Thermochimica Acta, 45 (1981) 167—176
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

QUANTITATIVE DETERMINATION OF CRISTOBALITE BY THERMAL METHODS

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(Received 22 October 1980)

ABSTRACT

Cristobalite was quantitatively determined in quartz samples fired between 1350 and 1490°C by thermal methods and specific gravity measurements. The amount of cristobalite was calculated from the thermal expansion coefficient, the area of the differential thermal expansion together with specific heat measurements and specific gravity determinations. The calculated values from the expansion coefficient and specific gravity are misleaing due to the presence of tridymite and glass in the samples. The results of differential thermal expansion compare well with those of specific heat measurements. Therefore, this method could be taken as a very precise measure for the quantitative determination of cristobalite. Also, the temperature of the peak indicates whether ordered or disordered cristobalite is present.

INTRODUCTION

Silica exists in three main polymorphic forms: quartz, cristobalite and tridymite. There are contradictions in the literature [1—6] about the existence of tridymite as a polymorphic form of silica. Workers in this field attribute its existence to the presence of a liquid phase formed by the addition of different mineralizers. Flörke [2] claimed that cristobalite and quartz are the only polymorphs of silica. "Each crystalline modification, however, exhibits two entirely different although superimposed expansions: the first type of expansion is brought about by increased atomic agitation with rising temperature, resulting in an increase in the bond length. The second occurs through an alteration in the bond angle and is responsible for a high—low inversion resulting in a sudden increase in volume over a narrow temperature range, while the former produces a slow regular increase in volume as the temperature is steadily raised" [7]. This inversion is accompanied by absorption of energy represented by an endothermic deflection in DTA.

Earlier workers in this field made use of the fact that quartz has different optical and thermal properties and a greater specific gravity than either cristobalite or tridymite, and attempted to assess the rate of conversion by means of the change in optical properties and thermal expansion or density of the fired body [8—11]. Precise measurements were not possible by these methods. DTA was also taken as a measure for the quantity of quartz in a ceramic material [12]. Flörke [13] declared that X-ray analysis gives a more precise determination of the phases.

The present work made use of the differential thermal expansion as a method for the quantitative determination of cristobalite following the quartz transformation. The results obtained are compared with those calculated from the heat of reaction, ΔH, measured by differential scanning calorimetry and those determined by specific gravity measurements.

EXPERIMENTAL

Raw materials

Raw quartz of 99.5% purity was chosen for the study (chemical analysis is represented in Table 1) together with a cristobalite sample prepared from silica gel (Merk) and 0.01 mole % FeO added as a mineralizer in the form of $FeSO_4$ fired in an electric globar furnace at 1500°C for 6 h, with intermediate mixing to ensure complete transformation into cristobalite as confirmed by X-ray analysis.

Sample preparation

Quartz was ground to pass 100 mesh sieve. Specimens in the form of cylinders (1.2 cm diameter and 2.5 cm height) were fabricated under a pressure of 5 KN cm^{-2} using dextrin as a binder, dried, then fired in a globar furnace between 1350 and 1490°C with a temperature interval of 50°C. The heating was carried out gradually to reach the maximum temperature in 2 days, soaked for 1 h at the maximum temperature, then cooled on the third day. The quantity of quartz transformed into cristobalite was determined by thermal means and specific gravity measurements.

Thermal analyses

Differential scanning calorimetry

The heat of reaction was determined for standard mixes prepared from cristobalite and quartz in the weight percentages 10—90%, and quartz samples were treated at the different temperatures. Twenty-five mg of the

TABLE 1

Chemical analysis of the raw quartz sample

Constituting elements	Percentage
SiO_2	99.65
Al_2O_3	0.18
Fe_2O_3	0.58
Na_2O	0.12
Loss on ignition	0.15
Total	100.83

samples were moulded in a capsule scanned against an empty reference capsule in a No. 900600, 902 Dupont DSC cell. The run was carried out in an atmosphere of nitrogen with a heating rate of 20° C min^{-1} and a sensitivity of 0.5 mcal sec^{-1} in.^{-1}. Isothermal heating at the peak temperatures of quartz and cristobalite (573 and 250°C, respectively) was followed at a rate of 2 min in^{-1}. The heat of reaction was calculated from the following equation

$$\Delta H = \frac{A}{W} 60BE\ \Delta q$$

where A = area of the peak, W = weight of the sample = 25 mg, B = time in.^{-1}, Δq = sensitivity = 0.5 mcal sec^{-1} in.^{-1}, E = cell constant = 1.15. The figure of 60 B $E\Delta q$ was kept constant for all runs. The area was measured from the height of the respective peak multiplied by the width at half height. Standard curves for quartz and cristobalite were then constructed (Figs. 1 and 2). The heat of reaction was then calculated for the experimental quartz samples fired at different temperatures and the amounts of the respective phases were determined from the standard curves.

Thermo-mechanical analysis, TMA

The reversible linear thermal expansion for the quartz specimens fired at different temperatures was measured using No. 900 902, cell 943 Dupont thermo-mechanical analyser. The run was carried out up to 300°C at a heating rate of 5°C min^{-1} and a sensitivity of 1 mil in.^{-1}. Meanwhile, the

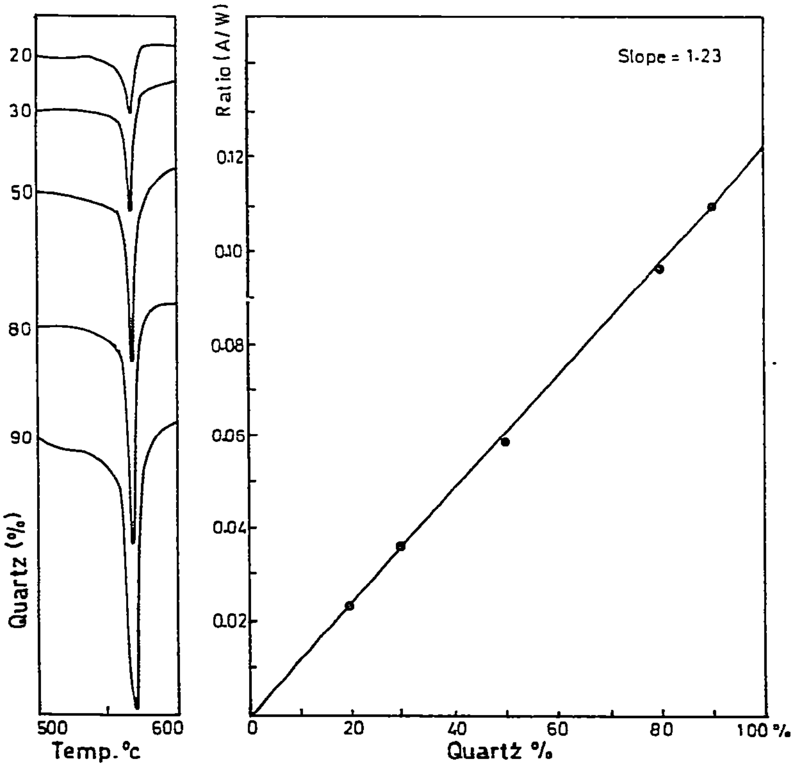

Fig. 1. Standard curve for the quantitative determination of quartz.

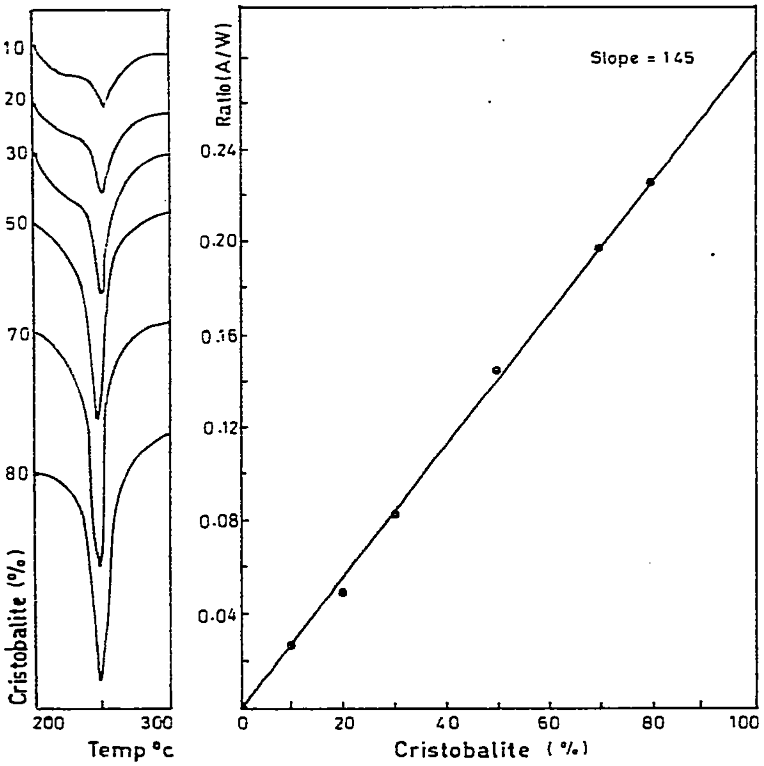

Fig. 2. Standard curve for the quantitative determination of cristobalite.

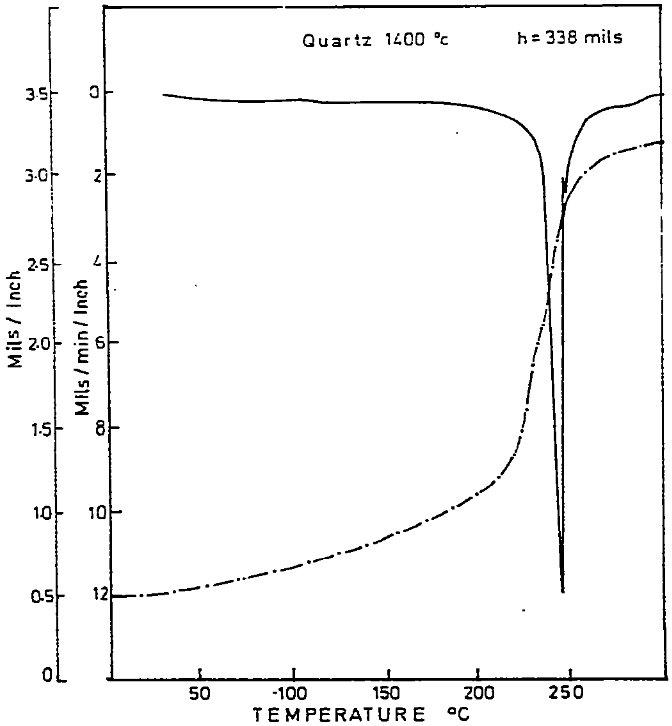

Fig. 3. A representative curve for the thermal expansion of the quartz sample fired at 1400°C. · — · — ·, TMA; ———, DTMA.

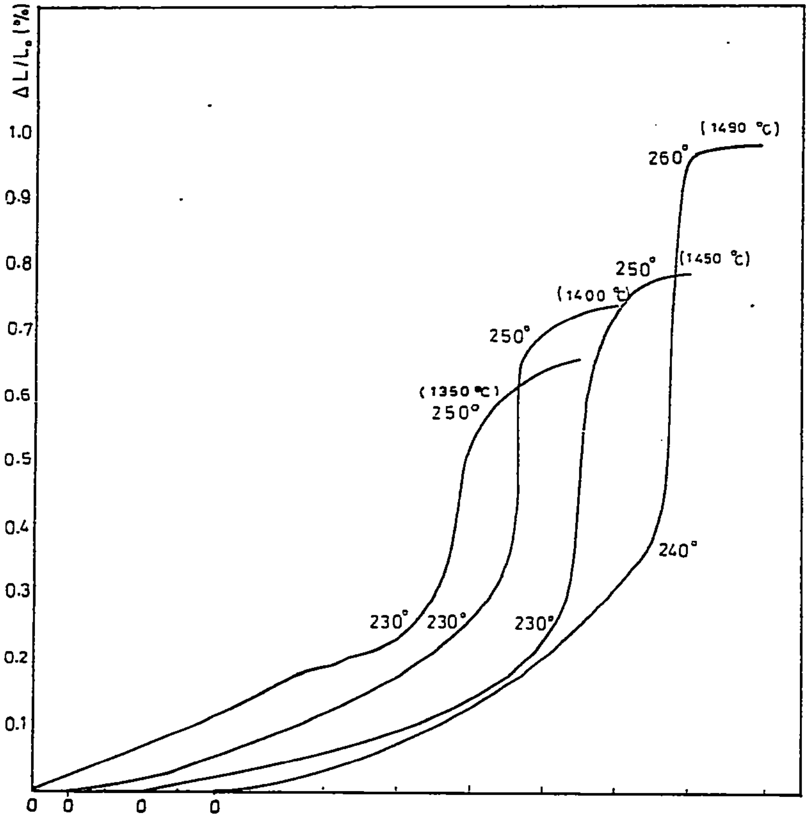

Fig. 4. Reversible linear thermal expansion curves of the samples under investigation.

derivative was traced at a sensitivity of 2 mil $\min^{-1}$ in.^{-1}. A representative curve of the run is shown in Fig. 3. The percent of quartz transformed into cristobalite was determined from both curves (Figs. 4 and 5). The mean expansion coefficient was first determined from the results of Fig. 4 and inserted in the following equation given by Turner [14]

$$\alpha = \frac{[\alpha' E' P'/d'] + [\alpha'' E'' P''/d'']}{[\alpha' E'/d'] + [\alpha'' E''/d'']}$$

where α = mean expansion coefficient of the samples between 20 and 300°C, α' and α'' = mean expansion coefficient of quartz and cristobalite at 20—300°C, d' and d'' = specific gravity of quartz and cristobalite, respectively, E' and E'' = elastic modulus of quartz and cristobalite, respectively. The results obtained are represented in Fig. 6 (curve d). The amount of cristobalite was also determined from the ratio of the area of the derivative obtained from the formula

$$\text{Area} = \frac{L \times \Delta q \times b}{R \times L_0}$$

where L = height of the derivative curve, L_0 = height of sample, Δq = sensitivity chosen = 2 mil $\min^{-1}$ in.^{-1}, R = heating rate = 5°C $\min^{-1}$, b = width at

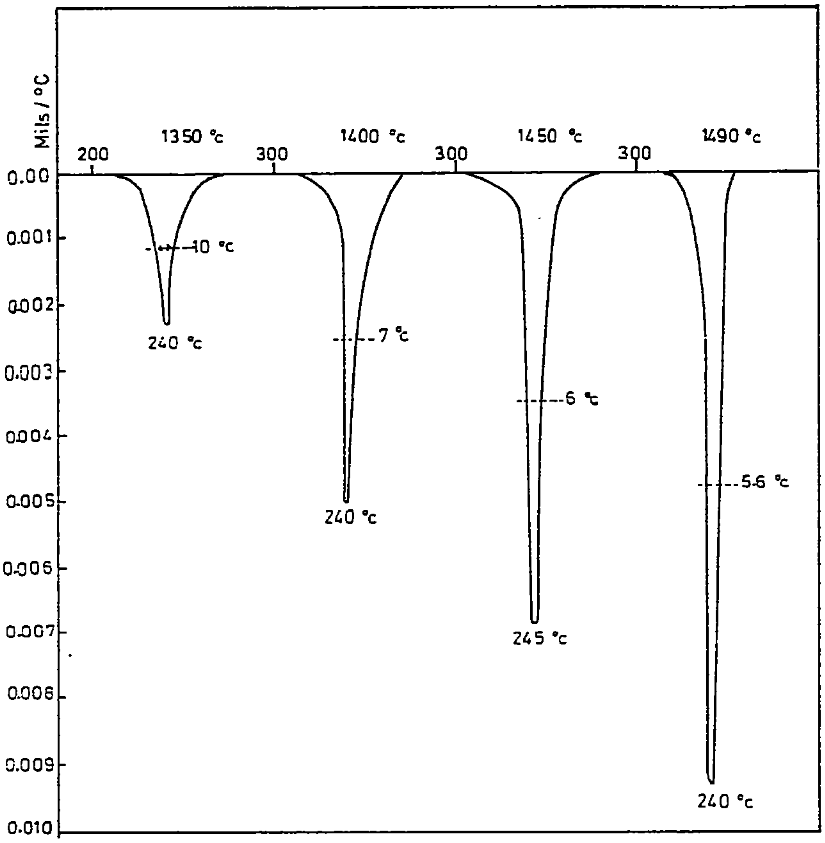

Fig. 5. Differential thermal expansion curves for the samples under investigation.

half height of the peak (°C $\mathrm{in.}^{-1}$), with respect to that obtained for a pure cristobalite sample scanned under the same conditions. The results obtained are represented in Fig. 6 (curve b).

Specific gravity

Specific gravity measurements were carried out for the quartz samples fired at different temperatures according to the ASTM specifications C 329-56 (1970). The amount of quartz transformed into cristobalite was calculated from the formula [15]

$$\frac{(1-x)}{d'} + \frac{x}{d''} = \frac{1}{D}$$

where d' and d'' = specific gravity of quartz and cristobalite, respectively, D = specific gravity measured for the different samples. The results obtained are shown in Fig. 6 (curve c). The amount of cristobalite obtained by the different methods is given in Table 3.

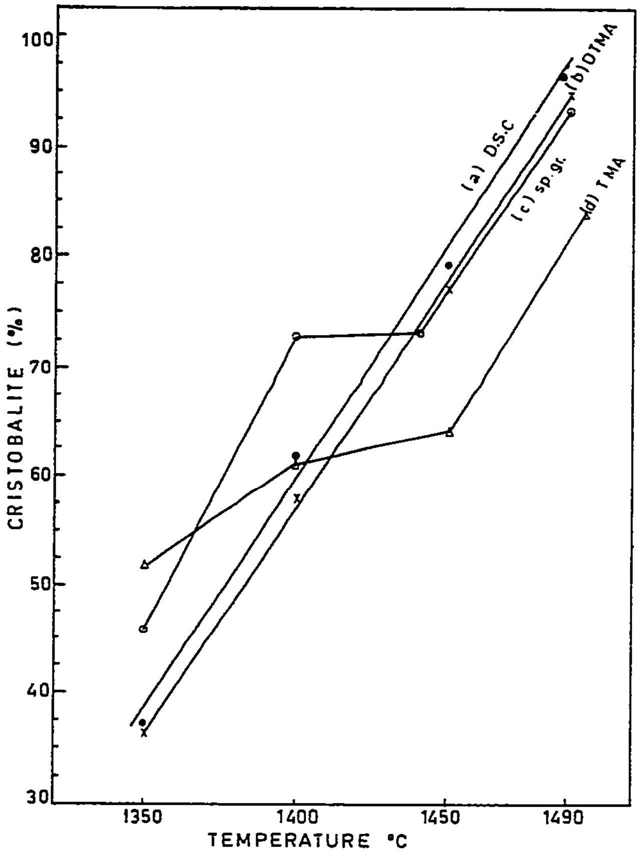

Fig. 6. Results of quantitative determinations of cristobalite by the different methods.

RESULTS AND DISCUSSION

The quartz sample was ground to pass 100 mesh sieve, i.e. maximum particle size of the material was 150 μm, as the early transformation of quartz to cristobalite is catalyzed when the material is ground sufficiently fine and heated to a high temperature. The transformation commences in pure material at defects on the surface produced by grinding, or within the crystal, then propagates by diffusion of a reaction layer throughout each particle [16]. Chemical analysis of the quartz sample (Table 1) reveals the

TABLE 2

Porosity of the samples under investigation

Temp. (°C) of treatment of quartz sample	Bulk density (g cm^{-3})	Specific gravity (g cm^{-3})	True porosity (%)
1350	1.75	2.48	29.43
1400	1.73	2.40	27.91
1450	1.69	2.39	29.28
1490	1.62	2.34	30.76

presence of 0.5% impurities in the form of Fe_2O_3, Al_2O_3 and Na_2O. These oxides act as mineralizers for cristobalite formation and are capable of forming a liquid phase at the firing temperature. Transformation proceeds rapidly to completion in the presence of a liquid phase [16].

The results of porosity of quartz specimens (Table 2) show that the present range of firing did not affect the porosity very much. Usually the porosity of the moulded specimens has little effect on the thermal expansion coefficient of the material [14]. The type and content of phases developed by firing together with the rate of heating and temperature of maturing are more effective.

The results of thermal expansion are represented in Fig. 4. The curves show that the temperature of commencement of expansion due to cristobalite occurs at 230—240°C, while the completion of expansion takes place at 250—265°C, with a temperature interval between the start and finish equal to 20—25°C. The extent of expansion at this temperature interval is best seen from the results of the differential thermal expansion curves (Fig. 5). The content of cristobalite determined by DTMA (Fig. 6, curve b) is in good agreement with the results of DSC (Fig. 6, curve a). The specific gravity results (Fig. 6, curve c) are similar to those of TMA (Fig. 6, curve d), but differ considerably from those of DSC and DTMA. The measurement of thermal expansion was carried out up to 300°C, as extending the test temperature above 400°C may change the state of order of the cristobalite present in the samples [13,17]. The chosen heating rate was 5°C min^{-1}. The temperature of commencement of expansion is greatly affected by the heating rate. Flörke [13] has shown that at a heating rate of 1°C min^{-1}, the temperature remained at 260°C, but was shifted to 270°C when the rate was changed to 5°C min^{-1}.

The shape of the thermal expansion curve of cristobalite is greatly affected by the degree of disorder of the crystal lattice. Well-ordered cristobalite has a critical temperature at which the inversion from the low to the high form takes place. Usually this inversion occurs at 270°C , it is sharp and the temperature interval does not exceed 5°C. This temperature is shifted to a lower temperature when either the content or the degree of order of cristobalite is low. The height of the thermal expansion curve (Fig. 3) is not indicative of the content of cristobalite present, but does give some indication of its degree of order, e.g. cristobalite formed in the quartz sample fired at 1350°C is disordered while that found in the sample fired at 1490°C is well ordered. Flörke has also shown that the amount of cristobalite affects the temperature of commencement of inversion. In this case it is shifted to a lower temperature when the material is not totally formed of cristobalite.

The mean expansion coefficient of a material is greatly affected by the type and content of phases present. The presence of tridymite and glass changes the mean expansion coefficient of the material, as tridymite in this temperature interval (20—300°C) has a high expansion coefficient of 35×10^{-6} °C^{-1}, while that of glass is 0.4×10^{-6} °C^{-1}. Therefore the calculation of the amount of cristobalite in the material based on the determination of the expansion coefficient from the cumulative curve will show higher cristobalite content when tridymite is present and low cristobalite content when tridy-

TABLE 3

Content of cristobalite as determined by the different methods

Temp. of treatment of quartz sample (°C)	Method					
	Specific gravity		DSC		DTMA	TMA
	Quartz (%)	Cristobalite (%)	Quartz (%)	Cristobalite (%)	Cristobalite (%)	Cristobalite (%)
1350	53.93	46.07	59	37	36.5	52.03
1400	26.96	73.04	33.5	61.5	58.08	61.04
1450	26.66	73.34	26	69	67.39	64.45
1490	9.09	90.91	3.5	95	95.3	82.02

mite is absent and glass is present. In both cases the results will be misleading. This is visualized by the results of quartz samples fired at 1350°C and 1490°C. Thus the thermal expansion curve of the sample fired at 1350°C shows a step at 165°C, indicating the presence of tridymite, i.e. the amount of cristobalite calculated from this curve represents both tridymite and cristobalite. Therefore the value calculated from TMA was higher than the values determined by DSC and DTMA. The quartz sample fired at 1490°C, on the other hand, shows a lower value. Usually glass is formed at this particular temperature, as indicated from the results of DSC for the respective amounts of cristobalite and quartz (Table 3) and the absence of the tridymite deflection in the expansion curve (Fig. 4). Glass, with an expansion coefficient much lower than cristobalite, will cause the lowering of the mean expansion coefficient of the sample, so the content of cristobalite calculated from the expansion coefficient will be low.

The specific gravity results are similarly affected by the presence of tridymite and glass, with specific gravity values of 2.26 g cm^{-3} and 2.2 g cm^{-3}, respectively. The considerably low specific gravity of tridymite compared with quartz, 2.65 g cm^{-3}, greatly affected the value of cristobalite calculated by this method for the sample fired at 1350°C. It gave a value in between those obtained by DSC and DTMA and TMA. The content of glass, on the other hand, affected the value of cristobalite calculated for the sample fired at 1490°C, and gave a value higher than TMA but lower than DSC and DTMA.

The values obtained by DTMA in the temperature interval of 50°C between 225 and 275°C compare well with the results of DSC (Fig. 6). This temperature interval covers the range of existence of cristobalite whether ordered or disordered. Therefore the results of the calculation of the amount of cristobalite from DTMA curves are more reliable than TMA. This method could be taken as a very precise measure for the quantitative determination of cristobalite. The degree of order of cristobalite can be deduced from the temperature of the DTMA peak.

ACKNOWLEDGEMENTS

The authors of this work wish to express their thanks to Dr. M. Abdel-Maksoud and Dr. N. Ghoneim for kindly carrying out the thermal runs.

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