The preparation of nano-crystallized cristobalite under hydrothermal conditions

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Crystalle silica experiences a series of polymorphic phase transformation from cristobalite to tridymite and to quartz upon cooling to room temperature at atmospheric pressure. Both the higher temperature polymorphs of cristobalite and tridymite are known to exist metastably at room temperature and atmospheric pressure [1, 2], although quartz is believed to be the thermodynamically most stable phase under such conditions.

Cristobalite particulates are produced in foundries, diatomaceous earth and ceramics and pottery industries [3]. They are also formed naturally during volcanic eruptions. Usually, cristobalite is thought to be formed at high temperature [4–6] and/or under high pressure [7, 8]. Co-doping with Na_2O and Al_2O_3, Chin-Hsiao Chao, *et al.* [9] successfully prepared crystalline phase of only β-cristobalite by sintering at 1100 °C for 48 hr.

Previously, a number of workers have found many intermediate phases before the formation of stable phase, quartz when amorphous silica is crystallized under hydrothermal conditions. Crorwin *et al.* [10] showed that either cristobalite or quartz was produced in a fixed time, and formation of quartz was favored by high pH. Campbell and Fyfe studied the rate of crystallization of amorphous silica in alkaline solutions, and found that the path of crystallization was always: amorphous silica → cristobalite → quartz [11]. That is to say, cristobalite should be crystallized together with quartz before amorphous silica is crystallized to be quartz completely.

It was well reported that quartz was prepared with alkaline solution by using amorphous silica as starting material under hydrothermal reaction conditions [12−15], and a lot of researches had been done on molecular dynamics simulations and phase transition of cristobalite [16–18]. In this paper, using amorphous silica as starting material, the preparation of nano-crystallized cristobalite, the influence of chemical solutions and reaction conditions on the crystallization of cristobalite under hydrothermal reaction conditions are investigated.

The starting material was the commercial silica gel (Nipsil-VN3, SiO_2 98.63 wt%, Nippon Silica Industrial Co. Ltd., Japan), which consisted of fine spherical particles with the average diameter of 18 nm. The specific surface area determined by the BET method was 160 m^2/g and the amount of absorbed water was 9.1 wt%. It was used for hydrothermal treatments without being dried.

Hydrothermal treatments were carried out in a Hastelloy-C lined autoclave with the inner volume of 20 ml. The amorphous silica was mixed with different chemical solutions of various concentrations and ultrasonically dispersed for 15 min. The autoclave was heated to the desired temperature at a heating rate of about 10 °C/min. and the charge of the autoclave was agitated during hydrothermal treatments with the autoclave rotating in the oven. After the hydrothermal treatments, the products were washed with distill water, ultrasonically dispersed in acetone, and then vacuum dried. The XRD patterns of the products were collected on a Rigaku RTP300 RC diffractometer with a diffracted beam monochromator of 40 kV, 100 mA. Typically, patterns were taken between 5 and 70° (2θ) with a step of 0.02°, and a scanning speed of 4°/min. The morphology was observed with a transmission electron microscope maker and model.

The kind of chemical solution has a great effect on the crystallization of cristobalite. When the amorphous silica was treated with KF, NaF and NaOH solution with different concentrations, respectively, the effectivity of chemical solution increased in order from KF, NaF to NaOH. When 1.0 g amorphous silica was treated with 15 ml 0.33 M chemical solution at 300 °C, as shown in Fig. 1, in NaOH solution, the amorphous silica was crystallized to be quartz, and in the KF and NaF solutions, the tetragonal and cubic phase of cristobalite was prepared respectively.

Using 1.0 g SiO_2 mixed with 15 ml 0.33 M NaF solutions as starting material, when the hydrothermal reaction was carried out at 200 °C for 24 hr, the amorphous silica could not crystallize to be cristobalite (see Fig. 2). Cristobalite could be prepared at 300 °C. When the amorphous silica was hydrothermally treated at 400 °C, it would be crystallized to be quartz.

The crystallinity of cristobalite increased with increasing the hydrothermal reaction time. Under the condition of 1.0 g amorphous silica mixed with 15 ml

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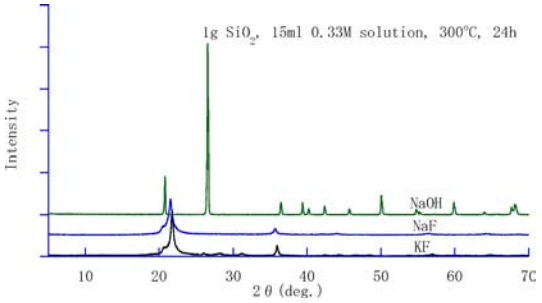

Figure 1 The influence of chemical solutions on the crystallization of critobalite.

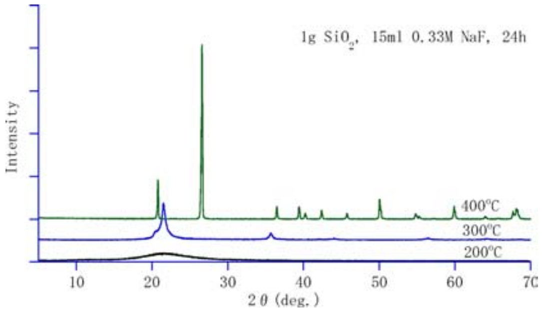

Figure 2 The influence of reaction temperature on the crystallization of critobalite.

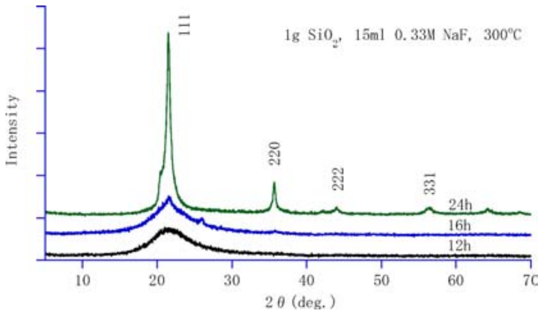

Figure 3 The influence of reaction time on the crystallization of critobalite.

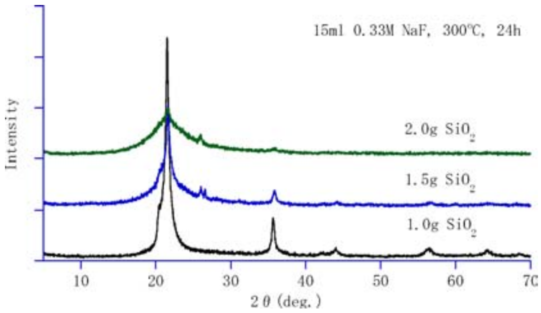

Figure 4 The influence of the amount of amorphous silica on the crystallization of cristobalite.

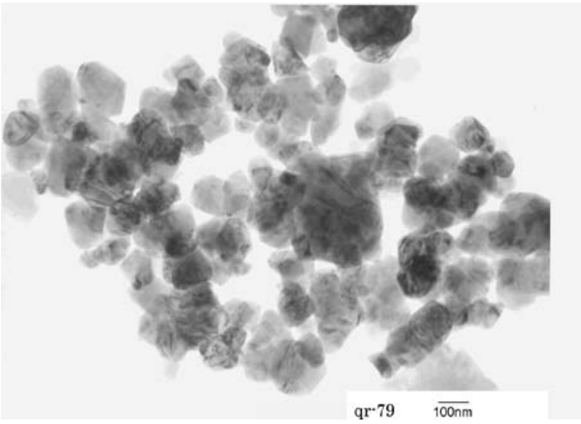

Figure 5 The TEM image of critobalite.

of 0.33 M NaF solution, the amorphous silica started to crystallize after being heated at 300 °C for 16 hr. The amorphous silica crystallized to be cubic phase of cristobalite perfectly at 300 °C for 24 hr, as shown in Fig. 3.

The crystallinity of cristobalite decreases with increasing the ratio of the amount of amorphous silica to the concentration of chemical solution. To keep the concentration of NaF solution constant, the amount of amorphous silica increased from 1.0 to 2.0 g, the crystallinity of product decreased as shown in Fig. 4. If the concentration of chemical solution was very high, the amorphous silica was crystallized to quartz quickly, and it was also difficult to get cristobalite. So the ratio of the amount of amorphous silica to the concentration of chemical solution should be adjusted according to the kind of chemical solution.

When the ratio of the amount of amorphous silica to the concentration of chemical solution is low, i.e. the amount of amorphous silica is comparatively small, the inner surface of autoclave becomes the main source of nuclei, the particle size of the products, which is formed on the innner surface and were large and aggregated. On the other hand, when the ratio is high, i.e. the amount of amorphous silica is comparatively large, the nuclei formed on the inner surface of amorphous silica and in the suspension, were small, due to the large amount of nuclei, and they were also aggregated because of their tight osculation.

After hydrothermal reaction, the autoclave was cooled down to the room temperature. According to the XRD patterns of the samples prepared at different cooling speeds, the later has an effect on the phase of cristobalite. High cooling speed benefits to get cubic phase of cristobalite.

Using amorphous silica as starting material, well-dispersed nano-crystallized cubic phase of cristobalite can be prepared under mild hydrothermal reaction conditions. Its Transmission Electron Microscope image is shown in Fig. 5. The hydrothermal conditions, such as reaction temperature, reaction time and the ratio of amorphous silica to the concentration of chemical solution have a great effect on the crystallization of cristobalite.

References

1. L. DUFFRÈNE and J. KIEFFER, *J. Phys. Chem. Solids* **59** (1998) 1025.
2. C. -H. CHAO and H.-Y. LU, *Mater. Sci. Eng.* **A328** (2002) 267.
3. D. R. HEMENWAY, M. P. ABSHER, L. TROMBLEY and P. M. VACEK, *Amer. Ind. Hyg. Assoc. J.* **51** (1990) 363.
4. T. KINGETSU, K. ITO, M. TAKEHARA and H. MASUMOTO, *Mater. Res. Bull.* **33** (1998) 731.

5. M. Y. A. MOLLAH, S. PROMREUK, R. SCHENNACH, D. L. COCKE and R. GÜLER, *Fuel* **78** (1997) 1277.
6. V. B. PROKOPENKO, L. S. DUBROVINSKY, V. DMITRIEV and H. -P. WEBER, *J. Alloys Compd.* **327** (2001) 87.
7. L. S. DUBROVINSKY, N. A. DUBROVINSKAIA, S. K. SAXENA, F. TUTTI, S. REKHI, T. LE BIHAN, GUOYIN SHEN and J. HU, *Chem. Phys. Lett.* **333** (2001) 264.
8. Y. TSUCHIDA and T. YAGI, *Nature* **347** (1990) 267.
9. CHIN-HSIAO CHAO and HONG-YANG LU, *Mater. Sci. Engng.* **A328** (2002) 267.
10. CORWIN, HERZOG, OWEN, YALMAN and SWINNERTON, *J. Amer. Chem. Soc.* **75** (1953) 3933.
11. S. CAMPBELL and W. S. FYFE, *Amer. Mineral.* **45** (1960) 464.
12. K. YANAGISAWA, Y. ZHU, A. ONDA and K. KAJIYOSHI, *J. Mater. Sci.* **39** (2004) 2931.
13. K. BYRAPPA and M. YOSHIMURA, "Handbook of Hydrothermal Technology," (Noyes Publications, William Andrew Publishing, 2001) p. 53.
14. J. F. BERTONE, JOEL CIZERON, RAJEEV K. WAHI, JOAN K. BOSWORTH and VICKI L. COLVIN, *Nano Lett.* **3** (2003) 655.
15. K. J. LEE, K. W. SEO, H. S. YU and Y. I. MOK, *Korean J. Chem. Eng.* **13** (1996) 489.
16. LUCAS DUFFRÈNE and JOHN KIEFFER, *J. Phys. Chem. Solids* **59** (1998) 1025.
17. KEIJI YAMAHARA, KEIJI OKAZAKI and KATSUYUKI KAWAMURA, *J. Non-Cryst. Solids* **291** (2001) 32.
18. T. KINGTSU, K. ITO, M. TAKEHARA and H. MASUMOTO, *Mater. Res. Bull.* **33** (1998) 731.

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