*Thermochimica Acta*, 135 (1988) 335–340
Elsevier Science Publishers B.V., Amsterdam



# DETERMINATION OF QUARTZ IN CERAMICS BY DILATOMETRY

K.-H. SCHÜLLER [1], R. SLADEK [2] and P. HUSE [1]

1 Georg-Simon-Ohm-Fachhochschule Nürnberg, Fachbereich Werkstofftechnik, Nuremberg (Federal Republic of Germany)
2 Riedhammer GmbH & Co KG, Nuremberg (Federal Republic of Germany)

## ABSTRACT

Dilatometric curves can be used for a semi-quantitative determination of quartz in ceramic bodies, especially by an evaluation of the volume increase during the transition of low quartz to high quartz. The present study concerns parameters which may affect calibration curves. It proved that the magnitude of the anomaly in thermal expansion depends on several factors like grain size and disorder of the quartz. It is therefore discussed whether other sections of the thermal expansion curve give more reliable data for a determination of quartz.

## INTRODUCTION

Quartz is an important constituent in ceramic bodies which controls not only the forming and firing conditions of the crude body but also the properties of the final product. It is of considerable interest to know the amount of quartz in the fired body. Dilatometry can be applied as a rapid method for the determination of quartz /1/. The use of derivative dilatometric curves allows a more precise interpretation /2/; it has been demonstrated that then the disturbing effect of fine grain size of the quartz can be overcome.

The present investigation concerns certain parameters which affect the dilatometric determination of quartz in ceramics.

## BODY PREPARATION AND SELECTION OF PROPER EXPERIMENTAL CONDITIONS

The determination of quartz in ceramic materials by dilatometry is impaired by two effects:

1. Under certain conditions the pores have to be considered as a separate phase in the heterogeneous body /3/. Porosity can influence the volume change in the total system in the transition range of the quartz; the increase in the volume of quartz can be partly compensated by a decrease of the pore volume, particularly

*Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988*
0040-6031/88/$03.50 

in materials with an open porosity. So the effect registered in the dilatometer curve does not necessarily reflect the amount of quartz.

2. The anomaly in the dilatometer curve is spread over a wider temperature range when very fine quartz is introduced into the body /2/.

In the present study series of special bodies were prepared to provide data for calibration curves. The crude bodies contained 18 wt-% of potassium feldspar; this seemed to be a reasonable compromise between adequate vitrification and little dissolution of quartz. Quartz was introduced in amounts between 2 and 35 wt-%. The remainder of the body was china clay. The quartz was introduced in 4 types which differed in fineness (Table 1). The bodies were fired at 1100 °C, 1200 °C, 1300 °C, and 1400 °C respectively. However, only the samples fired at 1100 °C and 1200 °C could be considered further because of the strong transformation of quartz to cristobalite when applying higher firing temperatures. Even at a firing temperature of 1200 °C cristobalite started to appear. X-ray diffraction analyses proved however that the decrease in quartz was negligible. It proved moreover that up to 1200 °C almost no quartz was dissolved. It had to be accepted however that at these low firing temperatures the bodies did not vitrify completely; water absorption ranged between 1 and 3 %.

TABLE 1

Quartz types used in this study

| Type | Mean grain size |
|---|---|
| W 12 | 10.6 µm |
| SF 300 | 8.5 µm |
| Sillitin N 85 | 3.3 µm |
| SF 800 | 2.4 µm |

The specimens were prepared by isostatic pressing to avoid particle orientation. Test bars of 50 mm length were cut from the fired bodies. Dilatometric curves and derivative dilatometric curves were recorded up to 1000 °C with a heating rate of 5 K/min.

## DISCUSSION OF THE VARIOUS DILATOMETER CURVES

### Sensitivity of dilatometry

No anomaly at 573 °C could be detected when only 2 wt-% of quartz was introduced into the body. Anomalies due to quartz appeared only when its amount was 5 wt-% or more.

### Appearance of the curves in the transition range of quartz

Thermal expansion during the phase transformation of quartz can best be registered in derivative dilatometric curves. The deviation from the steady expansion appears in a broad peak which is the more broadened the finer and more disordered the quartz (Figure 1).

In some of the curves the transition from the anomaly to the steady expansion at higher temperatures occured in a sharp bend. This appeared to be more pronounced at low firing temperatures of the specimens.

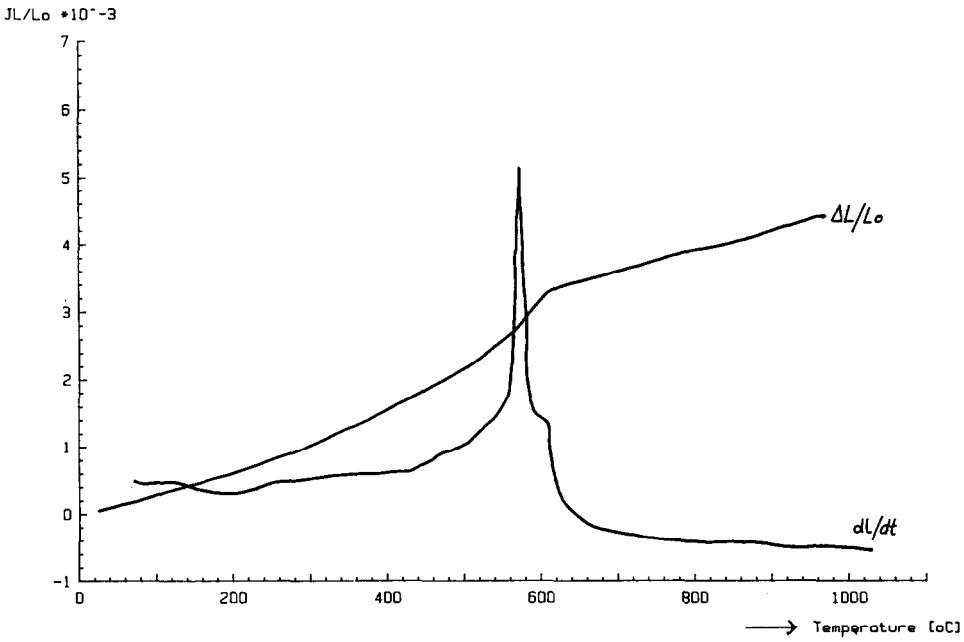


Fig. 1. Typical dilatometer curve and derivative dilatometric curve of the samples under consideration. Specimen with 20 wt-% quartz SF 300, fired at 1100 °C.

It proved that in samples fired at 1100 °C the anomaly started at lower temperatures down to about 500 °C when quartz was increased but it ended always around 620 °C. In samples fired at 1200 °C the anomaly started at 560 °C but the end of the peak was shifted to higher temperatures up to 700 °C with increasing quartz contents. No further experiments have been made hitherto to find the reason for this strange behaviour. Perhaps it has to be related to the remaining porosity.

It should be stressed that all the effects mentioned before were found to be reproducible.

In samples higher in quartz the broad peak was superimposed by a sharp peak at the transition temperature of low quartz to high quartz (Figure 1).

It was demonstrated formerly /2,4/ that quartz can be determined quite reasonably by dilatometry when the limits of the peak in the derivative curve are located by a special evaluation. The strange appearance in part of the curves obtained here impaired this special evaluation; it proved then extremely difficult to state the beginning and the end of the quartz transformation.

Comparison of the various types of quartz

The fine varieties of quartz - Sillitin N 85 and SF 800 - exhibited a more blurred anomaly and a less pronounced sharp peak at 573 °C. This was especially true for

Sillitin which is known to be a heavily disordered type of quartz. Dilatometry is therefore less suitable for a phase analysis of bodies containing heavily disordered quartz.

The various courses of volume change during the phase transformation of the quartz at 573 °C are most clearly reflected in the derivative dilatometric curves when materials of a given quartz content are compared. However, this causes some reservations against the evaluation of this part of the curve as a general method for a quantitative determination of quartz. This is valid at least when porous bodies or materials with disordered quartz have to be covered too.

Use of other parts of the dilatometer curves for evaluation

Forkel /4/ pointed out that the amount of quartz is reflected also in the steepness of the thermal expansion curve below the phase transformation. So we examined whether this part of the dilatometer curve can be used for a determination of quartz. Moreover we considered also the section above 700 °C; Kohler and Schneider /5/ found a volume decrease of quartz in this range so that the thermal expansion of the total system should be the lower the more quartz is present. To check this as a possibility of analytical evaluation we calculated the mean thermal expansion coefficients $\alpha_{250,500}$ and $\alpha_{725,975}$. The results are plotted in Figure 2.

It proved that the $\alpha_{250,500}$ values depend distinctly on the quartz grain size and on the firing temperature (Figure 2 a). So special calibration curves have to be applied for bodies with different raw materials and thermal history. The $\alpha_{725,975}$ values showed much less scatter (Figure 2 b) so that they offer the most promising approach for a semi-quantitative determination of quartz in ceramic bodies by dilatometry. No tests were made hitherto to find out to what extent a determination of this kind is impaired by the dissolution of quartz which would mean a replacement of the crystalline phase by an amorphous one of similar expansion behaviour. A combined consideration of $\alpha_{250,500}$ and $\alpha_{725,975}$ could help to overcome this problem.

## CONCLUSIONS

Dilatometer curves of ceramic bodies are affected by the type and fineness of the quartz introduced into the body and by the thermal pretreatment of the specimen. Obviously one has to expect also effects of the total body composition and of the intended porosity.

The run of the volume change during the structural change of quartz depends considerably on its grain size and disorder and moreover on composition and porosity of the total system. The phase transformation of quartz occurs in a certain temperature range around 573 °C /5/. The transition range is the more extended the finer and more disordered the quartz. This impairs the applicability of this volume change

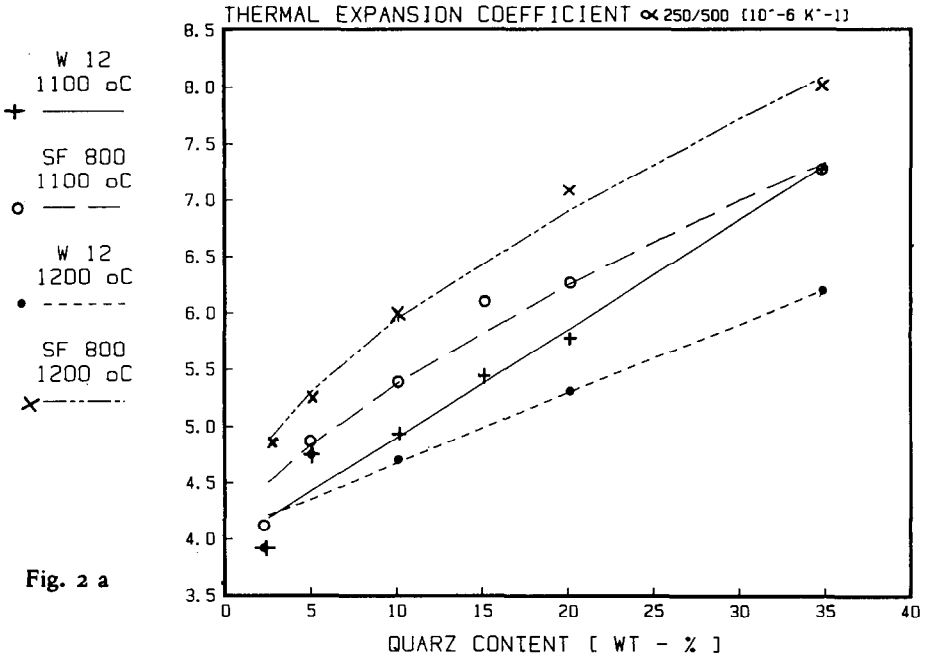


Fig. 2 a

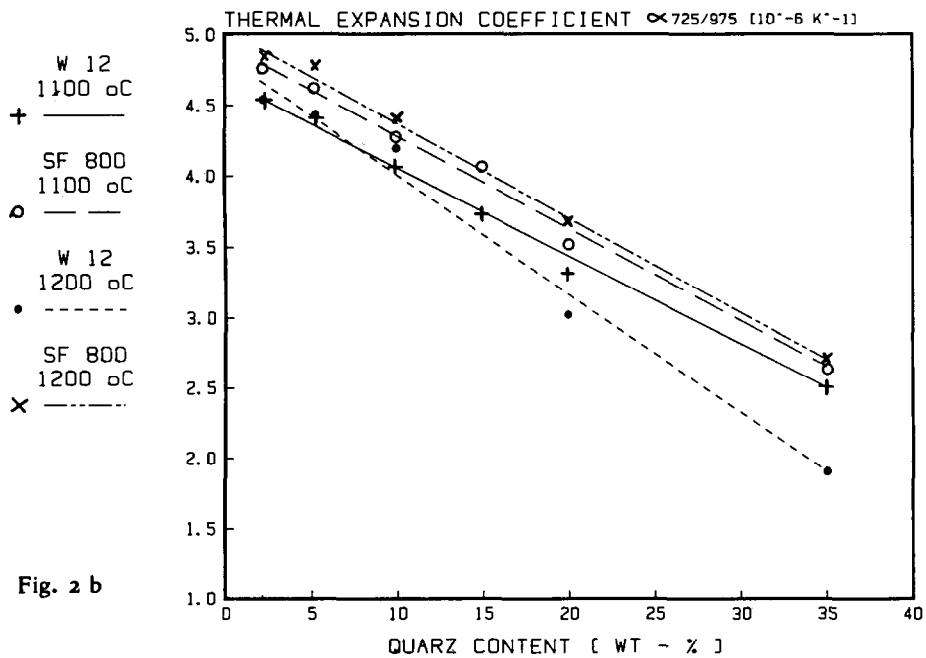


Fig. 2 b

Fig. 2. Thermal expansion coefficients of the specimens with quartz W 12 and quartz SF 800 respectively as a function of quartz content.

Fig. 2 a. $\alpha_{250,500}$ Fig. 2 b. $\alpha_{725,975}$

for a quantitative determination of quartz and necessitates separate calibration curves for various types of ceramic materials.

A more generally applicable dilatometric determination of quartz in ceramic materials can be provided through the thermal expansion coefficients below 500 °C and above 700 °C which are the more shifted the more quartz is present.

It should be pointed out that inspite of all the problems discussed here dilatometry has proved as a quick method for a semi-quantitative determination of quartz with a reasonable accuracy as long as similar types of ceramic materials are covered by the calibration curves in use /6,7/.

## REFERENCES


/1/ W. Lehnhäuser, Sprechsaal Keramik, Glas, Email, Silikate, **99** (1966), p. 78 - 84, 107 - 112, 140 - 150, 172 - 176

/2/ K. Schüller and P. Lindl, Trans. IXth Intern. Ceram. Congr., Brussels 1964, p. 139 - 148

/3/ K.-H. Schüller, Handbuch der Keramik, chapter III O 1, Verlag Schmid, Freiburg i. Brg., 1972

/4/ W. Forkel, Heidelberger Beitr. Miner. Petrogr., 5 (1955), p. 1 - 22

/5/ K. Kohler and G. Schneider, RADEX-Rdsch., 1965, Issue 4, p. 584 - 594

/6/ R. Sladek, Keram. Z., **39** (1987), p. 769 - 772

/7/ R. Sladek, Interceram, **34** (1985), p. 11 - 14