

METASTABLE QUARTZ-TYPE STRUCTURES FORMED FROM KAOLINITE BY SOLID STATE REACTION

E. R. SEGNI^T AND T. GELB, *Division of Building Research,
Commonwealth Scientific and Industrial Research Organization,
Melbourne, Australia*

ABSTRACT

Kaolinite reacts readily with MgO, FeO, ZnO, and CuO at temperatures between 750° and 1000°C to produce quartz-type structures associated with other crystalline phases. At higher temperatures and on prolonged heating the quartz structure breaks down with the concomitant formation of stable silicates and spinels.

INTRODUCTION

Quartz-type structures occurring along the join cordierite-silica in the ternary system MgO-Al₂O₃-SiO₂ were described by Schreyer and Schairer (1961). This phase had originally been described as an unstable form of cordierite by Rankin and Merwin (1918), who, however, did not recognize its relationship to quartz. Schreyer and Schairer were also able to show that "quartz" described by Schairer and Yagi (1952) when investigating the system FeO-Al₂O₃-SiO₂ was of a similar nature. The Mg²⁺- and Fe²⁺-bearing forms were obtained by crystallization from glasses in the temperature range 800° to 1050°C. The quartz structure was metastable, and inverted slowly to cristobalite on prolonged heating in the higher temperature range. Because the structure of these phases was basically that of quartz and existed over an extended range of compositions from pure silica, Schreyer and Schairer referred to them as quartz solid solutions. These forms were also comparable in structure to β-eucryptite, which Winkler (1948) had shown to have a high quartz structure in which Al³⁺ substituted for half the Si⁴⁺.

During our recent work on the reaction of kaolinite with various bases at temperatures below 1000°C (Segnit and Gelb, 1970, 1971; Segnit, Gelb, and Holland, 1972; and unpublished data) we encountered several cases where a similar quartz-type structure (quartz solid solution) was produced by solid state reaction at least as low as 750°C. The only other comparable case of formation of this type of structure appears to be that of Bradley and Grim (1951), who quenched high quartz structures from montmorillonite at 1000°C, the resulting phase being, according to Schreyer and Schairer, a quartz solid solution.

EXPERIMENTAL

A well-crystallized kaolinite from Mt. Egerton, Victoria, was used. It commonly contained up to about 4 percent quartz; the chemical composition of a typical sample was SiO₂ 45.8, TiO₂ 0.4, Al₂O₃ 39.6, Fe₂O₃ 0.3, CaO 0.5, Na₂O 0.1, K₂O 0.1, H₂O 13.9 percent. Mixtures of this material were prepared in specific mole proportions with analytical reagent quality MgO, ZnO, and CuO. Iron(II) oxalate was used as the source of FeO. The materials were mixed in a vibratory mixer, and pressed into pellets 2 cm diameter and 3–4 mm thick. The pellets (on platinum foil) containing MgO, ZnO, and CuO were fired in air in electric muffle furnaces at various temperatures between 700° and 1100°C. The pellets containing iron(II) oxalate were fired in a tube furnace in an atmosphere of nitrogen in the presence of carbon to remove traces of oxygen.

The fired samples were examined by X-ray diffractometry. Microscope examination yielded little useful results, as the crystallite size of the preparations was mostly in the sub-micron range.

KAOLINITE-MgO REACTION

The sub-solidus equilibrium phases for the composition used (mole ratio kaolinite:MgO:SiO₂ of 1:5:1) are forsterite + cordierite + spinel. All samples were fired for 16 to 24 hours. After firing at 770°C for 24 hours some forsterite had formed, there was residual MgO, and a new weak peak with a spacing of approximately 3.45Å had appeared. In samples fired at higher temperatures spinel also appeared in the diffraction pattern, and the 3.45Å peak grew stronger. The latter peak reached maximum intensity in the sample fired at 830°C; associated phases were forsterite, spinel, and unreacted MgO. At higher temperatures the amount of forsterite and spinel increased as the new phase decreased; it was a relatively minor constituent at 910°C.

There was also a slight decrease in the spacing of the 3.45Å peak at higher temperatures. The development of the new phase, and the change in the spacing (using quartz impurity in the kaolinite as an internal standard) of its main diffraction peak with temperature is illustrated in Figure 1. Other weak broadened peaks not corresponding to the other crystalline phases could also be detected; these are recorded in Table 1, which shows the close correspondence with the diffraction pattern for the Mg-bearing quartz solid solutions crystallized from glass by Schreyer and Schairer. A diffraction pattern of a sample fired at 850°C is shown in Figure 2(a).

KAOLINITE-FeO REACTION

Three compositions with mole ratios of kaolinite:FeO of 1:1, 1:2, and 1:4 were fired for 16 hours. The sub-solidus equilibrium phases are iron cordierite + hercynite for the first, and iron cordierite

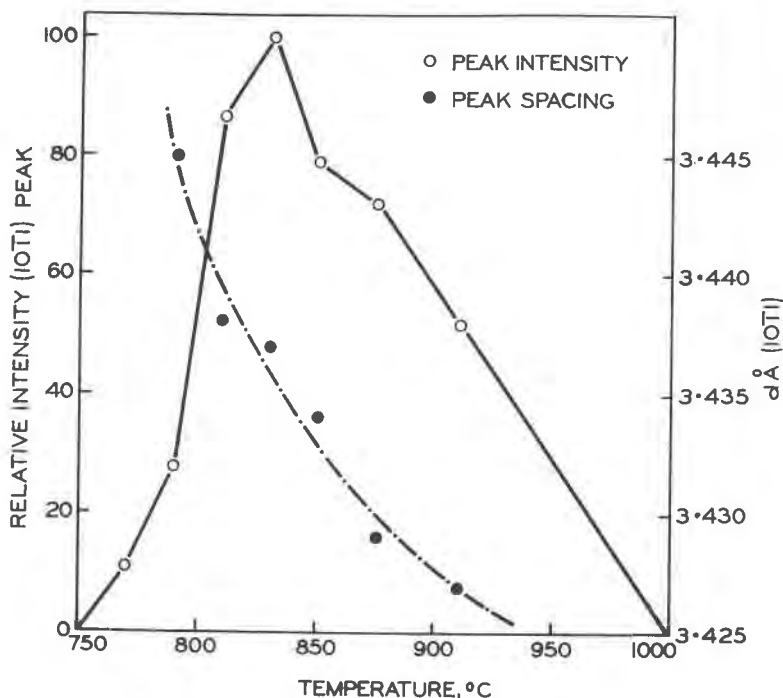


Fig. 1. Plot showing change in intensity and spacing of the $10\bar{1}1$ peak of the Mg-quartz solid solution with firing temperature.

+ hercynite + fayalite for the latter two samples. Hercynite and fayalite formed readily as low as 830°C ; no iron cordierite was detected even at 1100°C . In addition, a strong new peak at approximately 3.4 \AA appeared in all samples fired up to 1000°C . This peak was strongest in the 1:1 molar composition, in which it first appeared in the sample fired at 750°C and was still present at 1100°C . Additional weak peaks could be correlated with a quartz-type structure (Table 1). At 1100°C cristobalite was formed in all samples. The d spacing of the 3.4 \AA peak decreased with increase in both firing temperature and iron content of the sample (Table 2). A diffraction pattern of a sample fired at 830°C is shown in Figure 2(d).

KAOLINITE-ZnO REACTION

Mole ratios of kaolinite:ZnO of 4:1, 2:1, 1:1, 1:2, and 1:4 were fired for 16 to 24 hours. Sub-solidus equilibrium phases are gahnite + mullite + silica for the 4:1 and 2:1 compositions; gahnite + silica for the 1:1; and gahnite + willemite + silica for the 1:2 and 1:4 mixtures.

At firing temperatures from 750° to 810°C samples of mole ratio > 1:1 gave a strong diffraction peak ranging from 3.52–3.50 Å. The effect was most pronounced in the 1:1 and 2:1 compositions, and at 750°C; the samples of low zinc content gave much weaker

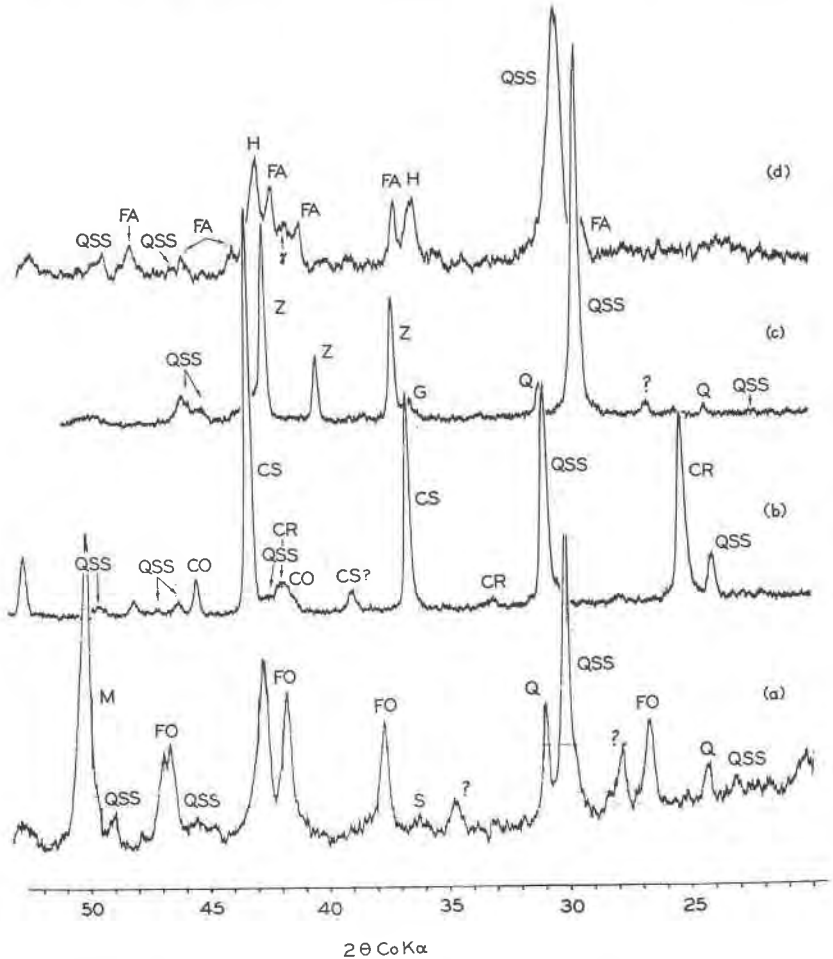


FIG. 2. X-ray diffraction patterns of metastable quartz structure

(a) Kaolinite-MgO fired at 850°C

(b) Kaolinite-CuO fired at 950°C

(c) Kaolinite-ZnO fired at 730°C

(d) Kaolinite-FeO fired at 830°C

Q = quartz; QSS = quartz solid solution; FO = forsterite;

M = MgO; S = spinel; FA = fayalite; H = hercynite; Z = ZnO;

G = gahnite; CR = cristobalite; CS = copper spinel; CO = CuO

peaks. Additional weak peaks could be allotted to a quartz-type pattern (Table 1). The new phase was accompanied by unreacted ZnO, which had almost disappeared by 810°C, at which temperature poorly developed willemite and gahnite were present. By 850°C willemite and gahnite were well developed. A characteristic diffraction pattern showing the quartz-type phase is reproduced in Figure 2(c).

KAOLINITE-CuO REACTION

A mixture of kaolinite and CuO of 1:1 molar proportion was fired up to 1000°C. The sub-solidus equilibria for the system CuO-Al₂O₃-SiO₂ are not known, but can be inferred from the work of Gadalla, Ford and White (1963) and Gadalla and White (1964) on

Table 1

Spacings of diffraction peaks of quartz and quartz solid solutions

1		2		3		4		5		6	
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
4.26	35	4.51	20	4.48	w	4.28	m	4.61	vw	4.31	w
3.34	100	3.45	100	3.43	vs	3.36	vs	3.51	vs	3.37	vs
2.46	12	2.60	6	*		2.46	mw	-		*	
2.28	12	2.30	4	2.30	vw	2.29	mw	2.33	w	2.29	vw
2.24	6	2.25	15	*		2.25	w	2.30	mw	2.24	vw
2.13	9	-		2.15	w	2.15	w	-		2.12	vw
1.98	6	2.08	10	2.01	w	1.99	w	2.03	vw	1.98	vw
1.82	17	1.86	30	1.86	mw	1.83	m	1.90	mw	1.83	vw

- absent

* obscured

Very weak lines generally very diffuse

- 1 Quartz
- 2 Mg-quartz solid solution (Schreyer and Schairer, 1961)
- 3 Mg-quartz solid solution from kaolinite reaction
- 4 Cu-quartz solid solution from kaolinite reaction
- 5 Zn-quartz solid solution from kaolinite reaction
- 6 Fe²⁺-quartz solid solution from kaolinite reaction

Table 2
 d spacings of 10 $\bar{1}1$ peak of Fe²⁺-quartz solid solutions derived
 from kaolinite-FeO reaction

Firing Temperature °C	Mole ratio kaolinite:FeO in original sample		
	1:1	1:2	1:4
	dÅ		
750	3.48	-	-
800	3.46	-	-
830	3.44	3.42	3.41
880	3.40	3.40	3.39
1000	3.37	3.37	3.36
1100	3.36	*	*

- No experiment

* No quartz solid solution formed

the copper oxide-silica and copper oxide-alumina systems, together with the highest temperature firing of our present work. On this basis, phases at equilibrium in the sub-solidus region for the 1:1 molar composition would probably be copper spinel + silica.

On firing for 16 hours at 900°C the sample gave a strong, sharp diffraction pattern of copper spinel, together with a strong sharp peak with a spacing of 3.365 Å. In addition, further weak peaks consistent with a quartz structure were identified, and a weak pattern of unreacted CuO. Refiring of this sample for 40 hours resulted in a considerable weakening of the quartz pattern, with a concomitant strengthening of the CuO pattern. After 16 hours at 950°C the reaction was similar (Fig. 2(b)), but at 1000°C the copper spinel was accompanied by well developed cristobalite and CuO instead of the quartz structure.

KAOLINITE WITH OTHER OXIDES

Large monovalent or divalent ions do not appear to produce these quartz-type structures on firing with kaolinite, nor do trivalent or tetravalent ions of similar size to Mg²⁺, Fe²⁺, Zn²⁺, and Cu²⁺. In our other investigations, we studied the reactions of kaolinite with Na₂O, K₂O, BaO, SrO, CaO, CdO, PbO, Al₂O₃, Fe₂O₃, and TiO₂. Despite vigorous reaction below 1000°C in a number of cases, there was no evidence of the formation of quartz-type structures. In addition, the reactions with NiO and CoO were studied. Despite the similarity in chemistry and ionic radius of the Ni²⁺ and Co²⁺ ions

to Fe^{2+} , no quartz-type phase was found in any sample fired between 450° and 1100°C .

DISCUSSION

Crystallinity

The low temperature of formation and the short firing times did not allow sufficient diffusion to take place to build well ordered crystallites of the quartz structures before breakdown of the metastable structure began. The relative strength of the $10\bar{1}1$ peak indicated that preferred growth had occurred in this structural plane, which is the favoured morphological direction in high quartz. The crystallite size of the preparations was too small to allow of identification of the quartz phase in the optical microscope.

Formation of the quartz solid solution

Replacement of Si^{4+} by Al^{3+} in the silicon oxygen tetrahedra requires concomitant stuffing of the open spaces to render the structure electrically neutral. The only ions thus far known to enter in this way are Li^+ , Mg^{2+} , Fe^{2+} , Zn^{2+} , and Cu^{2+} , with ionic radii ranging from 0.66 to 0.77 Å. Larger monovalent ions (Na^+ , K^+), larger divalent ions (Ca^{2+} , Sr^{2+} , Ba^{2+} , Cd^{2+} , Pb^{2+}), and trivalent ions of similar size (Fe^{3+} , Al^{3+}) do not form detectable amounts of solid solution on the breakdown of kaolinite, and it seems improbable that they are likely to do so.

Because of the complexity of its breakdown, kaolinite probably provides a favorable environment for the crystallization of the quartz structure. In the breakdown sequence of kaolinite–metakaolin→silicon spinel→mullite (Brindley and Nakahira, 1959), free silica is produced at each stage from the breakdown of the metakaolin. For pure kaolin this first occurs in the region of 925°C . However, metakaolin is a highly disordered structure and, especially in the presence of metal ions which readily form a spinel structure, free silica may be released at lower temperatures to form a stuffed quartz structure with a part of the foreign cations.

Schreyer and Schairer found Mg-bearing quartz solid solutions resembling both high and low quartz. The subsidiary peaks of the quartz solid solutions derived from kaolinite are too weak and diffuse to make a positive distinction between the two forms. The similarity of patterns 1 and 2 (Table 1) suggest that the structure is that of low quartz.

Metastability

Quartz solid solutions formed above the nominal quartz 867°C→tridymite transition in all cases except for the reaction with ZnO. The copper phase formed only above this temperature, but prolonged firing tended to destroy the structure, as Schreyer and Schairer found for the Mg phase. However, the disappearance of the quartz structure was not accompanied by the crystallization of another form of silica (except in the case of the CuO), but by the formation of new and/or stable phases.

Extent of solid solution

The Mg-quartz solid solution of Schreyer and Schairer extended to the cordierite composition, but was less extensive for the Fe²⁺ composition. Only a qualitative assessment of the extent of solid solution can be obtained for the phases derived from kaolinite. The large shift in the 10 $\bar{1}1$ spacing for the zinc composition indicated extensive solid solution. The small shift in the case of the copper phase was surprising, but significant solid solution evidently occurs as on prolonged firing at 900°C the breakdown of the quartz structure was accompanied by a release of CuO. The change in spacing of the 10 $\bar{1}1$ peak for the Mg²⁺ and Fe²⁺ phases indicated an appreciable amount of solid solution. The effect of temperature is not pronounced, but can be detected, for example, in the Mg²⁺ solid solution (Fig. 1). In the latter case a contributing factor could have been more rapid diffusion at higher temperatures causing a closer approach to maximum solid solution for a given composition.

Formation of stable phases

The formation of the quartz solid solution largely occurred when the stable sub-solidus phases did not form readily. Schreyer and Schairer crystallized cordierites from glass at least as low as 900°C, but it does not form until much higher temperatures by solid state reaction. The lowest temperature at which cordierite appears to have been detected in a solid state reaction is 1140°C (Segnit and Holland, 1971) from a mixture of clinocllore and kaolinite. The situation is probably similar with iron cordierite, which we did not detect up to 1100°C. In the ZnO-kaolinite mixture the quartz solid solution was less prominent when the stable sub-solidus assemblage willemite-gahnite began to form readily. With the Cu composition, free silica was a major sub-solidus phase in any case; the quartz solid solution formed together with copper spinel at 900°-950°C, and above this temperature cristobalite began to replace the quartz structure. In

general, therefore, the quartz solid solutions appeared to have been precursor phases preceding the crystallization of the thermodynamically stable phases.

Non-formation of quartz solid solutions

Co^{2+} and Ni^{2+} , with ionic radii 0.72 and 0.69 Å respectively, might have been expected to behave in a similar manner to iron, but did not do so. In the case of the Co, this may be explained by the fact that the CoCO_3 formed Co_3O_4 below 500°C and this stable spinel-type structure effectively prevented further reaction of Co^{2+} with metakaolin. By 1000°C, diffusion was sufficient for direct reaction of the cobalt oxide with the aluminosilicates to form cobalt spinel (CoAl_2O_4) and cobalt olivine (Co_2SiO_4). No explanation can be given for the lack of reaction with NiO up to 1100°C.

Occurrence of quartz solid solutions

Quartz solid solutions of these types are not known in nature, nor have they been described from industrial products. In view of their metastable nature they are unlikely to be found, except possibly where material of suitable composition was heated for only a short time at moderately elevated temperatures. Such quartz solid solutions may therefore be sought in Fe^{2+} - or Mg^{2+} -rich sediments baked by lava flows or small intrusions. In industrial products, it is possible that quartz solid solutions might be detected in structural clay products such as bricks, tiles, and pipes fired at 900–1000°C under strong reducing conditions.

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