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Elasticity of $\alpha-\beta$ quartz measured by TMA [1]

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Abstract

The $\alpha-\beta$ transformation at 573°C is used for the identification by DSC of quartz in mineral mixtures. This transformation can also be observed in TMA curves due to the difference in thermal expansion of the two quartz modifications. In this study a special accessory for bending measurements has been used to determine the Young's modulus by bending within the transformation region. Oriented cuts of natural and synthetic quartz crystals parallel and perpendicular to the *c*-axis were measured. The results proved that this modulus is larger in the low-temperature than in the high-temperature form. During the $\alpha-\beta$ transformation, a significant change in the elastic behavior takes place: the quartz crystal becomes "softer" (H.G. Wiedemann, R. Riessen and A. Boller, in A.T. Riga and M. Naeg (Eds.) Material Characterization by Thermochemical Analysis, American Society for Testing and Materials, Philadelphia, 1991, p. 84). A pronounced difference in the modulus was found for quartz samples cut 45° at an angle to the hexagonal *c*-axis, the optimum direction for oscillator quartz.

INTRODUCTION

In thermal analysis, DSC measurements of the heat of the $\alpha-\beta$ phase transformation at 573°C [2] are used for the identification of quartz, e.g. $\alpha-\beta$ quartz in bauxite. This transformation is due solely to a change of the bond angle in the SiO_4 tetrahedra [3] that alters the symmetry from trigonal trapezoidal to hexagonal. The corresponding space groups are $D3^4$-P3 21 and D^36-P3 21, respectively [4].

The transformation can also be observed by TMA measurements. Figure 1 shows an expansion measurement from 510 up to 590°C. The expansion stops immediately after the change in the bond angle. These results explain in an unorthodox way why quartz glass is temperature "shock-proof"; its non-rupture, i.e. its resistance to breakage, means that there is only a very

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small change of expansion coefficient over a broad temperature range. Reproducible curves of synthetically grown quartz can be obtained only after the samples have been heated and cooled two or three times.

During the solid–solid phase change, rearrangement of the crystal lattice widens the bond angles. Hence the Young's modulus by bending should also be affected.

EXPERIMENTAL

A Mettler TA4000 system with a TMA40 measuring cell was used. The static or dynamic load is automatically applied by the TMA probe. Dynamic load TMA (DLTMA) is herein defined as the technique in which the deformation or flexure of a substance under changing load is measured as a function of the temperature while the substance is subjected to a controlled temperature program (dynamic or isothermal). The alternating load has a cycle time of 12 s. Hence, this technique provides simultaneous information on the influence of temperature and force. Figure 2 represents the cross section of the device for flexure measurements. Figure 3 shows the device with the cut crystal in measuring position. An automatically alternating load between 0.1 and 0.5 N was applied.

Figure 4 explains how the sampling of the quartz specimen was done with respect to the structure of a quartz crystal. One cut was taken parallel, another perpendicular to the c-axis, and a third at an angle of 45° to the hexagonal c-axis. The dimensions of the samples were: length, 18 mm (l); thickness, 0.8 mm (a); and width, 3 mm (s).

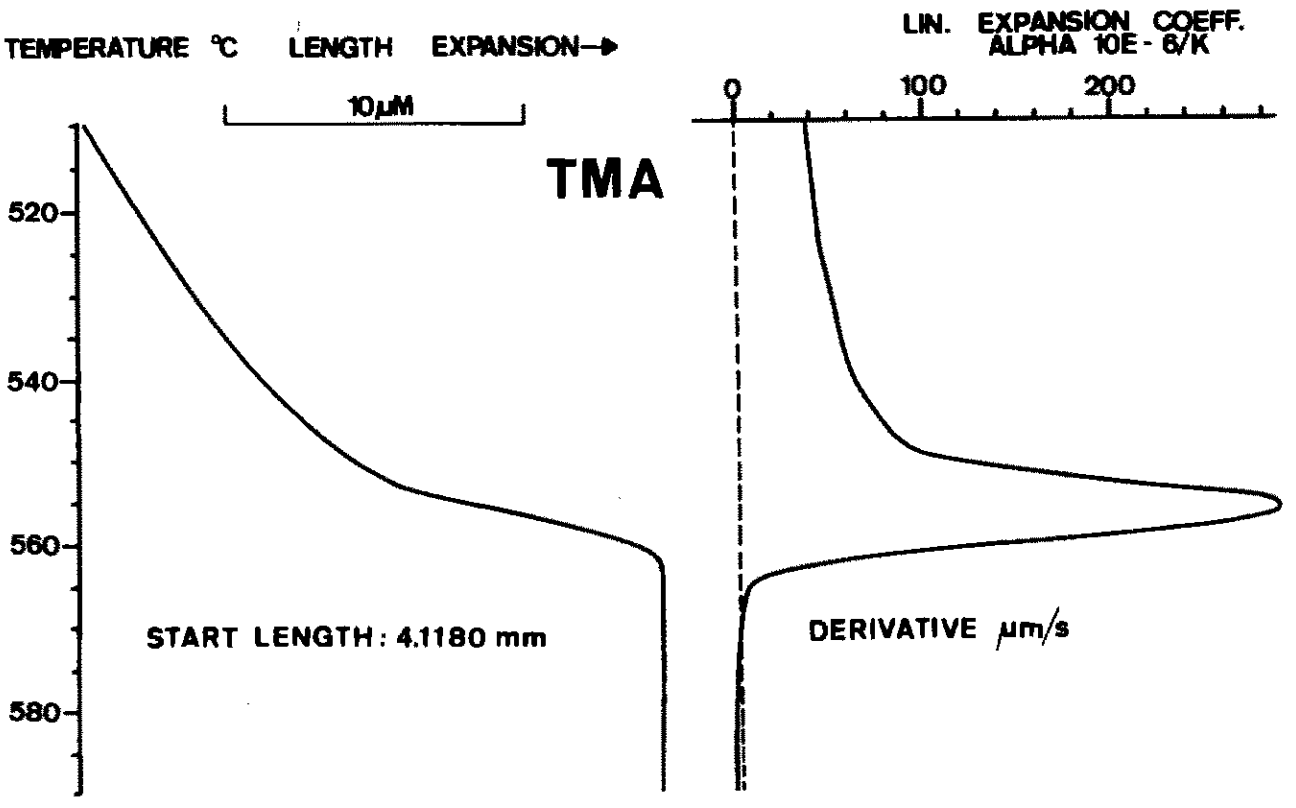

Fig. 1. TMA-curve of the $\alpha-\beta$ transformation of quartz and the corresponding temperature dependence of the linear expansion coefficient. Measured sample, c-cut (0001).

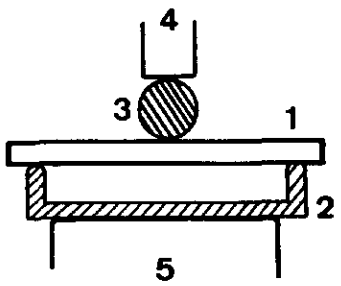

Fig. 2. Cross section of the bending accessory for the TMA40 to be put on sample support (5). The thin bar sample (1) is supported by the U-shaped device (2) and stressed by a central probe (4). A cylindrical bar (3) between probe and sample is placed to apply an equally distributed force. The support and cylindrical bar are made of Ni alloy.

RESULTS

The small forces applied in the TMA cell do not allow the measurement of large values of Young's moduli by compression. In this case, the modulus of bending may be measured. The formula for calculation of the Young modulus E (by bending) for rectangular bars (Fig. 2) is

$$E = (Fl^3)/(4sa^3b) \tag{1}$$

where E (MPa) is Young's modulus by bending, F (N) is the increase in force giving a flexure(s), l (mm) is the distance between supports (effective length of sample) = 17.0 mm, s (mm) is the flexure measured (the blank has to be subtracted), a (mm) is the sample thickness (vertical), and b (mm) is the sample width (horizontal).

This modulus of a single-crystal quartz was determined by using the accessory for bending measurements (Fig. 2 and 3). In the 568–576°C region where the α–β transformation takes place, the bending measurements show that the flexure is smaller in the low-temperature phase (see Fig. 5). Using the measurements in Fig. 5, the modulus was calculated (eqn.

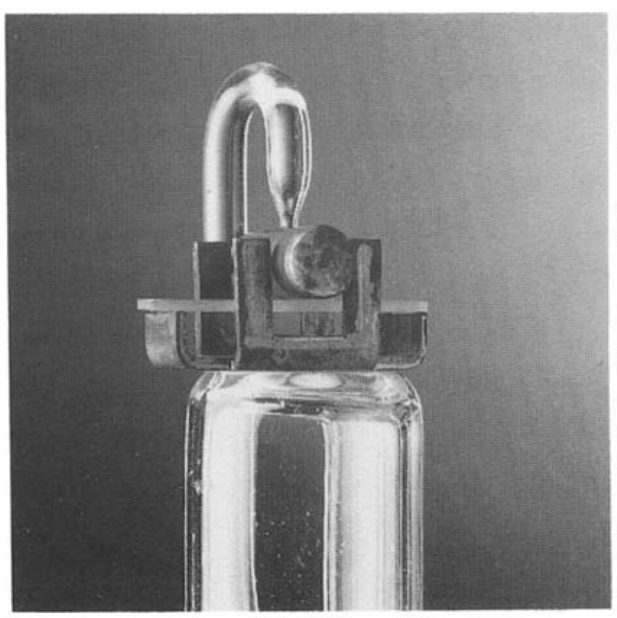

Fig. 3. Photograph of TMA bending accessory with quartz crystal slice.

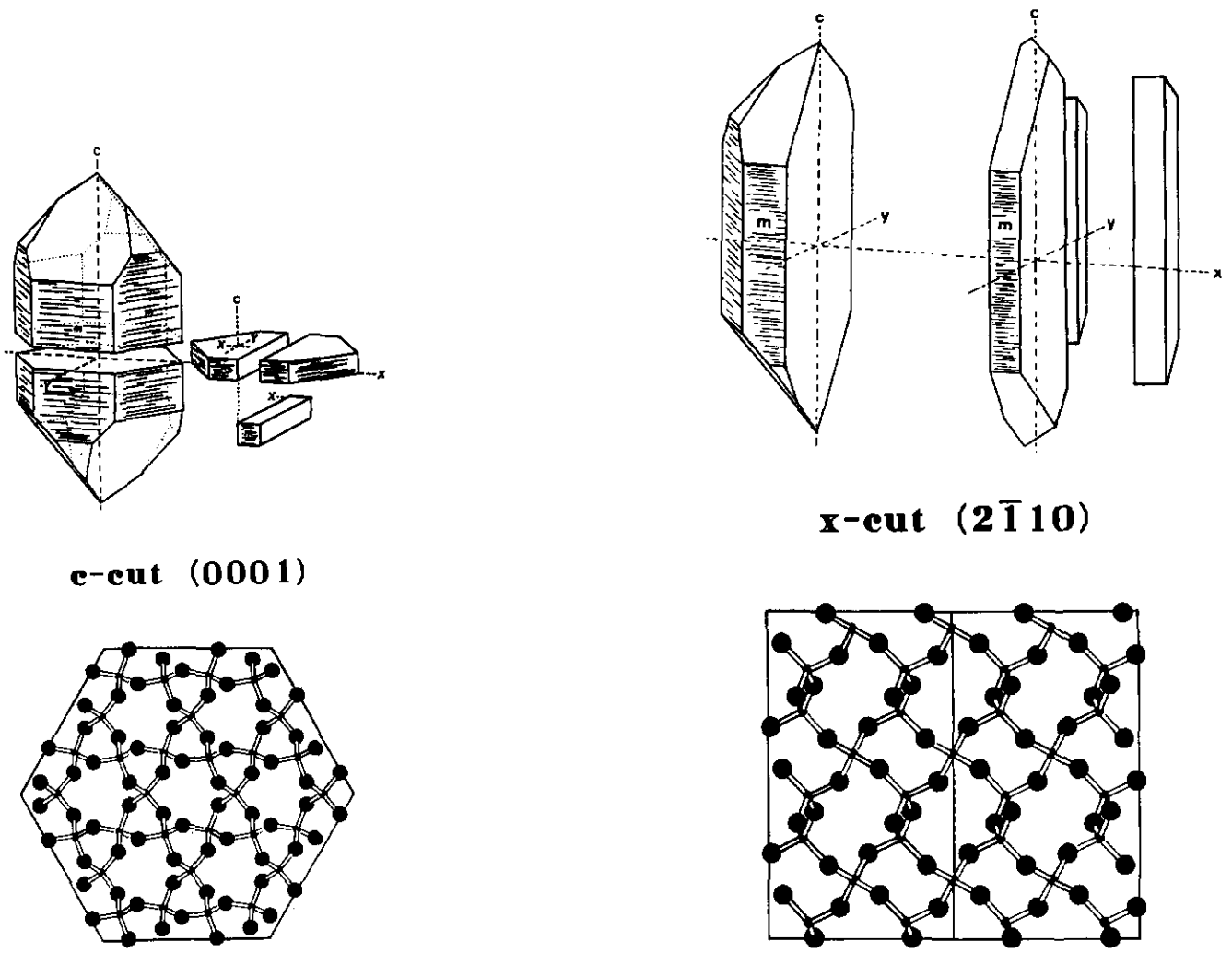

Fig. 4. Sample preparation [5] and structure of a synthetically grown crystal, crystallographic orientations of the c-cut (0001) and x-cut (2$\bar{1}$10).

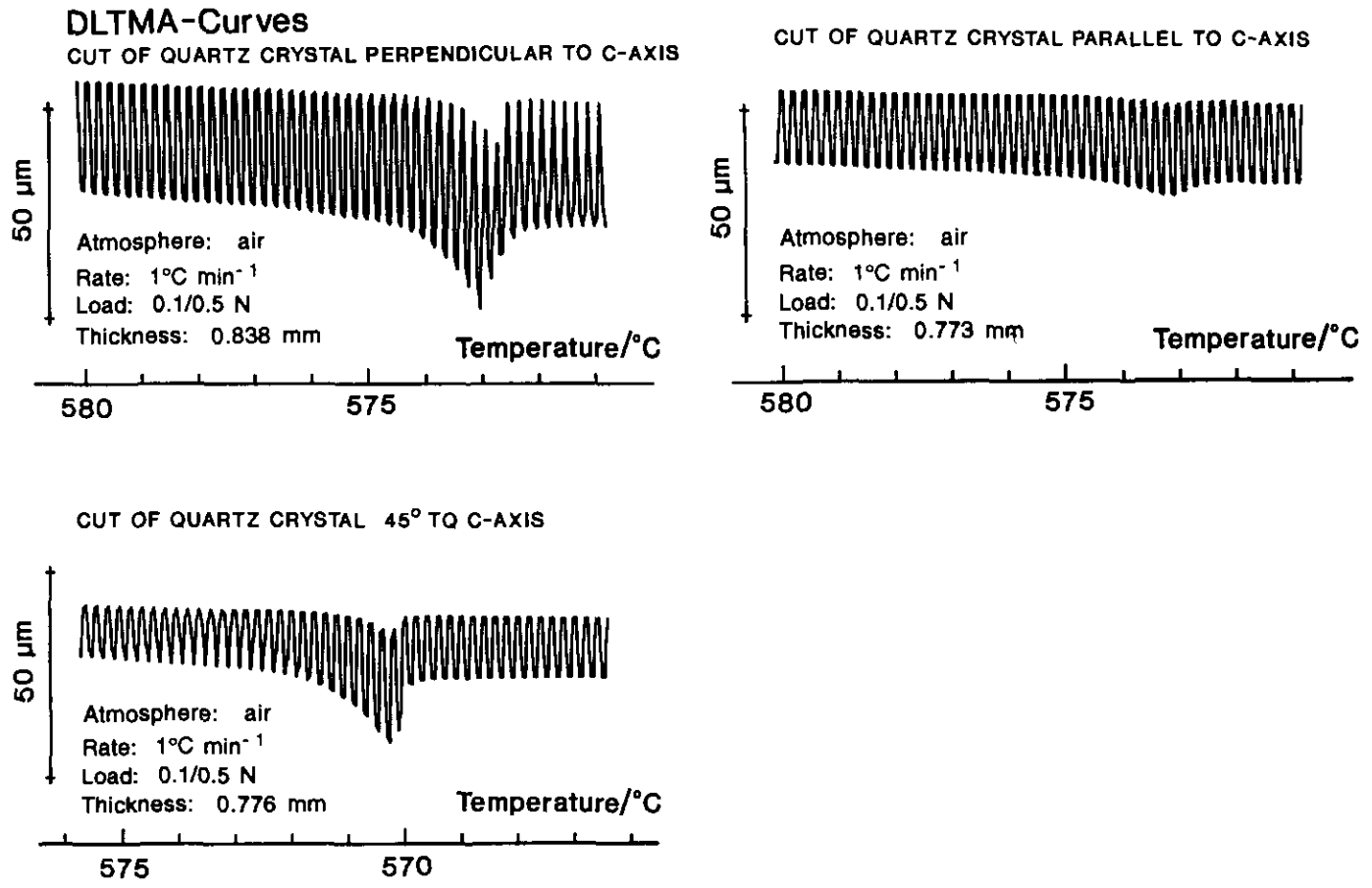

Fig. 5. Original tracings of DLTMA cooling curves for quartz cut in different orientations (flexure measurement during the transformation).

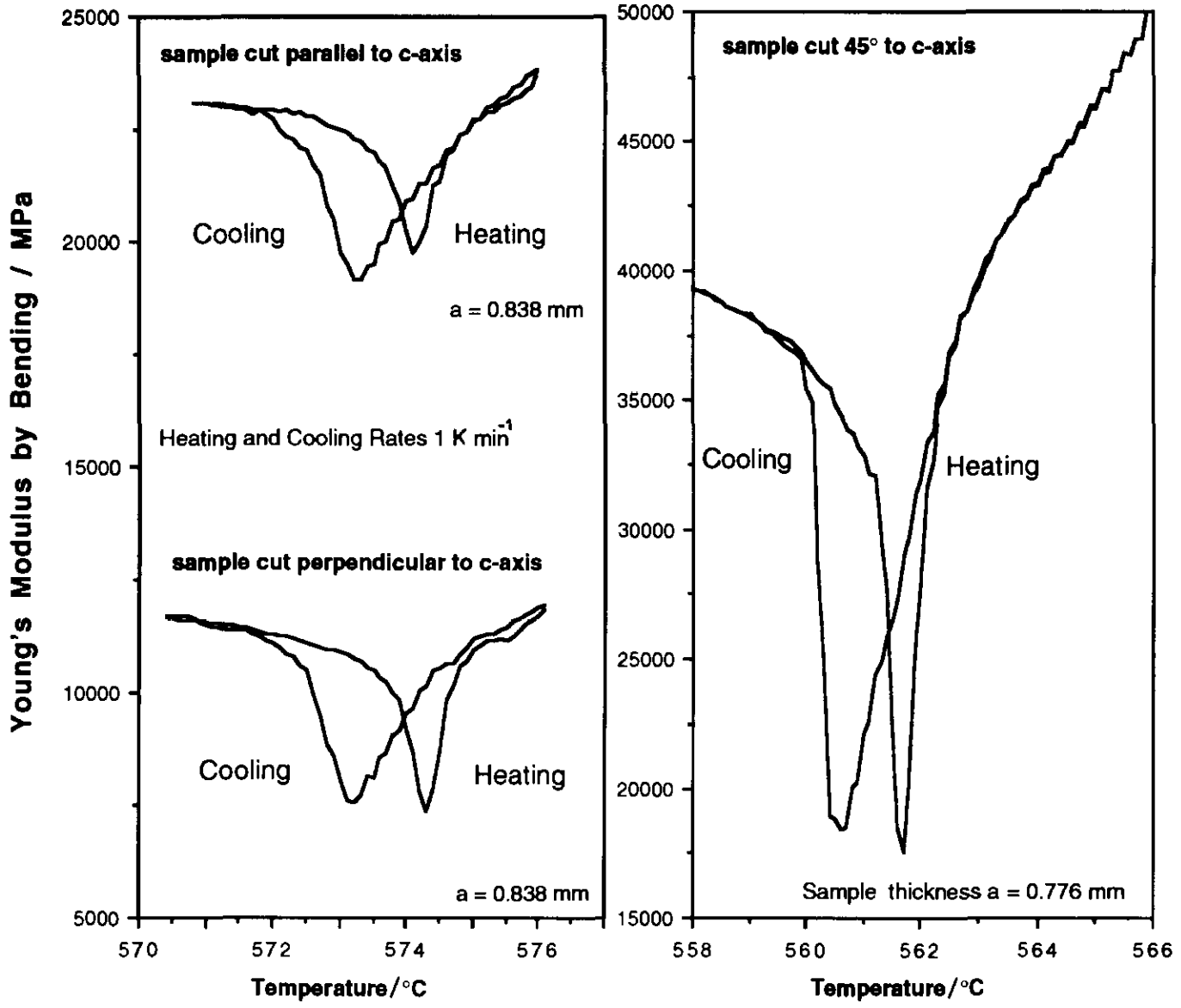

Fig. 6. Young's modulus by bending of quartz during transformation (cooling and heating) calculated from the measurements in Fig. 5. The accuracy of the temperature of the $\alpha-\beta$ transformation depends on heating rates, crystal cut, nature and sample size.

(1)) and the results for heating and cooling of quartz single crystals are presented in Fig. 6. The modulus changes during the transformation. The crystal becomes "softer", i.e. the modulus shows the weakening of the interatomic links. Furthermore, a pronounced difference in the flexure behavior and the magnitude of the modulus itself was observed in samples cut parallel, perpendicular and at an angle of 45° to the hexagonal c-axis (see Fig. 6).

Electron irradiation effects in quartz confirm the assumption of a "softening" during the $\alpha-\beta$ transformation [6]. Crystallization after irradiation is relatively slow at temperatures around the solid–solid transformation compared with the rate at low temperatures. At the transformation temperature, however, it is approximately as fast as the low-temperature rate.

CONCLUSION

TMA flexure measurements of the polymorphic transformation of quartz coincide with those provided by thermal expansion (Fig. 1), penetrometry

[7] and DSC studies [2]. Young's modulus by bending shows lower values during the α–β transformation. Hence, it is assumed that the reactivity of α–β quartz is increased in the transformation range.

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