THE STUDY ON THE EFFECTIVE FACTORS OF HYDROTHERMAL SYNTHESIS IN PREPARING HIGH QUALITY CRYSTALLINE α-QUARTZ POWDERS

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Abstract – In this study powders of high quality crystalline α-quartz were prepared by hydrothermal synthesis and parameters related to the preparation of the material were investigated. The degree of face development of the α-quartz crystal depended on the relative growth rates of a particular form that varies considerably with the degree of supersaturation, reaction temperature, concentration of mineralizers, and the amount of seed crystals in the feedstock. In the temperature range of 240-450°C and the pressure range of 100-300 atm, alkali hydroxides and alkali halides such as KOH, NaOH, Na₂CO₃, KF, and NaF were found to be the effective mineralizers. As the concentration of mineralizers increased, the particle size of crystalline α-quartz powders became smaller at lower reaction temperatures. The fractional size distribution of synthetic crystal powders depended on the hydrothermal conditions. As the reaction time and the amount of seed crystals increased, the width of particle size distribution became narrower. The weight mean particle size was in the range of 1 μm to 10 μm. The characterization of the products were carried out using XRD, SEM, PSA, FTIR, and Raman spectrometer.

INTRODUCTION

Quartz glasses have been widely used as a main element of the optical communications, such as optical disks and optical fibers. They have also been used for other purpose, such as quartz tube and infrared lamps, etc. [Ichinose, 1983; 鹽寄忠, 1987; 堂山 昌男, 1990; Ikeda, 1990]. In this study relatively simple experimental procedures and hardwares were used for hydrothermal operations, which enabled the production of the desired product with almost a 100% yield. The α-quartz crystals obtained have the shape of regularly edged rhombohedrons through the hydrothermal process. The products may be used as raw material in the manufacture of quartz glasses and quartz ceramics. Both advanced oxide powder producers and ceramic manufactures have worked on preparation of quartz crystal powders by means of hydrothermal synthesis [Lias et al., 1973; Dawson, 1988; Lee et al., 1995a, b].

Hydrothermal synthesis has been recognized as a viable chemical process for production of wide varieties of commercially important advanced ceramic powders [Geiger, 1995]. The advantages of the hydrothermal method include the powders being produced are very fine, uniform in particle size, and not agglomerated. It is a wet-chemistry technique for directly forming complex oxide powders. With improved control over powder homogeneity and particle uniformity, the process could give superior products of desired specifications [Dawson, 1988; Lee et al., 1995a; Ban, 1996; Jung, 1996]. Fine ceramic powders of uniform grain sizes having high crystallinity can be prepared by hydrothermal synthesis by imposing a subcritical or supercritical state to solutions whereby inorganic oxide compounds are extracted [Laudise and Ballman, 1958; Elwell and Scheel, 1975; Chernov, 1984; Barclay et al., 1992; Wold and Dwight, 1993; Byrappa, 1994; Mersmann, 1994; Brice, 1986]. The hydrothermal reaction replaces the high temperature calcination step required by the conventional sol-gel and coprecipitation techniques. The major difference between hydrothermal processing and the other technologies is that the former does not require high temperature calcination step. This, in turn, eliminates the need for milling. Powders are formed directly from solution via complex reactions which take place in high temperature water. By controlling these reactions, it is possible to produce anhydrous crystalline powders with controlled particle sizes and particle shapes [Dawson, 1988].

The hydrothermal process essentially consists in creating conditions that ensure the transformation of the crystallizing substance into a soluble state necessary supersaturation of the solution, and crystallization of the products. The supersaturation value may be controlled by changing the system parameters which determine the solubility of the reacting substance such as reaction temperature, pressure, types and concentration of mineralizers, and the temperature difference between the dissolution and growth zones [Chernov, 1984].

In recent years there has been good experimental progresses about the hydrothermal growth of various oxide ceramics. However, the most studies [Lias et al., 1973; Elwell and Scheel, 1975; Barclay et al., 1992; Byrappa, 1994] have been focused

on merely developing bigger and pure single crystals. The objective of this study is to obtain the optimum conditions by controlling the system parameters for producing high quality α-quartz crystal powders from raw materials, that will be used for quartz glasses and quartz ceramics.

EXPERIMENTAL PROCEDURE

Amorphous silicas were used as a nutrient to obtain optimum synthetic conditions of the hydrothermal reactions for high quality quartz crystal powders. The commercial silicas from Sigma Co. Ltd. and the other silicas prepared by the hydrolysis and alcoholysis of TEOS [Nogami and Moriya, 1980; Brinker et al., 1982b, 1986a; Yoon et al., 1994] which constitutes a waste material from electronic industries were used in these experiments. Small amounts of α-Quartz crystals were used as seed crystals. The seed crystal (0.05-0.5 wt%) was put into an autoclave with addition of mineralizers such as KOH, KF, KBr, KCl, NaF, NaOH, Na$_2$CO$_3$, LiF, LiOH to form quartz crystals. Mineralizers were added to increase solubility of the amorphous silica feedstock. The mixed feedstock was prepared by adding amorphous silica (10 g) and seed crystal into mineralizer solutions in different concentrations (0.005-5 wt%). The volume of the feedstock was kept constant throughout the experiments. After the autoclave apparatus was cooled, the product was filtered, and then washed successively with deionized water to remove impurities. The synthetic product was then dried in a freezing dryer. The chemicals used in this work were of extra pure reagent grade. The products were analyzed by X-ray diffractometer (XRD: MXP3, Mac Science Co.) using a monochromatic CuK$_α$ radiation, 40 kV, 20 mA, to determine the degree of the relative crystallinity of the products. The morphology of the product particles was observed using scanning electron microscope (SEM: Stereoscan 440, Leica Co.). Particle size analyzer (PSA: Master Sizer E, Malvern Co.) was used to investigate the size distribution and to determine the weight mean particle size. Fourier transform infrared spectrometer (FTIR: Magna-IR spectrometer 550, Nicolet Co.) and Raman spectrometer were used to investigate the unique spectral characteristics about the vibrational, chemical and structural properties of product and amorphous material. FTIR spectrometer was used to determine the crystallinity of the products by the KBr pellets. Raman scattering spectra were collected using a Spex Triplemated spectrometer (1877) with a Spex Industry CCD detector cooled to   133°C. A coherent Ar* Innova 70 (514.5 nm) was used as the exitation source. The laser power at the sample was approximately 10-20 mW, and scattered radiation was collected in a backscattered configuration.

RESULTS AND DISCUSSION

Experiments were performed to determine relevant factors and optimum conditions of hydrothermal reactions for preparing α-quartz crystal powders. Fig. 1 shows an example of the effect of reaction temperature on the formation of α-quartz crystals. This result illustrates the variation of the XRD patterns as the reaction temperature rises when 0.5 wt% seed crystals and 0.5 wt% KOH mineralizer were used. At higher tem-
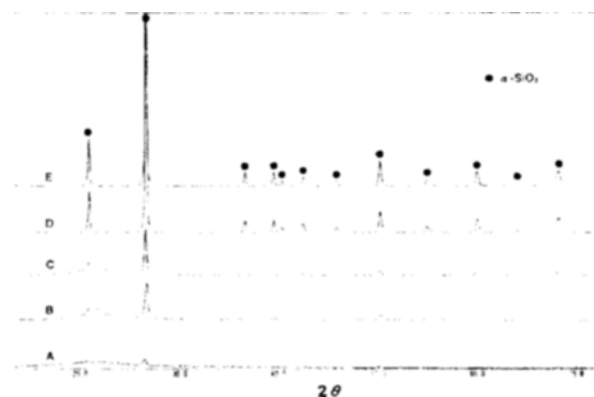

Fig. 1. XRD patterns of products formed at various reaction temperatures (A: 200°C, B: 225°C, C: 240°C, D: 260°C, E: 280°C, reaction time: 3 h, seed=0.5 wt%, with 0.5 wt% KOH).
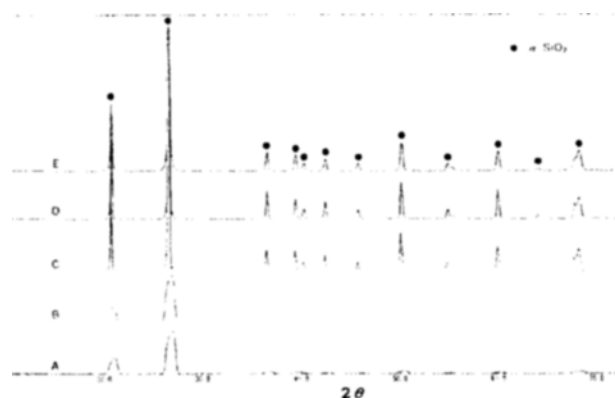

Fig. 2. XRD patterns of products formed with various reaction times (A: 1 h, B: 2 h, C: 3 h, D: 6 h, E: α-SiO$_2$, seed=0.5 wt%, at 400°C).

peratures, XRD patterns of the synthetic products reveal a crystalline phase. At temperatures over 240°C, α-quartz crystal was formed.

The XRD patterns in Fig. 2 show the extent of crystal formation of α-quartz as a function of the reaction time with 0.1 wt% KOH in the feedstock. After a 3 hours' reaction at 400°C, the phase of the crystalline product was obtained.

Fig. 3 shows the variation of XRD patterns of products with various mineralizers at their different concentration levels. As the concentration of mineralizers increased, XRD patterns of the synthetic products showed the crystalline phase. When the concentration of mineralizer KOH increased over 0.075 wt%, α-quartz crystal started to be formed.

Fig. 4 shows the XRD patterns of products formed with various types of mineralizers. The results show that a few alkali hydroxides and alkali halides such as KOH, NaOH, Na$_2$CO$_3$, KF, and NaF were found to be effective mineralizers.

Fig. 5 shows a SEM micrograph of α-quartz crystals formed with 0.075 wt% KOH. After a 3 hours' reaction at 400°C, synthetic α-quartz powders of the weight mean particle diameter of 2.03 μm with high crystallinity were obtained in uniform size of 1-3 μm with shapes of a rhombohedron.

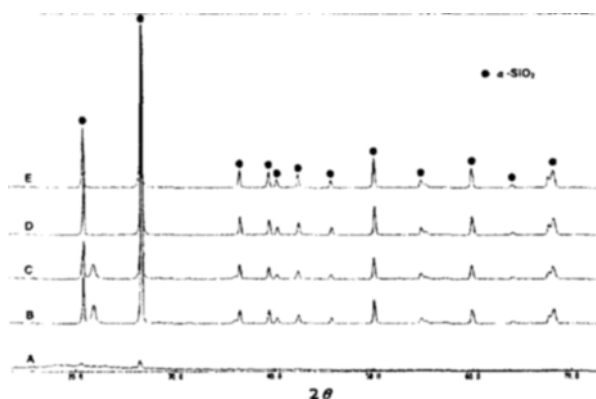Fig. 6 shows a SEM micrograph of α-quartz crystals formed

Fig. 3. XRD patterns of products formed with various concentration of mineralizers (A: No used, B: 0.025 wt% KOH, C: 0.05 wt% KOH, D: 0.075 wt% KOH, E: 0.1 wt% KOH, seed=0.5 wt%, at 400°C).
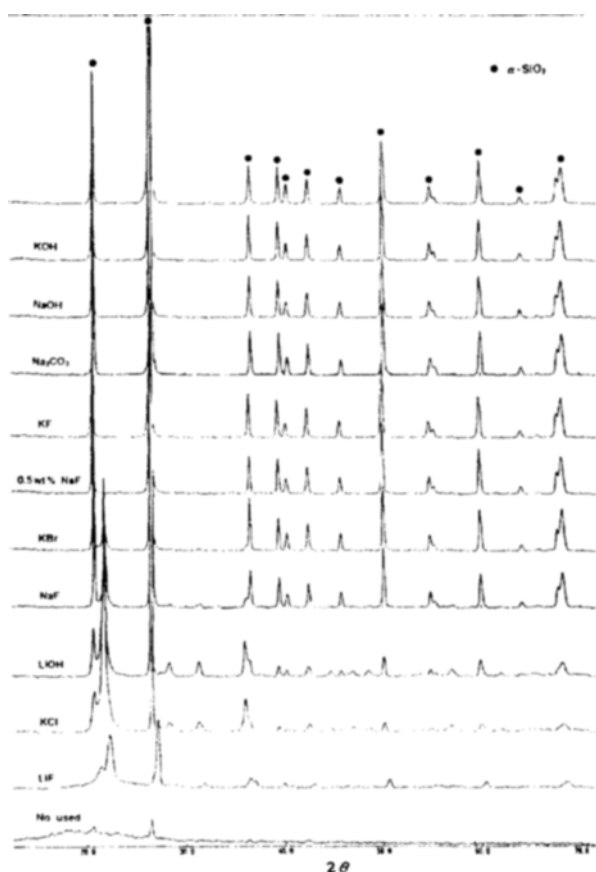

Fig. 5. SEM micrograph of α-quartz powder formed with 0.075 wt% KOH (reaction time: 3 h, seed=0.5 wt%, at 400°C).

Fig. 6. SEM micrograph of α-quartz powder formed with 0.5 wt% NaOH (reaction time: 3 h, seed=0.5 wt%, at 400°C).

Fig. 4. XRD patterns of products formed with various types of mineralizers (reaction time: 3 h, concentration of mineralizers=0.25 wt%, seed=0.5 wt%, at 400°C).

Fig. 7. SEM micrograph of α-quartz powders at 400°C TEOS was used to form amorphous silicas (reaction time: 3 h, seed=0.5 wt%, with 0.3 wt% KOH).

with 0.5 wt% NaOH. After a 3 hours' reaction at 350°C, synthetic α-quartz crystal powders of the weight mean particle diameter of 2.80 μm with high crystallinity were obtained which had shapes of a regularly edged rhombohedron.

Fig. 7 shows a SEM micrograph of α-quartz crystals formed using the feedstock of amorphous silica obtained from TEOS. After a 3 hours' reaction at 400°C, synthetic α-quartz crystal

powders of the weight mean particle diameter of 2.84 μm with high crystallite were obtained, but without a particular shape.

Fig. 8 shows a SEM micrograph of α-quartz crystal powder formed with 0.25 wt% KF. After a 3 hours' reaction at 400°C, synthetic α-quartz crystal powders of the weight mean particle
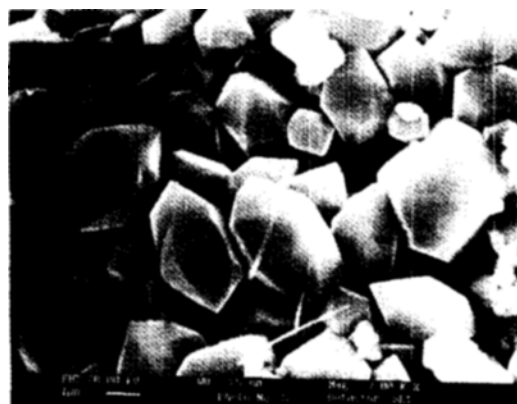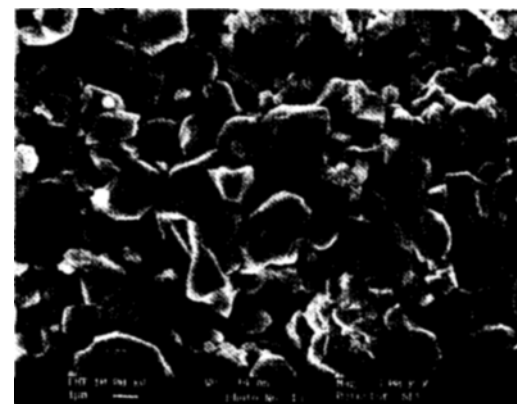
Fig. 8. SEM micrograph of α-quartz powders formed with 0.8 wt% KF(reaction time: 3 h, seed=0.5 wt%, at 400°C).

Fig. 10. SEM micrograph of α-quartz powders formed with 0.1 wt% Na₂CO₃(reaction time: 3 h, seed=0.5 wt%, at 350°C).

Fig. 9. SEM micrograph of α-quartz powders formed with 1.5 wt% NaF(reaction time: 3 h, seed=0.5 wt%, at 400°C).

Table 1. Summary of experimental results at different hydro-thermal conditions

Condition No.	Temperature (°C)	Reaction time (hour)	Mineralizer (wt%)	Mean particle size (μm)
Fig. 5	400	3	0.075 KOH	2.03
Fig. 6	350	3	0.5 NaOH	2.80
Fig. 7	400	3	0.3 KOH	2.84
Fig. 8	400	3	0.25 KF	4.47
Fig. 9	430	3	0.5 NaF	2.48
Fig. 10	400	3	0.1 Na₂CO₃	1.89

diameter of 4.47 μm with high crystallite were obtained having uniform size of 2-8 μm with shapes of a needle.

Fig. 9 shows a SEM micrograph of α-quartz crystal powder formed with 1.5 wt% NaF. After a 3 hours' reaction at 430°C, synthetic α-quartz crystal powders of the weight mean particle diameter of 2.48 μm with high crystallite were obtained which had shapes of a hexagonal structure.

Fig. 10 shows a SEM micrograph of α-quartz crystal powder formed with 0.1 wt% Na₂CO₃. After a 3 hours' reaction at 400°C, synthetic α-quartz crystal powders of the weight mean particle diameter of 1.89 μm with high crystallinity were obtained that had shapes of a regularly edged rhombohedron.

The results shown in Fig. 5 to 10 are summarized in Table 1.

These SEM micrographs showed that the external shape or the morphology of the α-quartz crystal varies considerably depending on the hydrothermal conditions. In Figs. 5, 6, and 10, the morphologies of α-quartz crystals are shown which consistent with shapes of rhombohedrons in hexagonal structures. Probably they could be grown in under similar hydrothermal environments. In Fig. 8, the particular features of interest are fast growth along an axis. This development of α-quartz crystals are probably due to high surface energy. If low energy faces are parallel to a unique crystallographic axis, then needle forms of α-quartz crystal are produced. From the literature

[Pamplin, 1975], the needle shapes of a α-quartz crystal shows an axial directional dislocation, that indicates the fast growth to the axial direction. The side faces of needles are low energy faces which grow only slowly, or not at all. And the supersaturation on the side faces must be sufficiently low to prevent a two-dimensional nucleation which would allow a radial growth.

Fig. 11 shows FTIR spectra of the prepared α-quartz powders with addition of mineralizers such as KOH, NaOH, Na₂CO₃, KF, and NaF at 400°C for a 3 hours' reaction. The FTIR spectra displays one dominant, highly polarized, peak at high frequency (1,100 cm⁻¹) and some weak peaks at lower frequencies (500, 700, 800 cm⁻¹). The result shows that the spectra of all the product are the same as that of a standard α-quartz powder with high crystallite shown in Fig. 10.

Fig. 12 shows Raman spectra of the products formed at different temperatures. The result shows the spectra of the products are very similar to that of standard α-quartz powder. After hydrothermal treatments above 300°C for a 3 hours' reaction, the result showed a good consistency for all samples. Spectra of crystalline products differ considerably from that of an amorphous silica. A strong, polarized peak at 466 cm⁻¹ and a weak shoulder at 205 cm⁻¹, which are characteristic of Raman spectrum of α-quartz powders was not observed in the spectrum of an amorphous silica in the range 200-600 cm⁻¹.

Fig. 13 shows the particle size distribution of α-quartz crystal powder formed with addition of 0.1 wt% KOH at 400°C for a 3 hours' reaction. This result shows that the mean particle diameter of the prepared α-quartz powders is 4.1 μm.
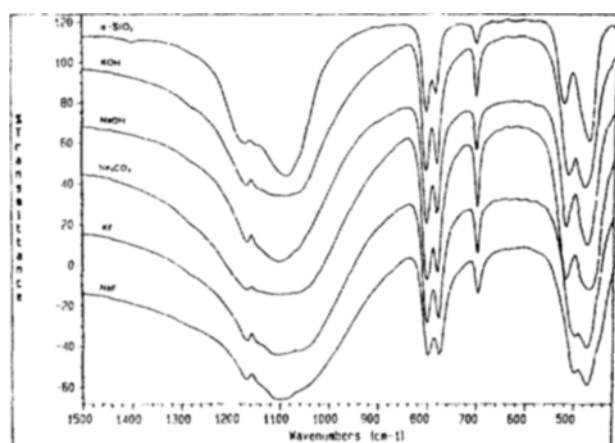
Fig. 11. FTIR spectra of α-quartz powders formed with various type of mineralizers(reaction time: 3 h, seed=0.5 wt%, at 400°C).

Fig. 13. Particle size distribution of α-quartz powders formed with 0.1 wt% KOH(reaction time: 3 h, seed=0.5 wt%, at 400°C).
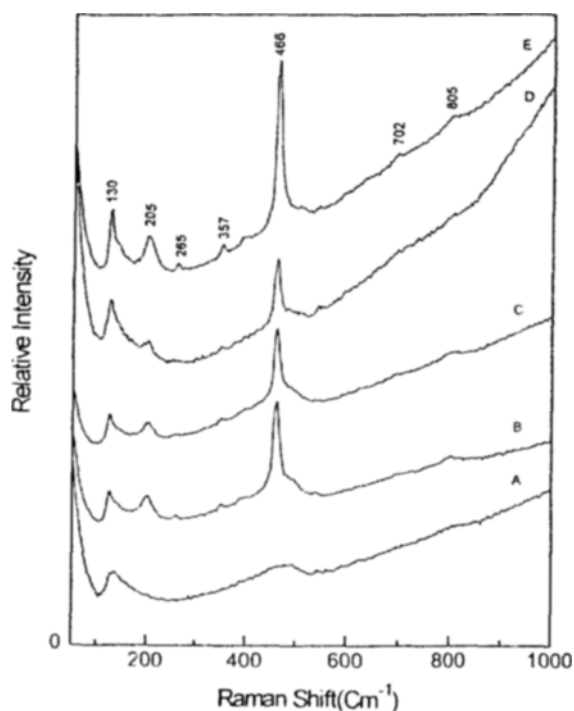

Fig. 12. Raman spectra of α-quartz powders formed at various reaction temperatures(A: amorphous silica, B: 300°C, C: 350°C, D: 400°C, E: α-SiO₂, reaction time: 3 h, seed=0.5 wt%, with 0.25 wt% KOH).

Fig. 14. Particle size distribution of α-quartz powders formed with 0.1 wt% KOH(reaction time: 6 h, seed=0.5 wt%, at 400°C).

Fig. 14 shows the particle size distribution of α-quartz crystal powders formed with addition of 0.1 wt% KOH at 400°C for a 6 hours' reaction. This result shows that the mean particle diameter of the prepared α-quartz powders is 4.31 μm. From the results shown in Figs. 13 and 14 we can see the effect of reaction time on the hydrothermal growth of α-quartz crystal powders. These results show that the particle size of the prepared α-quartz crystal powders increased as the reaction time increased. The hydrothermal reaction time also affected the particle size distribution. As the reaction time increased, the width
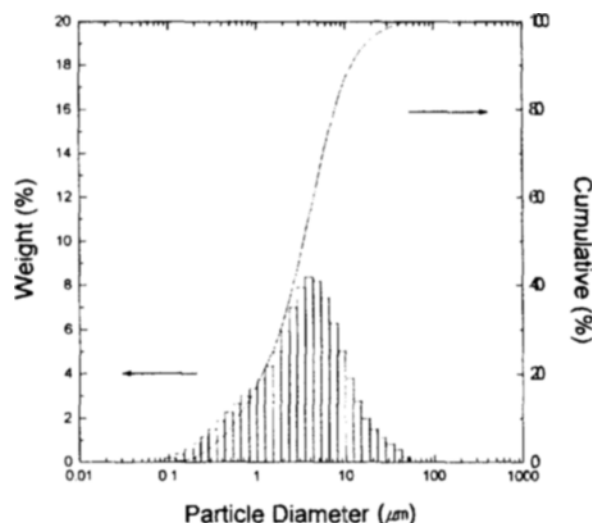
of particle size distribution became narrower.

Fig. 15 shows the particle size distribution of α-quartz crystal powders formed with addition of 0.8 wt% KOH at 400°C for a 3 hours' reaction. This result shows that the mean particle diameter of the prepared α-quartz powders is 2.39 μm. Figs. 13 and 15 show that the mean particle diameter of the prepared α-quartz crystal powders decreased as the concentration of the mineralizer increased.

Fig. 16 shows the effect of concentration of the mineralizer on the weight mean particle diameter of α-quartz crystal powders at 400°C for a 3 hours' reaction. This result shows that as concentration of the mineralizer increased, the weight mean particle diameter of synthetic products became smaller.
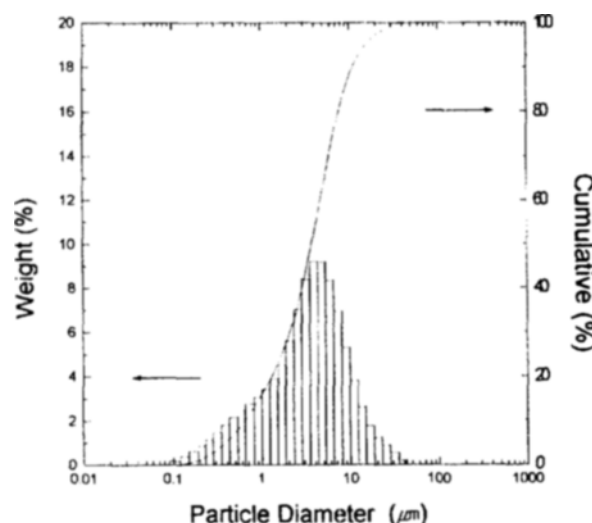
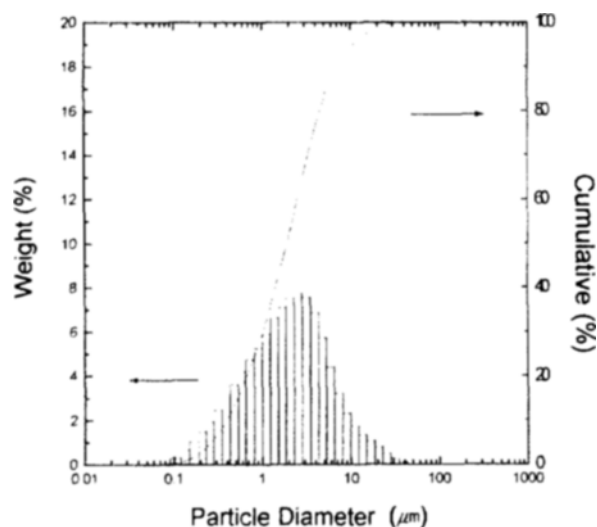Fig. 17 shows the intensity changes of synthetic products

Fig. 15. Particle size distribution of α-quartz powders formed with 0.8 wt% KOH(reaction time: 3 h, seed=0.5 wt%, at 400°C).

Fig. 17. Intensity change of synthetic α-quartz crystal face formed with concentration variation of seed crystals(reaction time: 3 h, concentration of the mineralizer: 0.25 wt% KOH, at 350°C).

Table 2. Summary of experimental results for hydrothermal synthesis

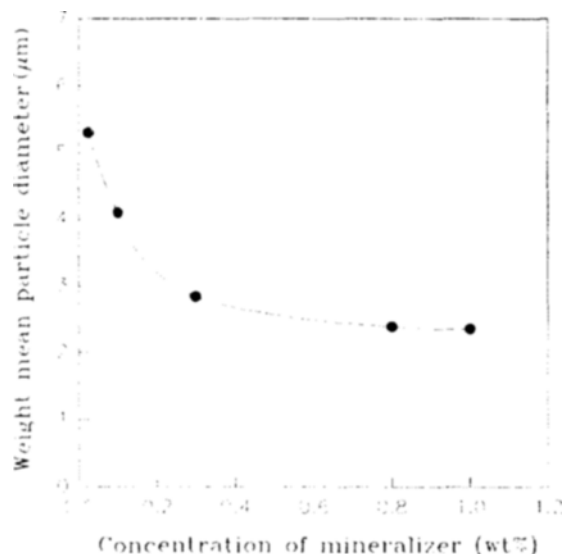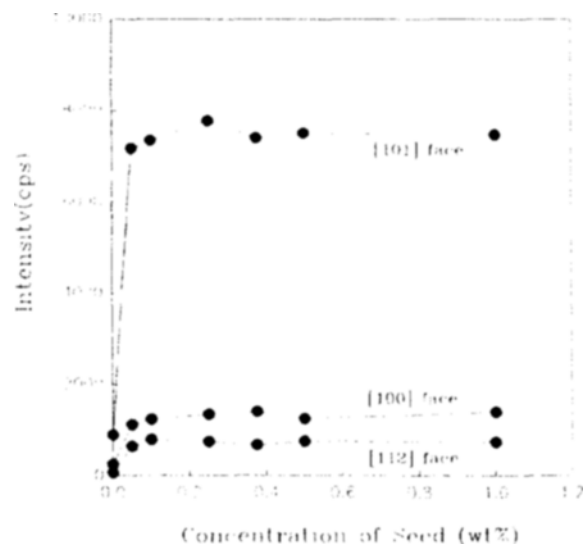| Condition No.	Temperature (°C)	Reaction time (hour)	Mineralizer (wt%)	Mean particle size (μm)
Fig. 11	400	3	0.25 All	1-10
Fig. 12	>300	3	0.25 KOH	1-5
Fig. 13	400	3	0.1 KOH	4.10
Fig. 14	400	6	0.1 KOH	4.31
Fig. 15	400	3	0.8 KOH	2.39
Fig. 16	400	3	0.5 KOH	2.36-5.29
Fig. 17	350	3	0.25	<5

Fig. 16. Effect of concentration of mineralizer on the weight mean particle diameter of α-quartz crystal powders at 400°C(reaction time: 3 h, seed=0.5 wt%).

formed with concentration variation of seed crystals for a 3 hours' reaction. The relative growth rates for three main crystal faces [101], [100], [112] are shown in Fig. 17. As this result shows, the [101] face is the fastest growing face, but the [112] face the slowest. As the amount of seed crystals increased, the effect of the seed crystals on formation of the crystal powders decreased. This result indicates that seed crystals affect significantly the crystal face formation of synthetic products.

The above results (from Figs. 11 to 17) were summarized in Table 2.

CONCLUSION

Fine crystallites of α-quartz of uniform particle sizes with

high crystallinity were prepared under hydrothermal conditions. The degree of α-quartz crystal face development depended on the relative growth rate of particular form that varies considerably with the degree of supersaturation, reaction temperature, concentration of mineralizers, and the amount of seed crystals in the feedstock.

The α-quartz powders were formed at the reaction temperature range of 240 to 450°C under the pressure range of 100 to 300 atm for a 3 hours' reactions. The crystal sizes were within the range of 0.1-100 μm, with the fractional size distribution depending on the hydrothermal condition. In the reactions mineralizers were added in order to increase the solubility of the amorphous silica feedstock. Alkali hydroxides and alkali halides such as KOH, NaOH, Na₂CO₃, KF and NaF were found to be effective mineralizers in the temperature and pressure ranges studied. Especially, KOH was found to be the most effective material for preparation of α-quartz crystal powders. For the powders prepared under the conditions of 0.25 wt% KOH, over 300°C and reaction time of 3 hours, Raman and FTIR spectra showed a good consistency among all products and the spectra of these powders showed the same as that of α-quartz powder with high crystallinity. The appearance of min-

eralizers and seed crystals in the medium affected significantly the crystal formation temperature and the morphology of synthetic products. The morphology of the α-quartz crystal powders was usually bounded by a small number of forms since fast growing face grow out leaving only the slowest growing face. The amount of α-quartz crystal powders increased as the reaction temperature and the concentration of mineralizers increased. However, as the concentration of mineralizers increased the size of the crystallites and the crystal formation temperature decreased. Hydrothermal reaction time also had an effect on the particle size distribution. As the reaction time and the amount of seed crystals increased, the particle size distribution became narrower. The weight mean particle size was in the range of 1 μm to 10 μm.

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