Characterization of starfruit-like PbWO$_4$ microstructured clusters synthesized by a solution route

Anukorn Phuruangrat$^{a, *}$, Titipun Thongtem$^{b, *}$ and Somchai Thongtem$^{c}$

$^a$Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
$^b$Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
$^c$Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Starfruit-like PbWO$_4$ microstructured clusters were synthesized by a solution route of Pb(NO$_3$)$_2$ and Na$_2$WO$_4$ in ethylene glycol. The product was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, Fourier transform infrared spectroscopy and photoluminescence spectroscopy. In this research, tetragonal PbWO$_4$ microstructured clusters in the shape of starfruits were detected. PL spectrum excited by 286 nm wavelength was divided into three individual components with the maximum blue emission at 390 nm (40.79%), 424 nm (30.30%) and green emission at 472 nm (28.91%).

Key words: Solution route, PbWO$_4$, Starfruit clusters.

Introduction

Recently, metal tungstate materials have attracted much attention because of their interesting luminescence behaviors, structural properties and potential applications [1-3]. Lead tungstate (PbWO$_4$) is one of such materials that has been increasing attention because of its technological importance as an inorganic scintillating crystals, interesting excitonic luminescence, thermoluminescence and stimulated Raman scattering (SRS) behaviors, due to its high density (8.3 g/cm$^3$), short decay time of less than 10 ns for large part of the light output and high irradiation damage resistance, small Moliere radius, fast decay time, non-hygroscopicity and low production cost [3-8]. There are two main polymorphs for lead tungstate. One is commonly found as stolzite with tetragonal crystal system and the other is rarely found as raspite with monoclinic crystal system, which transforms to stolzite irreversibly at around 400 °C [5]. PbWO$_4$ nano- and microstructures have been synthesized by several techniques: a surfactant-assisted wet chemical process [3, 5], hydrothermal [4, 12], sonochemical route [7, 9, 10], microwave irradiation [8, 13], microemulsion [11], Czochralski [14, 15], etc. However, these methods are required expensive equipment and high temperature process. Thus it is very interesting to develop a simple method for the preparation of PbWO$_4$ crystals.

In this study, microstructured PbWO$_4$ clusters in the shape of starfruits were successfully synthesized by a solution route. The structure, morphologies and properties were investigated and discussed in more detail.

Experiment

All chemicals were analytical grade and used without further purification. To synthesize the starfruit-like PbWO$_4$ microstructured clusters, 0.005 mole Pb(NO$_3$)$_2$ in 15 ml ethylene glycol was mixed with 0.005 mole Na$_2$WO$_4$ in 15 ml ethylene glycol, and followed by 24 h continuous stirring. Finally, white precipitates were synthesized, separated by filtration, washed with distilled water for removal of ionic remains and ethanol, and dried at 80 °C in an electric oven for 24 h.

The final product was characterized by X-ray powder diffraction (XRD) recorded on a Philips X’Pert MPD X-ray diffractometer equipped with a graphitic monochromatized Cu Kα radiation, using a scanning rate of 0.04 deg/s in the 2θ range of 10-60 °, HORIBA Jobin Yvon T64000 Raman spectrometer operating at 50 mW Ar green laser with 514.5 nm wavelength, Bruker Tensor 27 Fourier transform infrared (FTIR) spectrometer with KBr as a diluting agent and operated in the range of 400-4000 cm$^{-1}$, JEOL JSM-6335F scanning electron microscope (SEM) operating at 15 kV, JEOL JEM-2010 transmission electron microscope (TEM) at 200 kV accelerating voltage, and Perkin Elmer LS50B spectrophotometer using 286 nm excitation wavelength at room temperature.
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**Results and discussion**

XRD pattern of the as-synthesized PbWO\(_4\) powders processed by the solution method is shown in Fig. 1a. All diffraction peaks were specified as tetragonal stolzite PbWO\(_4\) structure with I4\(_1\)/a space group of the JCPDS No. 08-0476 [16]. The experimental lattice parameters were calculated using the plane spacing equation for tetragonal structure and Bragg’s law for diffraction [17], and were found to be \(a = b = 5.4221\) Å and \(c = 12.1300\) Å.

The total number of degree of freedom for the atomic vibration of body-centered primitive tetragonal (\(Z = 4\)) of PbWO\(_4\) with its S\(_4\)-symmetry. Group theory calculation shows 26 different vibrations: \(\Gamma = 3A_g + 5A_u + 5B_g + 5B_u + 5E_g + 5E_u\) for zero wavevector. They can be divided into internal and external vibrations. The internal vibrations correspond to the oscillations inside the [WO\(_4\)]\(^2-\) molecular groups with immobile mass centers. The external or lattice phonons correspond to the motion of the Pb\(^{2+}\) cations and the rigid molecular units. All the \(A_g\), \(B_g\) and \(E_g\) vibrations are Raman-active, those of \(4A_u\) and \(4E_u\) are infrared-active, \(1A_u\) and \(1E_u\) are acoustic vibrations, and \(3B_u\) vibrations are silent modes. For all 13 Raman actives, seven vibrations are internal modes of the [WO\(_4\)]\(^2-\) tetrahedral units and the remains are external - two rotations of \(A_g\) symmetry and four translation of \(2B_g\) and \(2E_g\) symmetries [7-9]. The \(\nu_{1f},\ \nu_2(A_g),\ \nu_3(B_g),\ \nu_3(E_g),\ \nu_4(B_u)\) and \(\nu_4(A_u)\) vibrations of starfruit-like PbWO\(_4\) microstructured clusters as shown in Fig. 1b were detected at 190, 332, 360, 750, 770 and 912 cm\(^{-1}\), respectively [10].

![Fig. 1](image1.png)

**Fig. 1.** (a) XRD, (b) Raman, (c) FTIR and (d) PL spectra of starfruit-like PbWO\(_4\) microstructured clusters.

![Fig. 2](image2.png)

**Fig. 2.** SEM images of the as-synthesized PbWO\(_4\) shaped like starfruits.

Fig. 1c shows a FTIR transmittance spectrum of the as-synthesized PbWO\(_4\) sample. For \(T_d\) symmetry, the vibrations for the [WO\(_4\)]\(^2-\) tetrahedral units are \(\Gamma_{T_d} = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_4(\nu_4)\). Only the \(F_2(\nu_3), \nu_4\) modes are IR active for the vibration stretching in the [WO\(_4\)]\(^2-\) tetrahedrons [7-9]. Therefore, a strong W-O stretching in [WO\(_4\)]\(^2-\) tetrahedrons was detected at 711-933 cm\(^{-1}\), and a weak W-O bending at 433 cm\(^{-1}\).

Morphology and structural characterization for the as-synthesized PbWO\(_4\) powders were investigated by SEM and TEM as shown in Figs. 2 and 3a & b. SEM images exhibited PbWO\(_4\) microstructured clusters shaped like starfruits with four ridges running along the long axes of each cluster. The ridges extended from the middle out to the two tips. Their average length and width are 2.50 and 0.80 µm. It should be noted that the starfruit-like PbWO\(_4\) were cylindrical hollow particles.

The selected area electron diffraction (SAED) patterns (Fig. 3c & d) of individual starfruit-like PbWO\(_4\) microstructured cluster were recorded from their top of...
the axis and at the ridges. They show bright diffraction spots which indicate that the product is good single crystalline in nature. The SAED patterns can be indexed to (0-24), (-4-44) and (-4-20) planes with [-1-10] as the zone axis of the tetragonal PbWO₄ structure, in consistent with the above XRD analysis.

Fig. 3. TEM images and SAED patterns of PbWO₄ shaped like starfruits.

Conclusions

Starfruit-like PbWO₄ microstructured clusters have been successfully synthesized by a solution route. A definite existence of the tetragonal PbWO₄ structure was confirmed by XRD and Raman analyses. SEM and TEM images showed that the product shaped like starfruits. PL spectrum showed emission peaks in the blue and green regions.

Acknowledgement

The research was supported by the National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency, Thailand.

References