



## Low-Temperature Synthesis and Structural Properties of PbMoO<sub>4</sub> Nanocrystals†

V.V. ATUCHIN<sup>1,2,3</sup>, O.P. ANDREEVA<sup>1</sup>, I.V. KOROLKOV<sup>4</sup>, E.A. MAXIMOVSKIY<sup>5</sup> and C.S. LIM<sup>6,\*</sup>

<sup>1</sup>Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia

<sup>2</sup>Functional Electronics Laboratory, Tomsk State University, Tomsk 634050, Russia

<sup>3</sup>Novosibirsk State University, Novosibirsk 630090, Russia

<sup>4</sup>Laboratory of Crystal Chemistry, Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk 630090, Russia

<sup>5</sup>Laboratory of Epitaxial Layers, Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk 630090, Russia

<sup>6</sup>Department of Advanced Materials Science & Engineering, Hanseo University, Seosan 356-706, Republic of Korea

\*Corresponding author: Tel/Fax: +82 41 6601445; E-mail: cslim@hanseo.ac.kr

Published online: 1 March 2014;

AJC-14751

Lead molybdate (PbMoO<sub>4</sub>) nanocrystals have been synthesized by coprecipitation method in aqueous solution. The phase composition and micromorphology of the reaction product have been evaluated by XRD and SEM analysis. The characteristic diameter of PbMoO<sub>4</sub> nanocrystals has been estimated as 100 nm.

**Keywords:** PbMoO<sub>4</sub>, Nanocrystal, Coprecipitation, XRD, SEM.

### INTRODUCTION

The family of molybdates and tungstates with Scheelite-like tetragonal structure in space group  $I4_1/a$  is widely studied because of their potential applications in such fields as photoluminescence, photocatalysis, laser techniques and nanotechnology<sup>1-7</sup>. Lead molybdate (PbMoO<sub>4</sub>) is a representative member of this family, and crystal structure of this compound<sup>8,9</sup> is shown in Fig. 1. The structure is appeared as a framework formed by corner-linked PbO<sub>8</sub> polyhedrons and MoO<sub>4</sub> tetrahedra. The PbMoO<sub>4</sub> crystals possess optical band gap of 2.94 eV and show high chemical stability in the air. The well faceted plates of wulfenite, PbMoO<sub>4</sub>, were found in several geological deposits and they are typically coloured with transition metal admixtures<sup>10,11</sup>. Comparatively, synthetic PbMoO<sub>4</sub> crystals are colourless and they are transparent over spectral range of  $\lambda = 0.4-5.5 \mu\text{m}$ <sup>12,13</sup>. The PbMoO<sub>4</sub> crystals can be activated with lanthanoid and transition metals that promises for using of doped crystals as lasing hosts and luminescent materials<sup>12,14-17</sup>. Previously, several methods were tested for preparation of the PbMoO<sub>4</sub> powder products, and the micro-morphology and physical properties of the particles have been shown to be strongly dependent on the starting reagent selection and reaction conditions<sup>18-23</sup>. In the present

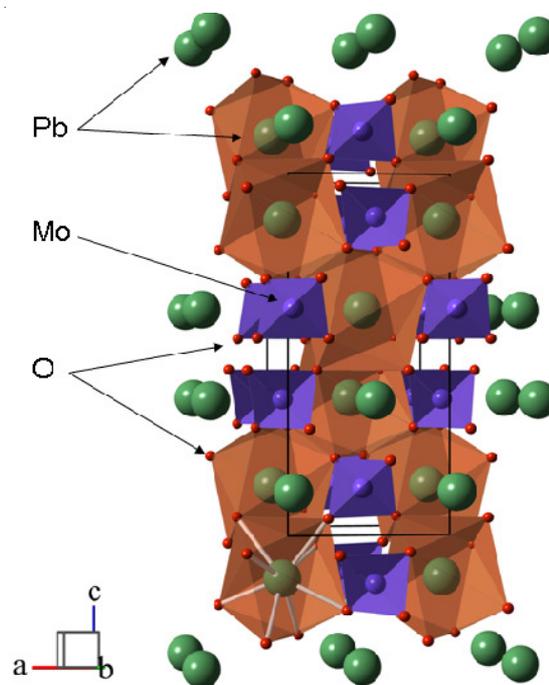


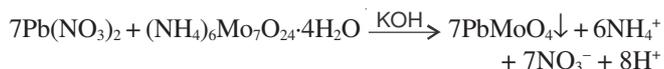
Fig. 1. Crystal structure of PbMoO<sub>4</sub>, space group  $I4_1/a$

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

study, the low-temperature precipitation method is developed to prepare the  $\text{PbMoO}_4$  microcrystals with uniform morphology. Earlier, similar precipitation techniques in water-based solutions were successfully used for the preparation of several simple oxides with different micromorphology and now it is interesting to reveal the potentials of this method for the synthesis of binary oxides<sup>24-28</sup>.

### EXPERIMENTAL

The  $\text{PbMoO}_4$  powder was prepared by the coprecipitation method in water *via* interaction of lead nitrate  $\text{Pb}(\text{NO}_3)_2$  (99.5 %, Reachim, Russia) with excess of ammonium heptamolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (> 99 %, Reachim, USSR) in the presence of potassium hydroxide  $\text{KOH}$  (> 95 %, Korea) at room temperature. The proposed equation of reaction is:



Initially, 0.005 mol of  $\text{Pb}(\text{NO}_3)_2$  were dissolved in 50 mL of distilled water by stirring. Dry ammonium heptamolybdate (0.001 mol) was poured into solution and then 50 mL of water were added. Slightly turbid mixture had pH 4-5. Because the  $\text{MoO}_4^{2-}$  ions are absent at such pH to generate  $\text{PbMoO}_4$ , the pellets of  $\text{KOH}$  were added to the reaction mixture one by one until the pH approached to 7. The reaction mixture was stirred for 90 min. The resulting white precipitate was separated by centrifugation and carefully washed with distilled water. Then, while washing sediment was boiled once in 10 mL of distilled water for 10 min at 100 W in microwave Samsung G2739NR to remove the contaminations. Finally, the white sediment was dried at 50-100 °C for 10 h.

XRD analysis was performed by Shimadzu XRD-7000 diffractometer ( $\text{CuK}_\alpha$  radiation, Ni-filter, 5-60°  $2\theta$  range). A polycrystalline sample was slightly ground with hexane in an agate mortar, and the resulting suspension was deposited on the quartz sample holder. The smooth thin layer formed after drying. Indexing of the diffraction pattern was carried out using data for compounds reported in the PDF database [Powder Diffraction File, PDF-2 release 2010]. The study of the surface morphology and elemental composition were performed on scanning electron microscope "Hitachi S-3400N" equipped with energy dispersive spectrometer "Oxford Instruments". The conductive coating was not applied, study was carried out in a low vacuum mode. The accelerating voltage was 20 kV.

### RESULTS AND DISCUSSION

The XRD of  $\text{PbMoO}_4$  is shown in Fig. 2. The major phase is  $\text{PbMoO}_4$  as it was found by comparison with available structural data<sup>8</sup>. There are two weak intensity peaks related to unknown admixture. The unit cell parameters were estimated as  $a = 5.428(2)$  and  $c = 12.111(3)$  Å that is in reasonable relation with earlier data of  $a = 5.434$  and  $c = 12.107$  Å<sup>8</sup>. The coherent scattering volume was estimated using Sherrer formula to be ~ 100 nm.

As it shown by SEM observation, the final powder product was formed by slightly agglomerated nanocrystals with typical diameter of 100 nm. The representative SEM pattern is shown in Fig. 3. Such morphology is formed due to swift precipitation and the short time of nanocrystal formation is not enough for

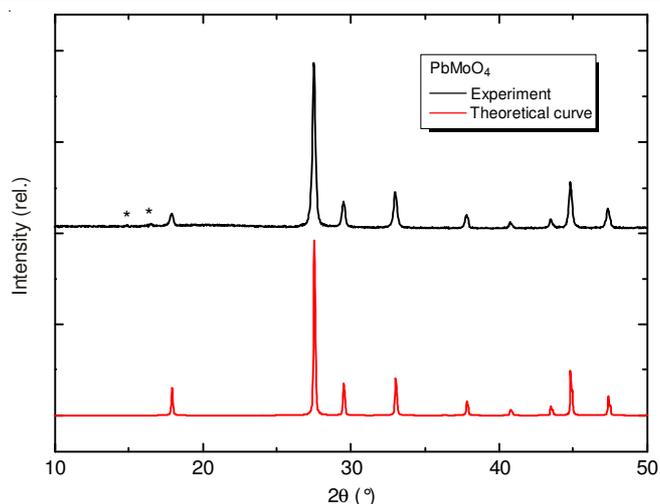


Fig. 2. XRD graph of  $\text{PbMoO}_4$ . Unindexed peaks are marked with asterisks

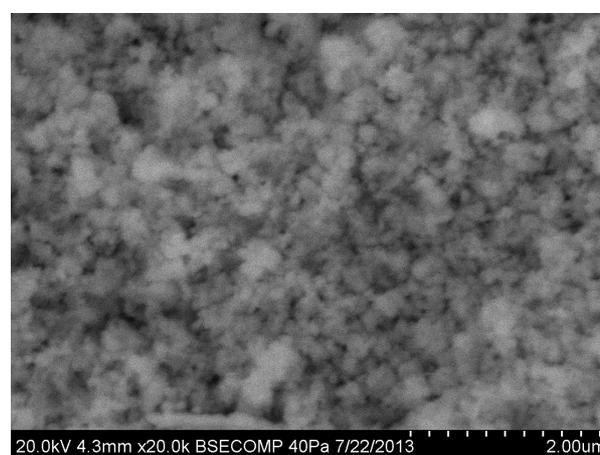


Fig. 3. SEM image of the  $\text{PbMoO}_4$  powder

facet generation. Chemical composition of the powder, determined with EDS analysis, is shown in Table-1. The values are in good relation with nominal composition of  $\text{PbMoO}_4$ . This result indicates that chemical precipitation reaction in aqueous solutions can be successfully used for the preparation of molybdates with predictable phase and chemical compositions. Now, it is topical to test the  $\text{PbMoO}_4$ -based reaction products when different doping agents are added into the solution<sup>29-32</sup>. As it seems, this is a promising way for the creation of new doped and composite systems. Above this, the reaction speed supposedly can be tuned by special agents and this may yield the faceted  $\text{PbMoO}_4$  nanocrystals.

Element	Wt. (%)	At. (%)
OK	17.62	66.43
MoL	28.38	17.84
PbM	54.01	15.72
Total	100.00	100.00

### Conclusion

The  $\text{PbMoO}_4$  nanocrystals with characteristic diameter of 100 nm were formed by coprecipitation method in aqueous solution. The phase composition and micromorphology of the

reaction product were evaluated by XRD and SEM measurements. The technique can be developed for the synthesis of doped PbMoO<sub>4</sub> nanocrystals.

### ACKNOWLEDGEMENTS

This study is partly supported by the Ministry of Education and Science of the Russian Federation.

### REFERENCES

1. T.T. Basiev, A.A. Sobol, Yu.K. Voronko and P.G. Zverev, *Opt. Mater.*, **15**, 205 (2000).
2. J.H. Ryu, J.W. Yoon, C.S. Lim, W.C. Oh and K.B. Shim, *Ceram. Int.*, **31**, 883 (2005).
3. F.E. Osterloh, *Chem. Mater.*, **20**, 35 (2008).
4. T. Thongtem, A. Phuruangrat and S. Thongtem, *J. Nanopart. Res.*, **12**, 2287 (2010).
5. C.S. Lim, *Asian J. Chem.*, **24**, 1523 (2012).
6. O.D. Chimitova, V.V. Atuchin, B.G. Bazarov, M.S. Molokeev and Z.G. Bazarova, *Proc. SPIE*, **8771**, 87711A (2013).
7. C.S. Lim and V.V. Atuchin, *Proc. SPIE*, **8771**, 87711O (2013).
8. C. Lugli, L. Madici and D. Saccardo, *Neues Jahrb. Miner. Monatsh.*, 281 (1999).
9. T.C. Ozawa and S.J. Kang, *J. Appl. Cryst.*, **37**, 679 (2004).
10. E.S. Leonardsen, H. Pauly, O.V. Patersen and J.G. Rønsbo, *Bull. Geol. Soc. Den.*, **29**, 145 (1981).
11. W.E. Wilson and M.J. Origlieri, *Mineral. Rec.*, **38**, 67 (2007).
12. A.A. Kaminskii and S.N. Bagayev, *Laser Phys.*, **11**, 1142 (2001).
13. V. Musinschi, M. Caraman and C. Musinschi, *Moldovan J. Phys. Sci.*, **10**, 65 (2011).
14. M.E. Doroshenko, T.T. Basiev, S.V. Vassiliev, L.I. Ivleva, V.K. Komar, M.B. Kosmyna, H. Jelínková and J. Šulc, *Opt. Mater.*, **30**, 54 (2007).
15. D. Piwowarska, S.M. Kaczmarek, P. Potera, P. Sagan and M. Berkowski, *Opt. Mater.*, **31**, 1798 (2009).
16. N.R. Aghamalyan, G.G. Demirkhanyan, R.K. Hovsepyan, R.B. Kostanyan and D.G. Zargaryan, *Opt. Mater.*, **35**, 1714 (2013).
17. Y.N. Gorobets, B.P. Nazarenko and A.N. Shekhovtsov, *Funct. Mater.*, **20**, 158 (2013).
18. V.M. Anandakumar and M.A. Khadar, *Phys. Status Solidi A*, **205**, 2666 (2008).
19. J.C. Sczancoski, M.D.R. Bomio, L.S. Cavalcante, M.R. Joya, P.S. Pizani, J.A. Varela, E. Longo, M.S. Li and J.A. Andrés, *J. Phys. Chem. C*, **113**, 5812 (2009).
20. M. Hashim, C. Hu, X. Wang, X. Li and D. Guo, *Appl. Phys. Sci.*, **258**, 5858 (2012).
21. D.B. Hernández-Uresti, A. Martínez-de la Cruz and J.A. Aguilar-Garib, *Catal. Today*, **212**, 70 (2013).
22. M. Shen, X. Zhang, K. Dai, H. Chen and T. Peng, *CrystEngComm*, **15**, 1146 (2013).
23. K. Dai, Y. Yao, H. Liu, I. Mohamed, H. Chen and Q. Huang, *J. Mol. Catal. Chem.*, **374-375**, 111 (2013).
24. V.V. Atuchin, T.A. Gavrilova, S.A. Gromilov, V.G. Kostrovsky, L.D. Pokrovsky, I.B. Troitskaia, R.S. Vemuri, G. Carbajal-Franco and C.V. Ramana, *Cryst. Growth Des.*, **9**, 1829 (2009).
25. C.V. Ramana, V.V. Atuchin, I.B. Troitskaia, S.A. Gromilov, V.G. Kostrovsky and G.B. Saupe, *Solid State Commun.*, **149**, 6 (2009).
26. I.B. Troitskaia, T.A. Gavrilova and V.V. Atuchin, *Phys. Procedia*, **23**, 65 (2012).
27. V.V. Atuchin, I.B. Troitskaia, O.Yu. Khyzhun, V.L. Bekenev, Yu.M. Solonin, *Appl. Mech. Mater.*, **110-116**, 2188 (2012).
28. V.V. Atuchin, B.I. Kidyarov and I.B. Troitskaia, *Ferroelectrics*, **444**, 137 (2013).
29. W.C. Oh, J.G. Choi, C.Y. Park and C.S. Lim, *J. Ceram. Proc. Res.*, **12**, 435 (2011).
30. C.S. Lim, *Mater. Res. Bull.*, **47**, 4220 (2012).
31. L. Zhu, Z.D. Meng, C.Y. Park, T. Ghosh and W.C. Oh, *Ultrason. Sonochem.*, **20**, 478 (2013).
32. C.S. Lim, *Asian J. Chem.*, **25**, 6251 (2013).