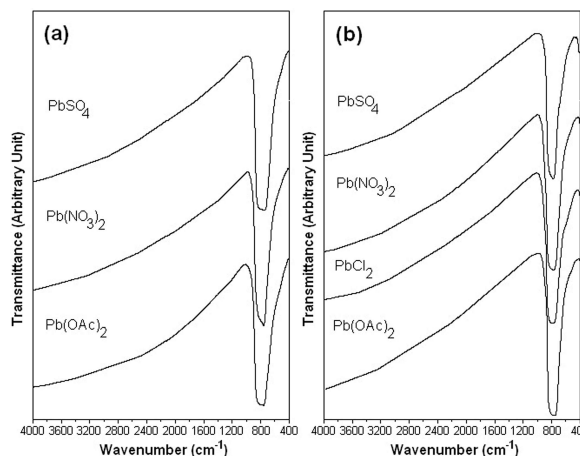


Fig. 2. FT-IR spectra of (a) PbMoO_4 and (b) PbWO_4 synthesized from different lead sources by microwave radiation.

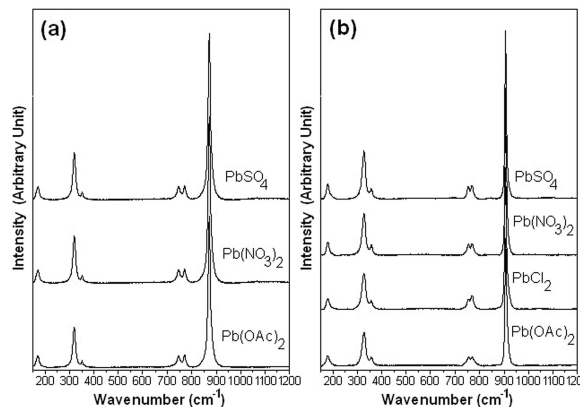


Fig. 3. Raman spectra of (a) PbMoO_4 and (b) PbWO_4 synthesized from different lead sources by microwave radiation.

(JCPDS# 08-0475) [13]. SEM images of PbWO_4 (Fig. 5) show the PbWO_4 samples containing a number of nanoparticles clustered together in groups of $2\text{ }\mu\text{m}$ to $4\text{ }\mu\text{m}$.

EDX characterization of PbMoO_4 revealed Pb peaks at 2.35 keV (M_α line), 2.44 keV (M_β line), 10.55 keV (L_α line) and 12.61 keV ($L_{\beta 1}$ line). The Mo peaks were detected at 2.29 keV (L_α line), 2.40 keV ($L_{\beta 1}$ line) and 2.52 keV ($L_{\beta 2}$ line), including the O peak at 0.53 keV ($K_{\alpha 1,2}$ line). The Pb:Mo:O atomic ratio of PbMoO_4 characterized by EDX is very close to its stoichiometric value. For the EDX characterization of PbWO_4 ,

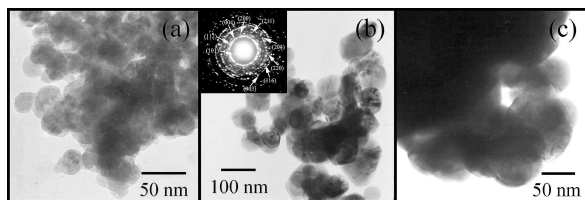


Fig. 4. TEM images and SAED pattern of PbMoO_4 synthesized from (a) lead acetate, (b) lead nitrate and (c) lead sulfate as lead sources by microwave radiation.

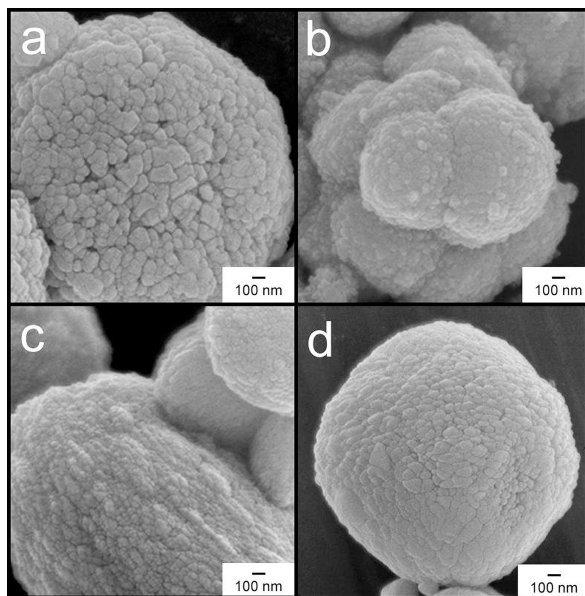


Fig. 5. SEM images of PbWO_4 synthesized from (a) lead acetate, (b) lead chloride, (c) lead nitrate and (d) lead sulfate as lead sources by microwave radiation.

the energy peaks for Pb and O are almost of the same value as those of PbMoO_4 , including the W peaks detected at 1.78 keV (M_α line), 1.84 keV (M_β line), 8.40 keV (L_α line) and 9.67 keV ($L_{\beta 1}$ line) [18]. The composition of PbWO_4 is in accordance with its stoichiometric value, as well.

Photoluminescence (PL) of PbMoO_4 (Fig. 6a) was determined by photoluminescence spectroscopy at room temperature. The spectra exhibit blue emission at 412 nm attributed to the charge diffusion within the $(\text{MoO}_4)^{2-}$ complexes in accordance with the literature [1, 19, 20].

Zhang et al. [19] have reported that PL spectrum of PbMoO_4 nanocrystals presents a blue emission peak at ca 450 nm due to the charged diffusion within the $(\text{MoO}_4)^{2-}$ units and weak green emission band at 550 nm due to the existence of Frenkel defects. Emission spectra of PbWO_4 at room temperature (Fig. 6b) show blue emission peak at 394 nm due to the charge diffusion of $(\text{WO}_4)^{2-}$ complexes in accordance with other reports [6, 21, 22]. Saraf et al. [21] reported a strong PL emission in blue phosphor and a weak PL emission in yellow and red components of PbWO_4 caused by $^1T_2 \rightarrow ^1A_1$ diffusion of electrons within $(\text{WO}_4)^{2-}$ tetrahedrons and defects associated with oxygen. Comparing PbMoO_4 and PbWO_4 synthesized from different lead salts, PL emissions of PbMoO_4 synthesized from $\text{Pb}(\text{NO}_3)_2$ and PbWO_4 synthesized from PbCl_2 show the strongest intensities. The electronic diffusion in the best crystal is the highest. The results indicate that PL emission depends on degree of crystallinity which should be enhanced to improve photoluminescence efficiency [11].

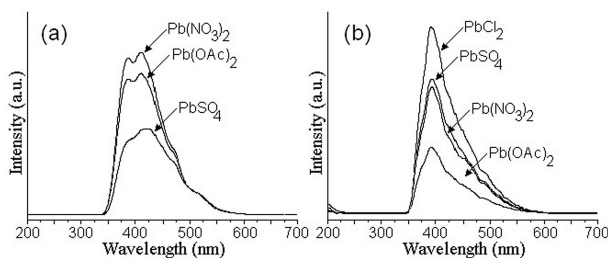


Fig. 6. PL emission of (a) PbMoO_4 and (b) PbWO_4 synthesized from different lead sources by microwave radiation.

4. Conclusions

Nanocrystalline PbMoO_4 and PbWO_4 were successfully synthesized in propylene glycol by microwave radiation. Phase crystallization, morphology and photoluminescence were controlled by the kinetics of anions. Photoluminescence of PbMoO_4 and PbWO_4 showed the highest emission at 412 nm and 394 nm, respectively.

Acknowledgements

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References

- [1] SPASSKY D.A., IVANOV S.N., KOLOBANOV V.N., MIKHAILIN V.V., ZEMSKOV V.N., ZADNEPROVSKI B.I., POTKIN L.I., *Radiat. Meas.*, 38 (2004), 607.
- [2] MAURERA M.A.M.A., SOUZA A.G., SOLEDADE L.E.B., PONTES F.M., LONGO E., LEITE E.R., VARELA J.A., *Mater. Lett.*, 58 (2004), 727.
- [3] HUO L., CHU Y., *Mater. Lett.*, 60 (2006), 2675.
- [4] AN C., TANG K., SHEN G., WANG C., QIAN Y., *Mater. Lett.*, 57 (2002), 565.
- [5] HU X., ZHU Y., *Langmuir*, 20 (2004), 1521.
- [6] BABIN V., BOHACEK P., BENDER E., KRASNIKOV A., MIHOKOVA E., NIKL M., SENGUTTUVAN N., STOLOVITS A., USUKI Y., ZAZUBOVICH S., *Radiat. Meas.*, 38 (2004), 533.
- [7] DING T., ZHANG J., LONG S., ZHU J., *Microelectron. Eng.*, 66 (2003), 46.
- [8] ZHAO Y., LIAO X., HONG J., ZHU J., *Mater. Chem. Phys.*, 87 (2003), 149.
- [9] CHEN D., TANG K., SHEN G., SHENG J., FANG Z., LIU X., ZHENG H., QIAN Y., *Mater. Chem. Phys.*, 82 (2003), 206.
- [10] CHEN D., SHEN G., TANG K., LEI S., ZHENG H., QIAN Y., *J. Cryst. Growth*, 260 (2004), 469.
- [11] RYU J.H., KOO S., CHANG D.S., YOON J., LIM C.S., SHIM K.B., *Ceram. Int.*, 31 (2005), 883.
- [12] RYU J.H., KOO S., YOON J., LIM C.S., SHIM K.B., *Mater. Lett.*, 60 (2006), 1702.
- [13] *Powder Diffraction File*, JCPDS-ICDD, 12 Campus Boulevard, Newtown Square, PA 19073-3273, USA, 2001.
- [14] JAYARAMAN A., BATLOGG B., UITERT VAN L.G., *Phys. Rev. B*, 31 (1985), 5423.
- [15] PHURUANGRAT A., THONGTEM T., THONGTEM S., *Curr. Appl. Phys.*, 10 (2010), 342.
- [16] PHURUANGRAT A., THONGTEM T., THONGTEM S., *J. Cryst. Growth*, 311 (2009), 4076.
- [17] BASIEV T.T., SOBOL A.A., VORONKO Y.K., ZVEREV P.G., *Opt. Mater.*, 15 (2000), 205.
- [18] *X-ray Absorption and Emission Energy*, Oxford Instruments Analytical, Halifax Rd., High Wycombe. Bucks HP12 3SE, UK.
- [19] ZHANG J., ZHAO T., ZOU L., GAN S., *J. Photoch. Photobiol. A*, 314 (2016), 35.
- [20] SCZANCOSKI J.C., BOMIO M.D.R., CAVALCANTE L.S., JOYA M.R., PIZANI P.S., VARELA J.A., LONGO E., LI M.S., ANDRÉS J.A., *J. Phys. Chem. C*, 113 (2009), 5812.
- [21] SARAF R., SHIVAKUMARA C., BEHERA S., NAGABHUSHANA H., DHANANJAYA N., *Spectrochim. Acta A*, 136 (2015), 348.
- [22] RYU J.H., KOO S.M., CHANG D.S., YOON J.W., LIM C.S., SHIM K.B., *Ceram. Int.*, 32 (2006), 647.

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