Journal of Thermal Analysis, Vol. 49 (1997) 1409-1415

TEMPERATURE DEPENDENCE OF THE CRISTOBALITE α–β INVERSION

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Abstract

The cristobalite α–β inversion has been studied using DSC on cristobalites produced by firing high purity quartz with and without addition of a mineraliser. If no mineraliser was used, the inversion temperatures and hysteresis on heating and cooling increased with firing temperature. Firing time had little or no effect on inversion temperature. When a mineraliser was used, the same general trend was observed with increases in firing time at low temperatures leading to splitting of the inversion peak. The amount of mineraliser added had little effect. Tridymite inversions were also observed. The results are explained in terms of the degree of order of the cristobalite structure.

Keywords: cristobalite inversion, quartz, silica polymorphism, tridymite

Introduction

Silica has three distinct crystalline forms at atmospheric pressure: quartz, cristobalite and tridymite. All three of these polymorphs also have high and low temperature forms. Thus as well as the reconstructive transformations between the polymorphs there exist displacive transformations between the low and high temperature forms on heating and cooling.

In the high temperature form of cristobalite the oxygen atoms are arranged in the manner of cubic close packing and the low temperature form is a distorted version of the high temperature form in which the Si–O–Si bond angle changes, while the silicon atoms remain in tetrahedral sites with respect to the oxygen atoms. If cristobalite is formed at high temperatures then an idealised three layer, ABCABC..., structure is produced. However, two-layer tridymite stacking sequences, AC′AC′..., where C′ is related to C by a rotation of 180°, may occur in addition to the three layer structure in cristobalites produced at lower temperatures. In this case the phase produced may be referred to as disordered cristobalite, C_D, or disordered tridymite, T_D, depending on which of the stacking sequences is most prevalent [1].

A thorough differential scanning calorimetry (DSC) study has been made of the displacive transformation (α–β inversion) in cristobalites produced from high purity quartz with and without addition of a mineraliser. The effects of firing time and temperature on the inversion temperature and hysteresis have been investigated. X-ray diffraction data for these samples have been presented elsewhere [2].

0368–4466/97/ $ 5.00

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Experimental

Iota quartz (Unimin Corporation, USA), which is a very pure form of quartz with a maximum of 35 ppm impurities (Table 1), was used throughout this study.

50–100 g of Iota quartz contained in an alumina crucible was heated at 5°C min^{-1} to a given soaking temperature between 1100 and 1700°C. The soak temperature was maintained for a prescribed time ranging between 1 and 50 h, except in the 1100°C case where a dwell time of 350 h was used, after which the sample was furnace cooled at 3°C min^{-1} to room temperature. At temperatures below 500°C the cooling rate will have been slower than that specified as the natural cooling of the furnace in this temperature range was slower than 3°C min^{-1}. The furnace temperature was checked using a Pt/Pt:Rh 13% thermocouple connected to a microcomputer thermometer (Jenco Electronics Ltd., model 700H). The furnace temperature was always within 6°C of the programmed temperature over the 15 cm range in the centre of the furnace within which all the samples were fired.

Table 1 Impurity levels in Iota quartz (data provided by suppliers)

Element	Maximum amount/ppm	Typical amount/ppm
Al	25	20
Li	2.0	1.0
Na	2.0	1.0
Fe	2.0	0.9
K	2.0	0.9
Ca	2.0	0.7
Cu	0.1	<0.08
Cr	0.01	<0.01

In addition samples were prepared using 0.10, 0.25, 0.50 and 1.00 mass % sodium carbonate as a mineraliser. The appropriate mass percent of the mineraliser was accurately weighed and finely ground with a small amount of Iota quartz before being thoroughly mixed with the remaining Iota quartz necessary to make the sample up to the required mass (normally 50 g). The prepared samples were placed in alumina crucibles and heated at 5°C min^{-1} to a given soaking temperature between 1100 and 1600°C. The soak temperature was maintained for a prescribed time ranging between 1 and 50 h, after which they were furnace cooled at 3°C min^{-1} to room temperature.

The products were examined by DSC using a DuPont 2000 DSC connected to a PC. In each case finely powdered samples, of mass 5.0±0.2 mg, were weighed into aluminium sample pans and covered with an aluminium lid. The covered pan was compressed to form a flat disc. The samples were heated, in an atmosphere of flowing nitrogen, at a rate of 10°C min^{-1} to 600°C. They were maintained at 600°C for 10 min and then cooled at the same rate. The DSC was calibrated before each use and the temperatures recorded are accurate to ±2°C.

Results and discussion

For the pure quartz samples the inversion temperatures on heating and cooling and the extent of hysteresis of the inversions are given in Table 2. No cristobalite inversions were observed in the samples fired at 1100 and 1300°C and no tridymite inversions were observed in any of the samples. The cristobalite inversion temperature increased from 225 to 269°C with increasing firing temperature but was relatively independent of dwell time. There was marked hysteresis on heating and cooling for the cristobalite inversion and this also increased with firing temperature. Samples fired at 1500 and 1600°C had more than one maximum to the cristobalite inversion peak (Fig. 1); in Table 2 the less major of these two peaks and its corresponding hysteresis is given in brackets. In some cases the secondary maximum occurred as a shoulder either on the high or low temperature side of the major peak and this is indicated in Table 2 by 's'. The increase in inversion temperature and extent of hysteresis with firing temperature are evidence of the production of a better ordered cristobalite at high temperatures [3, 4].

The cristobalite inversion temperatures for samples fired with a mineraliser at 1100, 1300, 1400, 1500 and 1600°C are given in Tables 3–7 respectively. A typical trace is shown in Fig. 2. In addition to the cristobalite inversions seen in the samples fired without a mineraliser, endotherms due to the tridymite inversions were also seen in many of the samples. The most commonly occurring tridymite inversion was at around 113°C but another, smaller inversion was often seen at around 165°C. Some samples which contained tridymite also had an endotherm at approxi-

Table 2 Cristobalite inversion temperatures and hysteresis for samples prepared from Iota quartz. Secondary maxima and corresponding hystereses are given in bracket. 's' indicates that the secondary maximum is a shoulder rather than a separate peak

T_{firing}/ °C	Dwell time/ h	Cristobalite inversion/°C(±0.2°C) heating	cooling	Hysteresis/ °C
1400	1	225	211	14
	5	222	208	14
	50	225	210	15
1500	1	234	220	14
	5	238 (251)	222	16 (29)
	15	239 (252)	224	15 (28)
1600	1	(265s) 271	230	(35) 41
	3	258 (269s)	229	29 (40)
	5	(259) 271	228	(31) 43
	15	(263s) 274	229	(34) 45
	50	268	227	41
1700	15	269	228	41

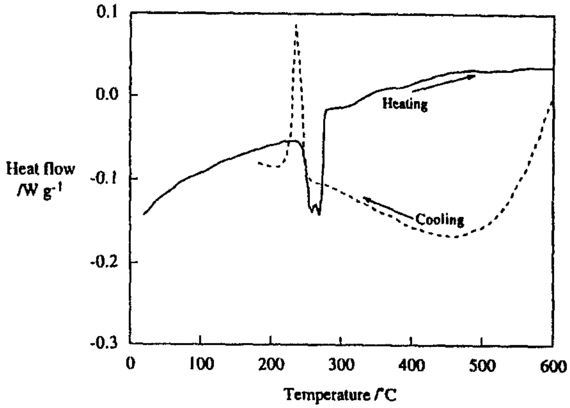

Fig. 1 DSC trace of cristobalite produced by firing pure quartz at 1600°C for 5 h showing splitting of the inversion peak on heating

mately 85°C. It is not clear whether this was a tridymite inversion or whether it was caused by some other phase. Adsorbed water is thought to be an unlikely explanation as this peak only appeared in samples which displayed tridymite inversions and it occurred at a fairly constant temperature; the temperature at which adsorbed water is apparently lost may vary considerably depending on the amount present in the sample.

As with the samples fired without a mineraliser the cristobalite inversions were in some cases double peaked and in others had shoulders either to the high or low temperature side of the main peak. The less major of these two peaks and its corresponding hysteresis is again given in brackets in Tables 3–7. In many cases the secondary maximum occurred as a shoulder either on the high or low temperature side of the major peak and this is indicated by 's' in Tables 3–7.

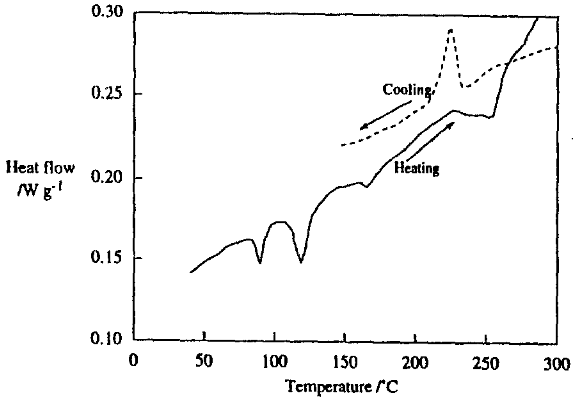

Fig 2 DSC trace of cristobalite produced by firing pure quartz with 1 mass % sodium carbonate at 1400°C for 15 h. The tridymite inversions can be seen on heating

Table 3 Cristobalite and tridymite inversion temperatures for samples fired at 1100°C with Na_2CO_3 as a mineraliser. Secondary maxima and corresponding hystereses are given in brackets. 's' indicates that the secondary maximum is a shoulder rather than a separate peak

%	Dwell time/	Cristobalite inversion/°C			Tridymite
Na_2CO_3	h	heating	cooling	hysteresis	inversions/°C
0.1	5	235	223	12	none
	15	230 (242s)	215 (224)	15 (18)	none
	50	226 (246s)	212 (221)	14 (25)	none
0.25	5	233	224	9	none
	15	229 (243s)	215 (224)	14 (19)	none
	50	225 (244s)	212 (223)	13 (21)	117
0.5	1	256	231	25	none
	5	234	224	10	none
	15	229 (246s)	213 (224)	16 (22)	119
	50	223 (246s)	210 (224)	13 (22)	117, 160
1.0	1	254	230	24	none
	5	233	225	8	115
	15	227 (246s)	211 (223s)	16 (23)	116
	50	221 (246s)	209 (224)	12 (22)	116, 160

Table 4 Ciystobalite and tridymite inversion temperatures for samples fired at 1300°C with Na_2CO_3 as a mineraliser. Secondary maxima and corresponding hystereses are given in brackets

%	Dwell time/	Cristobalite inversion/°C			Tridymite
Na_2CO_3	h	heating	cooling	hystereses	inversions/°C
0.5	15	228	212 (221)	(7) 16	117
1.0	15	226	(210) 220	6 (16)	87, 118, 162

Cristobalite formed at 1100°C in the presence of 0.5 and 1% of sodium carbonate after short firing times had an unexpectedly high inversion temperature; as this cristobalite is formed in the early stages of firing it is likely to be disordered and thus it would be expected to have a low inversion temperature. Anomalously high inversion temperatures under such conditions have also been observed by Grimshaw [5]. The high inversion temperatures may be due to hindrance of the inversion by the alkali metal ions. Longer firing times lead to lower inversion temperatures as greater numbers of tridymite stacking sequences, which can more readily accommodate the alkali ions, are generated. Meanwhile the tridymite peak heights increase as the firing time increases.

Table 5 Crystobalite and tridymite inversion temperatures for samples fired at 1400°C with Na_2CO_3 as a mineraliser. Secondary maxima and corresponding hystereses are given in brackets. 's' indicates that the secondary maximum is a shoulder rather than a separate peak

% Na_2CO_3	Dwell time/ h	Cristobalite inversion/°C			Tridymite inversions/°C
		heating	cooling	hysteresis	
0.1	1	233	216	17	none
	5	(226) 254	227 (210)	27 (16)	none
	15	(230) 254	228 (210)	26 (20)	none
	50	233, 265	231, 216	34, 17	none
0.25	1	238	223	15	none
	5	(238) 255	227 (212s)	28 (26)	none
	15	(229) 256	228	28	115
	50	(233) 267	232 (215)	35 (18)	none
0.5	1	241	224	17	86, 118
	5	(229) 253	227 (213s)	26 (16)	115, 167
	15	(232) 254	227	27	88, 116
	50	(233) 252	226	26	88, 117, 164
1.0	1	236	223	13	87, 117
	5	229, 249	225 (210s)	24 (19)	84, 115, 164
	15	(233) 252	226	26	88, 117, 164
	50	253	226	27	87, 116, 159

Table 6 Crystobalite and tridymite inversion temperatures for samples fired at 1500°C with Na_2CO_3 as a mineraliser. Secondary maxima and corresponding hystereses are given in brackets

% Na_2CO_3	Dwell time/ h	Cristobalite inversion/°C			Tridymite inversions/°C
		heating	cooling	hysteresis	
0.5	15	269	230	39	none
1.0	15	265 (270)	229	36	86, 113
5.0	15	263 (275)	228	35	86, 115

The inversion temperatures for samples fired at 1300 and 1400°C were generally low and again tridymite endotherms which increased in magnitude with firing time were observed. The high cristobalite inversion temperatures seen in samples fired to 1500 and 1600°C (Tables 6 and 7) are comparable to those shown in Table 2 and indicate that this cristobalite was well ordered. Tridymite inversions were seen in samples fired at 1500°C but not in those fired at 1600°C.

Table 7 Cristobalite and tridymite inversion temperatures for samples fired at 1600°C with Na_2CO_3 as a mineraliser. Secondary maxima and corresponding hystereses are given in brackets. 's' indicates that the secondary maximum is a shoulder rather than a separate peak

% Na_2CO_3	Dwell time/ h	Cristobalite inversion/°C		
		heating	cooling	hysteresis
0.1	1	(235s) 270	231 (217s)	39 (18)
	5	270	231	39
	15	270	231	39
0.25	1	(236s) 271	230	41
	5	270	232	38
	15	271	233	38
0.5	1	272	229	43
	5	271	234	37
	15	271	230	41
1.0	15	272	234	38

Conclusions

When pure quartz was fired without a mineraliser cristobalite formation only occurred for firing temperatures of 1400°C and above with a more rapid transformation at higher temperatures. Cristobalite formed at 1400 and 1500°C had a low α–β inversion temperature and small extent of hysteresis as measured by DSC indicating that it was disordered.

When pure quartz was fired with a mineraliser, cristobalite was formed even at 1100°C. However, tridymite was also formed for all firing temperatures except 1600°C. These results have been confirmed by XRD [2]. Cristobalites formed at 1400°C again had a low α–β inversion temperature and extent of hysteresis as measured by DSC indicating that it also was disordered.

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We are grateful for the award of an S.E.R.C. CASE award in conjunction with Specialist Refractory Services to SJS. Helpful discussions have been held with Mr. D. W. Bailey and Dr. P. Watkins.

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