Effect of Cations on Crystallization of Amorphous Silica (Part 3)

著者	TOMITA Katsutoshi, SONODA Atsushi, KAWANO Motoharu
journal or publication title	鹿児島大学理学部紀要=Reports of the Faculty of Science, Kagoshima University
volume	30
page range	27-36
URL	http://hdl.handle.net/10232/00012455

Rep. Fac. Sci., Kagoshima Univ.
No. 30, 27~36, 1997.

Effect of Cations on Crystallization of Amorphous Silica (Part 3)

Katsutoshi TOMITA[1], Atsushi SONODA[2] and Motoharu KAWANO[3]

(Received August 25, 1997)

Keywords : Amorphous silica, Quartz, Cristobalite, Tridymite, Crystallization.

Abstract

In this study amorphous silica was used as a starting material for various experimental analysis, and the effects of cations on its crystallization were investigated. The amorphous SiO_2 was heated at 800 ℃ and 600 ℃ in the presence of Na_2SO_4, K_2SO_4, NaOH and KOH, each treated separately, and the original amorphous silica was also subjected to heat at 600 ℃ with NaOH and KOH. When a small amount of Na_2SO_4 was added to original amorphous silica, cristobalite was formed after heating at 800 ℃ for 17 days, but when a large amount of Na_2SO_4 was added, cristobalite was formed only after heating at 800 ℃ for 23 days. When a small amount of K_2SO_4 was added to amorphous silica, cristobalite was formed after heating at 800 ℃ for 10 days, and with a large amount of K_2SO_4 added, cristobalite was produced after heating for 23 days. At 800 ℃, when a small amount of NaOH was added, silica minerals such as quartz, tridymite, cristobalite and sodium-silicate were formed, but when the amount of NaOH was increased, quartz, tridymite and sodium-silicate were the only minerals produced. With the application of a small amount of KOH at 800 ℃, quartz, tridymite and cristobalite were formed, however, if a large amount of KOH was added, tridymite, cristobalite and potassium-silicate were produced. At 600 ℃, when a small amount of NaOH was added, only cristobalite was formed after heating for 10 days, and when a small amount of KOH was applied, no products were formed. In this experiment, the results indicate that the process of amorphous silica transformation in the presence of various cations are different from each other and the inclusion of impurities has a great effect on the formation of silica minerals from the original amorphous silica.

Introduction

In nature some cristobalites, tridymites and quartz are often found in opal and is known that some of these crystals were formed under lower temperatures than its ordinary crystallization temperature. One of the reasons is considered to be due to impurities (Jones and Segnit, 1971, 1972), and it was confirmed by Kagawa *et al.* (1991) using natural amorphous silicas, but as they used natural samples, effects of cations were not investigated in detail. Crystallization of quartz from amorphous silica is reported (Carr and Fyfe, 1958; Imanaka *et al.*, 1989; Mizutani, 1966; Sakamoto *et al.*, 1986, 1988), but researchers concerning effects of cations on crystallization of amorphous silica are not so many. Tomita and Kawano (1992, 1993) presented studies on this cation effects using amorohous silica of guaranteed chemical reagent as a starting material, with observations made at 500 ℃, 600 ℃, 800 ℃ and 1000 ℃. In their experiments chlorides such as NaCl, KCl and LiCl were used, and in this experiments the effects of cations such as Na_2SO_4, K_2SO_4, NaOH and KOH were investigated.

[1] Department of Earth and Environmental Sciences, Faculty of Science, kagoshima University, 21-35, Korimoto 1-chome, Kagoshima 890, Japan.

[2] Toko Kensetsu Co., Ltd., 15-31 Kengun Honmachi, Kumamoto City, 862 Japan.

[3] Department of Environmental Sciences and Technology, Faculty of Agriculture, Kagoshima University, 21-24, Korimoto 1-chome, Kagoshima 890, Japan.

Experimental procedure

Amorphous silica powder of guaranteed chemical reagent was used as a starting material, and the amorphous silica was put into a porcelainous crucible with sulfates such as Na_2SO_4, K_2SO_4, NaOH and KOH. The mixtures were subjected to different levels of temperatures 600 ℃ and 800 ℃. Particle sizes of 0.063-0.2mm of amorphous silica were used. After continuous heating for desired periods of time the samples were washed with pure water for several times. The washed samples dried in air were identified for its mineral components with an X-ray diffractometer. The microstructures of the samples were observed using a scanning electron microscope.

Results

1) Reaction at 800 ℃

Effect of Na_2SO_4

In this experiments three kinds of mixtures were prepared. When a mixture of 3g of amorphous silica and 0.3g of Na_2SO_4 was heated at 800 ℃, the amorphous silica was converted to cristobalite after heating for 17 days. Quartz was formed after heating for 30 days in addition to cristobalite. The progressive change was clearly detectable on the X-ray diffraction patterns. The X-ray diffraction patterns of the reaction products are shown in Fig. 1. It was confirmed that any kinds of silica minerals were not formed after heating at 800 ℃ for 25 days without presence of Na_2SO_4 from the amorphous silica.

When a mixture of 3g of amorphous silica and 1g of Na_2SO_4 was heated at 800 ℃, cristobalite was formed after heating for 23 days, and formation of quartz was not observed even after heating for 30 days. X-ray powder diffraction patterns of the reaction products showed almost the same patterns as those of reaction products from the mixture of amorphous silica (3g) and Na_2SO_4 (0.3g).

When a mixture of 1.5g of amorphous silica and 1.5g of Na_2SO_4 was heated at 800 ℃, only a small

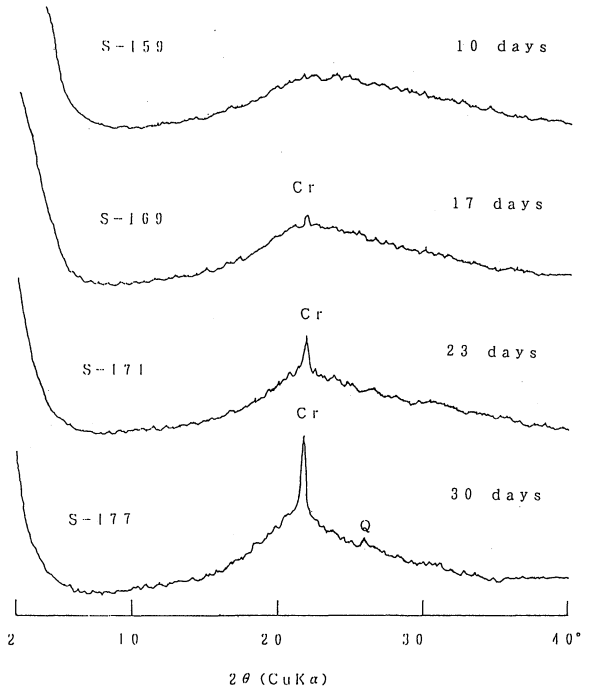

Fig. 1. X-ray powder diffraction patterns of the mixture of amorphous silica (3g) and Na_2SO_4 (0.3g) after heating at 800 ℃ for various time.
Cr : cristobalite, Q: quartz.

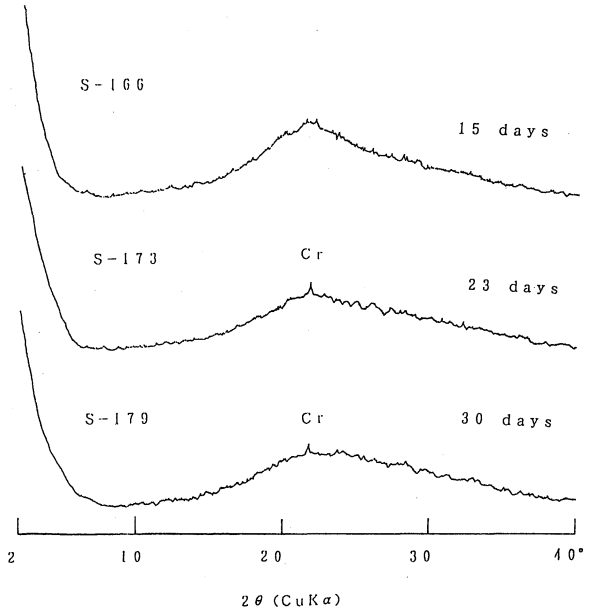

Fig. 2. X-ray powder diffraction patterns of the mixture of amorphous silica (1.5g) and Na_2SO_4 (1.5g) after heating at 800 ℃ for various time.
Cr : cristobalite.

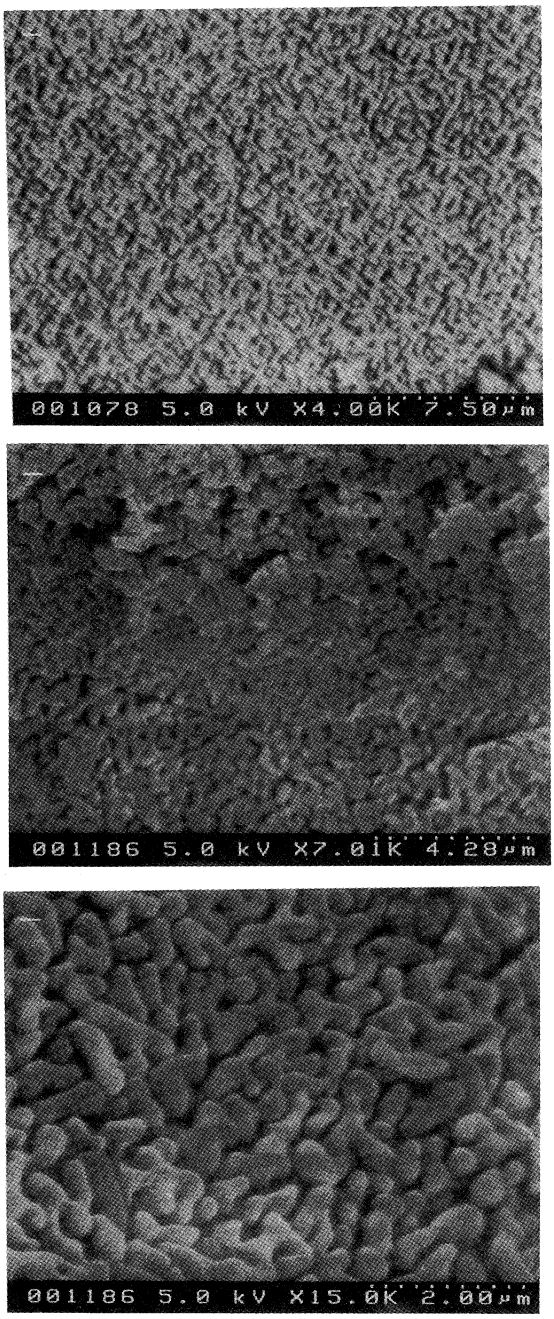

Fig. 3. Scanning electron micrographs of the products from the mixtures of amorphous silica and Na_2SO_4 after for 30 days.
(A) Product from the mixture of amorphous silica (3g) and Na_2SO_4 (0.3g).
(B) Product from the mixture of amorphous silica (3g) and Na_2SO_4 (1.0g).
(C) Product from the mixture of amorphous silica (1.5g) and Na_2SO_4 (1.5g).

Table 1. Experimental conditions and products at 800℃

Run No.	Amorphous silica (g)	Na_2SO_4 (g)	Time (day)	Products
S-141	3	0.3	1	
S-151	3	0.3	4	
S-157	3	0.3	7	
S-159	3	0.3	10	
S-169	3	0.3	17	Cri
S-171	3	0.3	23	Cri
S-177	3	0.3	30	Cri, Q
S-142	3	1	1	
S-147	3	1	2	
S-153	3	1	5	
S-160	3	1	10	
S-165	3	1	17	
S-172	3	1	23	Cri
S-178	3	1	39	Cri
S-143	1.5	1.5	1	
S-148	1.5	1.5	2	
S-154	1.5	1.5	5	
S-161	1.5	1.5	10	
S-166	1.5	1.5	15	
S-173	1.5	1.5	23	Cri
S-179	1.5	1.5	30	Cri

Cri: cristobalite, Q: quartz

amount of cristobalite was formed after heating for 23 days, and only cristobalite was formed after heating for 30 days. X-ray powder diffraction patterns of the reaction products are shown in Fig. 2. Only a small amount of cristobalite was formed after heating for 30 days.

Scanning electron micrographs of the products from the mixtures of amorphous silica and Na_2SO_4 are shown in Fig. 3. Round crystals of cristobalite are observed. In the Fig. 3 C, early stage of cristobalite formation is observed. The results of experimental products are listed in Table 1.

Effect of K_2SO_4

Three kinds of mixtures were prepared. When a mixture of 3g of amorphous silica and 0.3g of K_2SO_4 was heated at 800 ℃, the amorphous silica was converted to cristobalite after heating for 10 days. Quartz was not formed after heating for 30 days, but amount of cristobalite increased in accordance with heating time. The X-ray diffraction patterns of the reaction products are shown in Fig. 4.

When a mixture of 3g of amorphous silica and 1g of K_2SO_4 was heated at 800 ℃, cristobalite was

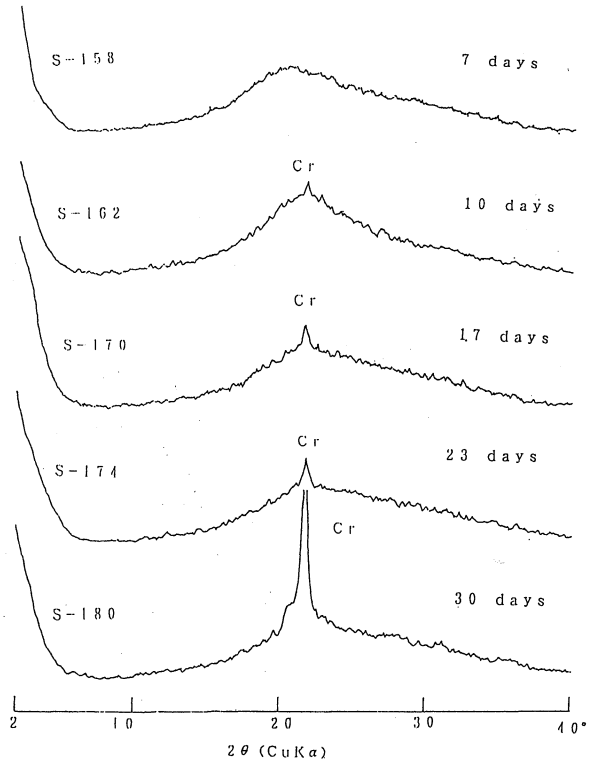

Fig. 4. X-ray powder diffraction patterns of the mixture of amorphous silica (3g) and K_2SO_4 (0.3g) after heating at 800 ℃ for various time.
Cr: cristobalite.

formed after heating for 23 days, and formation of quartz was not observed even after heating for 30 days. X-ray powder diffraction patterns of the reaction products showed almost the same patterns as those of reaction products from the mixture of amorphous silica (3g) and K_2SO_4 (0.3g).

When a mixture of 1.5g of amorphous silica and 1.5g of K_2SO_4 was heated at 800 ℃, only a small amount of cristobalite was formed after heating for 23 days, and only cristobalite was formed after heating for 30 days.

Scanning electron micrographs of the products from the mixtures of amorphous silica and K_2SO_4 are shown in Fig. 5. Peanut-shaped crystals of cristobalite are observed. The shape was formed by the sticking round crystals. The results of experimental products are listed in Table 2.

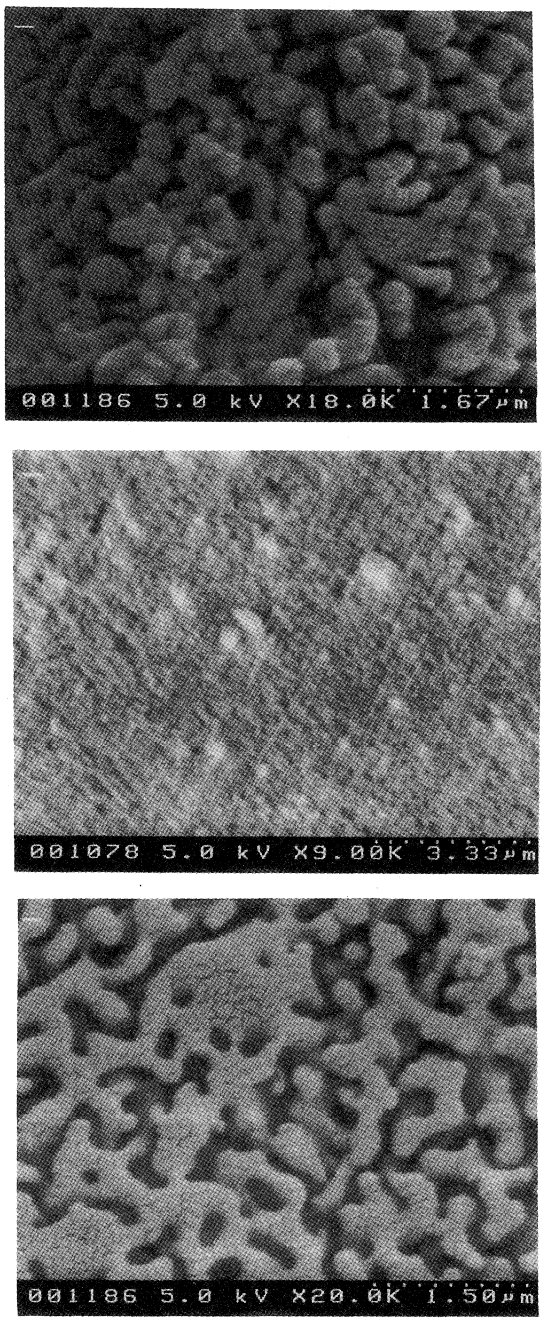

Fig. 5. Scanning electron micrographs of the products from the mixtures of amorphous silica and K_2SO_4 after for 30 days.
(A) Product from the mixture of amorphous silica (3g) and K_2SO_4 (0.3g).
(B) Product from the mixture of amorphous silica (3g) and K_2SO_4 (1.0g).
(C) Product from the mixture of amorphous silica (1.5g) and K_2SO_4 (1.5g).

Table 2. Experimental conditions and products at 800℃

Run No.	Amorphous silica (g)	K_2SO_4 (g)	Time (day)	Products
S-144	3	0.3	1	
S-152	3	0.3	4	
S-158	3	0.3	7	
S-162	3	0.3	10	Cri
S-170	3	0.3	17	Cri
S-174	3	0.3	23	Cri
S-180	3	0.3	30	Cri, Q
S-145	3	1	1	
S-149	3	1	2	
S-155	3	1	5	
S-163	3	1	10	
S-167	3	1	17	
S-175	3	1	23	Cri
S-181	3	1	39	Cri
S-146	1.5	1.5	1	
S-150	1.5	1.5	2	
S-156	1.5	1.5	5	
S-164	1.5	1.5	10	
S-168	1.5	1.5	15	
S-176	1.5	1.5	23	Cri
S-182	1.5	1.5	30	Cri

Cri: cristobalite, Q: quartz

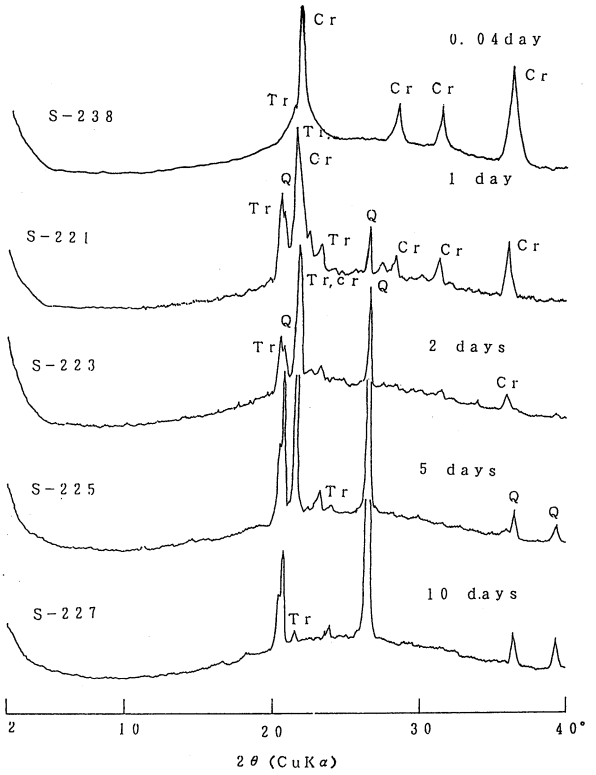

Fig. 6. X-ray powder diffraction patterns of the mixture of amorphous silica (2g) and NaOH (0.1g) after heating for various time.
Cr: cristobalite, Q: quartz, Tr: tridymite.

Effect of NaOH

Four kinds of mixtures were prepared for this experiments. When a mixture of 2g of amorphous silica and 0.1g of NaOH was heated at 800 ℃, tridymite, quartz and cristobalite were formed after heating for one day. Amount of cristobalite decreased and that of quartz increased in accordance with heating time up to 10days. Cristobalite disappeared after heating for 10 days. X-ray powder patterns of the products are shown in Fig. 6.

When a mixture of 3g of amorphous silics and 0.3g of NaOH was heated at 800 ℃, tridymite and quartz were formed after heating for one day, sodium silicate ($Na_2Si_4O_9$) was also formed beside these minerals. Tridymite disappeared after 10 days heating and quartz was the dominant product after 10 days' heating. X-ray powder patterns of the products are shown in Fig. 7.

When a mixture of 3g of amorphous silica and 1g of NaOH was heated at 800 ℃, tridymite, quartz and sodium silicate were formed after heating for one day, and tridymite disappeared after heating for 10 days. Quartz was the dominant mineral after 10

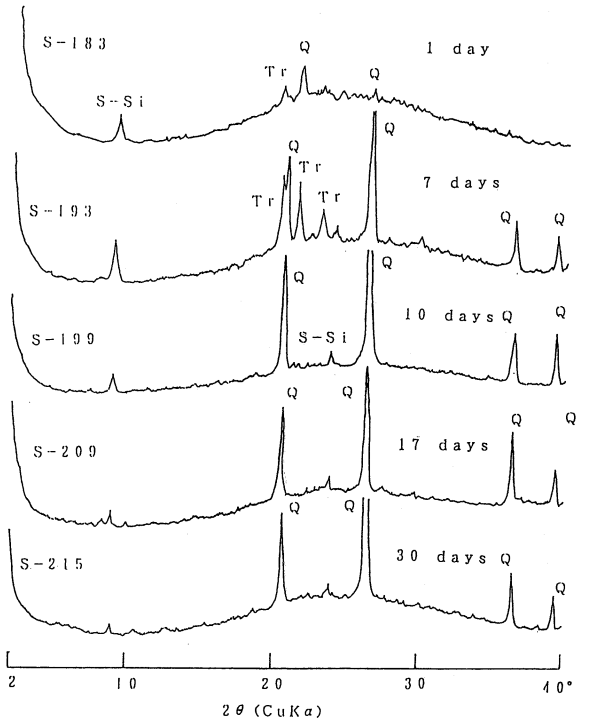

Fig. 7. X-ray powder diffraction patterns of the mixture of amorphous silica (3g) and NaOH (0.3g) after heating at 800℃ for various time.
Tr: tridymite, Q: quartz, S-Si: sodium silicate.

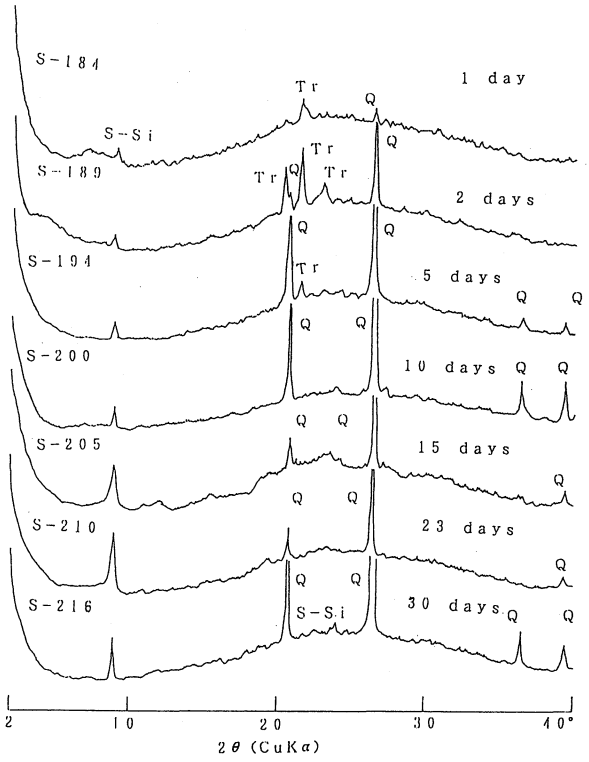

Fig. 8. X-ray powder diffraction patterns of the mixture of amorphous silica (3g) and NaOH (1g) after heating at 800℃ for various time.
Q: quartz, Tr: tridymite, S-Si: sodium silicate.

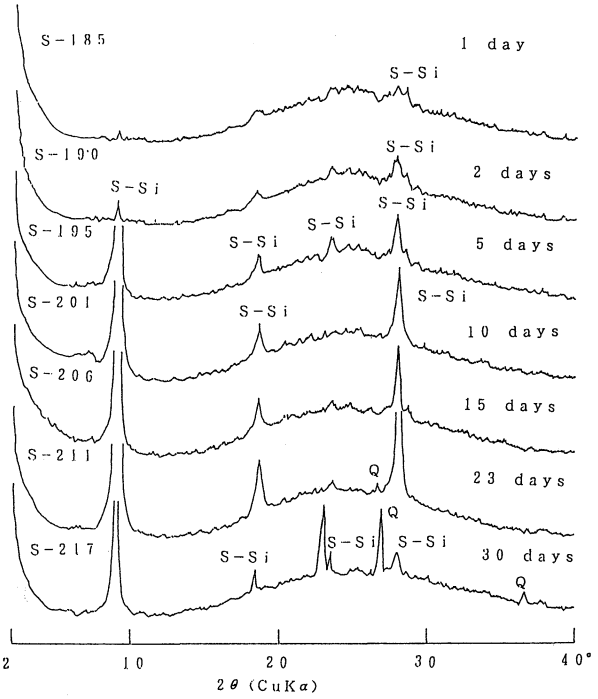

Fig. 9. X-ray powder diffraction patterns of the mixture of amorphous silica (1.5g) and NaOH (1.5g) after heating at 800℃ for various time.
Q: quartz, Tr: tridymite, S-Si: sodium silicate.

Fig. 10. Scanning electron micrographs of the products from the mixtures of amorphous silica and NaOH after for 30 days.
A. Product from the mixture of amorphous silica (3g) and NaOH (0.3g).
B. Product from the mixture of amorphous silica (3g) and NaOH (0.3g).

days' heating. X-ray powder diffraction patterns are shown in Fig. 8.

When a mixture of 1.5g of amorphous silica and 1.5g of NaOH was heated at 800 ℃, only sodium silicate was formed by heating less than 15 days, and quartz was formed after 23 day' heating. Amount of quartz increased after 23 days in accordance with heating time.

X-ray powder patterns of the products are shown in Fig. 9. Scanning electron micrographs of some products are shown in Fig. 10. Quartz is observed in Fig. 10 A, and sodium silicate shows lath-

Table 3. Experimental conditions and products at 800℃

Run No.	Amorphous silica (g)	NaOH (g)	Time (day)	Products
S-228	2	0.1	0.04	Cri, Tr
S-221	2	0.1	1	Tr, Cri, Q
S-223	2	0.1	2	Tr, Cri, Q
S-225	2	0.1	5	Tr, Q
S-227	2	0.1	10	Tr, Q
S-183	3	0.3	1	Tr, Q, So-Si
S-193	3	0.3	7	Tr, Q, So-Si
S-199	3	0.3	10	Q, So-Si
S-209	3	0.3	17	Q, So-Si
S-215	3	0.3	30	Q, So-Si
S-184	3	1	1	Q, Tr
S-189	3	1	2	Q, Tr, So-Si
S-194	3	1	5	Q, Tr, So-Si
S-200	3	1	10	Q, So-Si
S-205	3	1	15	Q, So-Si
S-210	3	1	23	Q, So-Si
S-216	3	1	30	Q, So-Si
S-185	1.5	1.5	1	So-Si
S-190	1.5	1.5	2	So-Si
S-195	1.5	1.5	5	So-Si
S-201	1.5	1.5	10	So-Si
S-206	1.5	1.5	15	So-Si
S-211	1.5	1.5	23	So-Si, Q
S-217	1.5	1.5	30	So-Si, Q

Cri : cristobalite, Q : quartz,
Tr : tridymite, So-Si : sodium silicate

shaped crystals (Fig. 10 B). The results of the products are listed in Table 3.

Effect of KOH

Four kinds of mixtures were prepared for this experiments. When a mixture of 2g of amorphous silica and 0.1g of KOH was heated at 800 ℃, a large amount of tridymite and cristobalite was formed after heating for one day. Quartz was formed after two days' heating. Amount of tridymite increased in accordance with heating time up to 10 days, and amounts of quartz and cristobalite did not change. X-ray powder patterns of the products are shown in Fig. 11.

When a mixture of 3g of amorphous silica and 0.3g of KOH was heated at 800 ℃, only tridymite was formed after heating for one day, and amount of tridymite increased in accordance with heating time. Cristobalite was formed after 7 days and quartz was formed after 10 days. Tridymite and quartz increased

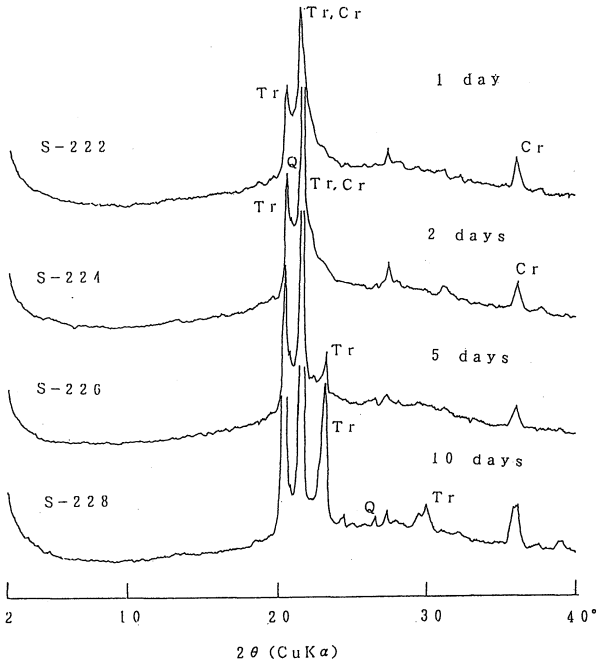

Fig. 11. X-ray powder diffraction patterns of the mixture of amorphous silica (2g) and KOH (0.1g) after heating at 800℃ for various time.
Cr : cristobalite, Q : quartz, Tr : tridymite.

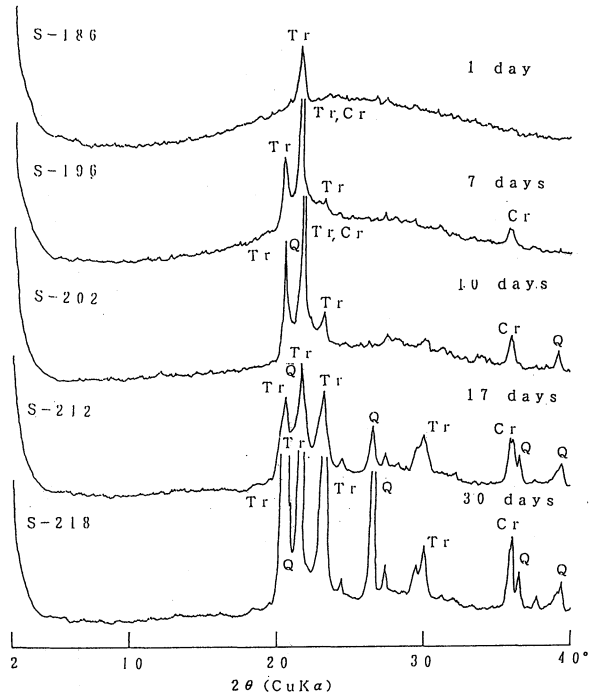

Fig. 12. X-ray powder diffraction patterns of the mixture of amorphous silica (3g) and KOH (0.3g) after heating at 800℃ for various time.
Tr : tridymite, Q : quartz, Cr : cristobalite.

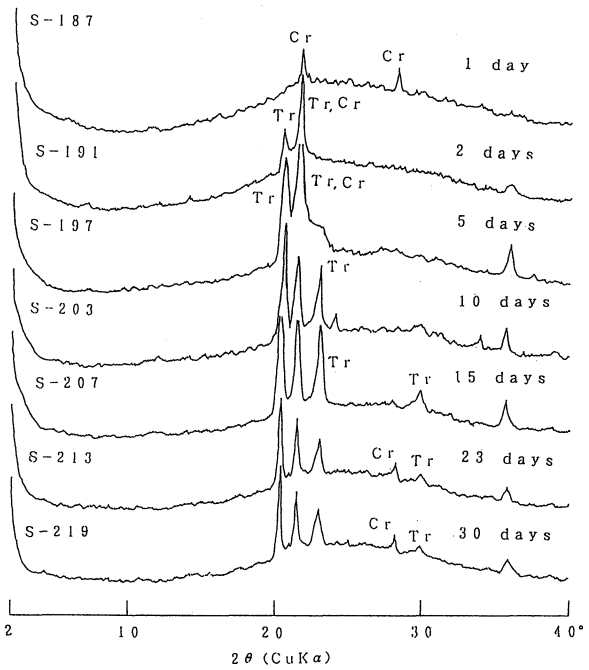

Fig. 13. X-ray powder diffraction patterns of the mixture of amorphous silica (3g) and KOH (1g) after heating at 800℃ for various time.
Cr : cristobalite, Tr : tridymite.

in accordance with time up to 30 days. X-ray powder patterns of the products are shown in Fig. 12.

When a mixture of 3g of amorphous silica and 1g of KOH was heated at 800 ℃, only cristobalite was formed after heating for one day, and tridymite was formed together with cristobalite after two days' heating. Quartz was not formed even after heating for 30 days. X-ray powder diffraction patterns of the reaction products are shown in Fig. 13.

When a mixture of 1.5g of amorphous silica and 1.5g of KOH was heated at 800 ℃, only potassium silicate was formed after heating up to 30 days. Scanning electron micrographs of some products are shown in Fig. 14. Quartz is observed in Fig. 14A, and platy tridymite crystals are observed in Fig. 14B. The results of the products are listed in Table 4.

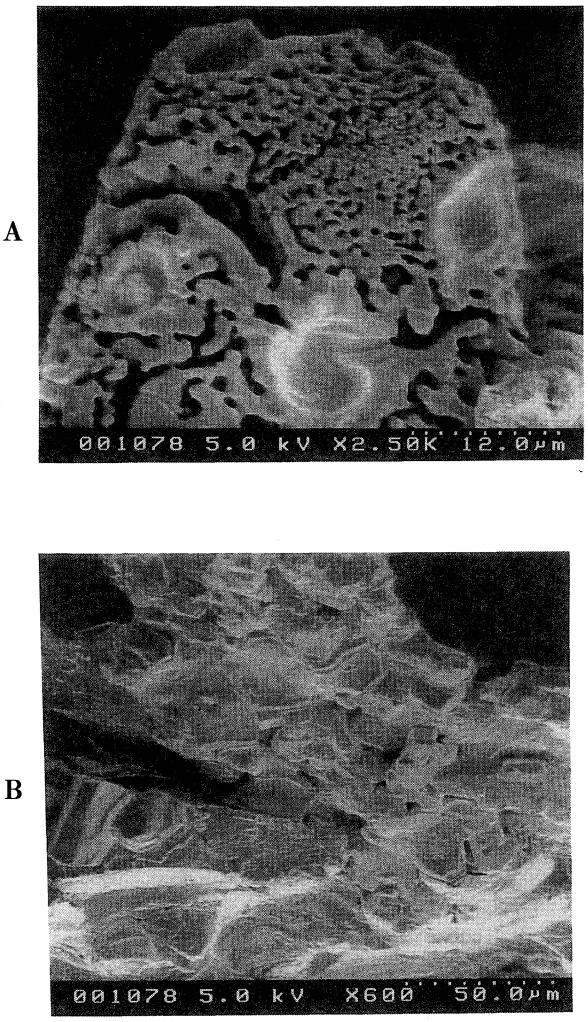

Fig. 14. Scanning electron micrographs of the products from the mixtures of amorphous silica and KOH after for 30 days.
A. Product from the mixture of amorphous silica (3g) and KOH (0.3g).
B. Product from the mixture of amorphous silica (3g) and KOH (0.3g).

Table 4. Experimental conditions and products at 800℃

Run No.	Amorphous silica (g)	KOH (g)	Time (day)	Products
S-222	2	0.1	1	Tr, Cri
S-224	2	0.1	2	Tr, Cri, Q
S-226	2	0.1	5	Tr, Cri, Q
S-228	2	0.1	10	Tr, Cri, Q
S-186	3	0.3	1	Tr
S-196	3	0.3	7	Tr, Cri
S-202	3	0.3	10	Tr, Cri
S-212	3	0.3	17	Tr, Cri, Q
S-218	3	0.3	30	Tr, Cri, Q
S-187	3	1	1	Cri
S-191	3	1	2	Tr, Cri
S-197	3	1	5	Tr, Cri
S-203	3	1	10	Tr, Cri
S-207	3	1	15	Tr, Cri
S-213	3	1	23	Tr, Cri
S-219	3	1	30	Tr, Cri
S-188	1.5	1.5	1	P-Si
S-192	1.5	1.5	2	P-Si
S-198	1.5	1.5	5	P-Si
S-204	1.5	1.5	10	P-Si
S-208	1.5	1.5	15	P-Si
S-214	1.5	1.5	23	P-Si
S-220	1.5	1.5	30	P-Si

Cri : cristobalite, Q : quartz,
Tr : tridymite, P-Si : potassium silicate

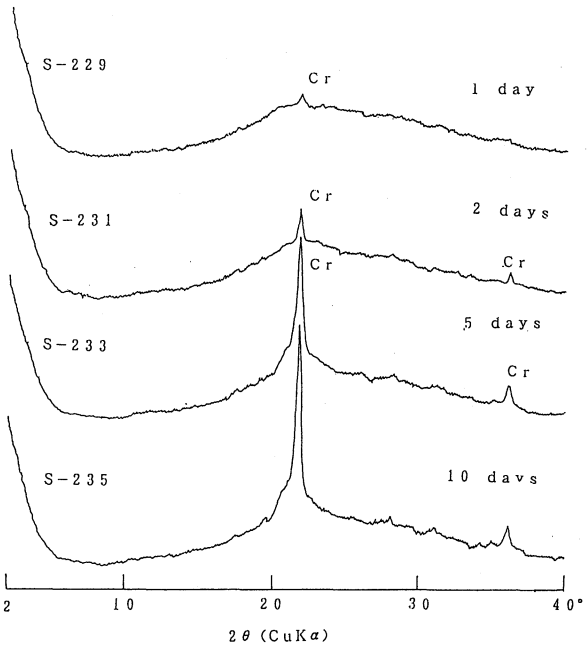

Fig. 15. X-ray powder diffraction patterns of the mixture of amorphous silica (2g) and NaOH (0.1g) after heating at 600 ℃ for various time.
Cr : cristobalite.

2) Reaction at 600 ℃

Effect of NaOH

When a mixture of 2g of amorphous silica and 0.1g of NaOH was heated at 600 ℃, only cristobalite was formed after heating for one day, and amount of cristobalite increased in accordance with heating time. Only cristobalite was formed up to 10 days' heating. X-ray powder diffraction patterns of the products are shown in Fig. 15.

Effect of KOH

When a mixture of 2g of amorphous silica and 0.1g of KOH was heated at 600 ℃, no crystalline form was produced even after heating up to 10 days.

Discussion

When the amorphous silica alone was heated at 800 ℃ for 25 days without adding any cations, no crystalline form was produced. When heated at 800 ℃ under the existence of Na_2SO_4, cristobalite was commonly formed, and quartz was formed after prolonged heating time. When heated at 800 ℃ under the existence of K_2SO_4, cristobalite was formed after heating for 10 days and amount of cristobalite increased in accordance with heating time. Tridymite was not formed under the existence of Na_2SO_4 and K_2SO_4. When NaOH was added, cristobalite, tridymite and quartz were formed after heating at 800 ℃ for one day, and amount of quartz increased in accordance with heating time. When much amount of NaOH was added, cristobalite and tridymite were not formed, and only quartz was formed after heating for more than 23 days. When heated at 800 ℃ under the existence of KOH, tridymite and cristobalite were formed after heating for one day. Quartz was formed under existence of a small amount of KOH, and cristobalite and tridymite were also not formed under existence of much amount of KOH. Amount of quartz increased in accordance with heating time. Hydrothermal experiments on the transformation of amorphous silica were carried out by Mizutani (1966), and he concluded that amorphous silica was converted to low-quartz through an intermediate phase of low-

cristobalite. Refering this facts, in this expeiment, when a small amount of NaOH was added, the result was similar to that of Mizutani (1966). It is difficult to explain why tridymite was not formed under the existence of both Na_2SO_4 and K_2SO_4. The results of this experiment indicate that the conversion mechanisms of amorphous silica to cristobalite, tridymite and quartz are not so simple under the existence of large amount of cations. Further experiments are necessary to clarify the conversion mechanisms.

References

Carr, R. M. and Fyfe, W. S. 1958. Some observations on the crystallization of amorphous silica. *Amer. Mineral.*, **43**, 908-916.

Imanaka, Y., Yamazaki, K., Aoki, S., Kamehara, N. and Niwa, K. 1989. Effects of alumina addition on crystallization of borosilicate glass. *Yogyo-Kyokai-Shi*, **97**, 3, 309-313.

Jones, J. B. and Segnit, E. R. 1971. The nature of opal-I. Nomenclature and constituent phases. *Jour. Geol. Soc. Australia*, **18**, 1, 57-68.

Jones, J. B. and Segnit, E. R. 1972. Genesis of cristobalite and tridymite at low temperature. *Jour. Geol. Soc. Australia*, **18**, 4, 419-422.

Kagawa, H., Tomita, K. and Kawano, M. 1991. Effect of cations on crystallization and phase transition of silica materials. *Rep. Fac. Sci. Kagoshima Univ. (Earth Sci. & Biol.)*, **24**, 1-22.

Mizutani, S. 1966. Transformation of silica under hydrothermal conditions. *The Jour. Earth. Sci. Nagoya Univ.*, **14**, 1, 56-88.

Sakamoto, C., Fujii, S., Sugie, Y. and Shiotsu, S. 1986. Crystal growth of α-quartz from a silica gel using alkali halide flux. *Yogyo-Kyokai-shi*, **95**, 10, 1062-1067.

Sakamoto, C., Fujii, S., Sugie, Y. and Sakurai, K. 1988. Crystal growth of α-quartz and by-production of lithium silicate in NaBr-LiCl type flux. *Yogyo-kyokai -shi*, **96**, 7, 768-772.

Tomita, K. and Kawano, M. 1992. Effect of cations on crystallization of amorphous silica (Part 1). *Rep. Fac. Sci. Kagoshima Univ. (Earth Sci. & Biol.)*, **25**, 1-18.

Tomita, K. and Kawano, M. 1992. Effect of cations on crystallization of amorphous silica (Part 2). *Rep. Fac. Sci. Kagoshima Univ. (Earth Sci. & Biol.)*, **26**, 1-16.