Low-Temperature Synthesis and Structural Properties of PbMoO₄ Nanocrystals†

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Lead molybdate (PbMoO₄) 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 PbMoO₄ nanocrystals has been estimated as 100 nm.

Keywords: PbMoO₄, 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 nanotechnology¹⁻⁷. Lead molybdate (PbMoO₄) is a representative member of this family, and crystal structure of this compound^{8,9} is shown in Fig. 1. The structure is appeared as a framework formed by corner-linked PbO₈ polyhedrons and MoO₄ tetrahedra. The PbMoO₄ crystals possess optical band gap of 2.94 eV and show high chemical stability in the air. The well faceted plates of wulfenite, PbMoO₄, were found in several geological deposits and they are typically coloured with transition metal admixtures^{10,11}. Comparatively, synthetic PbMoO₄ crystals are colourless and they are transparent over spectral range of $\lambda = 0.4\text{--}5.5\ \mu\text{m}$ ^{12,13}. The PbMoO₄ crystals can be activated with lanthanoid and transition metals that promises for using of doped crystals as lasing hosts and luminescent materials^{12,14-17}. Previously, several methods were tested for preparation of the PbMoO₄ 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 conditions¹⁸⁻²³. In the present

Fig. 1. Crystal structure of PbMoO₄, space group $I4_1/a$

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study, the low-temperature precipitation method is developed to prepare the 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 oxides²⁴⁻²⁸.

EXPERIMENTAL

The 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 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 MoO_4^{2-} ions are absent at such pH to generate PbMoO_4 , the pellets of 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 (CuK_α radiation, Ni-filter, 5-60° 2 θ 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 PbMoO_4 is shown in Fig. 2. The major phase is PbMoO_4 as it was found by comparison with available structural data⁸. 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 $c = 12.107$ Å⁸. 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 PbMoO_4 . Unindexed peaks are marked with asterisks

Fig. 3. SEM image of the 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 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 PbMoO_4 -based reaction products when different doping agents are added into the solution²⁹⁻³². 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 PbMoO_4 nanocrystals.

TABLE-1 CHEMICAL COMPOSITION OF FINAL POWDER PRODUCT		
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 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 PbMoO₄ nanocrystals.

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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, *Moldovian 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).