行政院國家科學委員會補助專題研究計畫
出席國際會議心得報告

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計畫類別：☑個別型計畫　　□整合型計畫

計畫編號：NSC 90－2116－M－002－008

執行期間： 90 年 8 月 1 日至 91 年 9 月 30 日

計畫主持人：黃武良

本出席國際會議心得報告包括以下應繳交之附件：

☑會議發表論文一份

執行單位：國立台灣大學地質科學系

中 華 民 國 91 年 8 月 14 日

行政院國家科學委員會專題研究計畫
出席國際會議心得報告

超高壓礦物的退向變質反應動力學之研究

計畫編號：NSC 90-2116-M-002-008
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出席第五屆國際熱水溶液反應(solvo-thermal reaction)會議報告

會議簡介及參加過程

國際熱水溶液反應會議的主要目標是集合學術界及工業界致力於熱水溶液反應的技術及科學的研究，並提昇此方面的研究在遠期或近期工業上或地質學上之應用。第五屆國際熱溶液反應會議於今年(2002)七月二十二日至二十六日在美國 East Brunswick, New Jersey 舉行。本會議是由美國結晶生長協會、美國陶瓷學會、美國地球物理學會、材料學會等合辦。全世界十幾國學者專家與會，共發表 127 篇論文，本人受邀與會發表論文，題目為「Nanoquartz : Synthesis in Neutral Solution at High Pressure」。專題研討會主題包括：(1)Kinetics and diagnostic methods; (2)Thermodynamics, solubility, phase diagrams and modeling; (3)Waste processing; (4)Organic, organometalic and Metallo-organic synthesis; (5)Geothermal/Geological processes; (6)Inorganic materials synthesis and processing; (7)Novel materials; (8)Single crystal materials; (9)Film growth; (10)Nanomaterials 等。其中本人參與的主要包括：Geothermal/Geological processes、Nanomaterials、Inorganic materials synthesis and processing。

與會心得

(一)Geothermal and Geological processes

本 session 主要以礦物在高溫高壓下的相變及化學反應動力學為主。其中重要的研究成果包括 chlorite 在熱水溶液中之穩定性的研究(S. Aja)，以及 cordierite 在熱水及 CO_2 環境下的平衡關係(A.V. Ganesha et al.)。此等研發的成果有助於吾人了解熱水換質作用及高溫接觸變質作用下礦物的轉換機制。

(二)Nanomaterials

本 session 研討奈米材料的合成與性質，是為本會議最熱門的議題，其中不乏創新的發現，例如：

(1)以微波熱水合成奈米級的 α-Fe_2O_3，做為紅色的顏料(K. Katsuki and S. Komarneni)。

(2)以熱水法處理氧化鈦膠體做為太陽能電池的材料(Tomiha et al.)。

(3)熱水法合成超細的氧化物粉末的晶形與粒度的控制研究(Burukhin et al.)。

(4)在超臨界條件下，以熱水法合成奈米級的金屬氧化物(T. Adschiri)。

(5)在超高壓下合成奈米多晶質石英(W. L. Huang)。

(6)熱水條件下合成奈米材料(B. Gersteu et al.; B.A. Korgel et al.; H. Wakayama et al.; S. Komarneni)。

本研討會的成果顯示高壓高溫熱水法在奈米材料的合成上有相當重要地位，國內在此方面研究甚少，未來國內的礦物學及實驗岩石學的專家應可往此方面發展。

(三)Iorganic material synthesis and processing

本 session 為本國際會議傳統性的主題研究，目前甚多工業用的材料乃由熱水法合成，其中最著名的是石英單晶的合成。本研討會中發表含 Ge 的石英的合成及性質，Ge-quartz 的特殊性質將擴展石英做為壓電材料的應用(V.S. Balitsky et al.)；本 session 中另一重要的研究，是以熱水法合成 Oxycarbonate 的超導體性質(K. Byrappa et al.)，以及微波熱水法合成工業用 silica 材料(B.L. Newalkar et al.)。在結晶生長技術方面，在 Heat Field Rotation 條件下，以熱水方法生長單晶，已開始引起注意。

建議

熱水反應合成材料廣泛地受到工業界的重視，高溫高壓熱水合成研究最早應用於礦物學及實驗岩石學的合成及相變化研究，近年來已廣泛地應用在氧化物單晶或多晶質粉末、陶瓷、沸石等的合成。此等技術在地質科學界相當普遍。建議國內地質科學界同材料界密切合作，進行跨領域的合作研究。此等研究成果不但在探討地球內部物理化學現象具有相當學術價值，並且可能在材料或奈米技術上有實際的貢獻。

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JOURNAL OF CRYSTAL GROWTH

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In Press July 2002

Nanoquartz: synthesis in neutral solutions at high pressures

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Received 18 June 2002; accepted 1 July 2002
Communicated by M. Schieber

Abstract

Polycrystalline quartz was synthesized from amorphous silica with sea- and distilled-water at temperatures from 50°C to 450°C, and pressures from 50 to 3000 MPa. The results show that pressure enhances significantly the transformation rates of amorphous silica to quartz, thus shortening the time for the grain to grow before completion of the transformation. This leads to the finding of a new condition to synthesize polycrystalline nanoquartz crystals in near-neutral solutions at pressures above 500 MPa. The minimum average grain size of single-phase nanoquartz synthesized so far is 80 nm (with $\sigma = 0.2$ nm) at 300°C, 2500 MPa (2.5 GPa) and 20 h. The study concludes that well crystallized nanoquartz powder with desired grain sizes may be synthesized by selecting properly the experimental conditions, in particular, the pressure.

PACS: 61.46.+w; 61.50.Ah; 61.82.Rx; 64.40.+i

Keywords: A1. Silica transformation; A2. Nucleation and growth; B1. Coesite; B1. Nanoquartz; B1. Polycrystalline quartz

1. Introduction

The importance of nanocrystals in the study of fundamental solid-state science and its applications has been well recognized [1]. The physical and chemical properties of nanocrystals have been reported to vary significantly with the particle size [2]. Rios et al. [3] in the study of the polymorphic transition between α and β nanoquartz from agate samples revealed that the excess entropy of the nanoquartz crystals is significantly different from that of larger quartz crystals. Quartz is by far the most widely used crystals for resonant frequency transceivers and other applications; its size-dependent piezoelectric property, if exists, should be of great interest to many researchers. Although the study of nanoquartz is still of academic interest, its significance as important industrial material may be realized as soon as its phase behavior is well understood.

In order to characterize the size-dependant phase behavior of quartz, crystals of a variety of sizes, particularly, in the nanometer range should first be available. Rios et al. [3] used natural nanoquartz as the starting material for studying phase behavior while J. Bertone (http://www.nano-net.rice.edu) used synthetic nanoquartz in the study of compressibility as a function of size.

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0022-0248/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-0248(02)01589-0

Although the natural sample can be used for studying the properties of the nanoquartz, its application is hindered by the difficulty in obtaining the samples with the desired particle size and size distribution for a specific study. The necessity and importance in developing synthetic techniques to produce nanoquartz is increasingly recognized.

Nanoscale, non-crystalline silica has been synthesized and widely used as materials with a variety of applications [4]. Syntheses of large single crystals of quartz [5–8] and polycrystalline quartz in the micrometer range [9–14] are also well studied. However, the synthesis of polycrystalline quartz crystals of nanometer size, to the author's best knowledge, has not been officially reported although the nanoquartz crystals have been synthesized in alkaline solutions under hydrothermal conditions by L.C. Lee (pers. comm.), and independently by J. Bertone. These studies claimed the synthesis of nanoquartz crystals under conditions similar to those of other previous studies [15–17]. The present study reports the experimental conditions, the morphology and size distributions of the synthetic nanoquartz crystals in near-neutral solutions and at high pressure up to 3000 MPa.

2. Experimental procedures

The starting material used in the experiments is a natural diatomite (amorphous silica, opal-A) from Monterey Formation, California. The sample was purified using dilute HCl to remove the trace amount of carbonates. The experimental solutions used were mainly seawater with some exceptions where distilled water was used. High-pressure experiments were performed using the piston-cylinder apparatus, similar to that described by Boyd and England [19], using half-inch diameter pressure vessels. The starting sample powder (4–6 mg, <40 μm grain size) with seawater at fluid/solid mass ratio of 1:1 was electric-arc sealed in a gold capsule (4 mm length, 2 mm OD, and 0.127 mm wall thickness). Temperatures measured with chromel–alumel thermocouples, were precise to +3°C and are considered accurate to +10°C. The furnace assemblies were constructed from graphite, talc and pyrophyllite. All runs were brought to a final pressure with the "piston-out" [19]. The pressures reported are nominal, and are considered accurate to +5 percent. Experiments at pressures of 200 MPa and below were performed in cold-sealed pressure vessels of standard size [18].

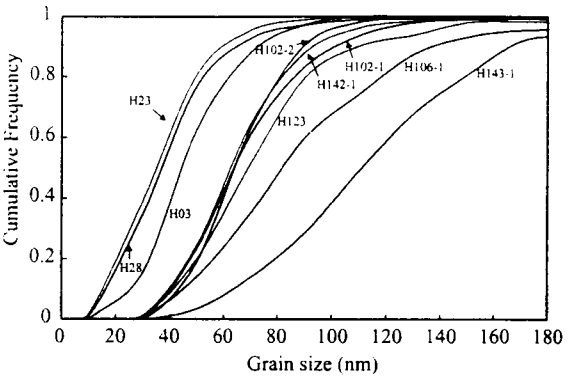

Fig. 1. Size distribution of nanoquartz grains synthesized at a variety of conditions. Each curve was marked by a run number: H123 (450°C, 500 MPa, 2 h, $\xi = 0.9$); H28 (300°C, 1500 MPa, 5 h, $\xi = 0.67$); H03 (400°C, 1000 MPa, 5 h, $\xi = 0.79$); H142-1 (450°C, 1500 MPa, 1.2 h, $\xi = 1$); H102-1 (300°C, 2500 MPa, 20 h, $\xi = 1$); H102-2 (300°C, 2500 MPa, 20 h, $\xi = 1$, distilled water); H123 (450°C, 500 MPa, 2 h, $\xi = 0.9$); H143-1 (450°C, 3000 MPa, 0.5 h, $\xi = 1$). All runs except H102-2 were done in seawater. Abbreviation: h, run duration in hours; ξ, extent of amorphous silica to quartz transformation.

Grain sizes were measured using SEM photographs of the run products. The outlines of the grain for each sample were manually traced on transparent paper from the SEM photographs and then scanned and digitized. The grain sizes and aspect ratio of the samples from all the experiments were determined from the grain outlines using an image analysis software, ImageTool 2.0, developed by the University of Texas Health Center, San Antonio. The calculated Feret diameters of the grains were statistically analyzed using Microsoft Excel. The average diameter and size distribution were plotted in Fig. 1.

3. Experimental results and discussion

The results reveal a dramatic pressure effect on the transformation rate, which increases approxi-

mately by five orders of magnitude as pressure increases from 50 to 3000 MPa at 400°C. At a pressure of 300 MPa or higher, amorphous silica transforms directly into quartz without intermediate cristobalite. It is of interest to note that quartz, instead of coesite, nucleated and grew metastably at pressures in the coesite stability field [13] at temperatures below 450°C (run H103 in Fig. 1). This is consistent with the previous observation that quartz is an intermediate, metastable phase during the amorphous silica to coesite transformation at 450°C and 3000 MPa [23]. The results obtained from the limited amounts of data also show that the transformation rate and grain sizes are similar in seawater and distilled water (e.g. Runs H102-1 vs. H102-2 in Figs. 1 and 2A).

Most polycrystalline quartz crystals synthesized at high pressures (> 500 MPa) show average grain sizes ranging from 50 to 100 nm (Fig. 1) and aspect ratio from 1.31 to 1.64. They appear a variety of morphologies: anhedral, equi-dimensional shape for those grown at low temperatures (<250°C); quartz crystals synthesized at higher temperatures are subhedral to euhedral, and become more euhedral with increasing temperature and run time, suggesting the increase of crystallinity (Fig. 2). The larger grains and better crystal form synthesized at low pressures (< 500 MPa) are attributed to the higher temperatures and longer time required for the transformation. For the same temperature and run duration, the crystal form may be more euhedral at higher pressure.

The increase in the observed overall transformation rate with pressure is attributed more to the fast nucleation than the growth. The calculation of nucleation rates using the observed transformation

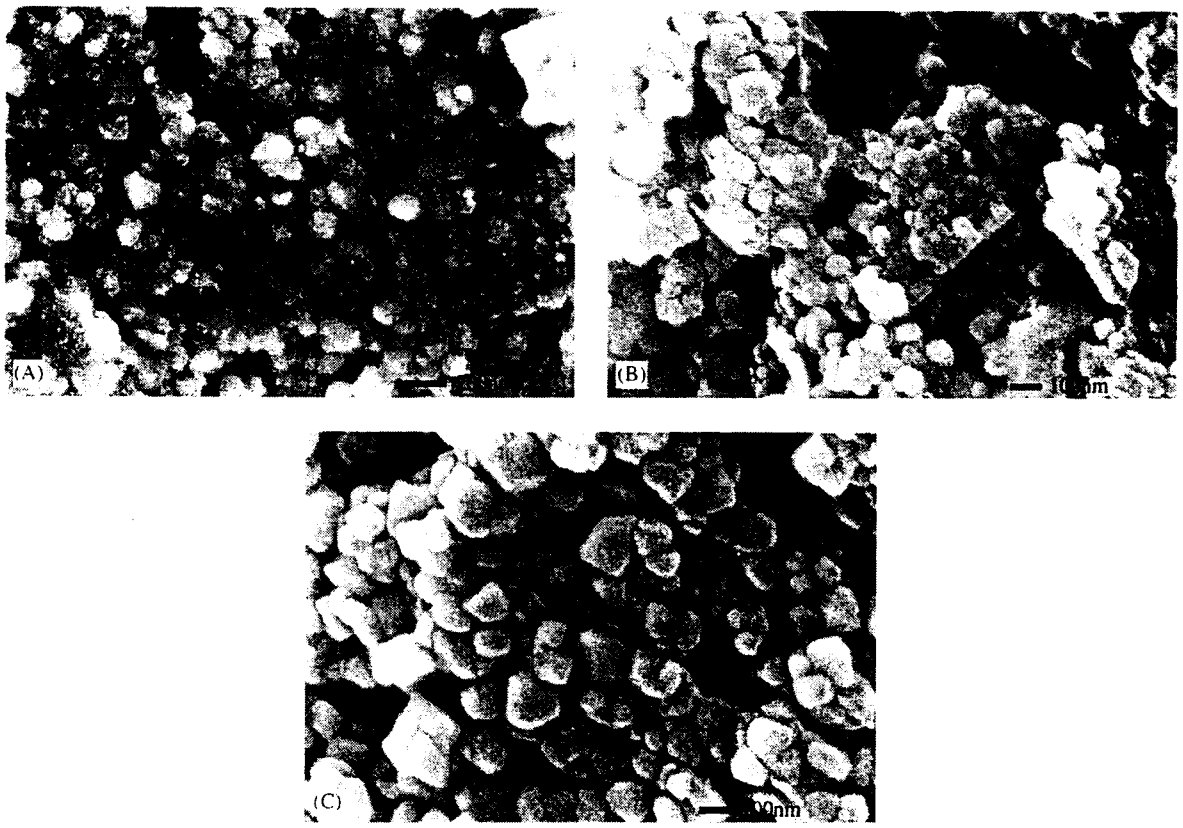

Fig. 2. SEM diagrams showing morphology nanoquartz synthesized at different temperature: (A) 300 C, 2500 MPa, 20 h (H102-1); (B) 400 C, 1000 MPa, 5 h (run H03); (C) 450 C, 500 MPa, 2 h (run H123). The scale bars for (A) is 200 nm, and for (B) and (C) are 100 nm.

and growth rates fitted to the rate equation for the grain-boundary nucleation and growth transformation [13] reveals that the pressure can significantly enhances both the nucleation and growth rates. It shows that the pressure effect is stronger on the nucleation than the growth. For instance, the nucleation rate increases by two orders of magnitude while the growth rate increases by only one order of magnitude as the pressure increases from 100 to 200 MPa at 400°C. The increase in the observed overall transformation rate with pressure is attributed more to the fast nucleation than the growth. It is generally believed that the particle size of neoformed crystals depends on the relative rates between nucleation and growth; the higher the nucleation rate relative to growth rate, the smaller the crystals formed. This has been confirmed by the SEM observations, which show that grain size indeed decreases significantly with increasing pressures. We have obtained so far the smallest grains (~80 nm) with complete transformation under conditions of 300°C, 2500 MPa and 20 h in near-neutral solutions (either seawater for run 102-1 or distilled water for run H102-2, Figs. 1 and 2A). Similar grain size (~100 nm) with complete transformation was obtained under higher-temperature conditions of 400°C, 2500 MPa and 1 h (run H106-1, Fig. 1). The runs at higher temperature (400°C) require only shorter time to complete the transformation, and therefore yield similar grain size as that at low temperature (300°C) even the growth rate is faster. This interpretation has been confirmed by other high-pressure experiments (Fig. 1). Quartz crystals with nanometer size (~50, 60 and 85 nm) were also synthesized, respectively, at three conditions (Fig. 1): (1) 300°C, 1500 MPa, 5 and 10 h (runs H28, and H23); (2) 400°C, 1000 MPa and 5 h (run H03); and (3) 450°C, 500 MPa and 2 h (run H123). However, the incomplete transformation of these three runs implies that the grains may continue to grow significantly until the completion is reached.

Similarly, the formation of nanoquartz crystals observed in alkaline solutions may also be attributed to the rapid transformation in alkaline solutions [15–17]. The higher transformation rates in both cases are believed to result from the higher degrees of silica supersaturation of solutions relative to quartz. The increase in solubility difference between quartz and amorphous silica with increasing pressure or hydroxyl ion concentration [28,16] accounts for the supersaturation. The relative slow transformation in neutral solutions at low pressures requires higher temperatures or longer time to complete the transformation and, the grain can therefore continue to grow to larger size and more euhedral shape. In contrast, the faster transformation in neutral solutions at higher pressures or in alkaline solutions requires only lower temperatures or shorter duration to complete the transformation, which leads to the smaller quartz grain. The present study suggests that the optimum conditions to grow polycrystalline quartz with nanoscale grain sizes and better crystal shape or crystallinity may be found by proper selections of experimental conditions, including the solution pH, temperature, and particularly pressure. Our future research effort focuses on the search for the conditions to grow nanoquartz with smaller particle size, and more uniformed particle distribution. This probably requires experiments in alkaline solutions at high pressure.

4. Conclusions

The present study reveals a new experimental condition, which synthesizes single-phase polycrystalline quartz crystals with average grain size as low as 80 nm from amorphous silica in near-neutral solutions at high pressures. In contrast, the quartz crystals synthesized at similar conditions but lower pressures have much larger size. This contrast is consistent with the observation that pressure enhances the nucleation rate more than the growth rate. The awareness of the pressure effect is useful for the present work and in the future study in search for the optimum conditions to synthesize well crystallized nanoquartz powder with uniform, desired grain sizes by selecting properly experimental conditions, including the solution composition, temperature and, in particular, the pressure.

5. Uncited references

[20,21].

Acknowledgements

The author wishes to thank Mr. Allen Hsu for his assistance in the laboratory. The research was supported by the Earth Sciences Section, National Science Council of ROC under grant nos. NSC 89-2116-M-002-055 and 90-2116-M-002-008.

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