Effect of Cations on Crystallization of Amorphous Silica (Part 2)

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Abstract

Amorphous silica of guaranteed chemical reagent was heated at temperatures 500 ℃, 600℃, 800℃ and 1000℃ under the existence of various chlorides such as NaCl, KCl and LiCl, and effects of which on crystallization of the amorphous SiO_2 were investigated. At 500℃, no crystalline form was produced when small amounts of NaCl and KCl were added, but with LiCl, quartz was evident after 25 days. At 600℃, cristobalite was formed under the existence of NaCl, and tridymite and cristobalite under the existence of KCl, both crystallizations resulting from 70 days heating. Quartz and lithium silicate were formed under the existence of LiCl in 25 days' heating. When NaCl was added at 800℃, both cristobalite and tridymite were formed in one-day's time, but the amount of tridymite gradually increased with heating time where by forming quartz after prolonged heating. With large amount of NaCl, however, only tridymite remained formed for up to 37days. With KCl was added at 800℃, tridymite and cristobalite likewise were formed under the existence of small amount, and only tridymite formed under the existence of large amount. Upon addition of LiCl, products varied depending upon the amounts added. At 1000℃, tridymite and cristobalite were formed in 7 days heating under the existence of NaCl and KCl.

Key words: Amorphous silica, Quartz, Cristobalite, Tridymite, crystallization.

Introduction

In nature 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 considered is due to impurities (Jones and Segnit, 1971, 1972) and this was confirmed by Kagawa *et al.*, (1991) using natural amorphous silicas, but effects of

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cations however were not investigated in detail. Crystallization of quartz from amorphous silica is likewise reported (Carr and Fyfe, 1958; Imanaka *et al.*, 1989; Mizutani, 1966; Sakamoto *et al.*, 1986, 1988), but again, researches concerning effects of cations on crystallization of amorphous silica are not so many. The authors of this paper (Tomita and Kawano, 1992), previously presented a study on this cation effects using amorphous silica of guaranteed chemical reagent as a starting material, with observations made only at 800℃ temperatures condition. In this experiments the authors investigated the effects of cations at 500℃, 600℃, 800℃ and 1000℃.

Experimental procedure

Amorphous silica powder of guaranteed chemical reagent was used as a starting material. Experiments were conducted using a porcelainous crucible where the mixture of amorphous silica with chloride such as NaCl, KCl and LiCl were placed. The mixtures were subjected to different levels of temperatures 500℃, 600℃, 800℃ and 1000℃. 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

Effect of NaCl

In this experiments four kinds of mixtures were prepared. When mixture of 3g of amorphous silica and 0.3g of NaCl was heated at 500℃, no crystalline form was produced after heating for 110 days. With temperature increased to 600℃, the amorphous silica was converted into cristobalite in 70 days. At 800℃, cristobalite and tridymite were formed in one day, and quartz crystals after 7 days. Amount of quartz increased in accordance with heating time, and the phase lasted up to 37 days. Tridymite and cristobalite were both formed at 1000℃ in 7 hours, but the amount of cristobalite decreased after 6 days. X-ray powder patterns of the reaction products after heating at 600℃, 800℃ and 1000℃ are shown in Fig. 1. Mixture of 3g of amorphous silica and 1g of NaCl heated at 500℃ produced no crystalline form. The mixture of 1.5g of amorphous silica and 0.5g of NaCl heated at 800℃ produced tridymite in 10 days, and small amount of quartz was formed in addition to the tridymite after 30 days. The mixture of 0.2g of amorphous silica and 0.2g of NaCl heated at 800℃, produced only tridymite in 10 days. Experimental conditions and products for these mixtures of amorphous silica and heated with NaCl are listed in Table 1. The products are arranged in order of amounts, and the first is the most abundant product. Effects of heating temperature and reaction time on the mixture of 3g of amorphous silica and 0.3g of NaCl on crystallization are shown in Fig. 2. The relationship between the value of (amorphous silica (g)/NaCl (g)) and reaction time at 800℃ is shown in Fig. 3. In Figures 2 and 3, marks at each points are in the order of produced amount in descending scale. It was observed in this experiment that monoclinic tridymite were always formed specially under the conditions of mixture of

1.5g of amorphous silica and 0.5g of NaCl heated at 800℃, and in a mixture of 0.2g of amorphous silica and 0.2g of NaCl also heated at 800℃.

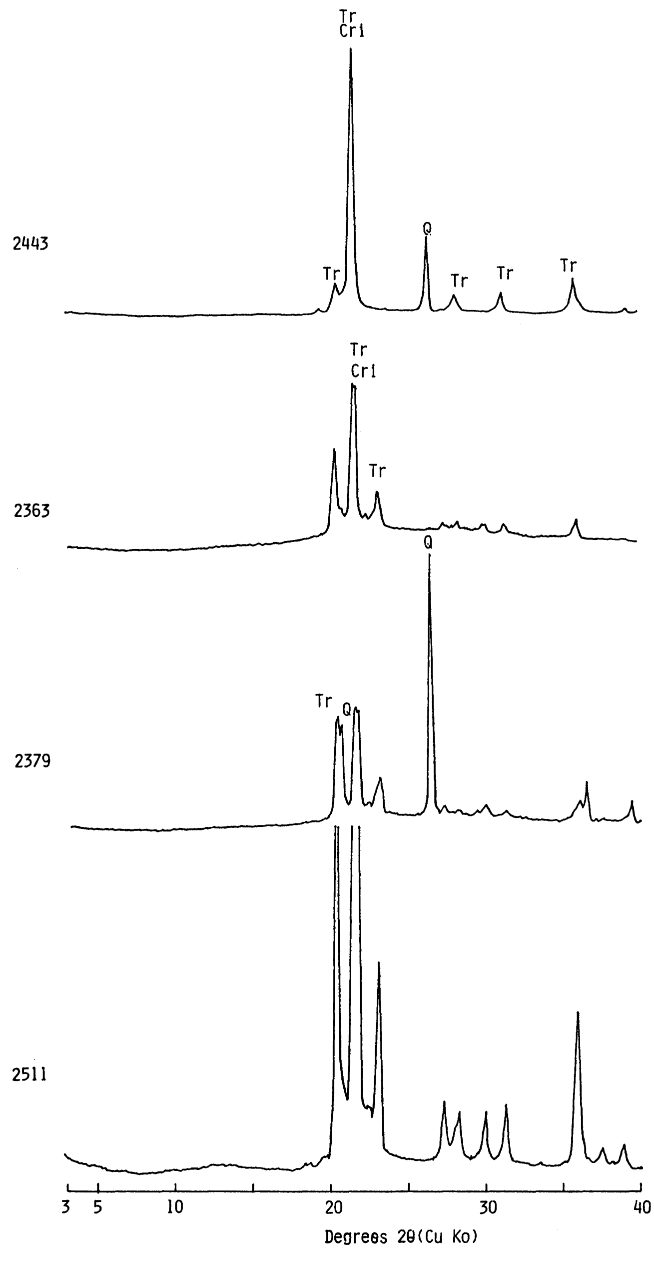

Fig. 1 X-ray powder diffraction patterns of the reaction products from the mixture of 3g of amorphous silica and 0.3g of NaCl heated at 600℃, 800℃ and 1000℃.
2443: 70 days at 600℃, 2363: 4 days at 800℃, 2379: 17 days at 800℃, 2511: 33 hours at 1000℃.
Tr: tridymite, Cri: cristobalite, Q: quartz.

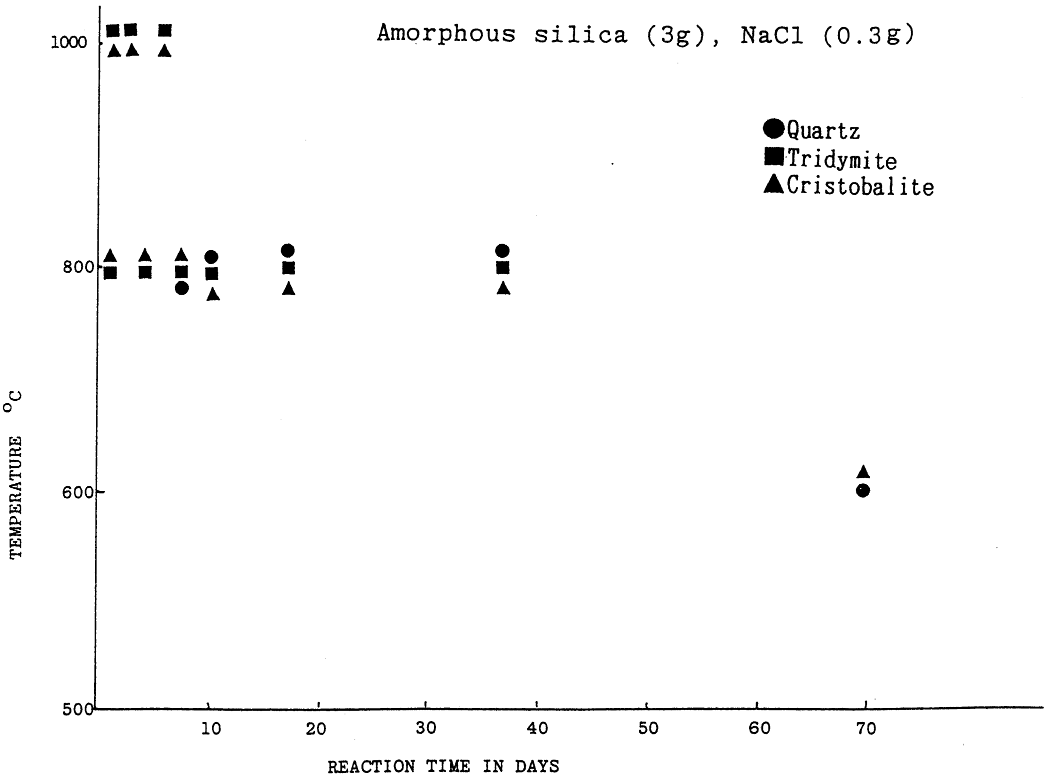

Fig. 2 Reaction products from the mixture of 3g of amorphous silica and 0.3g of NaCl under various conditions of time and temperature.

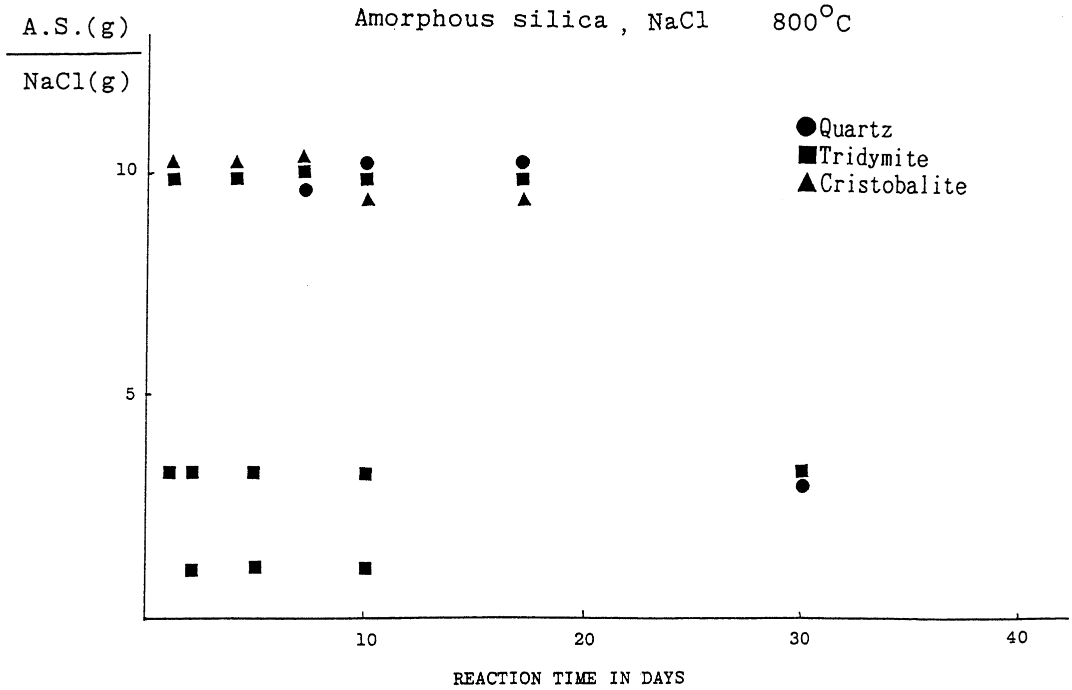

Fig. 3 Effects of amorphous silica (A.S.) (g) to NaCl (g) ratio on the reaction products.

Table 1. Experimental conditions and products.

Run No.	Amorphous SiO_2 (g)	NaCl (g)	Time (day)	Temperature (℃)	Products
2461	3	0.3	6	500	
2467	3	0.3	25	500	
2473	3	0.3	50	500	
2481	3	0.3	65	500	
2489	3	0.3	90	500	
2495	3	0.3	110	500	
2464	3	1	6	500	
2470	3	1	25	500	
2476	3	1	50	500	
2484	3	1	65	500	
2492	3	1	90	500	
2498	3	1	110	500	
2430	3	0.3	1	600	
2434	3	0.3	5	600	
2443	3	0.3	70	600	Tr, Cri, Q
2360	3	0.3	1	800	Cri, Tr
2363	3	0.3	4	800	Cri, Tr
2366	3	0.3	7	800	Cri, Tr, Q
2369	3	0.3	10	800	Q, Tr, Cri
2379	3	0.3	17	800	Q, Tr, Cri
2393	3	0.3	37	800	Q, Tr, Cri
2372	1.5	0.5	1	800	Tr
2374	1.5	0.5	2	800	Tr
2375	1.5	0.5	5	800	Tr
2378	1.5	0.5	10	800	Tr
2397	1.5	0.5	30	800	Tr, Q
2373	0.2	0.2	2	800	Tr
2376	0.2	0.2	5	800	Tr
2377	0.2	0.2	10	800	Tr
2505	3	0.3	0.29	1000	Tr, Cri
2511	3	0.3	1.375	1000	Tr, Cri
2530	3	0.3	6	1000	Tr, (Cri)

Cri: cristobalite, Tr: tridymite, Q: quartz

Effect of KCl

Three kinds of mixtures were prepared to investigate the effect of KCl. In a mixture of 3g of amorphous silica and 0.3g of KCl heated at 500℃, no crystalline form was produced after 110 days. When the mixture was heated at 600℃, the amorphous silica was converted into tridymite and cristobalite after heating for 70 days. Tridymite and cristobalite were likewise formed in one day after heating at a higher temperature at 800℃. Quartz was also developed in addition to the two crystals, after heating for 37 days. Amount of tridymite increased in accordance with heating time. The relationship between the weight percent of produced tridymite and reaction time is shown in Fig. 4. Only tridymite was formed at 1000℃ after heating for 7 hours, and the phase lasted up to 6 days. When a mixture of 3g of amorphous silica and 1g of KCl was heated at 500 ℃, no crystalline form was produced after 110 days. Only at 800℃ heating that tridymite was formed after two days, which lasted up to 30 days. No quartz observed when heated for 30 days. When a mixture of 3g of amorphous silica and 3g of KCl was heated, tridymite and small amount of cristobalite were formed after heating for 2 days, but only tridymite remained present after longer heating time up to 30 days. In the observations made in this experiment, monoclinic tridymite was generally produced under KCl conditions. Formation of quartz was not observed even after heating for 30 days. The X-ray powder diffraction patterns of the products after heating at 600℃, 800℃ and 1000℃ are shown in Fig. 5. The results of experimental products are

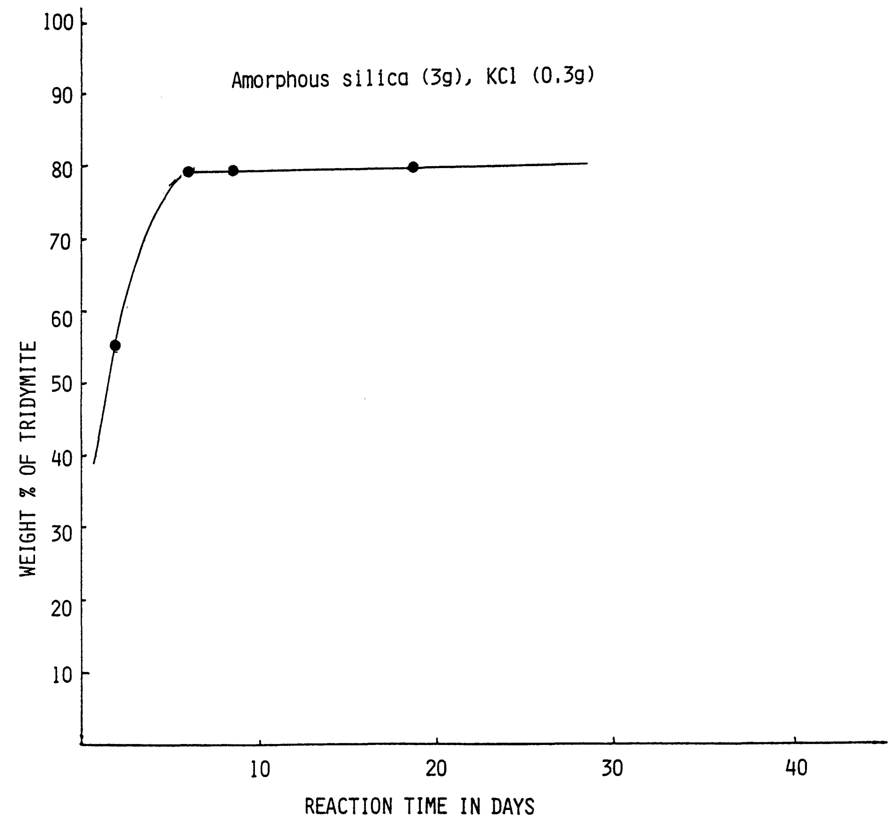

Fig. 4 Relationship between the weight % of produced tridymite and reaction time at 800℃ from the mixture of 3g of amorphous silica and 0.3g of KCl.

listed in Table 2, and weight percentage of produced tridymite after heating at 600℃, 800℃ and 1000℃ for various heating time are listed in Table 3. Effects of heating temperature and reaction time for a mixture of 3g of amorphous silica and 0.3g of KCl on crystallization are shown in Fig. 6. The relationship berween the value of (amorphous silica (g)/KCl (g)) and reaction time at 800℃ is shown in Fig. 7.

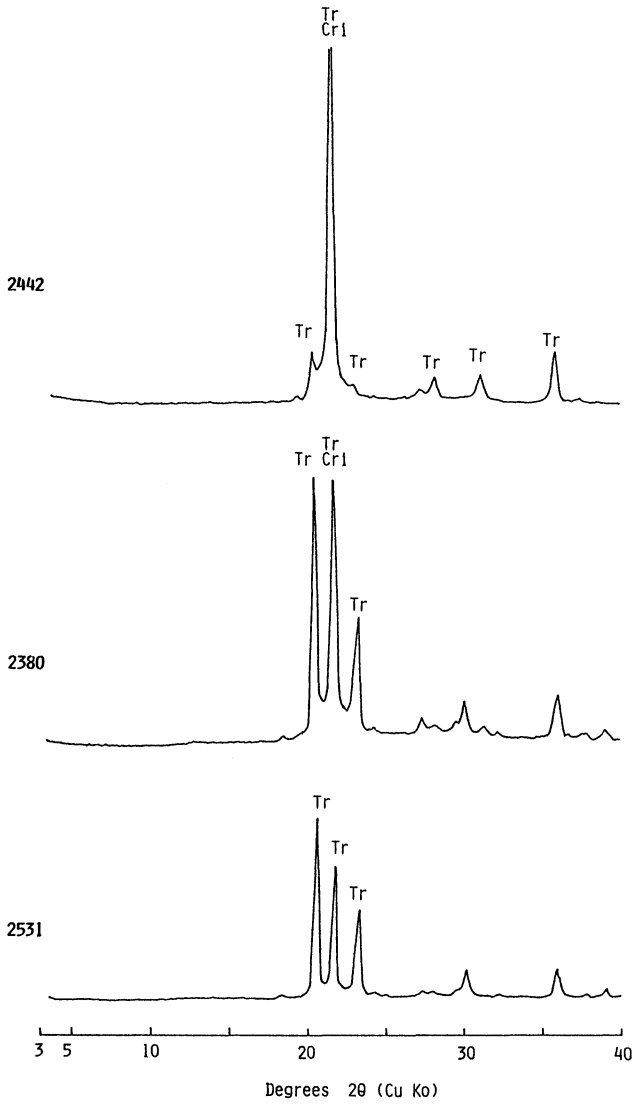

Fig. 5 X-ray powder diffraction patterns of the reaction products from the mixture of 3g of amorphous silica and 0.3g of KCl heated at 600℃, 800℃ and 1000℃.
2442: 70 days at 600℃, 2380: 17 days at 800℃, 2531: 6 days at 1000℃.
Tr: tridymite, Cri: cristobalite.

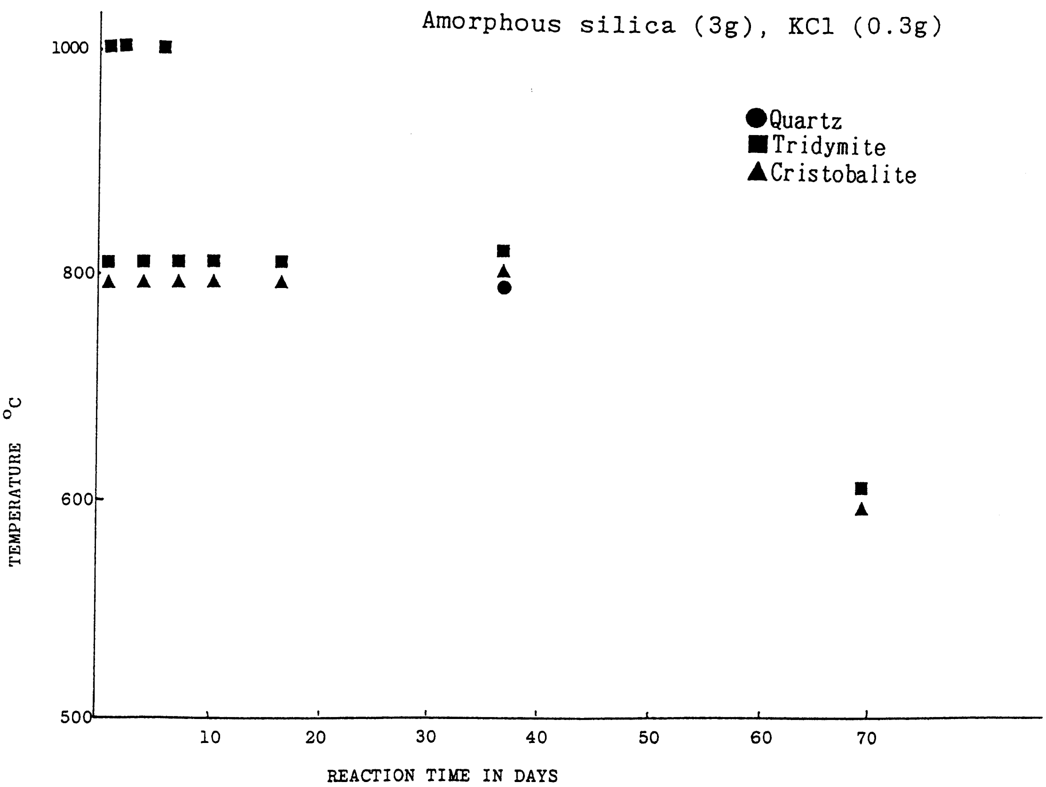

Fig. 6 Reaction products from the mixture of 3g of amorphous silica and 0.3g of KCl under various conditions of time and temperature.

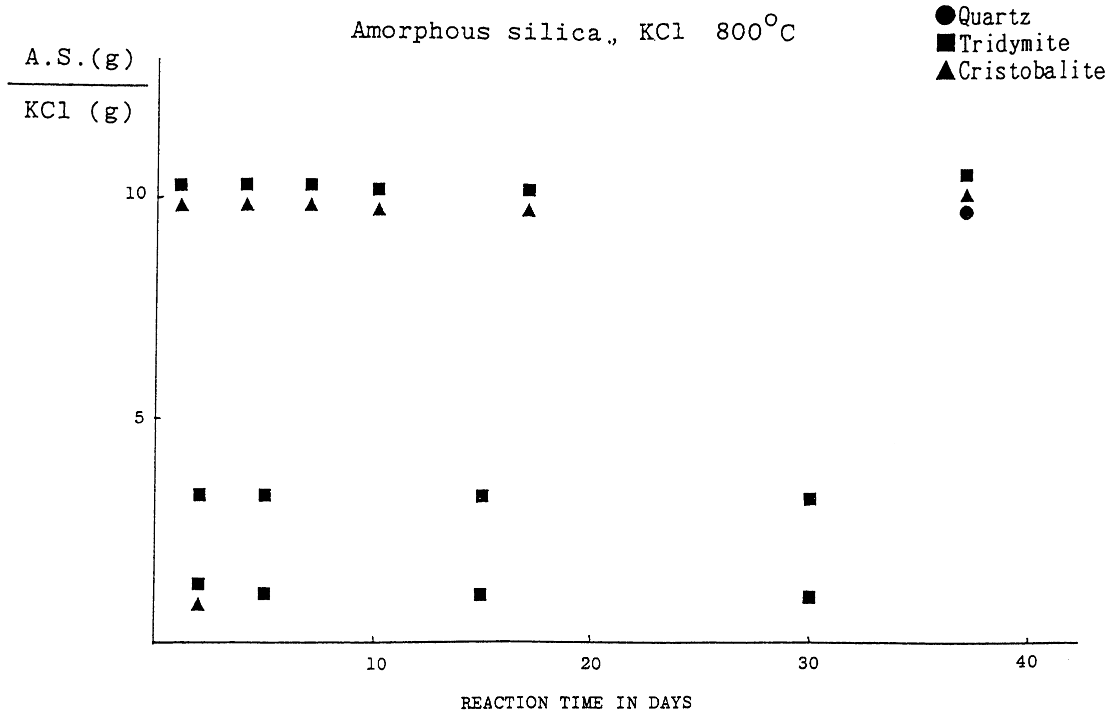

Fig. 7 Effects of amorphous silica (A.S.) (g) to KCl (g) ratio on the reaction products.

Table 2. Experimental conditions and products.

Run No.	Amorphous SiO_2 (g)	KCl (g)	Time (day)	Temperature (℃)	Products
2462	3	0.3	6	500	
2468	3	0.3	25	500	
2474	3	0.3	50	500	
2482	3	0.3	65	500	
2490	3	0.3	90	500	
2496	3	0.3	110	500	
2465	3	1	6	500	
2471	3	1	25	500	
2477	3	1	50	500	
2485	3	1	65	500	
2493	3	1	90	500	
2499	3	1	110	500	
2429	3	0.3	1	600	
2433	3	0.3	5	600	
2442	3	0.3	70	600	Tr, (Cri)
2361	3	0.3	1	800	Tr, Cri
2364	3	0.3	4	800	Tr, Cri
2367	3	0.3	7	800	Tr, Cri
2370	3	0.3	10	800	Tr, Cri
2380	3	0.3	17	800	Tr, Cri
2394	3	0.3	37	800	Tr, Cri, Q
2382	3	1	2	800	Tr
2384	3	1	5	800	Tr
2386	3	1	15	800	Tr
2390	3	1	30	800	Tr
2383	3	3	2	800	Tr, Cri
2385	3	3	5	800	Tr
2387	3	3	15	800	Tr
2391	3	3	30	800	Tr
2506	3	0.3	0.29	1000	Tr
2512	3	0.3	1.375	1000	Tr
2531	3	0.3	6	1000	Tr

Cri: cristobalite, Tr: tridymite, Q: quartz

Table 3. Weight percentage of tridymite in the experimental products

Reaction Temperature					
600℃		800℃		1000℃	
reaction time (days)	tridymite content (wt%)	reaction time (days)	tridymite content (wt%)	reaction time (hours)	tridymite content (wt%)
5	0	1	13	7	84
70	7	4	55	33	93
74	8	7	79	144	93
		10	80		
		17	80		
		37	80		

Effect of LiCl

Four kinds of mixtures were prepared to investigate the effect of LiCl. When a mixture of 3g of amorphous silica and 0.3g of LiCl was heated at 500℃, lithium silicate was formed after heating for 3 days, and had been constantly present until up to 110 days. When the mixture was heated at 600℃, quartz and lithium silicate were produced after one hour's heating, and these products remained present after heating for 100 days. When the mixture was heated to 800℃, quartz and lithium silicate were also formed after 37 days. Cristobalite and lithium silicate were formed at 1000℃ after 7 hours' heating, and tridymite was formed in addition to these minerals after heating for 33 hours. Lithium silicate disappeared after 6 days and quartz remained formed together with cristobalite and tridymite. When a mixture of 3g of amorphous silicate and 1g of LiCl was heated at 500℃, lithium silicate was formed after 3 days' heating, and the phase lasted up to 13 days. Quartz was formed in addition to lithium silicate, and the phase lasted from 25 days up to 110 days. When the mixture was heated at 600℃, quartz and lithium silicate were formed after 30 days and the phase lasted up to 100 days. When heated at 800℃, quartz, lithium silicate and cristobalite were formed in just one day. When mixture of 3g of amorphous silica and 0.1g of LiCl was heated at 800℃, quartz and tridymite were formed in 15 days, and tridymite disappeared after 25 days. When mixture of 3g of amorphous silica and 0.2g of LiCl was heated at 800℃, quartz, tridymite and cristobalite were formed in 15 days and the phase did not change when heated for 25 days. X-ray powder patterns of the reaction products from a mixture of 3g of amorphous silica and 0.3g of LiCl after heating at 500℃, 600℃, 800℃ and 1000℃ for various periods of heating time are shown in Fig. 8. The results of experimental products for the mixtures of amorphous silica and LiCl are listed in Table 4. Effects of heating temperature and reaction time for a mixture of 3g of amorphous silica and 0.3g of LiCl on crystallization are shown in Fig. 9. The relationship between the value of (amorphous silica (g)/LiCl (g)) and reaction time at 800℃ is shown in Fig. 10.

Table 4. Experimental conditions and products.

Run No.	Amorphous SiO_2 (g)	LiCl (g)	Time (day)	Temperature (℃)	Products
2446	3	0.3	3	500	(Li-Si)
2463	3	0.3	6	500	Li-Si
2469	3	0.3	25	500	Li-Si
2475	3	0.3	50	500	Li-Si
2483	3	0.3	65	500	Li-Si
2491	3	0.3	90	500	Li-Si
2497	3	0.3	110	500	Li-Si
2447	3	1	3	500	(Li-Si)
2466	3	1	6	500	Li-Si
2449	3	1	13	500	Li-Si
2472	3	1	25	500	Li-Si, (Q)
2478	3	1	50	500	Li-Si, (Q)
2486	3	1	65	500	Li-Si, (Q)
2494	3	1	90	500	Li-Si, (Q)
2500	3	1	110	500	Li-Si, (Q)
2428	3	0.3	1	600	Q, Li-Si
2432	3	0.3	5	600	Q, Li-Si
2425	3	0.3	30	600	Q, Li-Si
2441	3	0.3	70	600	Q, Li-Si
2444	3	0.3	100	600	Q, Li-Si
2426	3	1	30	600	Q, Li-Si
2445	3	1	100	600	Q, Li-Si
2362	3	0.3	1	800	Q, Li-Si
2365	3	0.3	4	800	Q, Li-Si
2368	3	0.3	7	800	Q, Li-Si
2371	3	0.3	10	800	Q, Li-Si
2381	3	0.3	17	800	Q, Li-Si
2395	3	0.3	37	800	Q, Li-Si
2396	3	1	1	800	Q, Li-Si, Cri
2398	3	1	3	800	Q, Li-Si, Cri
2502	3	0.1	15	800	Q, Tr
2517	3	0.1	25	800	Q
2503	3	0.2	15	800	Q, Tr, Cri
2518	3	0.2	25	800	Q, Tr, Cri
2507	3	0.3	0.29	1000	Cri, Li-Si
2513	3	0.3	1.375	1000	Cri, Tr, Li-Si
2532	3	0.3	6	1000	Cri, Tr, Q

Q: quartz, Li-Si: lithium silicate, Cri: cristobalite, Tr: tridymite

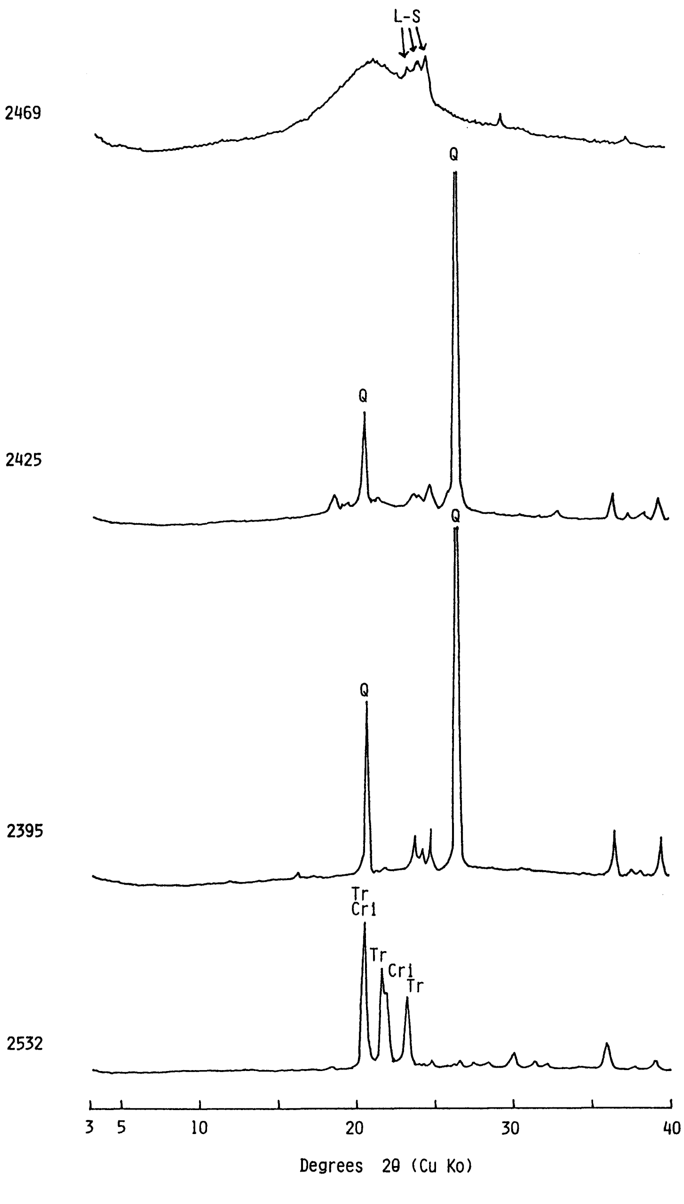

Fig. 8 X-ray powder diffraction patterns of the reaction products from the mixture of 3g of amorphous silica and 0.3g of LiCl heated at 500℃, 600℃, 800℃ and 1000℃. 2469: 25 days at 500℃, 2425: 30 days at 600℃, 2395: 37 days at 800℃, 2532: 6 days at 1000℃.
Tr: tridymite, Cri: cristobalite, Q: quartz, L-S: lithium silicate.

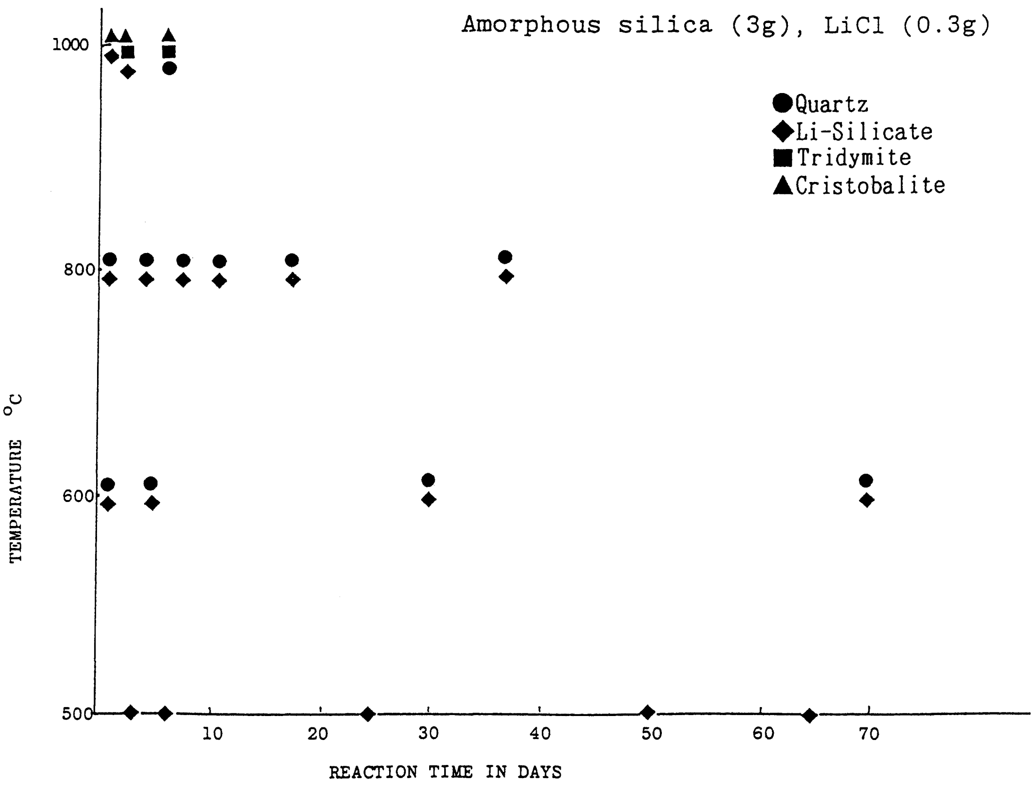

Fig. 9 Reaction products from the mixture of 3g of amorphous silica and 0.3g of LiCl under various conditions of time and temperature.

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 500℃ under the existence of NaCl and KCl, no crystalline form was produced, but with LiCl added, quartz was formed. At 600℃ conditions, quartz was likewise formed upon addition of LiCl in one day's heating. No crystalline form was produced when treated with NaCl or KCl. Cristobalite was evident after 70 days under existence of NaCl and tridymite and small amount of cristobalite were formed under existence of KCl. Based on this above mentioned observations, LiCl has a strong influence on crystallization of amorphous silica. The kinds of products vary under the existence of different cations. Products of 3g of amorphous silica under the existence of 0.3g of NaCl, KCl and LiCl at 800℃ are listed in Table 5. Amorphous silica was converted to quartz through an intermediate phase of cristobalite and tridymite under the existence of NaCl. With addition of KCl, tridymite and cristobalite were formed, in which tridymite was the dominant product. Only small amount of quartz was evident after 37 days. When LiCl was added only quartz and lithium silicate were formed. Cristobalite and tridymite were not formed. Kinds of products under the existence of 0.3g of NaCl, KCl and LiCl against 3g of amorphous silica at 1000℃ are listed in Table 6. It can be observed that kinds of products are different from each other. In this experiments, however, no other phases such as

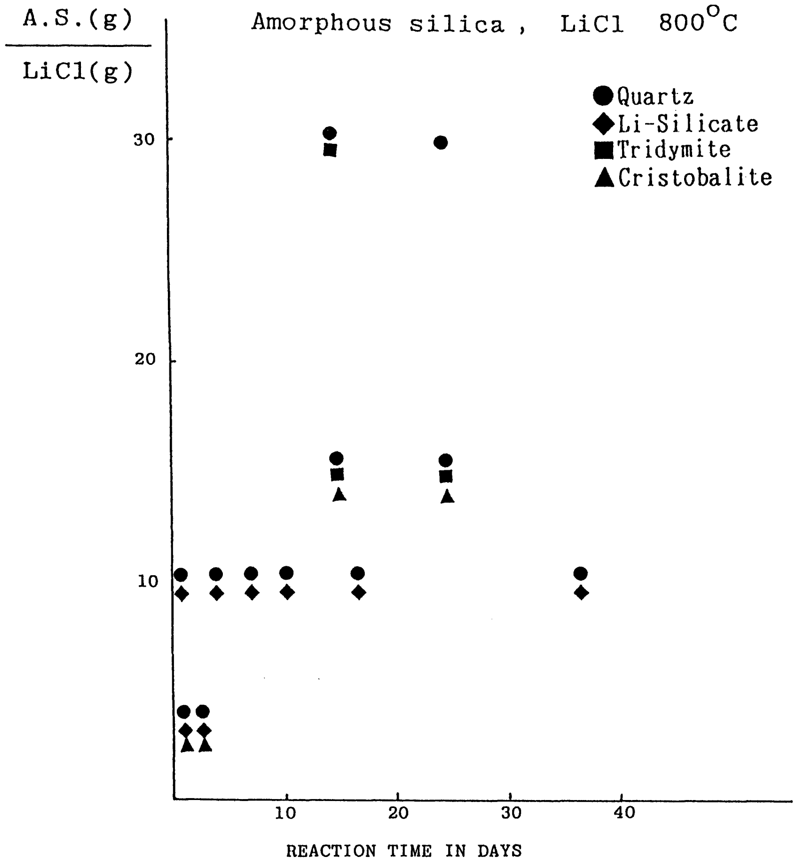

Fig. 10 Effects of amorphous silica (A.S.) (g) to LiCl (g) ratio on the reaction products.

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), but such phase was not observed in this experiments. Hydrothermal experiments on the transformation of amorphous silica carried out by Mizutani (1966), concluded that amorphous silica was converted to low-quartz through an intermediate phase of low-cristobalite. Refering to this facts, this experiment when small amount of NaCl was added, the result was similar to that of Mizutani (1966). But the results of this experiment clearly 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 vary under the existence of various amounts of cations. The mechanisms of these effects of cations on crystallization of amorphous silica will be reported in later papers.

Table 5. Experimental conditions and products at 800℃.

Run No.	Amorphous SiO_2 (g)	NaCl (g)	Time (day)	Products
2360	3	0.3	1	Cri, Tr
2363	3	0.3	4	Cri, Tr
2366	3	0.3	7	Cri, Tr, Q
2369	3	0.3	10	Q, Tr, Cri
2379	3	0.3	17	Q, Tr, Cri
2393	3	0.3	37	Q, Tr, Cri
		KCl (g)		
2361	3	0.3	1	Tr, Cri
2364	3	0.3	4	Tr, Cri
2367	3	0.3	7	Tr, Cri
2370	3	0.3	10	Tr, Cri
2380	3	0.3	17	Tr, Cri
2394	3	0.3	37	Tr, Cri, Q
		LiCl (g)		
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

Q: quartz, Li-Si: litium silicate ($Li_2Si_2O_5$), Cri: cristobalite, Tr: tridymite.

Table 6. Experimental conditions and products at 1000℃.

Run No.	Amorphous SiO_2 (g)	NaCl (g)	Time (hr)	Products
2505	3	0.3	7	Tr, Cri
2511	3	0.3	33	Tr, Cri
2530	3	0.3	144	Tr, (Cri)
		KCl (g)		
2506	3	0.3	7	Tr
2512	3	0.3	33	Tr
2531	3	0.3	144	Tr
		LiCl (g)		
2507	3	0.3	7	Cri, Li-Si
2513	3	0.3	33	Cri, Tr, Li-Si
2532	3	0.3	144	Cri, Tr, Q

Q: quartz, Li-Si: litium silicate ($Li_2Si_2O_5$), Cri: cristobalite, Tr: tridymite.

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