



Effect of Hydrochloric Acid on Formation of Nanocrystalline Bismuth Phosphate Synthesized *via* Hot Injection Method

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An attempt was made to synthesize nanocrystalline bismuth phosphate *via* hot injection method. The effect of hydrochloric acid concentration used during the synthesis process was investigated. The acid acted as oxidizing agent in producing PH_3 , the phosphorus source which reacted with bismuth acetate in 1-octadecene solvent. The XRD patterns showed the materials crystallized in cubic phase when 2 M or 4 M HCl were used. Meanwhile, a minor impurity phase of BiOCl was detected when higher concentration of 6 M or 8 M HCl was applied. It has been demonstrated that the particle size of these single phase materials ranged 5-7 nm. Interestingly, different particle shapes were observed in the bismuth phosphate materials that were prepared using varied concentration of HCl during synthesis process *via* hot injection method.

Key Words: Nanocrystalline, Bismuth phosphate, Hot injection method.

INTRODUCTION

Bismuth-based materials have been widely investigated for their various applications such as catalyst, ionic conductor, ion sensor, humidity sensor and separating radioactive elements, *etc.*¹⁻⁶. Of interest bismuth phosphate materials were synthesized previously *via* solid state reaction, hydrothermal synthesis and ball milling^{4,7}. However, the solid state reaction and hydrothermal synthesis required high temperature and long synthesis duration of 2-10 days, leading to a costly production process. Meanwhile, impurities of zirconia were always detected in ball milling prepared samples. In addition, the resulted materials were in micro size when the synthesis methods mentioned above were applied⁷.

In the last decade, more afford were made to synthesize nano materials since they may offer anomalous and interesting properties such as large surface area which could be important for improved performance as catalysts and ionic conductors^{4,8}. Recently, good quality and homogenized nanocrystals of indium phosphide (InP) and cadmium selenite (CdS) were successfully prepared *via* hot injection method⁹⁻¹². Accordingly, this method required shorter duration and lower reaction temperature compared to the others. Besides, this method was relatively simple as it was based on the nucleation and growth of the nanocrystals in hot amphiphile solution soon after the injection of precursor source. Nevertheless, the feasibility of synthesizing nanocrystalline bismuth phosphate materials *via* this method is unknown. Besides, effect of acid used in the

synthesis process is remained unclear. Therefore, in this research, we took the challenge to synthesize nanocrystalline bismuth phosphate material *via* hot injection method. The effect of HCl used in synthesis process on formation of nanocrystalline bismuth phosphate was reported.

EXPERIMENTAL

All the materials were synthesized *via* hot injection method as described at elsewhere with minor modification⁹. Firstly, mixture of 1-octadecene (Aldrich, 90 %) and myristic acid (Sigma, 99 %) was heated at 60 °C until a homogeneous and clear solution was formed. Then, sufficient amount of bismuth triacetate (Aldrich, 99.99 %) was added into the solution. The mixture was reheated up to 190 °C. On the other hand, HCl was injected to Ca_3P_2 in order to produce PH_3 that was flown and reacted with the bismuth contained mixture. Then, the mixture was left overnight, followed by process of filtration and washing with cold ethanol. Finally, the product was dried in oven at 100 °C for 2 days. In order to investigate effect of HCl on formation of nanocrystalline bismuth phosphate, different concentrations (2-10M) of HCl were injected during the synthesis process.

The phase and crystallinity of the synthesized materials were examined using powder X-ray diffraction employing a Siemens D5000. A scan rate of 0.05° was applied to record pattern in 2 θ range of 10-90°. The images of the products were captured by the JEOL-JSM-6701F field emitting scanning

electron which was equipped with EDX software. The transmission electron microscopy images were taken using a JEOL-JEM-2100. The microscope was operated at an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

All the dried samples appeared as fine and shining powder. Figs. 1 and 2 show the XRD patterns of the synthesized materials *via* hot injection method by using different concentrations of HCl. Results showed that XRD patterns of the materials prepared using 2 M and 4 M HCl were well matching with that of reported $\text{Bi}_{3.69}\text{P}_{0.31}\text{O}_{6.31}$ (PDF file number 43-0455) which was prepared by melting mixtures of Bi_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$ at 1000 °C for 2 min and quenching in ice water. The reported material crystallized in cubic Fm3m phase with $A = 5.4716 \text{ \AA}$. On the other hand, it had also been demonstrated that a mixed phase material consisted of $\text{Bi}_7\text{PO}_{13}$ and sillenite phase was obtained in material with Bi:P composition of 12:1 after solid state reaction at 800 °C for 2 days⁷. Obviously, our current finding indicates that a single phase bismuth phosphate material in cubic phase could be produced at lower temperature of 190 °C, even though the crystallinity of the resulted material was considerably low.

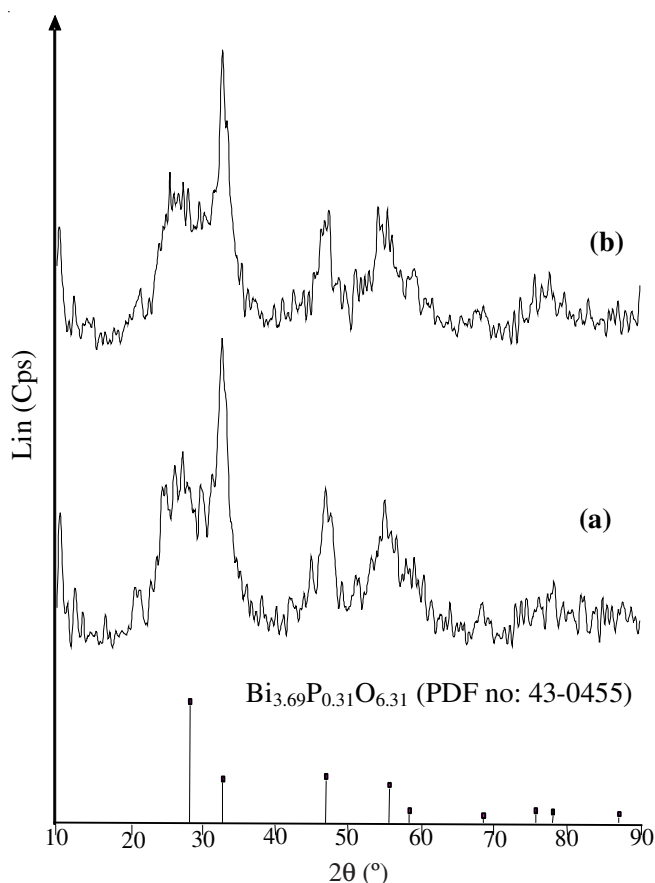


Fig. 1. XRD patterns of single phase bismuth phosphate prepared using (a) 2 M HCl; (b) 4 M HCl

Meanwhile, a tetragonal phase of BiOCl present as impurity when 6 M or 8 M HCl was used (Fig. 2). The phenomena implies the preference of bismuth precursor to react with the excess HCl rather than PH_3 , resulting in formation of

BiOCl . Apparently, a single phase material of BiOCl was detected in 10 M HCl prepared material. It is note-worthy that the crystallinity of the materials increased with increasing of concentration of HCl used in preparation procedure.

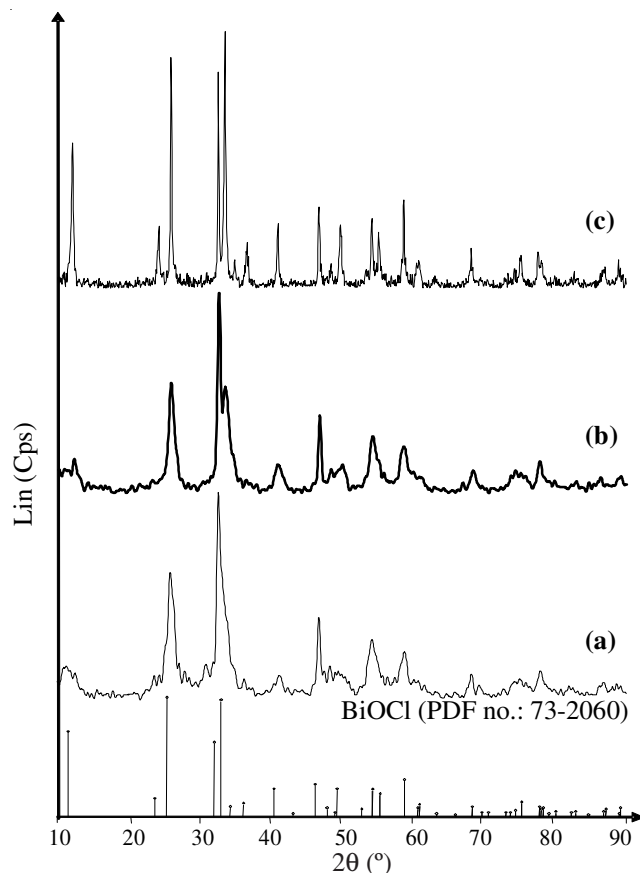


Fig. 2. XRD patterns of samples prepared using (a) 6 M HCl; (b) 8 M HCl; (c) 10 M HCl

FESEM micrographs of the synthesized bismuth phosphate materials are shown in Fig. 3. The surface morphology of these materials was homogenized and their particles were in spherical shape. It could be seen that the particles distribution of these materials was in bulky scale. For the mixed-phase materials prepared using 6 M and 8 M HCl, their particles were flower-like in shape. Meanwhile, BiOCl produced using 10 M HCl was inhomogeneous with the various particle shapes were observed. The observation strongly suggested concentration of HCl affected surface morphology of the materials formed.

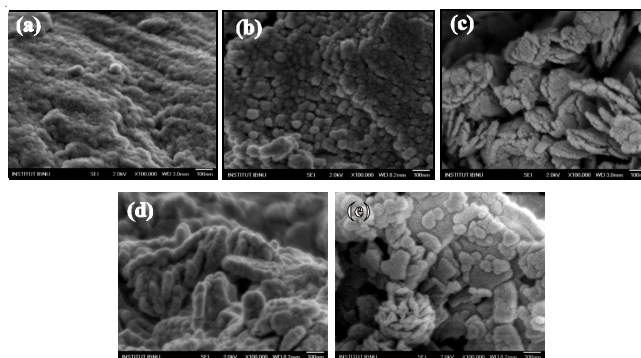


Fig. 3. FESEM micrographs of materials prepared using (a) 2 M HCl; (b) 4 M HCl; (c) 6 M HCl; (d) 8 M HCl; and (e) 10 M HCl

TEM images of the dispersed single phase bismuth phosphate materials were shown in Fig. 4. These materials were identified with mean diameters of 5 to 7 nm, indicating nanocrystalline bismuth phosphate materials were successfully synthesized *via* hot injection method. The synthesized materials using 2 M and 4 M HCl were fine and off-white in colour. Meanwhile, beige powder was obtained when 6-10 M HCl was used in synthesis process. In fact, the bismuth phosphate materials that were synthesized *via* high temperature solid state reaction and ball milling method were yellow in colour⁷. The discrepancies could be attributed to the formation of nanoparticles through hot injection method.

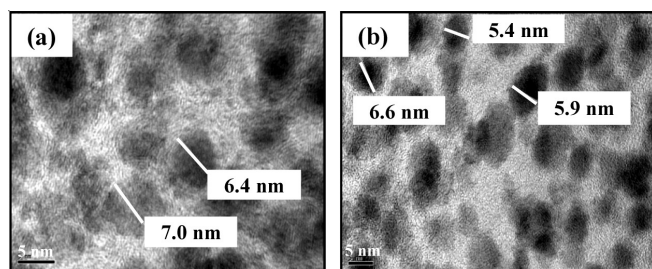


Fig. 4. TEM images of bismuth phosphate materials synthesized using (a) 2 M HCl and (b) 4 M HCl

On the other hand, elemental analysis using EDX revealed the ratios of Bi to P in the materials prepared were 9.7:1 and 10.5:1 using 2 M and 4 M HCl, respectively (Table-1). The results were in good agreement with that of suggested in pattern matching in XRD analysis where Bi:P = 11.9:1. However, further confirmation is needed for elemental composition determination by using other instrumental analysis such as ICP-MS. Besides, presence of both P and Cl was detected in 6 M and 8 M prepared materials, implying co-existence of bismuth phosphate and BiOCl as shown in the XRD results. Meanwhile, P was not found in 10 M HCl prepared material, strongly supporting our previous statement that claimed the formation of BiOCl. The decrease in P content with arising of HCl concentration indicates the lesser competency of PH_3 compared to HCl in the reaction with Bi precursor.

TABLE-1
ELEMENTAL ANALYSIS OF BISMUTH PHOSPHATE
MATERIALS PREPARED USING DIFFERENT
CONCENTRATIONS OF HCl

[HCl] /M	Bi (mass %)	P (mass %)	O (mass %)	Cl (mass %)	Bi:P ratio
2	96.64	1.48	1.88	-	9.7:1
4	96.07	1.36	2.57	-	10.5:1
6	92.64	1.23	2.14	3.96	-
8	90.81	0.96	2.20	6.03	-
10	87.74	-	2.41	9.85	-

Conclusion

Nanocrystalline bismuth phosphate materials have been synthesized *via* hot injection method. A single-phase material which crystallized in cubic phase was obtained in 2 M or 4 M HCl prepared materials. Particle size of these materials ranged 5-7 nm. Variation of particle shapes were observed when different concentrations of HCl were used.

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REFERENCES

1. C.K. Lee and C.S. Ong, *Solid State Ionics*, **117**, 301 (1999).
2. W.L. Liu, *J. Mater. Sci.*, **40**, 1827 (2005).
3. L. Dimesso, G. Gnappi and A. Montenero, *J. Mater. Sci.*, **26**, 4215 (1991).
4. F. Xue, H. Li, Y. Zhu, S. Xiong, X. Zhang, T. Wang, X. Liang and Y. Qian, *J. Solid State Chem.*, **182**, 1396 (2009).
5. M. Sheng, L. Gu, R. Kontic, Y. Zhou, K. Zheng, G. Chen, X. Mo and G.R. Patzke, *Sens. Actuators B*, **166-167**, 642 (2012).
6. G.J. Lumetta, J.C. Braley, J.M. Peterson, S.A. Bryan and T.G. Levitskaia, *Environ. Sci. Technol.*, **46**, 6190 (2012).
7. L. Wang, J. Tang and H. Yin, *Asian J. Chem.*, **25**, 2146 (2013).
8. Q.N. Pham, C. Bohnke, M.P. Lopez and O. Bohnke, *Chem. Mater.*, **18**, 4385 (2006).
9. L. Li, M. Protière and P. Reiss, *Chem. Mater.*, **20**, 2621 (2008).
10. L.J. Zhang, X.C. Shen, H. Liang, S. Guo and Z.H. Liang, *J. Colloid Interf. Sci.*, **342**, 236 (2009).
11. P.K. Jain, B.J. Beberwyck, L.K. Fong, M.J. Polking and A.P. Alivisatos, *Angew. Chem.*, **124**, 2437 (2012).
12. C. Banerjee, D.L. Hughes, M. Bochmann and T. Nann, *J. Chem. Soc., Dalton Trans.*, **41**, 7244 (2012).