

# A NEWLY DEVELOPED HIGH-TEMPERATURE CHAMBER FOR IN SITU X-RAY DIFFRACTION: SETUP AND CALIBRATION PROCEDURES

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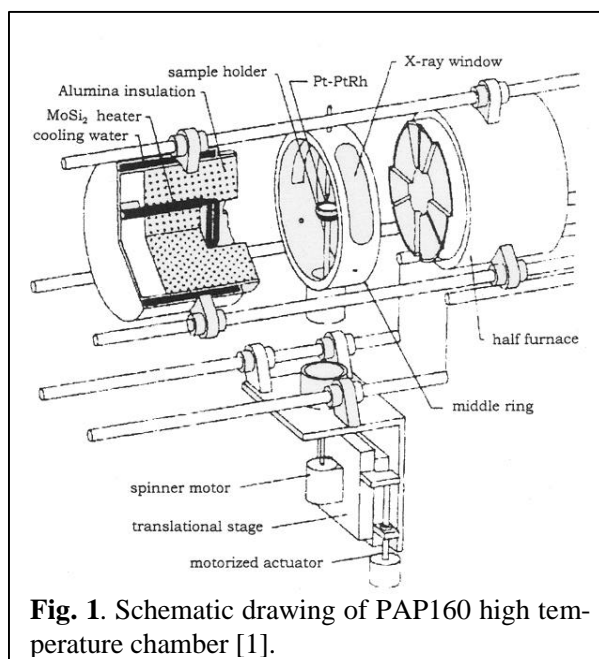
A new chamber for high temperature powder diffraction (PAP1600) has been developed based on the principles of the PMP1600 chamber. The implementation and the calibration procedures are described, together with some of the possible applications in materials science.

## 1. Introduction

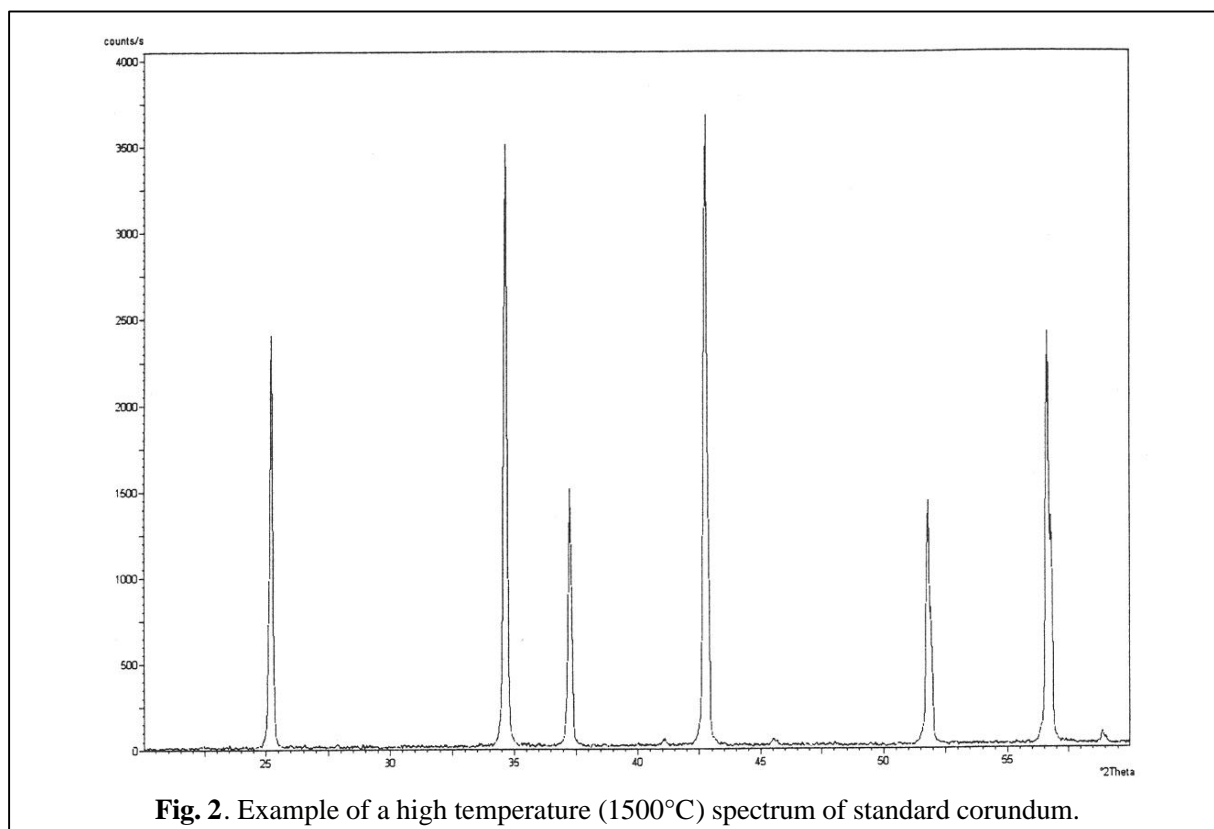
X-ray diffraction at non ambient conditions can be used for a variety of applications, including the study of dynamic processes that need to be investigated in situ. Examples of such processes are the reactions involving the solid state, phase transitions, crystallite growth, thermal expansion, etc. X-ray diffraction can be used as a very informative complement to other, more traditional, thermal analytical techniques (thermogravimetry, differential scanning calorimetry, etc.), thus effectively providing phase identification, texture analysis, and crystallite size measurement. The quality of the high temperature diffraction data measured on laboratory diffractometers is crucial to get satisfactory results. Three features are to be taken into account for the design of a new high temperature chamber for high resolution X-ray diffraction: the temperature homogeneity and stability of the sample, the correct measurement of the sample temperature, and the possibility to maintain the diffraction geometry optimized at all temperatures. In the case of the conventional Bragg-Brentano (or parafocusing) geometry, the latter condition translates directly into the possibility of maintaining the surface of the flat powder specimen tangent to the parafocusing circle upon temperature changes.

The PAP1600 chamber [1] is a general purpose resistance furnace, with a maximum working temperature of 1600°C. It is designed to be mounted on  $\theta$ - $\theta$  diffractometers to have the major advantage of a steady sample, with no chance for the sample to fallout or deform during the meas-

urement. This also guarantees a better temperature uniformity around the sample. The temperature stability is assured by two large alumina fibre blocks heated by two MoSi<sub>2</sub> resistances. The sample can be continuously rotated to achieve a better temperature homogeneity. The sample holder is composed by a dense alumina disk: to avoid thermal loss due to heat diffusion, the sample holder is supported by an alumina pole and the contact between the sample holder and the cold pole is kept to a minimum (virtually punctual). A schematic drawing of the chamber is shown in Fig. 1. The pole height is motor-controlled and it constantly keeps the sample surface at the goniometer



**Fig. 1.** Schematic drawing of PAP160 high temperature chamber [1].



**Fig. 2.** Example of a high temperature (1500°C) spectrum of standard corundum.

axis level, compensating for all thermal expansion effects of both the spinner and the sample. The fact that the parafocusing conditions are satisfied allows data of superb quality to be collected even at very high temperatures (as an example, see the diffraction spectrum of standard corundum at 1500°C, Fig. 2).

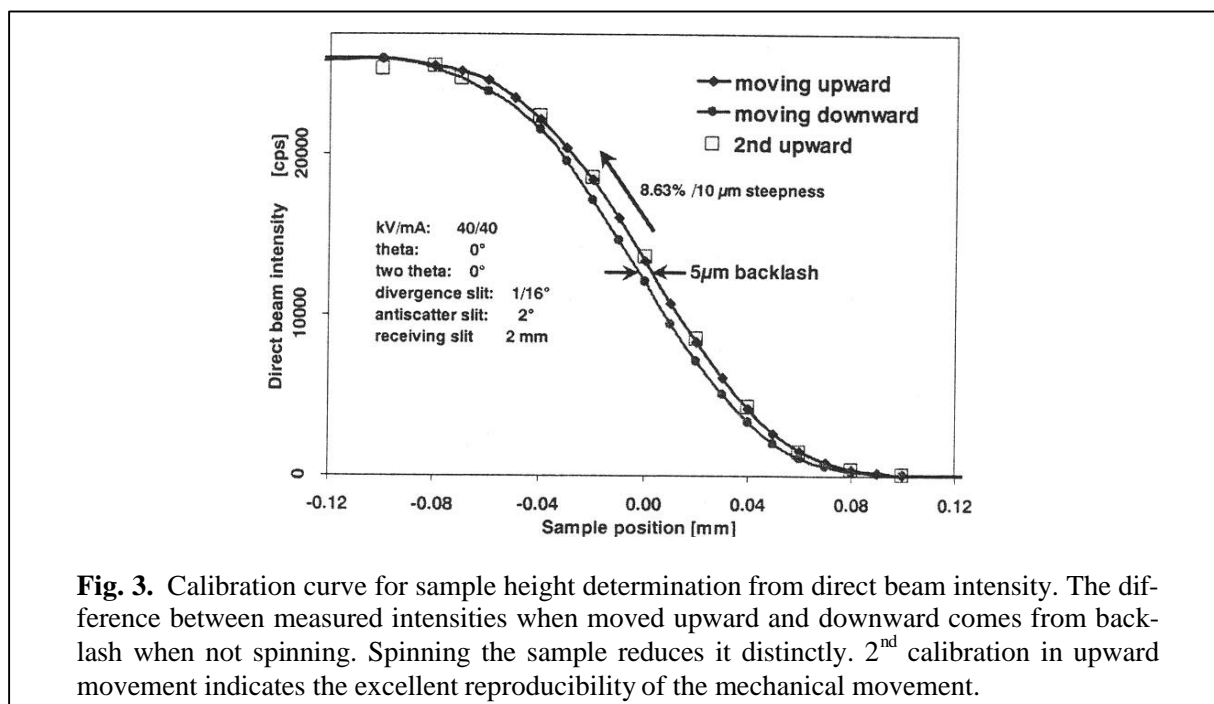
The temperature is measured by a type S thermocouple located as close as possible to the surface of the sample, where it does not interfere with X-rays. As the thermocouple can not be in direct contact with the sample, as in most heating systems, it is compulsory to carry out a temperature calibration, commonly performed using phase transitions with known  $T_c$ , which provides the temperature correction curve.

The chamber can also be used under vacuum or under a gas flux, so that the middle ring is equipped with the necessary feedthrough, gas inlet and outlet, and X-ray window. The use of bulk samples (possibly pressed pellets) ensures a better performance in terms of stable sample position and avoids  $\theta$  dependent intensity variations caused by undefined sample thickness in case of thin powder layers. This frequently happens at

high temperature because of the sintering of the powder particles.

## 2. Calibration of Sample Position

The sample with the sample holder is supported and rotated by a vertical ceramic shaft of 82 mm in length, which is fixed at its bottom end outside of the furnace. When the chamber is heated the shaft expands thermally and displaces the sample considerably from the goniometer axis, which is the optimal position. In order to avoid the sample displacement error, the pole thermal expansion is compensated by moving the shaft downwards when heating. This vertical translation is realised by a motorised precision stage connected to the shaft. This stage translates the shaft downwards as it expands. In this way the position of the sample remains unchanged during heating. For automatic adjustments the translation needs to be experimentally calibrated versus the thermal expansion of the shaft in the whole temperature range. A mere calculation is hardly possible because the temperature distribution along the shaft is unknown: one end of the shaft is heated in the furnace while the other is outside the chamber.



**Fig. 3.** Calibration curve for sample height determination from direct beam intensity. The difference between measured intensities when moved upward and downward comes from backlash when not spinning. Spinning the sample reduces it distinctly. 2<sup>nd</sup> calibration in upward movement indicates the excellent reproducibility of the mechanical movement.

The calibration measurement is carried out on the diffractometer using the sample attenuation of the incident X-ray beam. In this 'single edge' method the ceramic sample holder disk (25 mm in diameter and 6 mm in thickness) itself is generally used instead of a real edge.

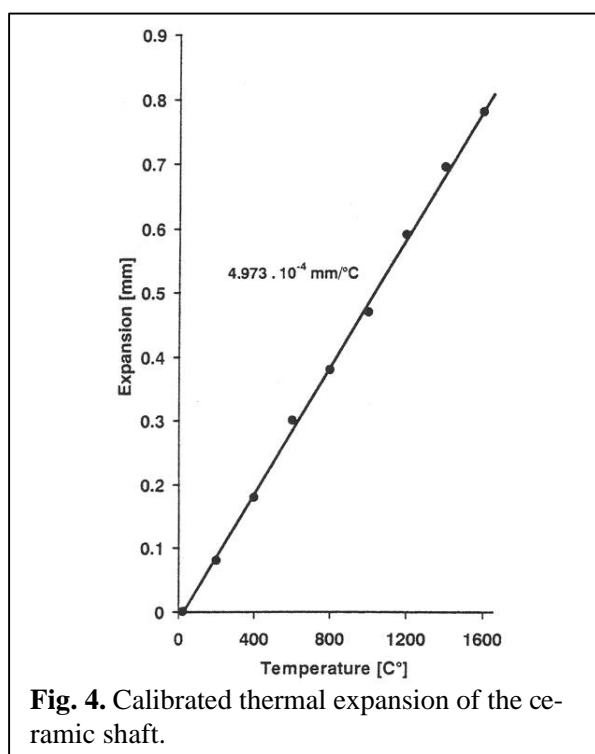
The calibration procedure starts by setting the goniometer  $\theta = 2\theta = 0^\circ$  position using a 200 $\mu\text{m}$  thick attenuating Cu filter in order to protect the detector from the direct beam. Using a narrow divergence slit of  $1/16^\circ$  and a goniometer radius of 23 cm the beam width at the sample position is about 0.23 mm. When the top of the sample holder is within this range, then a certain part of the beam is screened by the sample holder and therefore the beam intensity behind the sample holder-measured with wide receiving and antiscatter slits-is highly sensitive to the sample height. This measured intensity, as the function of the sample height, is plotted on Fig. 3. The height position relative to half of the original intensity is regarded as the reference height. This position found with this procedure is quite satisfactory for most measurements, however if very precise angular positions are required, for example to measure thermal expansion coefficients, then the sample position may be determined with even higher precision by mapping the measured intensity

( $0.863\% \cdot \mu\text{m}^{-1}$  sensitivity which was  $-220 \text{ cps} \cdot \mu\text{m}^{-1}$  in our case) and further by measuring the curve also in the opposite direction (i.e. by reversing the holder movement) to check for mechanical backlash. The case measurement reported in Fig. 3 evidenced a shift of about  $5\mu\text{m}$  due to the motor backlash. The backlash is actually lower if the sample holder is rotated. This backlash is mostly caused by the vacuum sealing, which creates friction with the shaft.

The furnace is then heated in  $200^\circ\text{C}$  steps up to the maximum temperature ( $1600^\circ\text{C}$ ). At each temperature step the system is thermally stabilized and then the procedure of sample height adjustment is repeated. The translation needed to adjust the sample position with respect to the reference position at RT is actually the thermal response of the shaft in the operating temperature range. The expansion of the shaft as a function of the temperature is plotted on Fig. 4. This linear function is then inserted in the software program that controls the sample vertical motor, the actual temperature is retrieved from the system and the sample position is automatically adjusted. In the system installed in our laboratory the maximum vertical compensation at  $1600^\circ\text{C}$  is 0.78 mm, and the linearity of the adjustment curve is excellent (Fig. 4: average compensation  $4.973 \cdot 10^{-4} \text{ mm } ^\circ\text{C}^{-1}$ ).

### 3. Temperature Calibration by Known Phase Transitions

The temperature calibration is generally performed in two steps. First of all the temperature effectively experienced by the sample is investigated by means of known phase transitions or melting points. This obvious procedure allows the evaluation of the discrepancy between the 'real' temperature inside the chamber and the 'virtual' temperature imposed by the controller and monitored by the Pt/Pt-Rh thermocouple. The temperature measured by the thermocouple is extremely stable at all temperatures, as the maximum variation with time is about 1°C at the highest temperature attainable. The materials used for the calibration



**Fig. 4.** Calibrated thermal expansion of the ceramic shaft.

are shown in Table 1.

The actual measurements were done at intervals of 1°C. In the case of the phase transitions, the measurements were bracketed both with rising and with decreasing temperature. The temperature difference between the two paths never exceeded 1°C. In the case of the  $\alpha$ - $\beta$  quartz transition the temperature was exactly the same within error.

The temperature range checked was as broad as possible. The results of the temperature calibration are shown in Fig. 5: the difference is more than 50°C at low temperatures (below 400°C), then it decreases until 1400°C, where imposed and experimental temperatures coincide. The calibration line reported in Fig. 5 has a slope of 0.9534, and the goodness of fit corresponds to an R of 0.9996. The curve extrapolation at higher temperatures was checked by means of the thermal expansion of standard materials.

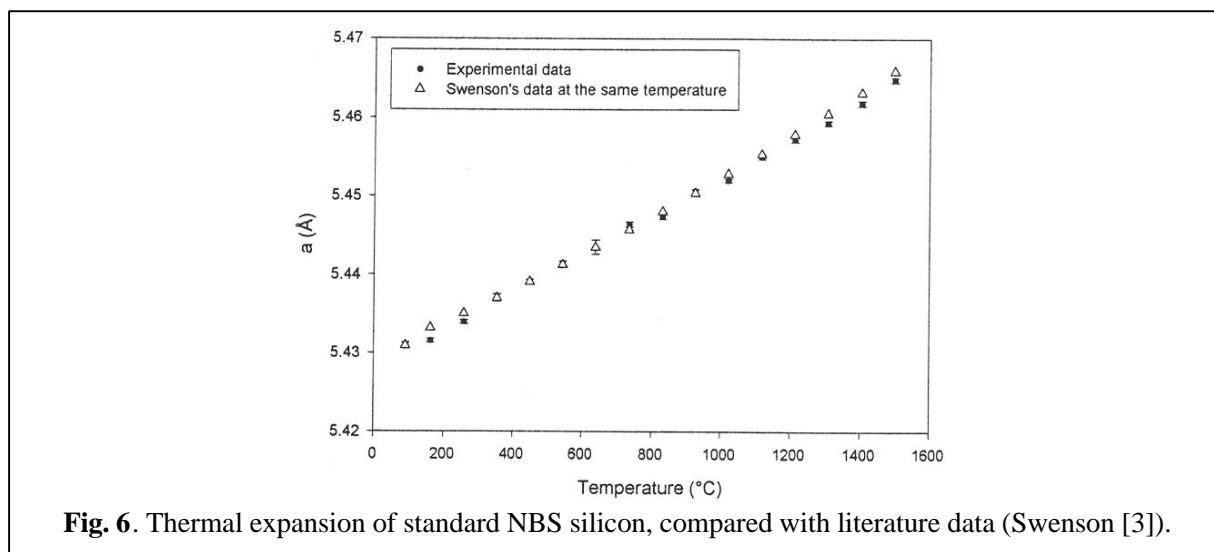
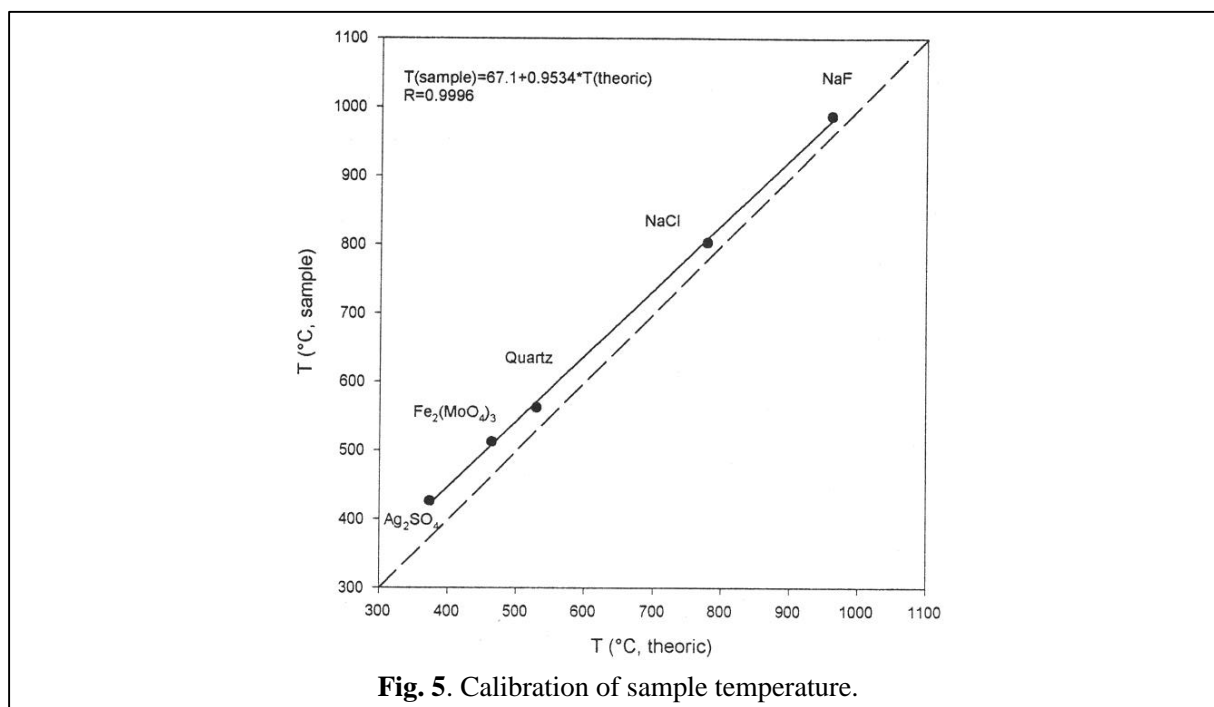
### 4. Thermal Expansion of Standard Materials

Once the temperature calibration curve is determined as described above, the second step allows a further check of the temperature reliability by measurement of the thermal expansion of standard materials, such as NBS silicon (NIST SRM 640b or SRM 640c). The measured lattice data are compared to those found in the literature (for example Swenson's [3] paper in the case of Si). This procedure has the great advantage of allowing the T calibration over the whole temperature range. Our preferred protocol is: (1) measurement of the thermal expansion data, (2) correct the nominal temperature with the previously obtained calibration curve, and (3) compare the corrected values with those reported in the literature.

In the present case silicon, corundum, and quartz were used in order to verify the temperature corrections applied by means of the previous

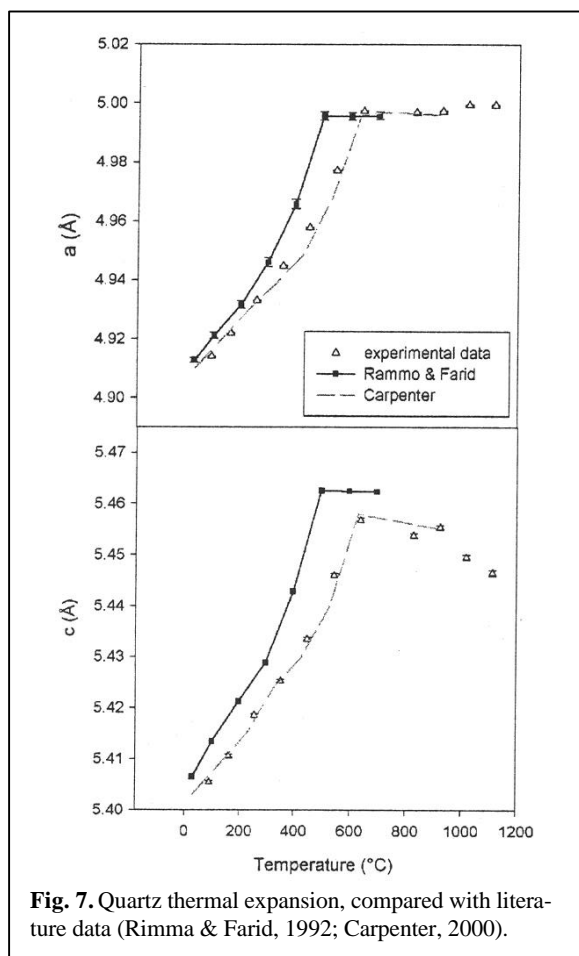
**Table 1.** Materials and corresponding transition/melting point temperatures (°C).

Phase transition	Melting point	Temperature
AgNO <sub>3</sub> orthorhombic-trigonal		165
	Pb	327.5
Ag <sub>2</sub> SO <sub>4</sub> orthorhombic-hexagonal		427
Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> monoclinic-orthorhombic		504
Quartz trigonal-hexagonal		573
	NaCl	803±3
	NaF	988



calibration. Thermal expansion of standard silicon was performed up to 1600°C in T steps of 100°C, using a heating rate of 20°C min<sup>-1</sup>. The Si lattice parameter was refined with the Rietveld method using the program GSAS [2], which allows proper treatment of the instrumental aberration parameters, such as the angular zero and the sample displacement parameters. The goniometer zero correction was refined at RT against the nominal silicon cell parameter, and then it was kept fixed for high temperature refinements. The results are

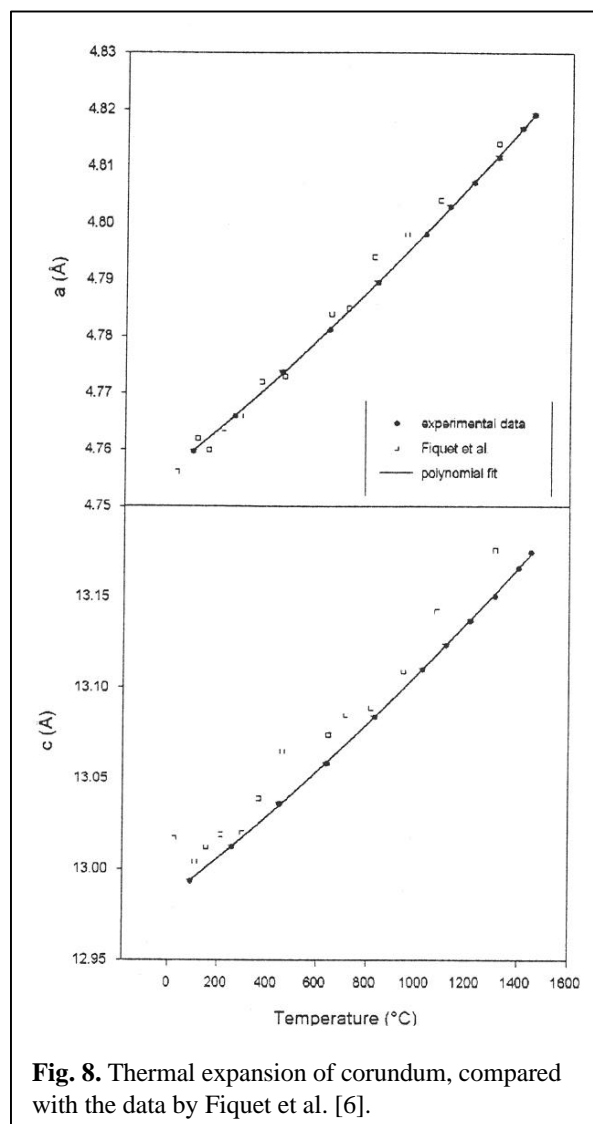
shown in Fig. 6. The temperature values were corrected using the previous calibration, and the silicon lattice parameter was calculated starting from the thermal expansion coefficient determined by Swenson [3]. The experimental results are in good agreement with literature data, with minor discrepancies in the low temperature range (150-300°C). These may be due to a small residual sample misplacement at these temperatures, as the specimen displacement coefficient was not refined in the Rietveld optimization.



**Fig. 7.** Quartz thermal expansion, compared with literature data (Rimma & Farid, 1992; Carpenter, 2000).

The other two standards used for temperature calibration were quartz and corundum (NBS SRM 674a). The results for quartz are shown in Fig. 7, where they are compared with the data of Rammo & Farid [4], and Carpenter [5]. The best agreement can be found for Carpenter's data, both in terms of the absolute values and in temperature calibration. Regarding the Rammo & Farid data, the overall temperature behaviour of cell parameters is the same, but the temperature is different. An incorrect temperature calibration by these authors is the most likely cause of the observed discrepancy.

The situation is a slightly different for corundum: the results are shown in Fig. 8 and compared with the data by Fiquet et al. [6]. There is a general agreement between the two data sets, although the data by Fiquet et al. show an evident large dispersion, especially concerning the *c* cell parameter, whereas our data show a rather smooth behaviour. This is a clear indication that the litera-



**Fig. 8.** Thermal expansion of corundum, compared with the data by Fiquet et al. [6].

ture data are affected by poor temperature homogeneity or stability.

## 5. Conclusions

The prototype PAP1600 high temperature chamber proved to be extremely successful for its temperature stability and homogeneity. The quality of the diffraction data is excellent even at the highest temperatures. An accurate temperature calibration is necessary to produce reliable results, especially if one wants to investigate phase transitions and reaction kinetics, where temperature control is especially important.

The comparison of the measured thermal expansion data of standard materials with available literature data showed a good agreement over the

whole temperature range.

The overall performance of the chamber, now available only as a prototype, in terms of temperature stability, homogeneity, reproducibility of the diffraction data, precision of the measured lattice parameters at HT, and quality of the powder spectra for structural refinements is very good and compares or exceeds those of most commercially available temperature chambers.

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