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Temperature of the Inversion in Cristobalite

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The inversion temperature of cristobalite prepared from pure precipitated silica gel was compared with that of less pure cristobalite, including material derived from quartz. All materials showed a variability in their inversion temperature which was dependent on their thermal history. However, evidence suggested that a sufficiently extended heat treatment at high temperatures would in each case produce a uniform product with invariant inversion temperatures attributable to the low-high and high-low inversions. It is proposed that the variability of the inversion temperature can be rationalized in terms of three rate processes dependent on the temperature of heat-treatment, viz., nucleation, ordering, and crystal growth. The effect of all other factors known to influence the inversion temperature is either to accelerate or retard the rate of one or more of these processes.

1. Introduction

Cristobalite, the high temperature crystalline form of silica, undergoes a rapid,[1] reversible inversion from a low-temperature tetragonal structure to a high-temperature cubic structure accompanied by a volume expansion of about 3.7 percent [1].[2] The inversion has been observed over a fairly wide range of temperature and is characterized by a hysteresis such that the inversion on cooling is invariably observed at a lower temperature than on heating. The peculiarities of the inversion have been investigated over a period of many years, but no clear understanding of the causes of the variation in the inversion temperature has been reached. Indeed, much conflict of opinion has been expressed both in and among reviews of the subject [2, 3, 4].

No precise agreement on the range of the inversion temperature exists, but recent investigators tend to quote values in the range of 200° to 280° C. However, the authors are not aware that a figure higher than 277° C has ever been observed. Moreover, because many of the systems studied have been neither homogeneous nor pure, it would seem more consistent to use a range extending from below 25° to 277° C, for cubic cristobalite has been shown to exist in opals even at room temperature.

The classical picture of the variability of the cristobalite inversion stems from the work of Fenner [5]. However, he raised many questions concerning the causes of the variability which still persist. Fenner investigated the possibility that the inversion temperature was dependent on the following variables: (1) Impurities within the material, (2) the thermal history of the material, (3) the source of the material (i. e., whether produced from quartz, tridymite, or amorphous silica), and (4) particle size. In recent years disorder within the structure has been added to this list. Furthermore, the postulation that more than one form of cristobalite exists has frequently recurred.

Fenner believed that impurities were not responsible for the variability, for he found a change in inversion temperature with heat treatment for cristobalite produced from quartz of 99.93 to 99.96 percent purity. More recently [6], however, an apparent double inversion in cristobalite has been associated with the presence of impurities, and the possibility in Fenner's work that the effect of impurities was masked by a larger effect due to the nature of the source material (quartz) should not be overlooked.

The temperature of formation of cristobalite is the variable most commonly associated with changes in its inversion temperature. Thus, Pierce and Austin [7] were able to show that the inversion temperature (from the thermal expansion curve) of cristobalite along the length of a used open-hearth furnace brick was almost linearly related to the temperature along the thermal gradient in the brick while in use. The higher the temperature at which the cristobalite was formed or heat treated, the higher was the inversion temperature.

The inversion temperature for the same heat treatment has been reported to be dependent, in some indefinite way, on the source of the silica. The experimental evidence is, however, again uncertain, for although Fenner reported that amorphous silica yielded a higher inversion temperature than quartz, Kondo, Yamuachi, and Kora [8] invariably found the opposite to occur. Various observers have noted that the state of subdivision of the quartz itself affects the rate at which cristobalite is formed,[3] but nowhere in the literature is it suggested that this fact alone makes direct comparison between the sources invalid on the "identical heat treatment" basis.

It is also invalid to associate changes in the particle size of the cristobalite with its inversion temperature, unless it is first shown that the particles are themselves the fundamental units undergoing inversion. In fact, no such association has yet been clearly demonstrated. Buerger [9], arguing from crystallographic concepts, has suggested that the correct variable in this context is crystallite size. If the crystallites are sufficiently small, then, clearly, a single particle may contain many of them. The surface of a crystallite, itself, represents a high degree of disorder and if the surface:volume ratio is high, a lowering of the inversion temperature may be expected. Flörke [10], from X-ray intensity considerations and dilatometric studies, has recently

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[1] It is probable that this inversion is more accurately described as gradual-rapid. The high and low forms of cristobalite have not been identified by the letters α and β, since these symbols are employed ambiguously in the literature.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The solid state transformation of any principal form of silica to any other principal form is always sluggish.

related the degree of crystallinity (extent of disorder) to the heat treatment and corresponding inversion temperature of various cristobalite samples. Cristobalite fired at lower temperatures had less sharp X-ray patterns, less marked expansion curves, and lower inversion temperatures.

Fenner speculated on the existence of more than one molecular species of cristobalite, and in 1926 Weil [11] reported two inversions (175° to 195° C and 217° to 245° C) in the same sample. More recently Plumat [12] has also noted an apparent double inversion, and Grimshaw, Westerman, and Roberts [13] reported the appearance and disappearance of two peaks in differential-thermal-analysis curves for a single sample subjected to successive heat treatments.

There have been very few attempts to associate any of the foregoing variables with changes in the hysteresis of the inversion temperature, even though the width of the hysteresis appears to be as variable as the inversion temperature itself. Unfortunately, a number of recent investigators have tended to record inversion temperatures for the low-high inversion only, hence there is less data available on the hysteresis. However, there appears to be no consistent support for the suggestion of Sosman [2, figure VII] that higher inversion temperatures yield wider hystereses. The only attempt known to the authors to explain the hysteresis on mechanistic principles is that of Mosesman and Pitzer [14]. They suggested that, on heating, a gradual rotation of the oxygen ions precedes the rapid alteration in bond length and direction. The rotation of the ions accounted for an anomalous rise in the specific heat before the rapid part of the inversion (accompanied by a latent heat effect) was observed. It may be postulated that, on cooling, the collapse of the structure from cubic to tetragonal symmetry cannot be effected until the rotation has ceased, and the inversion temperature on cooling is, therefore, lower lower than on heating.

In one of the reviews of the subject Dodd [3] concluded with the remarks: "It would seem that further research is needed based on very pure chemically precipitated silica subjected to controlled heat treatment under conditions precluding the possibility of contamination." It is very difficult to avoid minor contamination of powders at high temperature in any physically realizable furnace, but this investigation was an attempt to redetermine the cristobalite inversion temperature in accordance with Dodd's suggestion, and to compare the behavior of very pure cristobalite with less pure material, including material derived from quartz.

2. Preparation and Purity of Materials

General qualitative spectrochemical analyses of the various materials used in the investigation are summarized in table 1. These are analyses of

TABLE 1. *General qualitative spectrochemical analysis of source materials*

Elements	Source material							
	Amorphous silica				Quartz			Commercial silica brick
	Gel from tetraethyl orthosilicate			Reagent silicic acid	Madagascar 1,500° C 4 hr	Near Lisbon, Md. 1,500° C 18 hr	Synthetic 1,500° C 24 hr	
	Lot A	Lot D	Lot E					
Ag	—	—?	FT	T	T	—?	T	FT
Al	—?	FT	T	VW	W	W	W	0.6%
B	—	—	—	T	—	—	—	VW
Ba	—	T	T	VW	—	VW	VW	VW
Be	—	—	—	—	—	—	—	VW
Ca	—	T	FT	T	VW	T	T	2%
Cr	—	FT?	—	FT?	T	FT?	FT?	T
Cs	—?	—?	—?	—	—	—?	—	—
Cu	FT	FT	FT	W	—	VW	M	M
Fe	—?	FT	—?	VW	VW	T	VW	0.3%
K	—	T	—	T	—	T	T	W
Li	—?	FT	—?	FT	—	FT	FT	T
Mg	FT	T	FT	FT	VW	FT	FT	W
Mn	—	—?	—	—?	FT	—?	—?	VW
Mo	—	—	—	—	—	W	VW	—
Na	—?	[a]VW	[a]VW	VW	—	VW	VW	VW
Ni	—	—	—	—	—	—	—	T
Pb	—?	FT	—	T	—	T	T	T
Rb	—	—?	—	—?	—	—?	—?	—?
Si	VS	VS	VS	VS	VS	VS	VS	VS
Sn	—	—?	—	—?	—	—?	—?	—?
Sr	—	—	—	—	—	—	—	W
Ti	—	—	—	VW	VW	VW	—	W
V	—	—	—	T	—	T	T	VW
Zn	—	—	—	W	—	—	—	W
Zr	—	—	—	VW	—	—?	—?	W
Estimated Purity % Min	99.9998	[a]99.9854	[a]99.9876	99.7338	99.8579	99.7547	98.8547	95.4359
Estimated Purity % Max	—	[a]99.99854	[a]99.99876	99.97338	99.98579	99.97547	99.88547	96.93359

NOTE: In general the following concentration ranges are indicated by the symbols: VS greater than 10%; S, 1-10%; M, 0.1–1%; W, 0.01-0.1%; VW, 0.001–0.01%; T, 0.0001–0.001%; FT less than 0.0001%; (—), not detected.

[a] Flame Photometer analysis for sodium indicated none present which was not also obtainable by a blank run. The sodium detected in the blank run amounted to 0.00157%. Quantitative spectrochemical analysis indicated less than 0.002%. It seems probable therefore that lots D and E were as pure as lot A.

source materials as received or as prepared, and the compositions may have been modified slightly by subsequent heat treatment. Furthermore, deliberate impurity additions were made to some samples.

Our highest purity material was prepared by the hydrolysis of redistilled tetraethyl orthosilicate. The resulting gel was prepared in five lots (designated Lots A to E), which were first heated overnight to 110° C to remove most of the water. The lots were then crushed lightly in an agate mortar and heated for 24 hr at 360° C to remove the last traces of alcohol.[4]

Various impurities were added to individual samples of lots B to E. These were added to the extent of 1 mole percent of the substances given in tables of results (table 5), with the exception of iron oxide for which there was no certainty as to its valency state in association with silica. Aluminum and germanium oxides were added directly as powders to the silica gel, iron was added as the oxalate, calcium as the carbonate or the phosphate, and the other elements as carbonates. All additions were intimately mixed with the silica gel as fine reagent grade powders before heat treatment.

The remaining samples of amorphous silica and quartz (table 1) were not subjected to any chemical treatment before conversion to cristobalite. An analysis of a typical unused commercial silica brick is given for comparison.

Samples were heated to form cristobalite by a uniform procedure. They were placed in covered platinum boats, and heated at a steady rate of 2°/min in a Pt-Rh wound mullite tube furnace until some preselected maximum temperature had been attained. The maximum temperature was held for a specified time to within ±5° C, whence the samples were cooled at 4° C/min until the temperature had fallen to about 700° C. At this temperature the natural cooling rate of the furnace became less than 4°/min and the samples were permitted to cool at the natural rate to room temperature over a period of 12 to 24 hr.

After heat treatment the samples were ground to a fine powder (through a 200-mesh screen) with an agate pestle and mortar. The particle size distribution of these powders was not determined.

Minor deviations from this general method of preparation were followed with a few samples in order to study special effects, or because of the limited quantity of source material available. Such deviations are given in the sections 4 and 5 (Results and Discussion) when the inversion temperatures of such samples are discussed.

3. Apparatus and Experimental Procedure

In recent years both X-ray and differential thermal analyses have been added to the earlier optical and thermal expansion methods of studying the inversion. Both methods of analysis were used in this investigation, and the results were supplemented by observations with a hot-stage microscope and an electron microscope.

Differential thermal analysis (DTA) is a particularly useful routine technique and has been employed throughout this investigation. Both the theory of the technique and its application to the cristobalite problem have been recently reviewed [15], and will not be described in detail here. Grimshaw and Roberts [13, 15], and others, have reported that they were unable to obtain reliable inversion temperatures on cooling by the DTA method. However, in this investigation it was found that, by using a specially designed furnace, reliable inversion temperatures could be obtained both on heating and cooling.

Figure 1 shows the all-copper furnace which was constructed for the DTA apparatus. The furnace was intended for use only up to 300° C, and no difficulty with the oxidation of the copper was experienced if this temperature was not exceeded. Reproducible and uniform heating rates could usually be obtained using a manually controlled variable transformer. The furnace was allowed to cool naturally, with the heater power turned off. The rate of cooling could be varied by changing the furnace insulation, or by surrounding the furnace with a cold jacket. The cooling curve thus obtained was not, of course, a straight line over wide ranges of

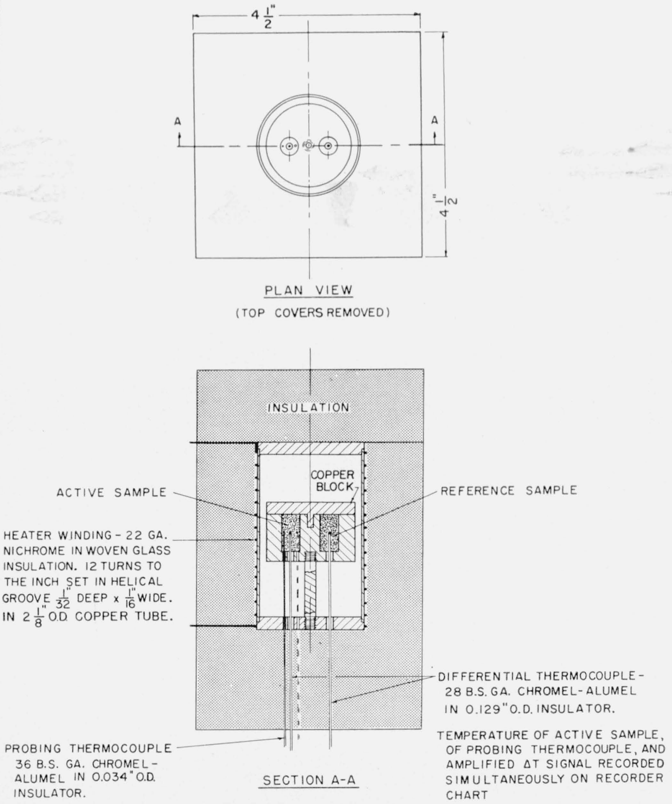

FIGURE 1. *Differential thermal analysis furnace.*

Alternative position of probing thermocouple shown with broken lines. The drawing is to scale. The insulation consists of cut sections of Class 28 insulating brick.

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[4] The prolonged, low-temperature heat treatment was necessary for the removal of alcohol without decomposition to a black carbonaceous deposit. Once formed the deposit could only be removed by prolonged heat treatment even at 1,550° C.

temperature, but could be approximated to a straight line over the limited range in which the inversion occurred. In the normal routine analysis of samples the insulation was as shown in figure 1 and yielded a cooling rate of about 4° C/min through the inversion range. The heating rate was, then, also set to approximate this figure.

As discussed in the following section (Results), it was found, rather surprisingly, that varying the heating and cooling rates gave significant changes in the temperatures at which peaks occurred in the differential-temperature (ΔT) curve. The figure of 4° C/min represented a compromise which gave relatively high peaks which were yet broad enough to give fair details of the singularity or multiplicity of their structure. Very slow rates were difficult to control with precision, while rapid heating and cooling tended to smear out significant differences in inversion temperature within a sample.

4. Results

4.1. Differential Thermal Analysis

Some traces of DTA records of particular interest are shown in figure 2. The bulk of the DTA results are, however, best presented in tabular form and are given in the sequence of tables 2 through 7.

In interpreting the data from the ΔT curves it has been assumed that peaks in these curves represent inversion temperatures. The difficulty here has been that frequently no single peak was obtained with a given sample, nor yet just two (as has been previously reported in the literature [13]). In fact, certain samples persistently gave so many peaks that it was difficult to resolve these from a continuous hump in the ΔT curve. There was abundant evidence that when two peaks occur close together one peak influences the apparent inversion temperature indicated by the other. The situation was further complicated because samples which gave very sharp, high peaks on heating through the inversion temperature often gave very skewed, double or even treble peaks on cooling. Except in cases where there was a definite skew in the peak obtained on heating, it was not possible to resolve the one peak into two identifiable peaks. The suggestion remained that the character of the inversion on heating was different from that on cooling. This suggestion was supported both by the readiness with which the inversion temperature on cooling was subject to variations not attributable to further high-temperature heat treatment, and by the fact that inversion temperatures on cooling were subject to greater fluctuations than inversion temperatures on heating.

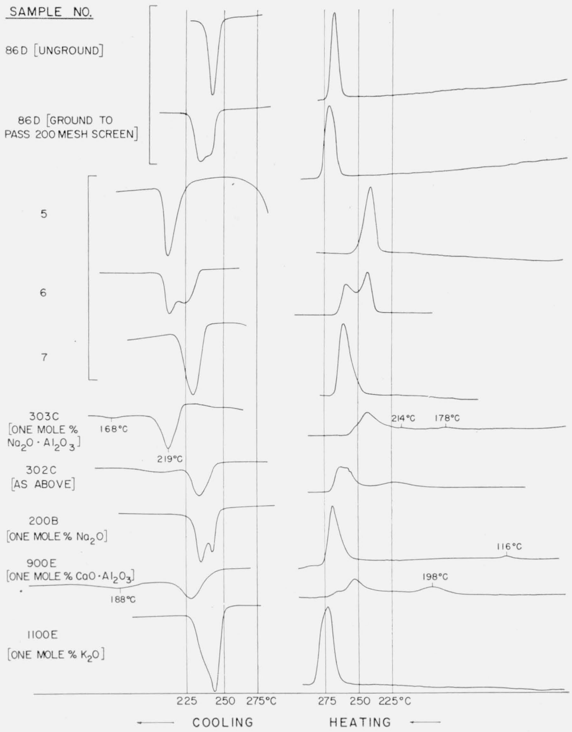

FIGURE 2. *Traces of typical differential temperature curves on heating and cooling at approximately 4° C/min.*

TABLE 2. *DTA of samples prepared from tetraethyl orthosilicate*

Sample No.	Peak temperatures obtained by heating and cooling at 4° C/min after stated heat treatments: Heat treatment, Maximum temperature	Heat treatment, Time	Heating, Peak temperature	Heating, Peak height	Cooling, Peak temperature	Cooling, Peak height
	° *C*	*hr*	° *C*		° *C*	
33A	1, 200	6	[a]	[a]	[a]	[a]
37B		24	[a]	[a]	[a]	[a]
55B		48	225?	------	205–15?	------
82D		192	253	74	221 229	59 35
84D		384	242 251	22 62	215 222	28 63
39	1, 250	12	[a]	[a]	[a]	[a]
43B		192	254	140	229	104
32A	1, 300	6	254–5	6	227	10
36B		12	255	46	232	41
38B		96	257	129	227 232	91 95
40B		192	257	143	232–3	143
45B	1, 350	6	[b]	[b]	[b]	[b]
46B		12	256–7	34	230 233	24 27
47B		48	261	128	237	126
48B		96	260–1	132	236	124
49B		192	262–3	142	238–9	134
50B	1, 375	6	258	6	232–3	5
53B		7½	258–9	50	236	46
52B		9	260	26	235 228	25 19
54B		10½	257	27	234	24
51B		12	266	135	240	128
31A	1, 400	6	266	157	241	148
57D		12	266	178	234 241	89 92
59D		96	266	196	225 241	53 94
79D		192	266	197	235 240	70 82
81D		408	266	207	224 240	40 86
30A	1, 500	6	268	184	242	175
78D		96	269	215	238 243	68 96
35B	1, 550	6	268	179	243	179
83D		48	270	212	238 244	103 168
34B	1, 600	6	267–8	187	242	181
56B	1, 650	6	270	172	236 244	101 171
86D	1, 700	18	272	174	235 241	122 111

[a] No observable peaks.
[b] No measurable peaks.

TABLE 3. *DTA of samples prepared from reagent silicic acid*

Sample No.	Peak temperatures obtained by heating and cooling at 4° C/min after stated heat treatment									
	Heat treatment		Peak 1				Peak 2			
	Maximum temperature	Time	Heating	Height	Cooling	Height	Heating	Height	Cooling	Height
	° C	*hr*	*° C*		*° C*		*° C*		*° C*	
14	1, 100	3	238	110	211	115	--------	--------	--------	--------
16		6	234–5	97	209–10	103	--------	--------	--------	--------
17		12	235	75	210	96	--------	--------	--------	--------
13	1, 200	3	243	87	214–5	90	--------	--------	--------	--------
5		6	241	101	214	105	--------	--------	--------	--------
15		12	241–2	67	215–6	82	--------	--------	--------	--------
18		24	234–5	94	209	103	--------	--------	--------	--------
20		48	235	89	210	90	--------	--------	--------	--------
26		192	244	37	216	34	252	119	225	119
28		384	(a)	(a)	220	96	251	129	228	67
11	1, 300	3	242–3	52	215–6	59	259	48	227	48
6		6	243	60	215–6	63	259	43	225	49
12		12	242	60	215	59	259	51	226–7	47
19		24	242–3	49	214–5	53	258	53	226–7	49
21		48	242	39	215	39	259	61	227–8	51
9	1, 400	3	242–3	50	216	55	260	51	229	46
3		6	241	157	214	157	--------	--------	--------	--------
10		12	242–3	51	216–7	59	260	44	227	43
24		192	--------	--------	--------	--------	269	135	235 239	81 83
25		408	--------	--------	--------	--------	267	125	224 238	39 75
2	1, 500	6	249–50	86	222	97	259	41	(b)	(b)
1		12	257–8	72	228–9	92	262–3	107	233–4	89
7	1, 550	6	--------	--------	--------	--------	261	107	230	99
27		48	--------	--------	--------	--------	270	129	237 244	63 93
8	1, 600	6	--------	--------	--------	--------	264	150	235–6	128

[a] Merged into Peak 2.
[b] Merged into Peak 1.

TABLE 4. *DTA*[a] *of samples produced from quartz*

Heat treatment		Peak temperatures ° C (Peak heights shown in parentheses)					
		Madagascar		Near Lisbon, Maryland		Synthetic	
Temperature	Hours	Heating	Cooling	Heating	Cooling	Heating	Cooling
1, 400	6	----------	----------	----------	----------	230 (41)	221 (42)
1, 500	4	238 (90)	218 (83)	----------	----------	----------	----------
	6	----------	----------	----------	----------	227 (81) 247 (10) 265 (3)	219 (83) 231 (13) 241 (3)
	12	----------	----------	240 (59) 246 (84)	227 (77) 231 (94)	----------	----------
	18	----------	----------	242 (78) 246 (99)	---------- 230 (108)	----------	----------
	24	----------	----------	----------	----------	232 (87) 249 (11)	216 (100) 230 (13)
1, 600	6	252 (91)	227 (101)	----------	----------	257 (131)	234 (126) 243 (23)
	12	264 (156)	233 (92)	----------	----------	262 (163)	236 (116) 244 (24)
	18	264–5 (172)	232 (77)	----------	----------	262 (160)	237 (106) 242–3 (20)
	24	265–6 (180)	233–4 (77)	----------	----------	----------	----------
1, 700	24	----------	----------	----------	----------	272 (142)	233[b] (116)

[a] DTA heating and cooling rate 4° C/min.
[b] Second peak merged into this at about 239° C.

Further comment on these observations will be given subsequently, both in this section and the following Discussion (section 5). First, however, some comment on the validity of identifying peak temperatures with inversion temperatures is warranted.

Apart from a consideration of the significance of the peaks as fundamental reference points, it is pertinent to question whether the peaks occurred at invariant temperatures for given samples. With the equipment used in this investigation the temperatures at which peaks occurred were reproducible to within less than ½° C for fixed heating (or cooling) rates. However, peak temperatures could be raised 7° to 8° C by increasing the heating rate from ⅛° to 35° C/min. Rapid cooling lowered the peak temperatures or suppressed higher temperature peaks

TABLE 5. *DTA of samples containing one mole percent of added impurities*

Impurity	Peak temperatures obtained by heating and cooling at 4° C/min from samples heated for 6 hr at stated temperatures (Peak heights in parentheses)									
	1,200° C		1,400° C		1,500° C		1,600° C		1,650° C	
	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
None	None	None	266 (157)	241 (148)	268 (184)	242 (175)	268 (187)	242 (181)	270 (172)	236 (61) 244 (109)
Al_2O_3	--------	--------	----------	----------	260 (92)	224 (58) 228 (63) 241 (18)	263 (122)	239 (127)	261 (116)	238 (117)
Na_2O	--------	--------	116 (6) 162 (1) 264 (73)	233 (49) 239 (51)	116 (3) 259 (89)	235 (75) 242 (63)	116 (2) 268 (100)	239 (81) 244 (90)	----------	----------
$Na_2O \cdot Al_2O_3$	[b] 178 (3) 214 (2) 242 (25)	167 (4) 219 (62)	214 (16) 220 (14) 229 (12) 256 (9)	190 (13) 202 (25) 214 (15) 232 (7)	250 (40)	224 (46)	214–223 (6) 258 (31) 263 (34)	206–213 (3) 234 (44)	----------	----------
MgO	None	None	255 (103)	226 (69) 232 (51) 238 (36)	263 (156)	238 (115)	264 (181)	240 (152)	----------	----------
Fe_xO_y[a]	None	None	252 (126)	222 (67) 226 (56) 241 (18)	255 (137)	225 (44) 233 (70) 242 (28)	265 (184)	234 (72) 239 (146)	----------	----------
Li_2O	116 (3) 173 (1) 246 (46)	223 (71)	116 (13) 171 (1) 262 (37)	233 (37) 238 (33)	115 (2) 266 (87)	237 (70) 243 (81)	117 (1) 263 (30) 272 (116)	238 (92)	----------	----------
CaO	--------	--------	245 (74) 258 (13)	221 (62) 227 (55)	264 (122)	230 (101)	268 (159)	234 (98) 242 (85)	----------	----------
$Na_2O \cdot Fe_2O_3$	--------	--------	247 (46) 249 (42)	218 (69) 240 (4)	249 (53) 258 (39)	226 (51) 233 (68)	----------	----------	----------	----------
$CaO \cdot Al_2O_3$	--------	--------	232 (22) 236 (25) 254 (6)	208 (37) 226 (10)	240 (20) 245 (19) 263 (3)	209 (35) 218 (21) 228 (9)	198 (9) 254 (23) 265 (7)	188 (7) 229 (36)	----------	----------
BaO	--------	--------	247 (70) 260 (15)	218 (56) 240 (15)	255 (36) 258 (36)	230 (87)	270 (175)	243 (147)	----------	----------
K_2O	--------	--------	117 (8) 263 (70)	232 (65)	272 (109)	237 (120) 243 (62)	272 (115)	243 (124)	----------	----------
$Ca_3(PO_4)_2$	--------	--------	----------	----------	258 (113) 268 (33)	233 (85) 239 (56)	268 (126)	239 (114)	----------	----------
GeO_2	--------	--------	----------	----------	270 (141)	244 (128)	----------	----------	----------	----------
$Al_2O_3 \cdot Ca_3(PO_4)_2$	--------	--------	----------	----------	237 (21) 242 (22) 257 (32) 261 (33)	215 (52) 228 (34) 237 (20) 244 (23)	----------	----------	----------	----------
$Li_2O \cdot Al_2O_3$	--------	--------	----------	----------	258 (57)	233 (78)	----------	----------	----------	----------
$K_2O \cdot Al_2O_3$	--------	--------	----------	----------	----------	----------	241 (9) 265 (32)	219 (11) 236 (38)	----------	----------
$MgO \cdot Al_2O_3$	--------	--------	----------	----------	----------	----------	251 (84) 266 (37)	230 (105)	----------	----------
$BaO \cdot Al_2O_3$	--------	--------	----------	----------	----------	----------	238 (?) 255 (47)	224 (75)	----------	----------

[a] Added as 2½% by weight of $FeC_2O_4 \cdot 2H_2O$.
[b] Heated 192 hr.

TABLE 6. *DTA of samples prepared from gel of different particle sizes*

Mesh size of gel		Peak temperatures obtained by heating and cooling at 4° C/min for stated heat treatments												
		Heated at 1,450° C for 6 hr							Heated at 1,600° C for 6 hr					
		Sample no.	Heating		Cooling				Sample no.	Heating		Cooling		
Through	On		Temperature	Height	Temperature	Height	Temperature	Height		Temperature	Height	Temperature	Height	Temperature	Height
			° C		° C		° C			° C		° C		° C	
325	-----	60D	259	130	227	98	-----	-----	74D	267	165	-----	-----	[a] 240	119
200	325	62D	263	153	229	111	-----	-----	73D	267	169	-----	-----	238	108
140	200	65D	266	146	231	[a] 99	-----	-----	72D	268	173	230	70	241	121
100	140	69D	267	160	231½	90	242	88	71D	266	167	230	85	240	98
80	100	64D	265	153	232	92	240	75	70D	266	181	233	63	242	155
40	80	63D	264	182	234	39	242	176	68D	267	221	-----	-----	245	210
20	40	61D	263	162	------	-----	241	149	67D	267	192	-----	-----	244	191

[a] These peaks markedly skewed in direction of other cooling peaks.

Table 7. *X-ray determination of inversion temperatures by change of structure*

Sample 67D[a]		Sample 71D[a]	
Temperature	Structure	Temperature	Structure
° C		*° C*	
Heating:		Heating:	
255–6	Tetragonal.	256	Tetragonal.
261	Cubic and small amount of tetragonal.	264	Cubic.
264	Cubic.		
Cooling:		Cooling:	
234	Cubic and trace of tetragonal.	231	Tetragonal and cubic.
225	Cubic and small amount of tetragonal.	226	
219	Tetragonal and trace of cubic.	220	Tetragonal.

[a] History of these samples is given in Table 6. The authors are indebted to W. Johnson and K. W. Andrews of the United Steel Cos., Central Research Laboratory, Rotherham, England, for making these determinations.

in favor of lower temperature peaks. The heating and cooling rates used for the routine analysis (4° C/min) gave peak temperatures which were about 2° C higher (or lower) than those obtained by the slowest rates. The exact error involved in passing through the inversion rapidly was difficult to determine, however, because of the multiple peak character of the ΔT curve for many of the samples.

For rapid, reversible inversions the recorded inversion temperature should be independent of the heating rate and identical with the temperature of a peak in the ΔT curve [15, 16, 17] (providing the thermocouples are located at the center of the specimens). Cristobalite is a substance whose individual crystallites may all have rapid inversions, but not identical inversion temperatures. Although the individual inversions take place only over a limited range of temperature, it is possible that the temperature at which the peak in the ΔT curve occurs may be fortuitous and dependent upon the distribution of the inversion temperatures among the crystallites of the sample. It was observed on a hot-stage microscope that all the crystallites of a sample do not, in fact, invert at the same temperature. (See also the paper by Chaklader and Roberts [18]). It has been suggested by Hargreaves [5] that, as an alternative to using the peak temperature, the temperature at which the ΔT curve first deviates from its base line yields a temperature more characteristic of a sample. With the apparatus and samples used in this investigation this temperature was 5° to 20° C lower than the peak temperature on heating, and in order to justify its acceptance it was necessary to determine whether the temperature gradient through the samples was negligible by comparison. An additional probing thermocouple was inserted into the outside of the cristobalite as shown in figure 1. The temperature registered by this thermocouple was then recorded on a chart along with the usual DTA data. It was thus possible to observe the temperature at which the ΔT curve first departed from its base line simultaneously with the temperature of the probing thermocouple (fig. 3). By this method it was possible to show that the initial departure of the ΔT curve from its base line was associated with temperature gradients in the sample, rather than with variations in the inversion temperature (fig. 3). The different inversion temperatures were fairly uniformly distributed throughout the samples. It was thus concluded that the peak in the ΔT curve provided the best estimate of the inversion temperature of a sample as a whole, notwithstanding the observation that no single temperature could be given for all the individual crystallites. Furthermore, it was, in general, desirable to correct for the significance of heating rates in converting observed peak temperatures to estimated inversion temperatures.

During the course of the investigation, it was observed that there were three extraneous factors involved in the experimental procedure which were sometimes significant in determining the inversion temperatures indicated by DTA. It appeared possible that peak temperatures could be changed

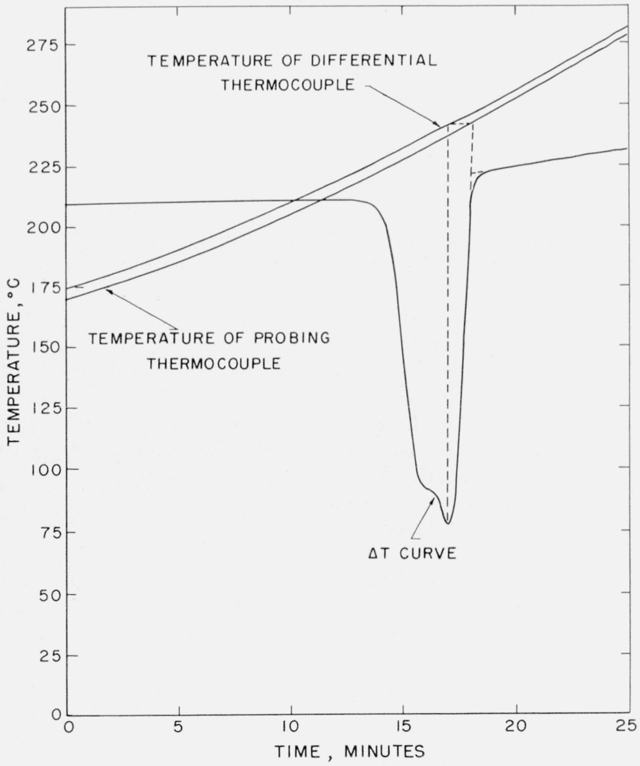

Figure 3. *Trace of a typical recorder plot of a cooling curve, showing that the initial departure of the differential temperature (△T) curve from its base line can be associated with a temperature gradient within the sample.*

The temperature gradient within the sample is shown by the different temperatures of the differential thermocouple (located in the center of the sample) and the probing thermocouple (located at the edge of the sample) at particular times.

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[5] Private conversation. We are indebted to Dr. J. Hargreaves (Research Laboratories of United Steel Companies, Rotherham, England) for first suggesting these possibilities. He has further noted that with samples he has prepared, the hysteresis in the inversion temperature is eliminated if this alternative criterion is employed. Within ±2° C (the error being largely due to the difficulty of locating the precise temperature at which the ΔT curve departs from its base line) many of the heating and cooling curves resulting from this investigation also show this effect (at about 250° C). The effect is, however, not consistent (and probably quite fortuitous). Hargreaves also found, however, that by using this criterion he was able to reconcile inversion temperatures determined by DTA with those obtained by Johnson and Andrews by X-ray methods [1].

(1) by quenching samples from high temperature following heat treatment, (2) by grinding the samples in the agate mortar after treatment, and (3) by cycling samples through the inversion in the DTA furnace.

The first factor was taken care of in the experimental procedure by cooling samples at a controlled rate. The effect of quenching a sample from high temperature was, however, investigated using a portion of sample 70D (table 6). The peak temperatures obtained were not significantly different from those of the unquenched sample (70D), but there was some small difference in the relative heights of the peaks obtained on cooling.

The data given in the tables of results are not corrected for the heating rate because of the difficulty of knowing the exact correction for each sample. In any case, the error involved with many of the samples is believed to be slight. The peak heights are given in arbitrary units, intended merely to indicate their relative heights.

It was not discovered until most of the samples had been analyzed that the process of grinding the samples for DTA had a significant effect on the peak temperatures obtained. The effect during heating was slight and barely detectable in most instances. However, there was good evidence that the second (lower temperature) peak obtained during cooling was at least in part attributable to grinding. For example, sample 86D (table 2) when analyzed without first being crushed or ground gave a peak on heating at 270° C, and a single sharp peak on cooling at 244° C. Successive crushing and grinding only slightly raised the heating peak but gradually introduced a new lower temperature peak on cooling which ultimately became dominant (fig. 2). This effect was noted with other samples, but not with those containing impurities. The results given in the tables are all for samples crushed to pass through a 200-mesh sieve.

The third factor observed was the antithesis of the foregoing, for with some samples the lower temperature cooling peak could be eliminated in favor of the higher temperature peak. This was achieved by cycling the temperature about the inversion points and observing the change in the peak temperature during successive cycles. The lower temperature peaks of samples 70D, 71D, and 72D (table 6) could all be eliminated by cycling the temperature in this way. However, it was not possible to remove the skewness from sample 74D by this technique. Moreover, when cycling samples containing impurities, only a slight effect was noted, which was of doubtful significance. The peak temperatures given in the tables of results are for samples subjected to a single heating and cooling in the DTA furnace.

4.2. X-Ray Analyses

The purpose of the X-ray analyses was twofold. First, an attempt was made to check the inversion temperature against observed changes in crystal structure; second, samples with different inversion temperatures were examined at room temperature for variations in inherent structure, order, and crystallite size.

The results of the inversion temperature determinations are given in table 7. It will be noted that there is a difference in the inversion temperatures as indicated by X-ray analysis and DTA. Because, however, there is an inherent difficulty of accurate temperature measurement in most high-temperature X-ray cameras, this lack of agreement is probably of little significance. Of perhaps greater significance is the range of temperature over which the inversion occurred, although, here again, some of this range may be due to temperature gradients within the sample.

The results of the structure and crystallite size investigations were deduced from counter diffractometer traces obtained by scanning over the angular region $2\theta=5°$ to 162°. The studies were made at room temperature using samples 35B (DTA peak 268° C), 43B (DTA peak 254° C), and 9 (DTA peaks 242° and 260° C). No appreciable differences in low angle scattering ($\theta=5°$ to 11°) were observed, indicating a crystallite size greater than 10A in all samples. Likewise, no significant differences in diffraction line intensities or peak positions were detected, suggesting identical or very closely similar atomic packing in the crystallite regions. Shifts in the X-ray diffraction patterns of the type described by Flörke [10] were, therefore, not a prominent feature of any sample. The width of the diffraction lines, however, varied markedly between the samples, especially at high angles.[6] The line profiles of sample 43B were wider than those of sample 35B throughout the scanning range, the high-angle peaks being very diffuse (fig. 4). The line broadening for the latter sample was very little more than that attributable to the experimental technique, indicating crystallites of size larger than 1000 A and of small internal strain. Attempts to

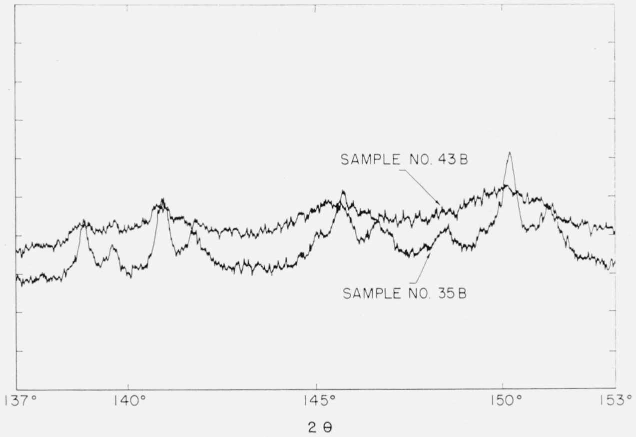

FIGURE 4. *X-ray diffraction line intensities for the angular region $2\theta=137-153°$.*

Sample 43B gave a DTA peak at 254° C during heating, and sample 35B gave a DTA at 268° C.

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[6] In Flörke's investigation [10] the diffraction patterns are shown only for low angles.

obtain the causes for the line broadening were based on a number of assumptions, none of which were fully justified, and whose cumulative errors precluded any reliable quantitative interpretation. Nevertheless, the following qualitative conclusions were almost certainly justified.

(a) The rate of broadening with Bragg angle was too great to be solely attributable to the small crystallite size in sample 43B. Significant crystallite strains appeared to exist.

(b) The ultimate crystallite size was likely to be of the order of 50A.

(c) The results for sample 9 were similar to those for sample 43, with the possibility of a wider crystallite size distribution.

5. Conclusions and Discussion

The results of the investigation even with the very pure material retain a certain lack of reproducibility and definitude. The lack of reproducibility was clearly inherent both in the nature of the samples (they were not homogeneous with respect to inversion temperature) and the experimental procedure, and even the most meticulous use of the techniques used in this investigation could hardly eliminate it. Some greater definitude in the results might have been obtained if samples had been heat treated longer, whereas now probable trends alone are indicated. It is, however, possible to draw a number of conclusions which appear justified by the results.

It is clear that the most important variable associated with variations in the inversion temperature is the time and temperature of heat treatment. In order to provide some cohesion to a discussion of the variability of the inversion temperature in general, it is first proposed that the actual inversion temperature of the crystallites can be associated with three rate processes dependent on the temperature of heat treatment. These processes are, first, nucleation of the cristobalite phase from the source material; second, an ordering effect whereby small, well-ordered, strain-free crystallites are developed; and last, grain growth from the well-ordered crystals. That, within a polycrystalline sample, there will be an interplay between these processes is obvious. The result of each process will be a net loss of energy of the system and an observed increase in the inversion temperature. It is believed that a careful study of the effect of heat treatment upon the inversion temperature over the range 1,100° to 1,700° C supports the conclusion that there are three stages involved.

Consider the temperatures obtained for the low to high inversion with the samples prepared from tetraethyl orthosilicate (table 2). (The high to low inversion will be discussed subsequently.) Up to 1,350° C, very little cristobalite was formed during short-term heating (6 to 12 hr), but there was evidence that freshly nucleated material in an amorphous matrix inverted at temperatures around 225° C. It is believed that the general concept of a temperature-dependent rate process for nucleation will be readily accepted without detailed argument, but the question of whether nucleation occurs at a surface or within the gel may still be a matter for speculation.

Following nucleation, further heat treatment yields a progressive increase in the inversion temperature until this reaches 266° C. The rate at which the inversion temperature increases is temperature-dependent; heat treatment at 1,200° C for 384 hr causes the inversion temperature to rise only to 251° C, whereas at 1,375° C heat treatment causes the inversion temperature to reach 258° C after 6 hr and 266° C after 12 hr. It appears that the attainment of an inversion temperature of about 266° C represents the completion of the second process, whereby the freshly nucleated material develops well-ordered, strain-free crystallites.

It was observed that the inversion temperature of 266° C was attained after only 6 hr heat treatment at 1,400° C, but that more extended heat treatment at this temperature (up to 408 hr) did not raise the inversion temperature further. Heat treatment at higher temperatures, however, yielded a further slow rise in the inversion temperature, the rate of rise again apparently increasing with the temperature of heat treatment. The highest peak temperature obtained by DTA of this material was 272° C, but it is not unlikely that more prolonged heating at high temperatures would raise the inversion temperature somewhat further. That the slow rise in inversion temperature can be associated with a rate process is clear, but it must be admitted that the proposal that the process is crystal growth is based on little more than speculation. The proposal does, however, seem a reasonable possibility and is in at least qualitative accord with the known slow growth of cristobalite crystals.

From the above broad proposal it is possible to suggest the effect of particular variables on the inversion temperature. It is suggested that the general effect of impurities, the source material, and the crystal or particle size is merely to vary the rate of the above processes. For it appears that all cristobalite, from whatever source, and of whatever purity, will ultimately invert at the same temperature if subjected to a sufficiently extended heat treatment.

As far as rates are concerned, however, the effect of even relatively small amounts of impurity are significant, for the inversion temperatures of the cristobalite prepared from reagent silicic acid (table 3) are significantly different from the results discussed above. First, it will be observed that the impurities which were present in this material accelerated the nucleation of the cristobalite, since cristobalite was formed in only 3 hr at a temperature as low as 1,100° C. However, they retarded the ordering process yielding DTA curves very typical of the "two-peak" type which have been reported before. Nevertheless, the end product of heat treating this material appears to be identical with the end product from tetra-ethyl orthosilicate. Indeed, it is striking that two materials can yield cristobalite samples which behave so differently after low-temperature heat treatment, yet which are indistinguishable after high-temperature treatment.

The effects of the deliberate impurity additions (table 5) were in general accord with the above remarks, but were more complex. With some impurities the attainment of a relatively stable end product was retarded, and with others accelerated. We did not obtain any evidence that the end product of samples containing impurities was any different from that of the pure materials. Hence one may be justified in concluding that cristobalite rejects impurities in its structure during heat treatment at high temperature. The alkali ions Na, Li, and K each produced small DTA peaks which were attributable to tridymite, but these peaks were not detected with any other impurity. We have not attempted to relate the size or valency of the impurity ions to the magnitude or sign of their effect on the proposed rate processes. At this stage speculation alone can suggest whether some of these would occupy interstitial sites in the silica structure, substitute themselves for the cation, merely attach themselves to the surface, or enter into new polycomponent systems. It may be significant, however, that the $Na_2O \cdot Al_2O_3$ and $CaO \cdot Al_2O_3$ impurities contributed a larger effect than any other variable studied, because aluminum plus an alkali or alkaline earth is known to substitute for silicon in the silica structure. These impurities contributed DTA peaks as low as 178° C, but the possibility exists that some of the peaks may be more properly attributed to impurity stabilized phases within the silica matrix. It should not be overlooked that tridymite itself may fit into this category.

A further important effect of the impurities concerns the number of DTA peaks obtained. It will be observed (table 2) that the single peak character of the inversion was characteristic of the very pure material, with the exception of one sample prepared at low temperatures. (We are still discussing the low-high inversion only.) On the other hand, impure specimens tended to give a multiplicity of peaks which at times became difficult to resolve from a continuous hump spread over 20° to 40° C. There seems to be no sound reason for interpreting these peaks in terms of a number of different forms of cristobalite, unless substantial supporting evidence is produced. It would appear to be more probable that the appearance and disappearance of these peaks is associated with a lack of homogeneity within the sample in terms of the rate processes previously described. The multiple peak character of the DTA curves can be attributed to a tendency for groups of crystallites within particular samples to reach distinct stages of development. Since impurities most commonly slow down that process following nucleation to which the inversion temperature is most sensitive, the spread of inversion temperatures should become more apparent. And it is with just those impure samples in which the ordering process proceeds most slowly that the multiple peaks are most obvious.

It should be clear, in terms of a rate process interpretation of the variability of the inversion temperature, that cristobalite produced from quartz is not going to give the same inversion temperature as gel for the same heat treatment, unless identical end products have been obtained. Before cristobalite can be nucleated from quartz, there has to be a breaking of bonds within the structure, and this is, energetically speaking, a more difficult and time-consuming process than is encountered with the gel. Our results are in accordance with this expectation. In addition, the result of heating quartz to 1,700° C for 24 hr suggests that the end product obtained is identical with that obtained from gel.

We turn now to a consideration of the high-low inversion. It has already been stated that the nature of the inversion on cooling indicated by DTA was different from that on heating. The question may, however, be asked: was there a *real* difference, or were the observations merely inherent in the experimental procedure?

It is believed the difference was real, first, because observations were apparently independent of such variables as the DTA heating rate which would be most likely to yield anomalies of this type. The probing thermocouple did not indicate that the magnitudes of the temperature gradients on heating were significantly different from those on cooling. Secondly, the X-ray data (table 7) also suggested that the inversion on cooling was spread over a wider temperature range than on heating. Thirdly, the inversion on cooling appeared susceptible to significant variations independent of any observable variation on heating. Furthermore, if the inversion is accepted as being of the gradual-rapid variety on heating it may, nevertheless, only be of the rapid variety on cooling. It may well be that the rapid inversion of the high form is retarded until such time as sufficient energy of rotation of the oxygen ions has been lost that all the structural changes within a crystallite can be effected at the same time.

On the basis of this interpretation it is possible to suggest why two DTA peaks were obtained on cooling when only one peak was obtained on heating. It may be postulated that, on cooling, DTA is more sensitive to small structural inhomogeneities (such as strain induced by grinding) within the sample. That is, that inhomogeneities which are smeared out by the gradual onset of rotation on heating are nevertheless observable on cooling. More exact heat-content data would be required to test this interpretation.

Apart from the general anomalies obtained for the high-low inversion, the variability of the inversion temperature was generally consistent with proposals given for the low-high inversion. There was a suggestion in the data that more prolonged heat treatment at higher temperatures was redeveloping the lower temperature peak at the expense of the higher temperature peak. However, no ready explanation could be found as to why the peak temperature gradually rose to about 244° C and then fell off with the development of the lower temperature peak, unless the more extensive heat treatment yielded samples which required more grinding and thus were subjected to greater strain.[7]

The lack of homogeneity within samples, the limitations of DTA techniques, and the anomalies obtained for the high-low inversion make an unequivocal identification of the temperatures of the inversion very difficult. Assuming that very slow heating rates yield a more accurate correspondence between peak temperatures and truly representative inversion temperatures, but that further heating of our samples would have slightly raised our peak temperatures, the best estimate we can give for the low-high inversion is 270° to 272° C. This value is for samples of well ordered, well developed crystals, and is somewhat lower than previously proposed maxima. Complete information on the heating rates used to determine inversion temperatures has not always been given in the literature. Indeed, it has been supposed that indicated inversion temperatures are independent of heating rates. In many instances, however, heating rates of 15° C/min and greater have been used and it seems probable that apparent inversion temperatures in the range 270° to 280° C are attributable to rapid heating rates. In this investigation it has been possible to obtain similar values by the use of rapid heating rates with samples which yielded peak temperatures of 272° C or lower during slow heating.

Similar considerations are pertinent to the identification of the temperature of the high-low inversion, although, in this case, we also have to contend with the anomalous multiple peak character of the inversion. Neglecting effects which are believed to be partially due to grinding, it appears that the inversion on cooling is about 26° C lower than on heating, yielding a value of 244° to 246° C.

The authors thank H. S. Peiser of the Bureau for his contributions to the understanding of the structural variations of our samples as indicated by X-ray analysis. David C. Ailion, now a graduate student at the University of Illinois, also assisted with the preparation of the pure silica samples and with the routine differential thermal analysis.

6. References

[1] W. Johnson and K. W. Andrews, An X-ray study of the inversion and thermal expansion of cristobalite, Trans. Brit. Ceram. Soc. **55,** 227 (April 1956).

[2] R. B. Sosman, The properties of silica, p. 126 (Chemical Catalogue Co., Inc., New York, N. Y., 1927).

[3] A. E. Dodd, The forms of silica, p. 209 in Ceramics, a symposium (edited by A. T. Green and G. H. Stewart, Brit. Ceram. Soc., Stoke-on-Trent, 1953).

[4] W. Eitel, The physical chemistry of the silicates, p. 618 (University of Chicago Press, Chicago, Ill., 1954).

[5] C. N. Fenner, The various forms of silica and their mutual relations, J. Wash. Acad. Sci. **2,** 471 (1912); The stability relations of the silica minerals, Am. J. Sci. **36,** 331 (1913).

[6] Laboratoire Central de l'Union des Verreries Mecanique Belges a Charleroi, Verre Silicates Ind. **13,** 166 (1948).

[7] R. H. H. Pierce, Jr., and J. B. Austin, A comparison of the thermal expansion of used silica brick from an insulated and an uninsulated open hearth furnace roof, J. Am. Ceram. Soc. **19,** 276 (1937).

[8] S. Kondo, T. Yamuachi, and Y. Kora, Inversion of quartz to tridymite, J. Soc., Chem. Ind. (Japan) [B] **40,** 233 (1937).

[9] M. J. Buerger, Cristallographic aspects of phase transformations, Chap. **VI,** p. 206 in Phase transformations in solids. Edited by R. Smoluchowski, J.E. Mayer, and W. A. Weyl (John Wiley & Sons, Inc., New York, N. Y., 1951).

[10] O. W. Flörke, Struckturanomalien bei Tridymit und Cristobalit, Ber. d. deut. Keram. Ges. **32,** 369 (1955) Uber die Hoch-Tief Umwandlung und die Thermische Ansolchnung von Cristobalit; ibid. **33,** 319 (1956); Structural anomalies in tridymite and cristobalite. Review of above papers by W. Eitel. Bull. Am. Ceram Soc. **36,** 142 (1957).

[11] R. Weil, Etude microscopique de la transformation α-β de la cristobalite naturelle, Compt. Rend. Acad. Sci. Paris **180,** 1949 (1925); Influence des impurities sur la temperature de transformation paramorphique de la cristobalite; ibid. **183,** 753 (1926).

[12] E. Plumat, Anomalies des transformations instantées de la tridymite et de la cristobalite, Verre Silicates Ind. **13,** COBEA Suppl. p. 81 (1948).

[13] R. W. Grimshaw, A. Westerman, and A. L. Roberts, Thermal effects accompanying the inversion of silica, Trans. Brit. Ceram. Soc., **47,** 269 (1948).

[14] M. A. Mosesman and K. S. Pitzer, Thermodynamic properties of the crystalline forms of silica, J. Am. Chem. Soc. **63,** 2348 (1941).

[15] R. C. Mackenzie and B. D. Mitchell, Chapter II, Apparatus and experimental technique of DTA; R. W. Grimshaw and A. L. Roberts, Chapter XI, The silica minerals in the differential thermal investigation of clays (edited by R. C. MacKenzie, Mineralogical Society, London, 1957).

[16] H. T. Smyth, Temperature distribution during mineral inversion and its significance in differential thermal analysis, J. Am. Ceram. Soc., **34,** 221 (1951).

[17] E. Deeg, Foundations of the theoretical treatment of differential thermal analysis. Practical applications, Ber. d. deut. Keram. Ges. **33,** 321 (1956).

[18] A. C. D. Chaklader and A. L. Roberts, Relationship between the constitution and properties of silica refractories, Trans. Brit. Ceram. Soc., **56,** 331 (1957).

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[7] The persistence of a single, often skewed, low temperature peak at about 233° C was also common with samples derived from quartz.