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Effect of Cations on Crystallization of Amorphous Silica (Part 1)

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Abstract

Amorphous silica of guaranteed chemical reagent was used for a starting material, and effects of cations on crystallization of amorphous SiO₂ were investigated. The amorphous silica was heated at 800 °C under the existence of NaCl, KCl and LiCl, respectively. When small amount of NaCl was added, cristobalite and tridymite were formed after heating for one day, and amount of tridymite increased gradually with increasing the heating time and quartz was formed after prolonged heating. When large amount of NaCl was added, only tridymite was formed up to 37 days. When KCl was added, tridymite and cristobalite were formed under the existence of small amount of KCl, and only tridymite was formed under the existence of large amount of KCl. When LiCl was added, only quartz and lithium silicate were formed.

Key words: Amorphous silica, Quartz, Cristobalite, Tridymite

INTRODUCTION

In nature some cristobalites, tridymites and quartz are often found in opal and it is known that these crystals were formed under lower temperatures than ordinarily crystallization temperature. One of the reasons is considered to be due to impurities (Jones and Segnit, 1971, 1972). 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 by some researchers (Carr and Fyfe, 1958; Imanaka *et al.*, 1989; Mizutani, 1966; Sakamoto *et al.*, 1986, 1988), but researches concerning effects of cations on crystallization of amorphous silica are not so many.

In this experiments the authors used amorphous silica of guaranteed chemical reagent as a starting material, and effects of some cations on crystallization of amorphous silica were investigated.

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Experimental procedure

Amorphous silica powder of guaranteed chemical reagent was used for a starting material, and the amorphous silica was put into a porcelainous crucible together with a chloride such as NaCl, KCl and LiCl.

The mixture was heated at 800 °C. Particle sizes of 0.063-0.2 mm were used for the experiment. After heating for desired periods of time the sample was washed with pure water for several times. The washed sample was dried in air, and minerals in the dried sample were identified with an X-ray diffractometer. The microstructures of the samples were observed using a scanning electron microscope.

Results

1. *Effect of NaCl*

In this experiments three kinds of mixtures were prepared. When a mixture of 3 g of amorphous silica and 0.3 g of NaCl was heated, the amorphous silica was converted into crystalline forms after heating for certain periods of time. Its progressive change was clearly detectable on the X-ray diffraction patterns. X-ray powder patterns of the starting material and the reaction products are shown in Fig. 1. The original amorphous silica shows a very broad diffraction pattern and cristobalite and tridymite were formed after heating for one day.

Quartz was formed after heating for 10 days in addition to cristobalite and tridymite, and after heating for 37 days, amount of quartz increased and formation of cristobalite was not observed. Scanning electron micrographs of the starting amorphous silica and products are shown in Fig. 2. Round crystals of cristobalite are observed in the product of one day's heating. Platy crystals of tridymite are observed in the products after heating for 7 days and 10 days besides cristobalite, and crystals of quartz are observed in the product after heating for 10 days.

When a mixture of 1.5 g of amorphous silica and 0.5 g of NaCl was heated, only tridymite was formed after heating for one day. The X-ray powder diffraction patterns of the amorphous silica and the products are shown in Fig. 3. Formation of quartz was not observed even after heating for 10 days, and after heating for 37 days quartz was formed. Scanning electron micrographs of the products are shown in Fig. 4. Platy crystals of tridymite are observed in the products.

When a mixture of 0.2 g of amorphous silica and 0.2 g of NaCl was heated only tridymite was formed up to 10 days' heating time. In this experiment monoclinic tridymite was always formed. Scanning electron micrographs of products are shown in Fig. 5. Platy crystals of tridymite are observed.

The results of experimental products are listed in Table 1.

2. *Effect of KCl*

Three kinds of mixtures were prepared to investigate the effect of KCl. When a mixture of 3 g of amorphous silica and 0.3 g of KCl was heated, the amorphous silica was converted into crystalline forms after heating for certain periods of time.

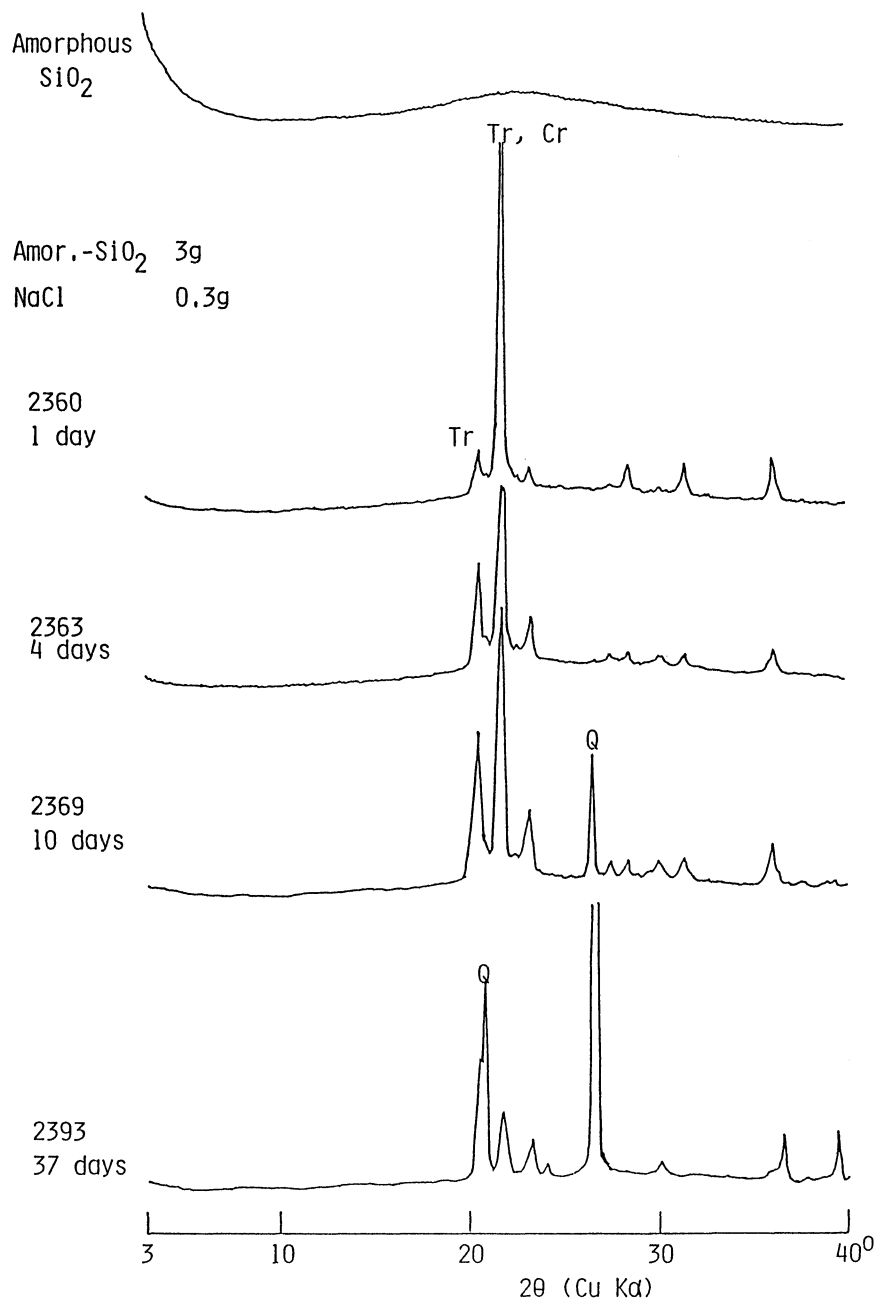


Fig. 1. X-ray powder diffraction patterns of the amorphous silica and products of the mixture of amorphous silica (3 g) and NaCl (0.3 g) after heating for various times. Tr: monoclinic tridymite, Cr: cristobalite, Q: quartz.

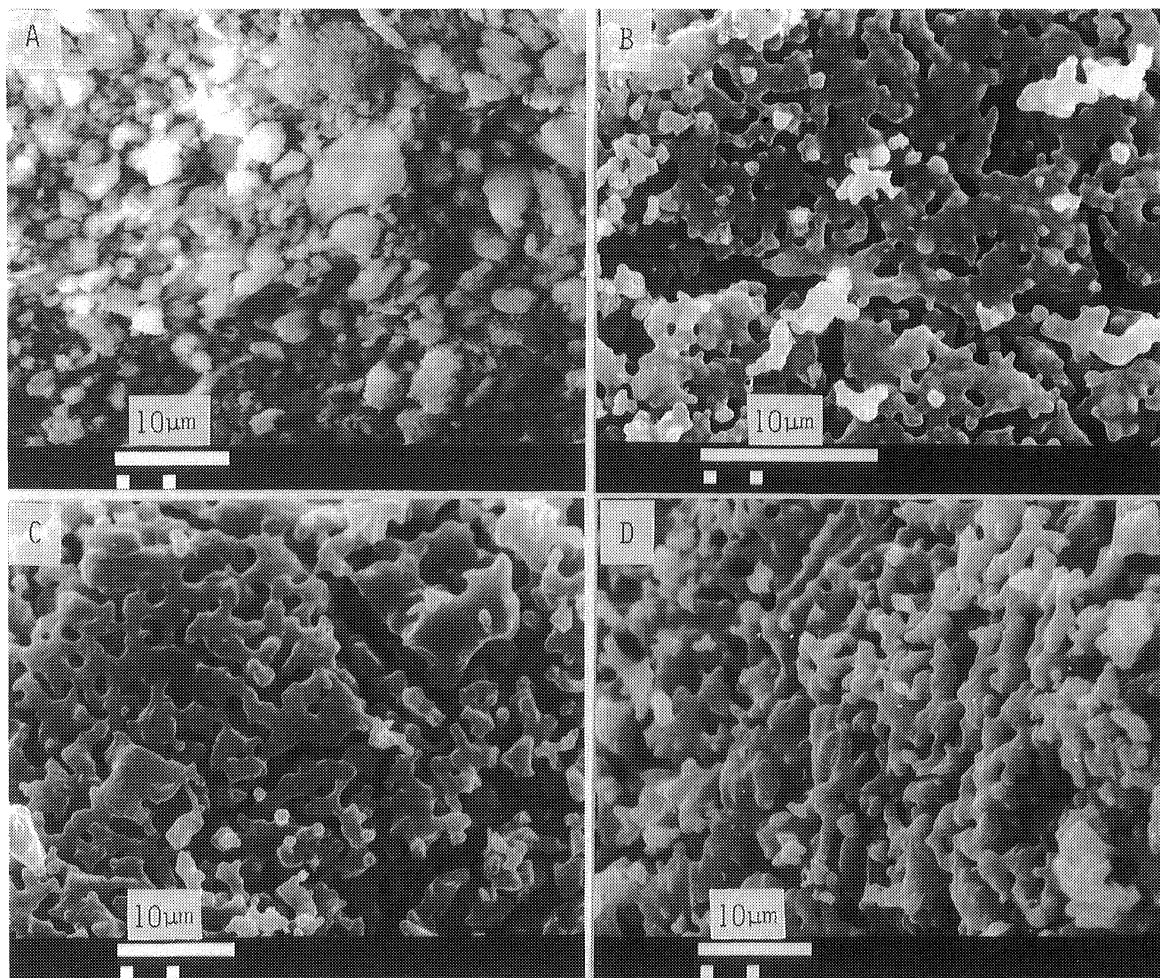


Fig. 2. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (3 g) and NaCl (0.3 g) after heating for various times. A. amorphous silica, B. product after heating for one day, C. product after heating for 7 days, D. product after heating for 10 days.

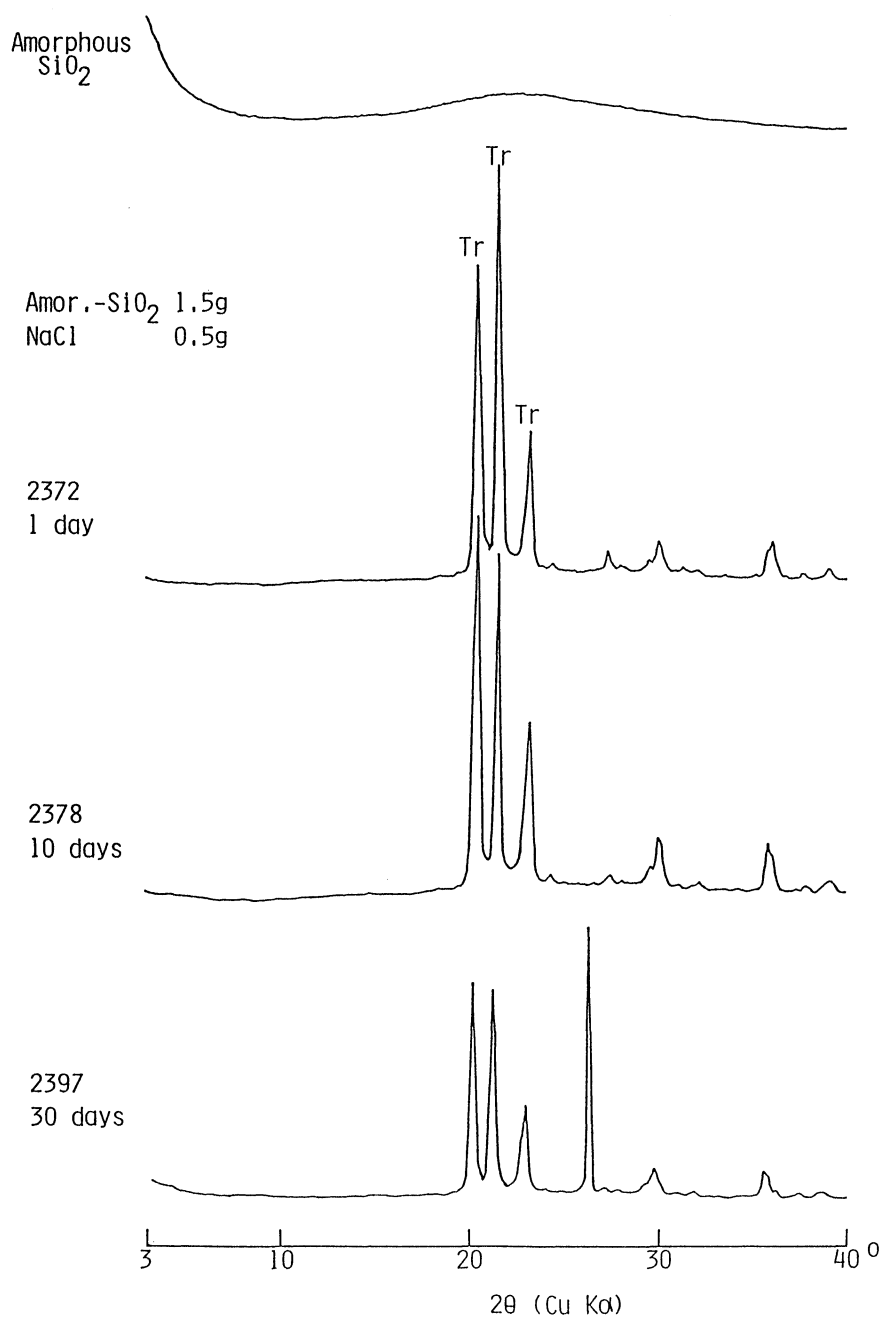


Fig. 3. X-ray powder diffraction patterns of the amorphous silica and products of the mixture of amorphous silica (1.5 g) and NaCl (0.5 g) after heating for various times. Tr: monoclinic tridymite.

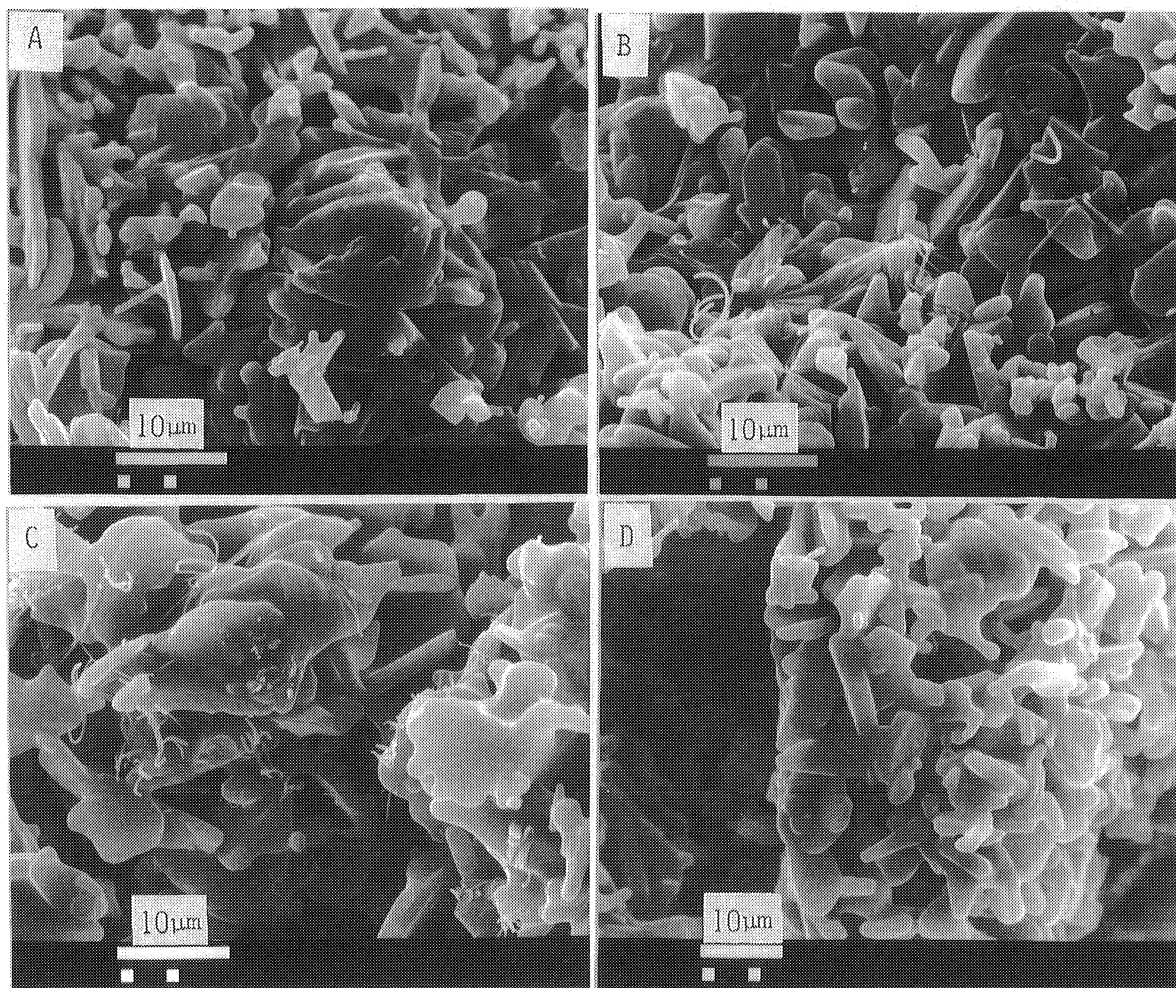


Fig. 4. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (1.5 g) and NaCl (0.5 g) after heating for various times. A. product after heating for one day, B. product after heating for 2 days, C. product after heating for 5 days, D. product after heating for 5 days.

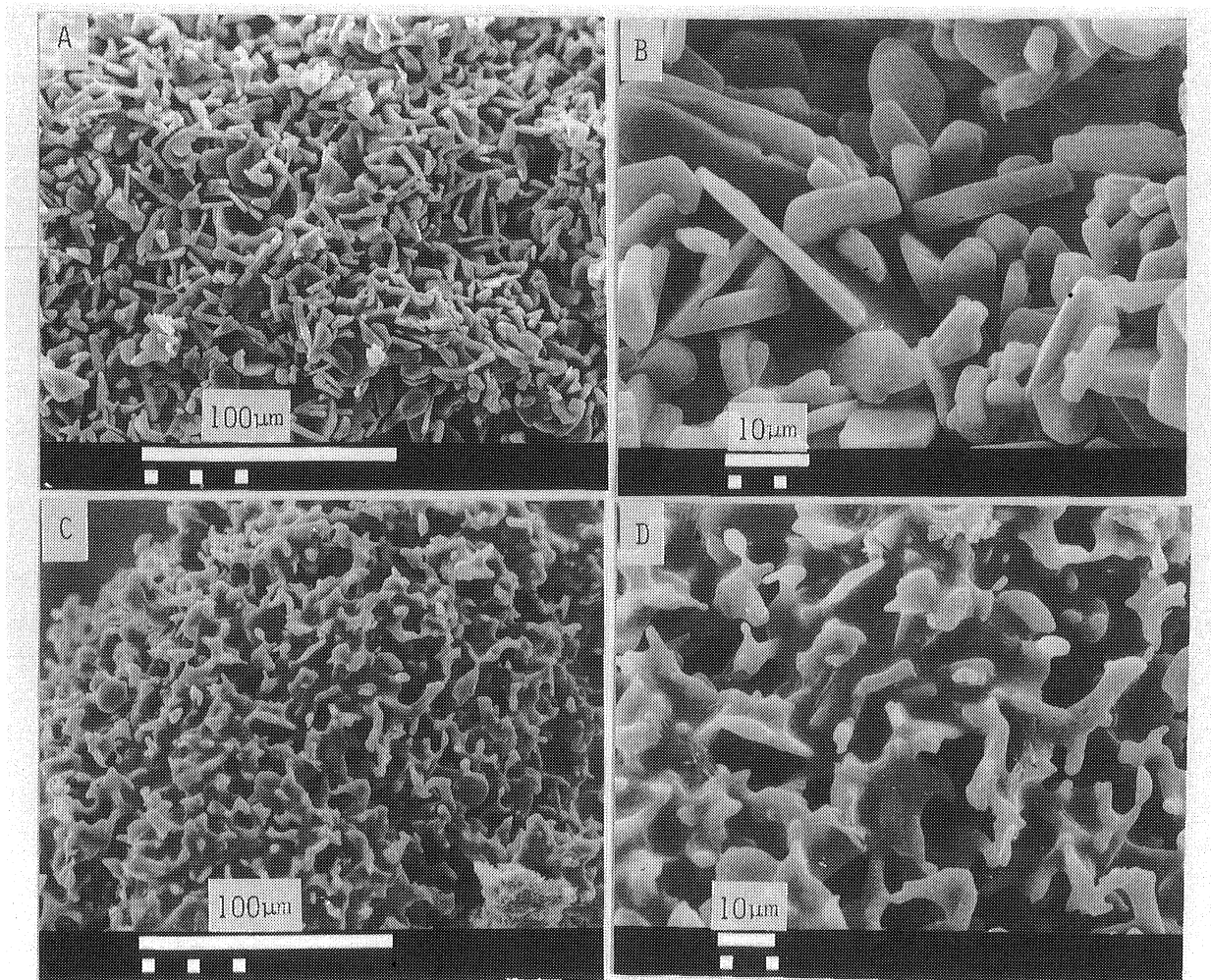


Fig. 5. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (0.2 g) and NaCl (0.2 g) after heating for various times. A. product after heating for 2 days, B. product after heating for 2 days, C. product after heating for 5 days, D. product after heating for 5 days.

Table 1. Experimental conditions and products.

Run No.	Amorphous SiO ₂ (g)	NaCl (g)	Time (day)	Products
2360	3	0.3	1	Cri, M-Tr
2363	3	0.3	4	Cri, M-Tr
2366	3	0.3	7	Cri, M-Tr, Q
2369	3	0.3	10	Q, M-Tr, Cri
2379	3	0.3	17	Q, M-Tr, Cri
2393	3	0.3	37	Q, M-Tr, Cri
2372	1.5	0.5	1	M-Tr
2374	1.5	0.5	2	M-Tr
2375	1.5	0.5	5	M-Tr
2378	1.5	0.5	10	M-Tr
2397	1.5	0.5	30	M-Tr, Q (?)
2373	0.2	0.2	2	M-Tr
2376	0.2	0.2	5	M-Tr
2377	0.2	0.2	10	M-Tr

Cri: cristobalite, M-Tr: monoclinic tridymite, Q:quartz

X-ray powder patterns of the starting material and the reaction products are shown in Fig. 6. Cristobalite and tridymite were formed after heating for one day, but quartz was not formed after heating for 17 days, and after heating for 37 days, quartz was formed.

Scanning electron micrographs of the products are shown in Fig. 7. Round crystals of cristobalite and platy tridymite are observed in the product of 4 days' heating. Platy crystals of tridymite are dominant in the products after heating for 7 days and 17 days, respectively.

When a mixture of 3 g of amorphous silica and 1 g of KCl was heated, only tridymite was formed after heating for two days. The X-ray powder diffraction patterns of the amorphous silica and the products are shown in Fig. 8. Formation of quartz was not observed after heating for 30 days. Scanning electron micrographs of the products are shown in Fig. 9. Platy crystals of tridymite are observed in the products.

When a mixture of 3 g of amorphous silica and 3 g of NaCl was heated, small amount of cristobalite was formed after heating for 2 days in addition to tridymite, but only tridymite was formed up to 30 days' heating time. In this experiment monoclinic tridymite was also always formed. Formation of quartz was not observed after heating for 30 days. Scanning electron micrographs of the products are shown in Fig. 10.

The results of experimental products are listed in Table 2.

3. Effect of LiCl

Three kinds of mixtures were prepared to investigate the effect of LiCl. When a mixture of 3 g of

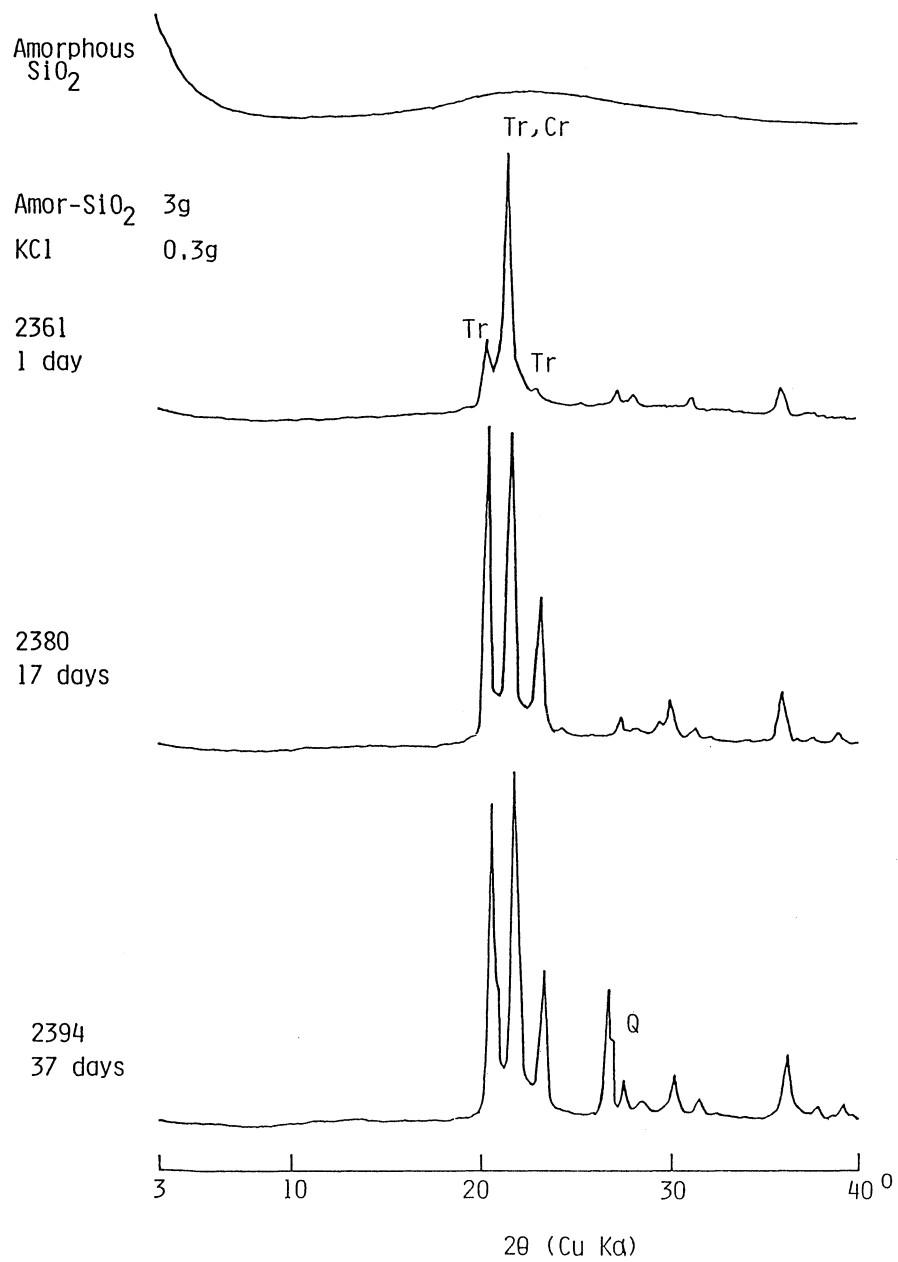


Fig. 6. X-ray powder diffraction patterns of the amorphous silica and products of the mixture of amorphous silica (3 g) and KCl (0.3 g) after heating for various times. Tr: monoclinic tridymite, Cr: cristobalite, Q: quartz.

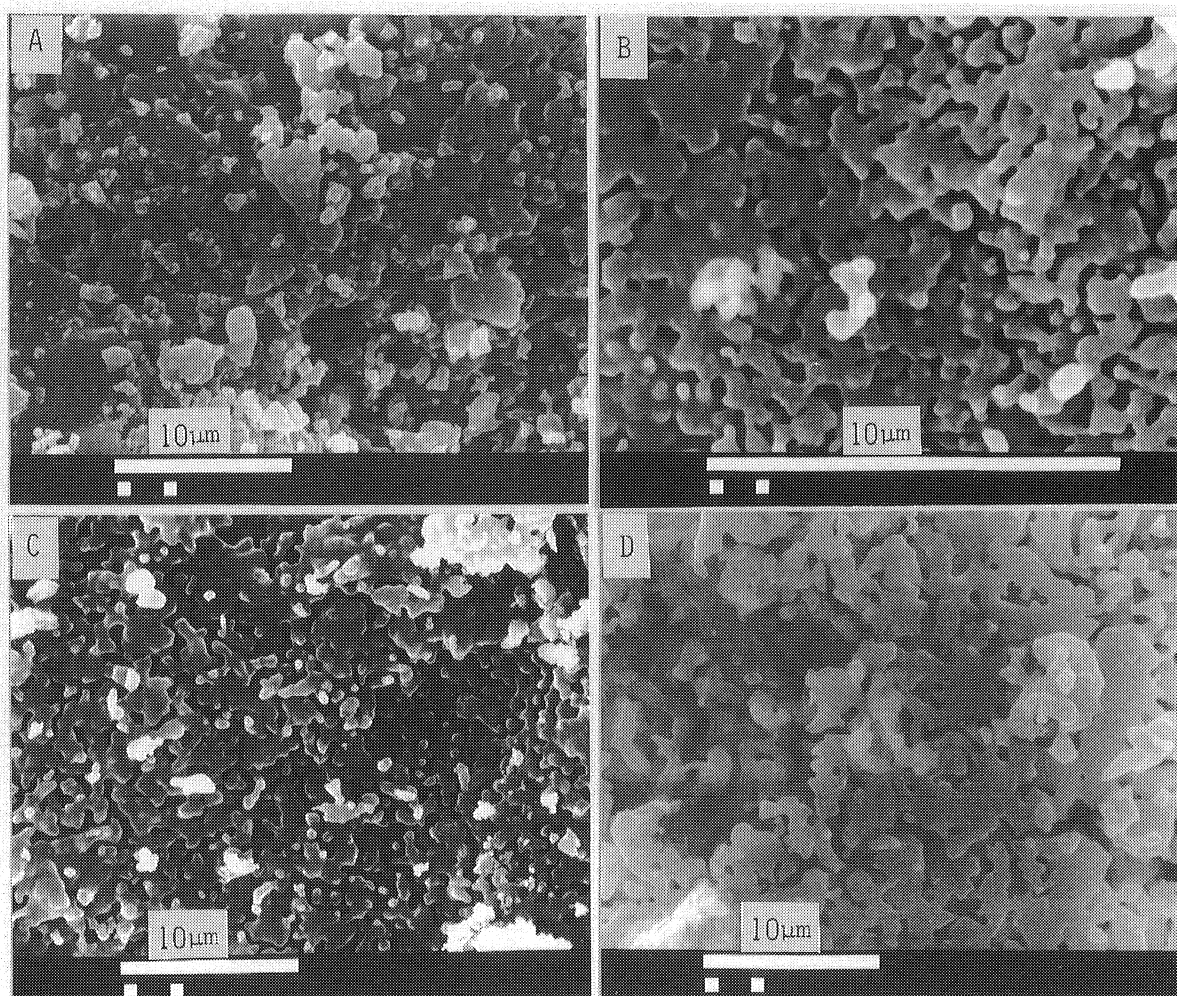


Fig. 7. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (3 g) and KCl (0.3 g) after heating for various times.
A. product after heating for 4 days, B. product after heating for 7 days, C. product after heating for 7 days, D. product after heating for 17 days.

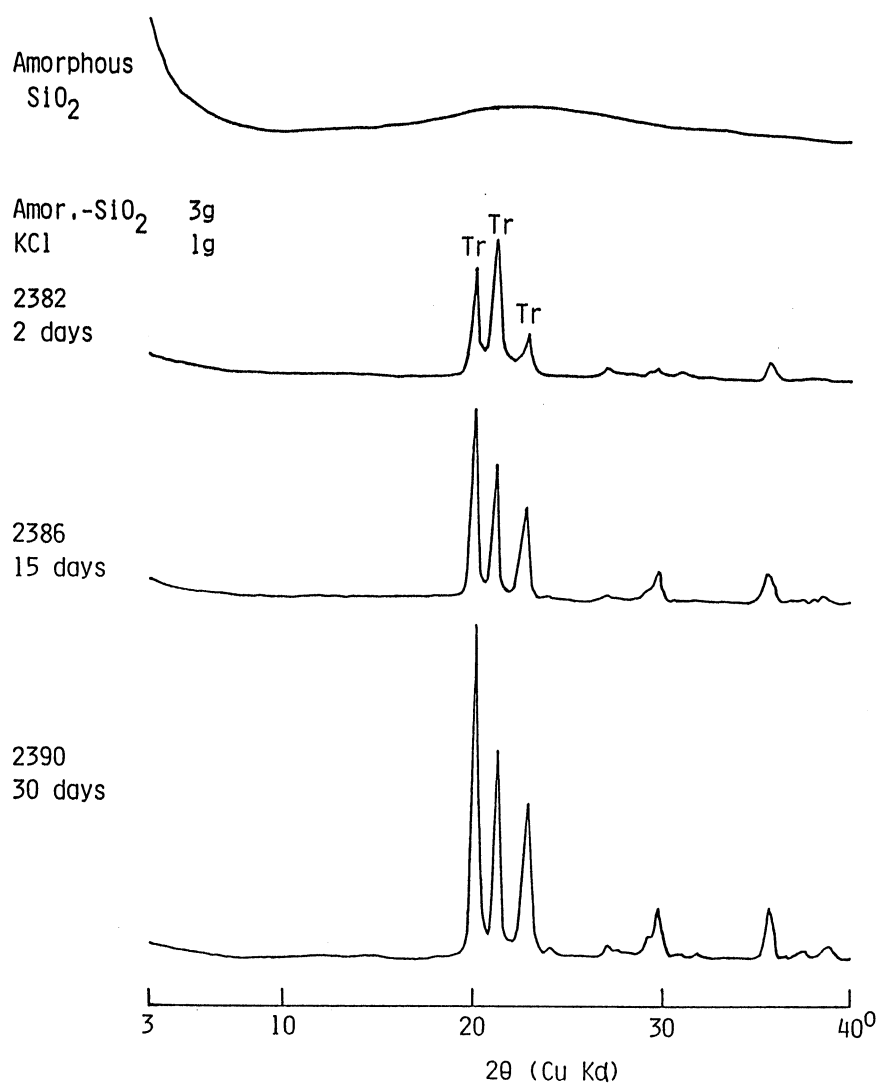


Fig. 8. X-ray powder diffraction patterns of the amorphous silica and products of the mixture of amorphous silica (3 g) and KCl (1 g) after heating for various times.
Tr: monoclinic tridymite.

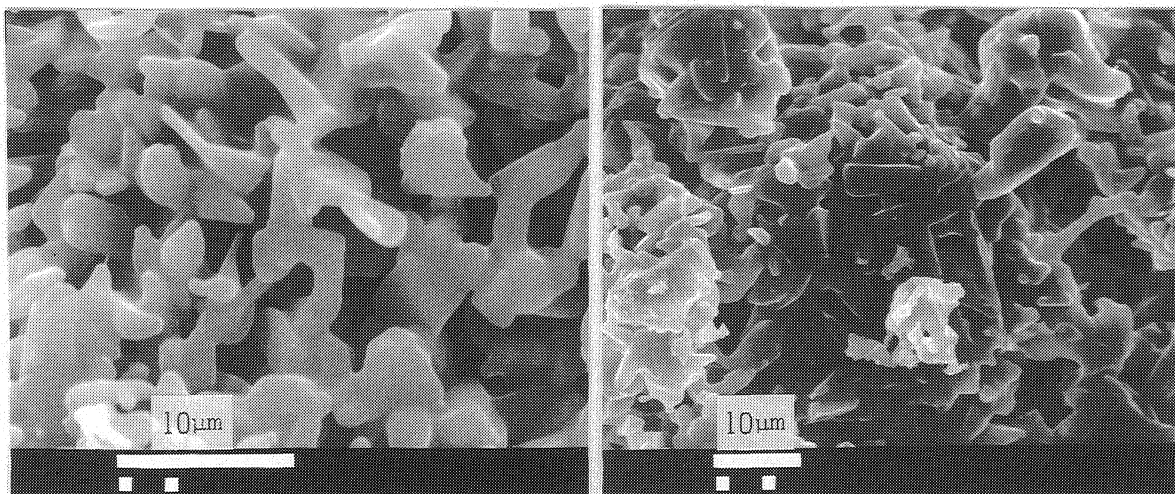


Fig. 9. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (3 g) and KCl (1 g) after heating for 10 days.

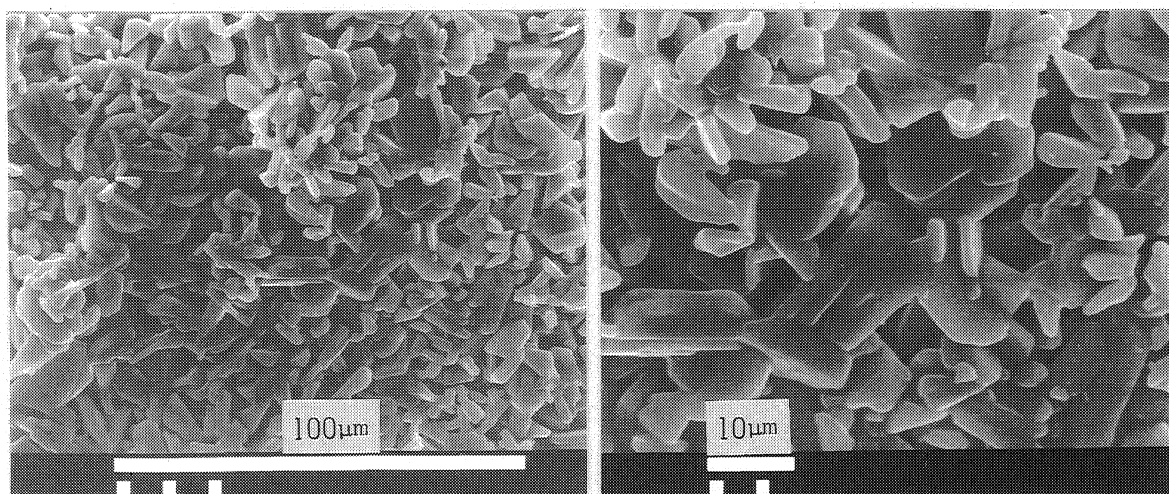


Fig. 10. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (3 g) and KCl (3 g) after heating for 10 days.

Table 2. Experimental conditions and products.

Run No.	Amorphous SiO ₂ (g)	KCl (g)	Time (day)	Products
2361	3	0.3	1	M-Tr, Cri
2364	3	0.3	4	M-Tr, Cri
2367	3	0.3	7	M-Tr, Cri
2370	3	0.3	10	M-Tr, Cri
2380	3	0.3	17	M-Tr, Cri
2394	3	0.3	37	M-Tr, Cri, Q
2382	3	1	2	M-Tr
2384	3	1	5	M-Tr
2386	3	1	15	M-Tr
2390	3	1	30	M-Tr
2383	3	3	2	M-Tr, Cri (?)
2385	3	3	5	M-Tr
2387	3	3	15	M-Tr
2391	3	3	30	M-Tr

Cri: cristobalite, M-Tr: monoclinic tridymite, Q: quartz

amorphous silica and 0.3 g of LiCl was heated, the amorphous silica was converted into crystalline forms after heating for certain periods of time. X-ray powder patterns of the starting material and the reaction products are shown in Fig. 11.

Quartz and lithium silicate (Li₂Si₂O₅) were formed after heating for one day, and same products were formed up to 37 days' heating. Cristobalite and tridymite were not formed.

Scanning electron micrographs of the products are shown in Fig. 12. Crystals of quartz are observed in the product of one day's heating. Fibrous crystals of lithium silicate are observed.

When a mixture of 3 g of amorphous silica and 1 g of LiCl was heated, quartz and lithium silicate were formed after heating for three days.

Scanning electron micrographs of the products are shown in Fig. 13. Crystals of quartz are observed in the product of one day's heating.

Platy crystals of lithium silicate are observed in the product after heating for one day.

The results of experimental products are listed in Table 3.

Discussion

Amorphous silica was converted to low-quartz through an intermediate phase of cristobalite and monoclinic tridymite under the existence of small amount of NaCl, whereas only monoclinic tridymite was formed under the existence of large amount of NaCl. When KCl was added, monoclinic tridymite and cristobalite were formed, and monoclinic tridymite was dominant product under the existence of small amount of KCl and only monoclinic tridymite was formed under the existence of large amount of KCl. Only small amount of quartz was formed after heating for 37 days under the existence of small

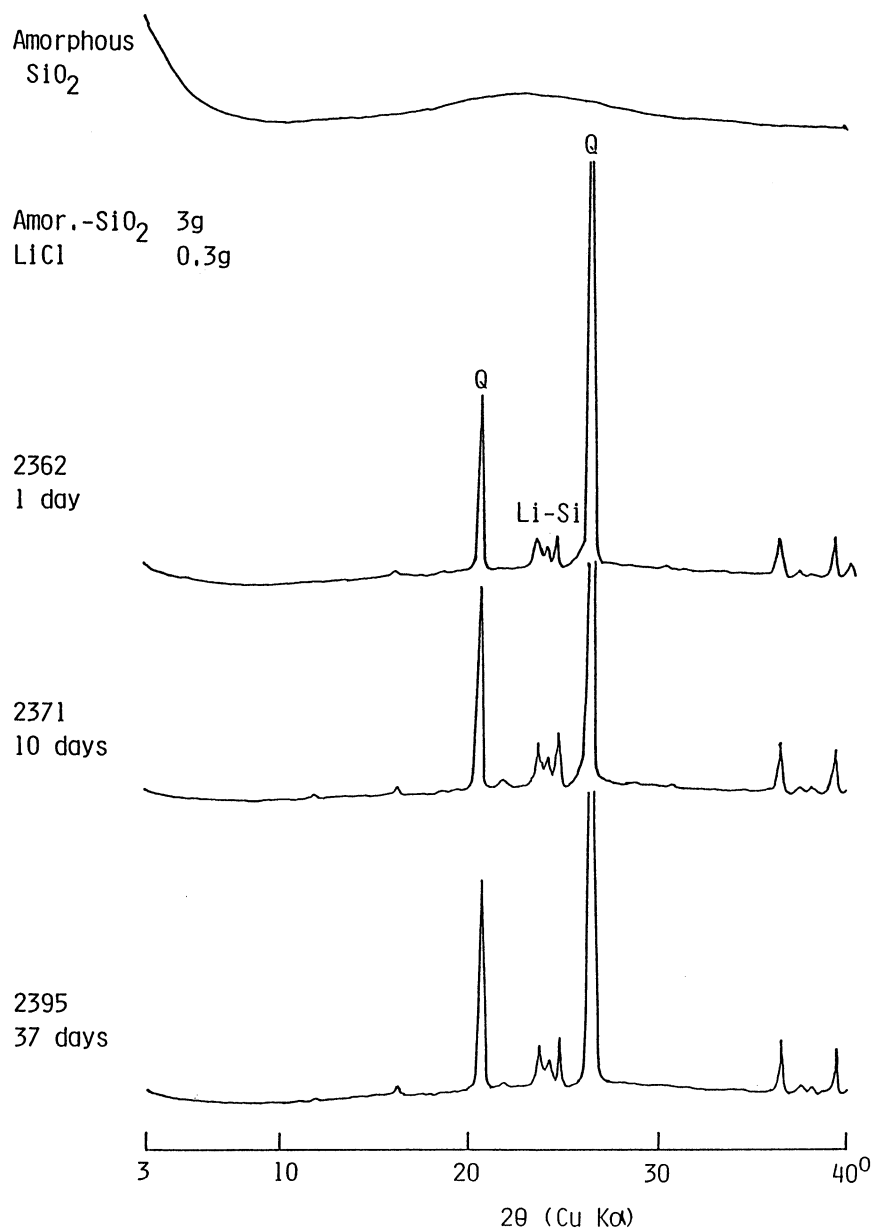


Fig. 11. X-ray powder diffraction patterns of the amorphous silica and products of the mixture of amorphous silica (3 g) and LiCl (0.3 g) after heating for various times. Q: quartz, Li-Si: lithium silicate.

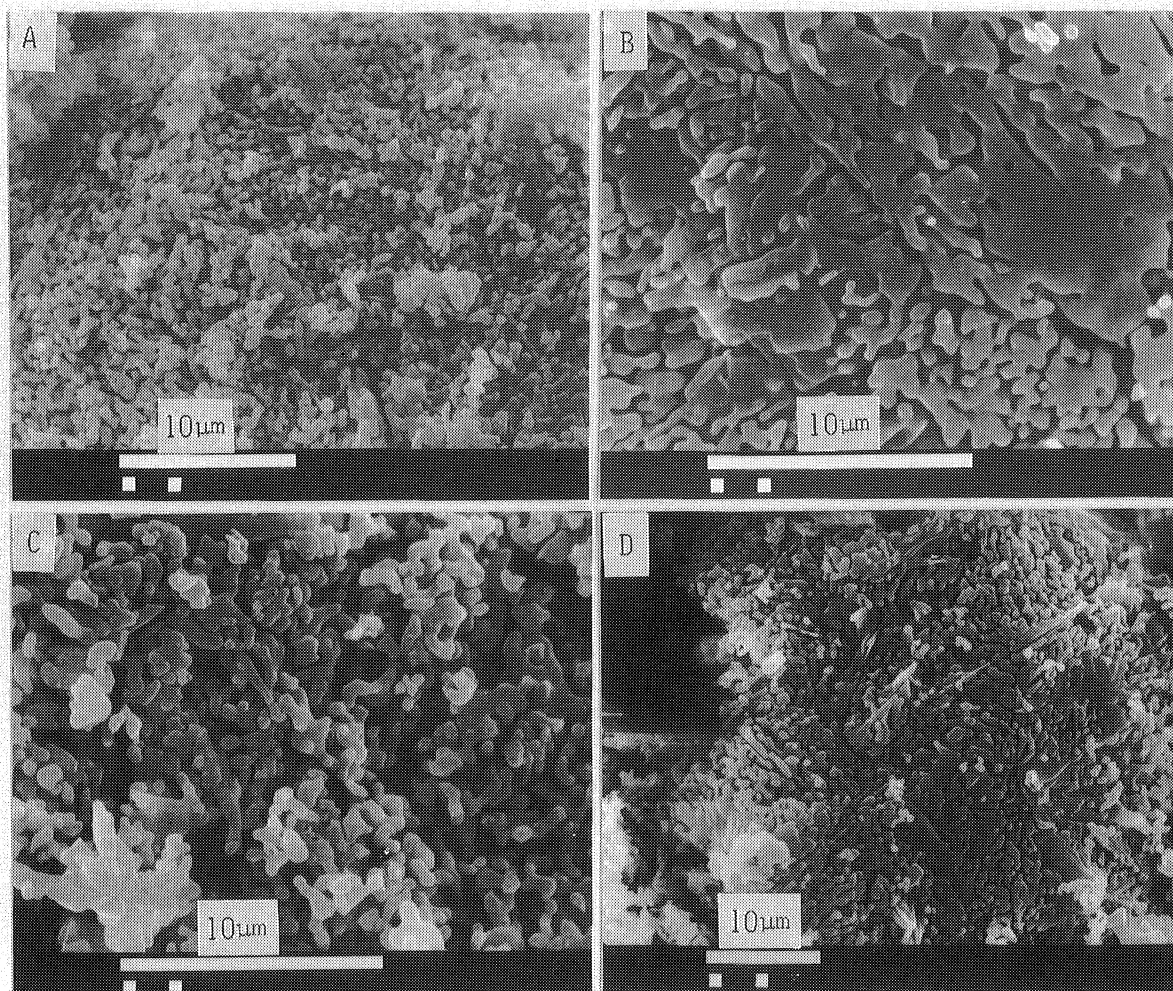


Fig. 12. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (3 g) and LiCl (0.3 g) after heating for various times. A. product after heating for one days, B. product after heating for one days, C. product after heating for 4 days, D. product after heating for 10 days.

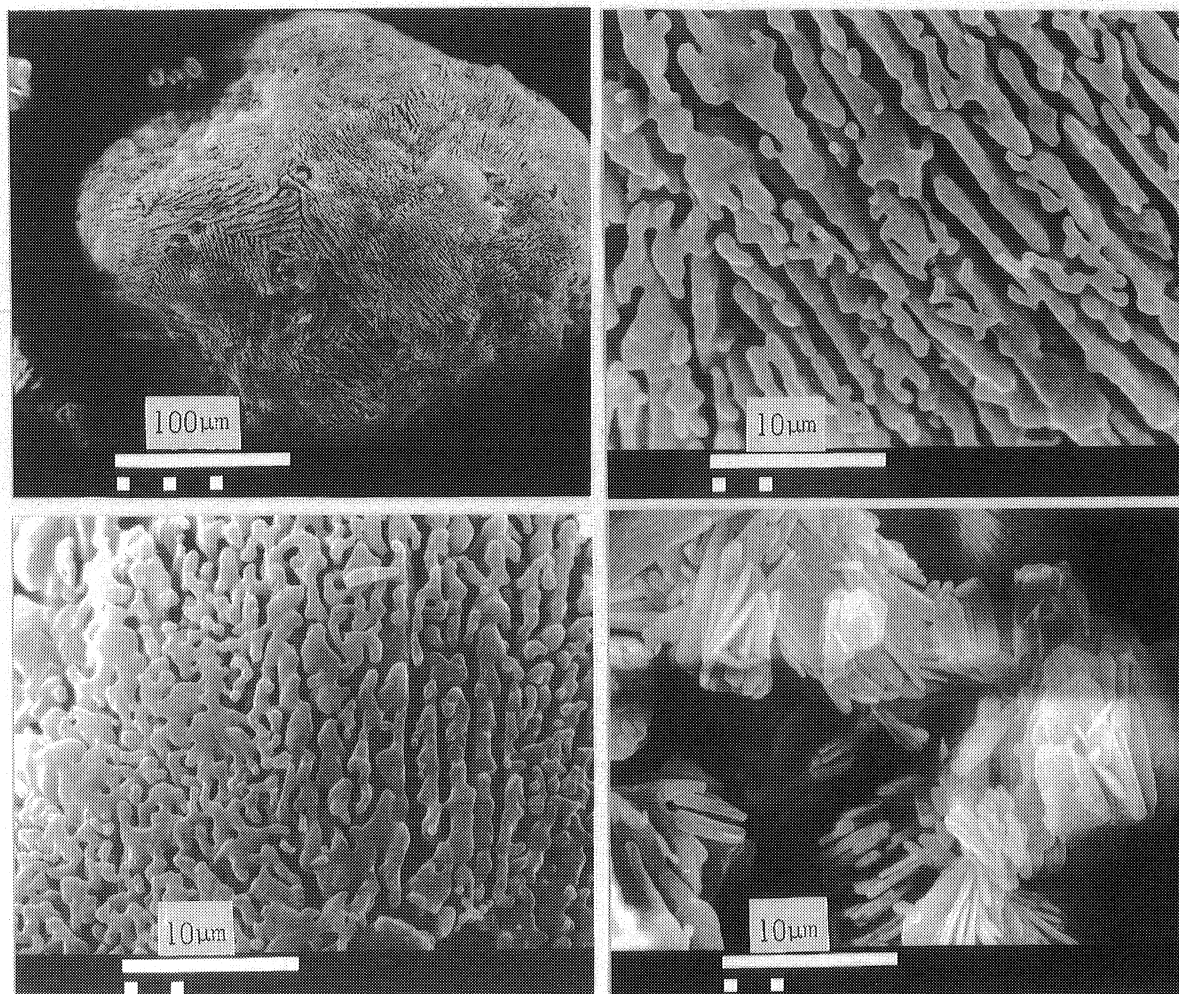


Fig. 13. Scanning electron micrographs of the amorphous silica and products of the mixture of amorphous silica (3 g) and LiCl (1 g) after heating for one day.

Table 3. Experimental conditions and products.

Run No.	Amorphous SiO ₂ (g)	LiCl (g)	Time (day)	Products
2362	3	0.3	1	Q, Li-Si
2365	3	0.3	4	Q, Li-Si
2368	3	0.3	7	Q, Li-Si
2371	3	0.3	10	Q, Li-Si
2381	3	0.3	17	Q, Li-Si
2395	3	0.3	37	Q, Li-Si
2396	3	1	1	Q, Li-Si
2398	3	1	3	Q, Li-Si

Q: quartz, Li-Si: lithium silicate (Li₂Si₂O₅)

amount of KCl. When LiCl was added only quartz and lithium silicate were formed. Cristobalite and tridymite were not formed. In this experiments, no other phases such as silica K which was formed when natural amorphous silicas were used (Kagawa *et al.*, 1991) were observed. Formation of silica K as an intermediate phase was reported by Carr and Fyfe (1958) and Mizutani (1966). 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. In this experiment when small amount of NaCl was added, the result was similar to that of Mizutani (1966). But 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. The ways of transformation under the existence of various cations are different from each other.

The mechanisms of the effects of cations on crystallization of amorphous silica will be reported in later papers.

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