Preparation of Crystal Quartz by Hydrothermal Synthesis

Songxia Li, Siqi Wang, Qi Xue, Jin Zhang and Ping Fan

Abstract Adopting high-purified $SiCl_4$ as raw material and taking Na_2CO_3 as mineralizer, crystallized SiO_2 was prepared with hydrothermal process. Particularly, the effect of processing temperature, precursor concentration and pH on the crystallization of SiO_2 were taken into consideration. To analyze the growing mechanism, the structure and morphologies of hydrothermal product were studied with XRD and SEM. The results showed three factors, including synthesis temperature, precursor concentration and pH, influenced the crystallization and morphologies of crystalline SiO_2 significantly. Proper hydrothermal processing, 220 °C hydrothermal environment, 1.2 mol/L precursor, pH 10.5 and Na_2CO_3 mineralizer, resulted in 8 μm well-crystallized columnar grain crystal. The crystallization process of SiO_2 followed the "dissolution-precipitation" mechanism in the hydrothermal synthesis and contained the aggregation-growth.

Keywords Hydrothermal process · Crystallized SiO_2 · Precursor concentration Temperature · pH

S. Li (✉) · S. Wang · Q. Xue · J. Zhang · P. Fan
School of Materials Science and Engineering,
Southwest Petroleum University, Chengdu 610500, China
e-mail: lisongxiay@163.com

S. Wang
e-mail: 346806743@qq.com

Q. Xue
e-mail: qxue01@163.com

J. Zhang
e-mail: jzhang@swpu.edu.cn

P. Fan
e-mail: 214692970@qq.com

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Introduction

As for the typically optical characters, thermal stability, inertia and irradiation performance, transparent SiO_2 was widely used in semi-conduct and astronavigation [1]. Limited by the shortage of raw material, smelting crystal was replaced by crystallized SiO_2 gradually.

The high-purity SiO_2 can be roughly divided into two categories: the inartificial one and the synthesis one, for which the former was purified with silica sand. Meanwhile, there were two ways to synthesize high-purity SiO_2: dry processing and wet processing (precipitation and hydrothermal). Wet processing was prior to the dry method in cost and security. The less soluble and immiscible material in closed container would be soluble if high temperature or high pressure, or both, were applied in the vessel which was stuffed with water, then material went through dissolution-crystallization [2]. In 1990s, researchers made SiO_2 by hydrothermal method which cost less, however, crystallized well, agglomerate slightly. This way was introduce to industrial crystal production [3]. With the research and development of hydrothermal processing, it became a competitive preparation processing to obtain oxide powders [4]. However, reports of the hydrothermal SiO_2 were mainly about crystalline ones rather than the powder ones.

In this paper, crystallized SiO_2 was prepared with hydrothermal processing by adopting high-purity $SiCl_4$ as raw material and taking Na_2CO_3 as mineralizer. The effects of these factors, including synthesis temperature, precursor concentration and pH, on the crystallization, particle the size and profile of SiO_2 were specifically studied. Based on the data, the growing mechanism was discussed.

Experimental

Rectification $SiCl_4$, $NH_3{\cdot}H_2O$(AR), Na_2CO_3 (AR), NaOH(AR) and deionized water were used in the experiment.

(1) Preparing crystal quartz with hydrolyzed $SiCl_4$. Firstly, $SiCl_4$ was hydrolyzed in $NH_3{\cdot}H_2O$. Then purging the precursor and drying it in 90 °C heating furnace. The certain pH liquor, stuffed reactor 80% volume, was consisted of Na_2CO_3 and hydrolyzed $SiCl_4$ which acted as mineralizer and precursor respectively. The reactor was heated under 140, 180, 220 and 260 °C respectively for a period of time then chilled in room temperature. Finally, cleaning the products with 1wt% hydrochloric acid and drying the sample under 90 °C again.

(2) Preparing the crystal quartz with the remnant hydrothermal liquor. To observe the crystallization, we vapored the remnant hydrothermal liquor to enrich

solution. The hydrothermal condition applied in the reactor as follows: 220 °C temperature, 30 h reacting time, pH 10.5 and 80% filling. Finally, cleaning the products with 1wt% hydrochloric acid and drying the sample under 90 °C.

(3) Analyzing the structure of specimen with XRD(DX-2000); Observing the micro-profile of sample by SEM(TM-1000).

Results and Discussion

Effect of Temperature on the Hydrothermal Reaction. Temperature was directly related to the powder quantity in practically manufacture was essential within the factors working on the hydrothermal system. Therefore 4 different temperature, 140, 180, 220 and 260 °C, were applied in the experiment. Figure 1 showed the XRD pattern of product derived from those series of hydrothermal temperature. When produced at 100 °C, the diffraction peaks of α-SiO_2 (PCPDF 65–0466) began to be detected. The diffraction peaks, however, showed typical characteristics of amorphous as they were lower and broader. Increasing the processing temperature up to 140 °C, the diffraction peaks of crystal α-SiO_2 were stronger and narrower. It meant that the crystallinity of the α-SiO_2 were better and higher than that of the 100 °C -produced sample. Further increasing the temperature, the diffraction pattern showed the similar multiple orientations of (100), (101), (110), (112), and (211) with the improvement of the intensity. It should be noted that when prepared at 260 °C, the intensity of the diffraction peaks decreased in comparison with the 220 °C -produced sample. Consequently, the crystal quartz grew in size and perfected in crystallization with rising temperature. But the size of crystal were thinned which resulted in the impairment of diffraction peak.

The morphologies of crystal quartz synthesized with different temperature were shown in Fig. 2. Increasing temperature, the boundary of quartz grain became sharp and clear, and the quartz revealed obvious columnar outline and perfected

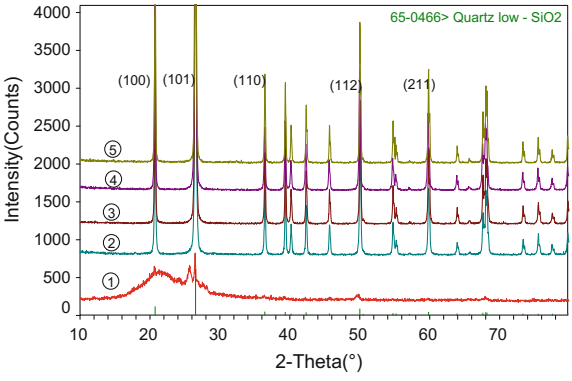


Fig. 1 XRD patterns of SiO_2 crystal obtained from different reaction temperature. ① 100 °C, ② 140 °C, ③ 180 °C, ④ 220 °C, ⑤ 260 °C

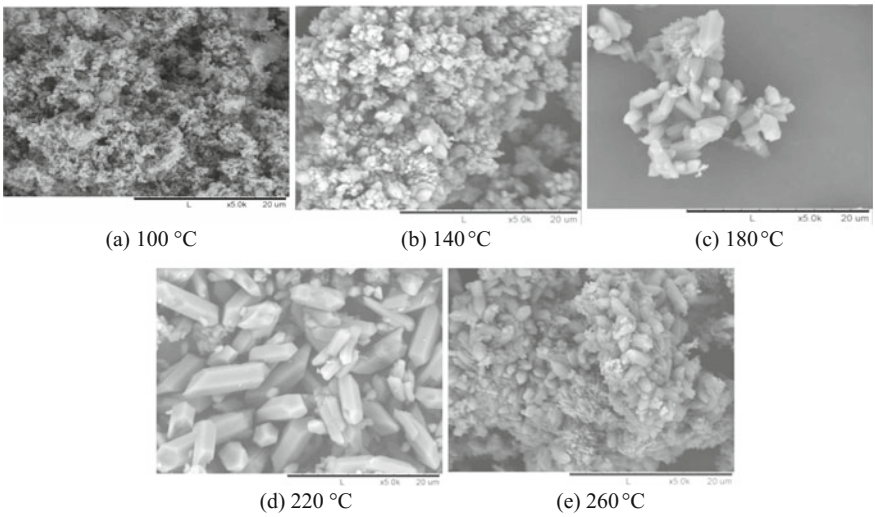


Fig. 2 SEM images of SiO_2 crystal obtained from different reaction temperature. **a** 100 °C **b** 140 °C **c** 180 °C **d** 220 °C **e** 260 °C

crystallization. Large bulk crystal SiO_2 enriched. On the other side, the thinned SiO_2 particles aggregated seriously as temperature was more than 220 °C. It can be interpreted as follows: rising temperature accelerated the dissolve rate of precursor and benefited the free energy of hydrothermal system, which attributed to the diffusion of Si–O directly and led to nucleation outweighing growth of particles indirectly [5]. All in all, 220 °C was the proper temperature for hydrothermal processing.

Effect of Precursor Concentration on the Hydrothermal Reaction. It was reported that the precursor concentration exerted a significant influence on the hydrothermal reaction [6]. To explore the influence of precursor concentration on the crystallization of quartz, different utility of precursor were adopted in the experiment with 30 h 220 °C treatment. The morphologies of products for each precursor concentration, were shown in Fig. 3. The crystal quartz seemed to be columnar shape as precursor concentration ranging from 0.8 to 1.4 mol/L. But the surface of the sample, 0.8 mol/L precursor concentration, disclosed numerous defects which may result from inadequate precursor. The crystal quartz particles thinned and aggregate seriously as precursor concentration ranging from 1.6 to 1.8 mol/L. And the outline of these particles was spherified. The reason for the phenomenon above was follows: Precursor concentration increase accelerated the growth rate of quartz. However, increasing precursor concentration was corresponded to rising viscosity of the liquid which impeded the diffusion of Si–O and impaired the dissolution of precursor, and all of these lessen the growth rate of quartz.

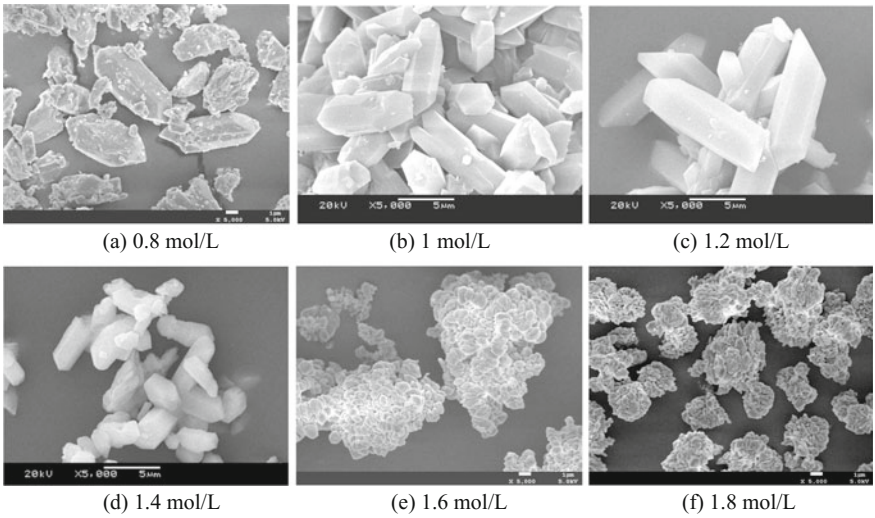
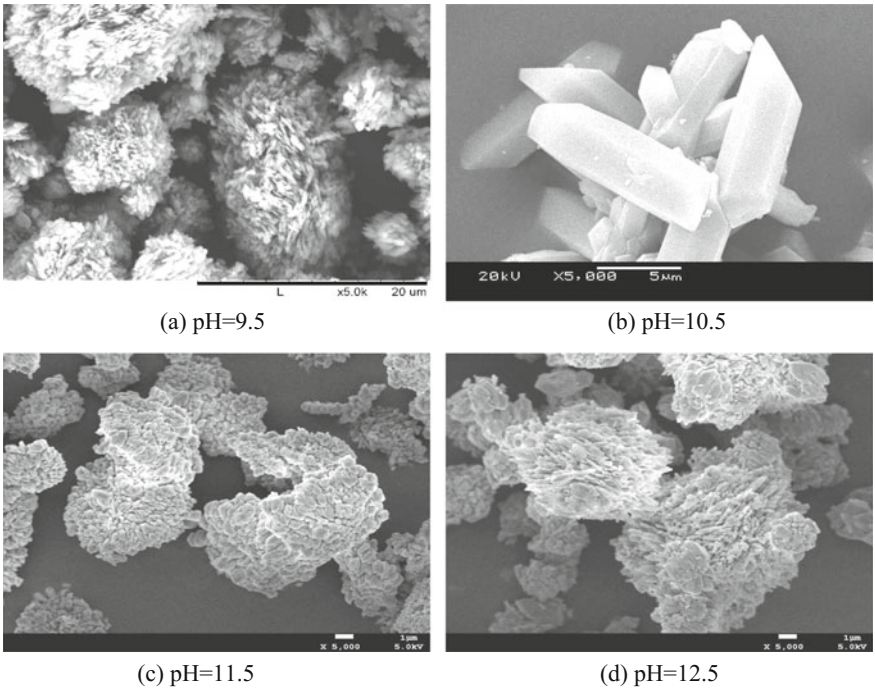


Fig. 3 SEM images of quartz prepared with different precursor concentration

Effect of pH on the Hydrothermal Reaction. The crystal SiO_2 was prepared by taking 1 mol/L precursor, stuffing 80% volume, using Na_2CO_3 as mineralizer in the experiment to find out proper pH. The specimen was accustomed to 30 h 220 °C heat and the adopted pH was set as pH9.5, pH10.5, pH11.5 and pH12.5, respectively. The morphologies of each product were scanned as Fig. 4. Low pH led to the weakness of SiO_2 solubility which resulted in thinning and pinning particles [7]. On the other side, high pH led to the obvious increase of precursor dissolution, thus the viscosity of liquid was improved, which greatly impacted on the crystallization of quartz [8]. Therefore pH needs to be controlled about 10.5.

Discussion on Crystallization Mechanism. There were two theories about the crystallization mechanism of hydrothermal processing, in situ crystallization and dissolution-crystallization. HERTL [9] prepared $BaTiO_3$ who considered crystal $BaTiO_3$ followed in situ crystallization. However, PINCELOUP [10] and Xu Hua-rui [11] who studied on the $BaTiO_3$ powder put forward dissolution-crystallization theory, and pointed out that bottleneck structure of particle was essential to the dissolution-crystallization progress. Weizhuo Zhong [12] insisted that the precursor dissolve in alkaline solution formed tetrahedron $Si(OH)_4$ and it nucleated and grew up with the supersaturation, which was obviously in favor of dissolution-crystallization theory. Moreover, the bottleneck theory, in Fig. 5, supported that crystallization just followed the rule of dissolution-crystallization. Otherwise, according to the Fig. 3a, b, the columnar quartz was derived from the gathering of amount small particles which made sense that aggregation growth also existed during the crystallization [13].



(a) pH=9.5 (b) pH=10.5

(c) pH=11.5 (d) pH=12.5

Fig. 4 SEM images of quartz prepared with different pH

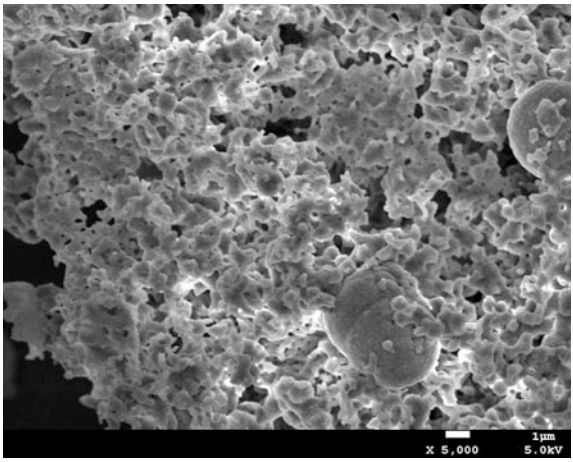


Fig. 5 SEM image of quartz prepared with remnant liquor

Conclusions

1. There are three factors, including synthesis temperature, precursor liquor concentration and pH, significantly involve the particle size and profile of crystalline SiO_2. Rising temperature was contributed to the size of columnar crystallized quartz. The particle size decreases and crystallization becomes non-columnar while the temperature is below 220 °C. The well-crystallization concentration of precursor is about 1.2 mol/L. Lower precursor concentration leads to defect of crystallization while higher concentration results in agglomeration. It is critical to keep the hydrothermal liquor pH 10.5. More or less pH will impair the crystallization of quartz and turn into small columnar crystallized quartz.
2. Taking Na_2CO_3 as mineralizer, hydrolyzing $SiCl_4$ as "Si source", the crystal quartz grows up under 140 °C or above. The growth of crystal follows the "dissolution-crystallization" rules, and sort of agglomeration either.

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References

1. D.B. Jin, X.M. Zhang, W.W. Zhou. Study on Processing Technology of High Purity Quartz. J. Chin. Nonferr. Metals Ind. **4**, 44–48 (2004)
2. W.E. Shi, C.T. Xia, B.G. Wang, et al. Development and application of hydrothermal method. J. Inorg. Mater. **11**, 193–206 (1996)
3. Byrappa K, Yoshimura M. *Handbook of Hydrothermal Technology* (William Andrew, 2012)
4. Yanagisawa K, Zhu Y, Onda A, et al. Hydrothermal synthesis of mono-dispersed quartz powders. J. Mater. Sci. **39**, 2931–2934 (2004)
5. B.C. Zhang, Q. Xue, J. Zhang et al, Synthesis of high purity micron-sized quartz from SiCl4 by hydrothermal method. Inorg. Chem. Ind. **45**, 33–35 (2013)
6. R.R. Xu. *Inorganic Synthetic Chemistry* (Higher Education Press, Beijing, 1991) pp. 221–223
7. X. Chen, X.Y. Qu, L.W. Qiu et al., Hydrothermal experiment research on characteristics and mechanisms of quartz dissolution. Bull. Mineral. Pet. Geochem. **34**, 1027–1033 (2015)
8. S. Nangia, B.J. Garrison, Reaction rates and dissolution mechanisms of quartz as a function of pH. J. Phys. Chem. A. **112**, 2027–2033 (2008)
9. W. Hertl, Kinetics of barium titanate synthesis. J. Am. Ceram. Soc. **10**, 879–883 (1988)
10. P. Pinceloup, C. Courtois, J. Vicens et al., Evidence of a dissolution—precipitation mechanism in hydrothermal synthesis of barium titanate powders. J. Europ. Ceram. Soc. **19**, 973–977 (1999)
11. H. Xu, L. Gao, New evidence of a dissolution—precipitation mechanism in hydrothermal synthesis of barium titanate powders. Mater. Lett. **57**, 490–494 (2002)
12. W.Z. Zhong, G.Z. Liu, S.K. Hua et al., Formation mechanism of the growth forms of SiO_2 and SnO_2 under hydrothermal conditions. J. Synth. Cryst. **23**, 1–7 (1994)
13. W.E. Shi, C.T. Xia, B.G. Wang, et al. Aggregation growth in ceramic powders prepared by hydrothermal method. Sci. Chin. (Series E) **27**, 126–133 (1997)