A new high temperature, high heating rate, low axial gradient capillary heater

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A new heater design, capable of fast heating and cooling to and from >1000°C, has been developed at the Swiss–Norwegian Beamlines, European Synchrotron Radiation Facility, France. The design uses a SiC head to distribute heat, and resistive Si₃N₄ heat cartridges to provide heat.

1. Introduction

Temperature is an important thermodynamic field that defines the stability and functional behaviour of many materials. Temperature-dependent diffraction is one of the most powerful tools for characterizing solid materials, providing atomic-level detail on the mechanisms underlying structural phase transformations (Tomaszewski, 1992; Whatmore, 2017; Bassett & Brown, 1990) and chemical reactions (Bojesen & Iversen, 2016; Eppl, 1994; Bassett & Brown, 1990), and untangling different contributions in the thermal expansion coefficients (James et al., 2001; Bassett & Brown, 1990) to name a few. Nowadays, measurements as a function of temperature are often performed at synchrotrons. Thanks to bright synchrotron radiation and modern fast large-area detectors, temperature-dependent diffraction has become one of the routine tools. However, designing an efficient heater to provide the temperature control is a challenge, especially for diffraction measurements where a large exit window is required to observe higher angle scattering.

Hot-air blowers are a common method for heating capillaries, but have some drawbacks in that they are often limited to low temperatures or low ramp rates, and large temperature gradients over millimeter-sized samples (Newton et al., 2019). They are, however, versatile because the directed air flow allows for an open environment for a capillary. They have a long history of use in synchrotron experiments (van Beek & Pattison, 2019; Norby, 1997; Grubb et al., 1984).

Resistive heaters are an attractive option. They provide heat through either conduction or radiation. Designs based around the use of ceramic elements surrounded by resistive wire have been used previously; the design by Chupas et al. (2008) is a well known example. This heater uses two ceramic pieces wrapped in kanthal wire above and below the capillary, and can reach 1000°C. One disadvantage of this design is the mechanical connection between capillary and heater which can make it difficult to align a sample. A later design incorporated a variable winding pitch in the resistive wire to give an intentional thermal gradient for measuring across a sample (O’Nolan et al., 2020). A similar, more enclosed, design for small-angle measurements was reported by Andreen et al.
(2003). In this device the capillary is placed inside a ceramic tube wrapped in resistive wire. It also featured a vacuum chamber to reduce air scattering of X-rays. A high-pressure (1.5 kbar) hydrothermal cell for extended X-ray absorption fine-structure spectroscopy (EXAFS) was reported by Hoffmann et al. (2000). The cell used 3.2 mm-diameter heat cartridges to provide temperatures up to 600°C.

Larger resistance furnaces have been used for X-ray diffraction experiments, notably Linkam furnaces used on a number of beamlines (Connor et al., 2018). These are capable of reaching high temperatures (1500°C) and ramp rates (200°C min⁻¹) (Oversluizen et al., 1995; Bras & Ryan, 1998) and seem like a good option for solid state measurements, though the enclosed system may limit sample environment options. Mirror furnaces, in which light from a lamp is focused to a very small point, are another option for very high temperatures, although the temperature gradient is necessarily high and temperature control is notoriously difficult (Proffen et al., 1995).

Doran et al. (2017) reported an infra-red tube furnace, in use at beamline 12.2.2 at the Advanced Light Source, capable of temperatures >1100°C. The design uses a SiC tube, in which a capillary is placed. The tube is heated by two infra-red lamps, which together run at 150 W with the furnace at 1200°C. The lamps are then surrounded by heat shielding. Two holes in the SiC tube act as an X-ray entry and exit window.

Energy-dispersive diffraction measurements also allow for a narrow exit window. Large reaction vessels with heating jackets were used in the early days of in situ crystallisation reactions in this way (Evans et al., 1995; Barnes et al., 1996).

Blichfeld et al. (2020) designed a resistive heater for thin film measurements capable of reaching temperatures of 1100°C at 1200°C min⁻¹ using a small hot-plate made from Si₃N₄ by Bach Resistor Ceramics. The cell featured an aluminium casing and Kapton windows which allowed for gas flow to regulate the atmosphere. This was used to measure the in situ crystallisation of epitaxial or textured thin films from solution deposition methods.

Microwave devices have been reported in hydrothermal reactors (Caffrey et al., 1990). As microwave radiation directly heats the reaction medium, it is potentially more efficient than convection or heat radiative methods, and can achieve high ramp rates (Schmidt et al., 2018). However, the application is limited to reactions in polar solvents.

Induction furnaces are used in high-temperature applications (Tang et al., 1998; Kudrna Prašek et al., 2018). They can be very efficient and reach temperatures >1500°C but have some disadvantages: it can be harder to control temperature if the sample itself is affected by the electric field, and they are more complex in design which can put constraints on sample environment.

There are, therefore, many options available for the heating of powder samples during diffraction or EXAFS experiments at synchrotrons that each have their advantages and disadvantages. Modern synchrotron sources and detector systems allow for measurements of 1 s per diffraction pattern or even faster. In spite of the many solutions that are already reported and tested, there is still a need for a fast heater (e.g. 60–120°C min⁻¹ temperature ramp rate that for 1 s exposure gives 1–2°C temperature sampling) that can reach temperatures above 1000°C and provides reliable and reproducible control of the temperature without a large gradient in the measured zone (that implies that the hot zone has to be larger than the zone irradiated by the beam). The heater has to be compatible with capillary sample holders, in situ and operando equipment, such as gas flow cells, and provide sufficiently large opening for both low-angle (small angles X-ray scattering, EXAFS) and high-angle (powder diffraction, pair distribution function) tools. Further design objectives comprise low thermal mass and a small axial thermal gradient especially important for operando space-resolved catalytic micro-flow reactors.

Here we report a design for a capillary heater which uses a SiC head piece and Si₃N₄ heat cartridges capable of reaching temperatures above 1000°C at a rate above 100°C min⁻¹.

2. Description

Two SiC head pieces with different designs were made: the ‘in-line’ piece and the ‘perpendicular’ piece, so called because of the relative directions of the heat cartridges with respect to the beam. These are each approximately 3 cm in their longest dimension. SiC was chosen due to its high thermal conductivity (>300 W m⁻¹ K⁻¹) (Yu & Levinstein, 2001), stability and resistance to thermal shock. They each have opening angles of 60°, making them suitable for synchrotron X-ray diffraction (XRD) and total scattering experiments. Both have two holes cut out to fit 3 mm heat cartridges made from Si₃N₄ with coiled resistive wire running through. These are part

![Figure 1](https://www.solidworks.com/)

*SolidWorks* (https://www.solidworks.com/) drawings of the (a) in-line and (b) perpendicular SiC head pieces.
82306B by Webasto, normally used as a flame sensor in combustion heaters. The capillary can be placed in the cut between the cartridge holes. Smaller holes (1 mm) between the capillary and heat cartridges are cut to fit reference thermocouples. Fig. 1 shows 3D drawings of the SiC heads. The heater is controlled with a Eurotherm Nanodac, with power supplied using a Delta Elektronika box.

Fig. 2 shows photographs of the two heaters in their frames. Water-cooling channels flow through them, with 6 mm tube adapters at the ends. The heat cartridges are connected in parallel.

The heater has been tested and calibrated using lattice parameters, determined using X-ray diffraction of Ag and Pt, as well as with the melting points of Pb, Ba(NO3)2, NaCl and Ag up to 1200 °C and 100 °C min⁻¹ [Fig. 3(a)]. A thermocouple log is shown in Fig. 3(c). These data were measured on the ‘in-line’ furnace. Lattice parameter calibrations were performed using a cubic relation; details are given in Appendix A. The software Tcal was used to quickly calculate the calibrated temperatures from the diffraction data; details are given in Appendix B.

The heater is useful for measuring phase and lattice parameter changes due to its wide temperature range [e.g. the melting of silver (and crystallisation of quartz) shown in Fig. 3(d)]. It can also be used in conjunction with gas flow or...
gas isobar cells for measuring, for example, gas adsorption or absorption, or (catalytic) chemical reactions. Due to the low thermal mass and high shock resistance, the cell is capable of high heating and cooling rates which can be useful in kinetic studies. At maximum rate, the heater cools from 1000°C to room temperature in less than 10 min, saving experiment time and cooling time for changing samples.

Higher temperatures (>750°C) can only be reliably achieved when applying radiation shielding to the heater. Shielding substantially reduced power consumption and therefore improves the lifetime of the cartridges. At 1100°C, the in-line furnace uses 183 W and 220 W with and without shielding, respectively – a 17% reduction. The difference is starker with the perpendicular heater, with power being reduced from 288 W to 178 W at 950°C – a 38% reduction (Fig. 4).

Fig. 5 shows the axial temperature distribution at 200°C and 800°C measured using two methods. The data for a thermocouple placed in a capillary are skewed such that higher temperatures are observed on one side of the heater than the other. This is the effect of thermal conduction in the thermocouple itself; when more of the thermocouple is in the heater, higher temperatures are observed. This experiment illustrates that a highly conducting sample will have a highly uniform temperature distribution. The second method used a thermocouple that was held mostly outside of the heater, with its tip in the capillary section to negate the effect of different temperature distributions within the thermocouple, resulting in less skew in the data. From these measurements we observe that the heater is within 1% of the maximum measured temperature within a 5 mm distance, both at 200°C and 800°C (using the bent thermocouple data); 2°C and 6°C, respectively. This is a substantial improvement on what we see from a hot-air blower which varies by 75% across 10 mm at the centre of the blower (Newton et al., 2019).

For capillary measurements we consider this 5 mm window of 1% variation to be a low gradient. Since the heater can be kept consistently in the same position with respect to the beam (we estimate this to be well within 1 mm), the sample-to-sample temperature variation is negligible, and will depend more on the sample’s thermal conductivity, quantity and how symmetrically it is placed in the heater.

3. Conclusion
We have designed and tested a new resistive heater for use on synchrotron beamlines. It is useful for high-temperature measurements (>1000°C) and ramp rates (>100°C min⁻¹)
and, with the prior assumption, one obtains
\[ T_{\text{max}} \quad 10^4 \]
\[ \text{where coefficients } b_i \text{ with a linear coefficient of thermal expansion} \]
\[ \text{where } \text{measured as a function of temperature, and} \]
\[ \text{approximated as a polynomial function,} \]
\[ \text{taken at 20°C} \]
\[ \text{as an argument. The source code (written in} \]
\[ \text{calibrant is refined against the room-temperature value, or it} \]
\[ \text{equal to the measured temperature at this point).} \]
\[ \text{can be fixed if desired, and used in equation (1) to determine} \]
\[ \text{as errors coming from the experimental instabilities.} \]
\[ \text{towards zero power through the} \]
\[ \text{the value at room temperature,} \]
\[ \text{i.e. zero power through the} \]
\[ \text{it neglects uncertainties for} \]
\[ \text{inversion pattern. The software can read file headers in the .cbf images} \]
\[ \text{and compared this with the value at room temperature,} \]
\[ \text{the calibration based on thermal expansion, as it} \]
\[ \text{this gives} \]
\[ \text{as well as errors coming from the experimental instabilities.} \]
\[ \text{the Swiss–Norwegian beamlines (SNBL, ESRF) are} \]
\[ \text{Acknowledgements} \]
\[ \text{The Swiss National Science Foundation (grant} \]
\[ \text{References} \]
\[ \text{Andreasen, J. W., Rasmussen, O., Feidenhans'l, R., Berg Rasmussen,} \]
\[ \text{Beek, W. van & Pattison, P. (2019).} \]
\[ \text{the beam time. The BM31 setup} \]
\[ \text{was funded by the Swiss National Science Foundation (grant} \]
\[ \text{Beek, W. van & Pattison, P. (2019).} \]
\[ \text{International Union of Crystallography.} \]
\[ \text{APPENDIX B} \]
\[ \text{Tcal} \]
\[ \text{We have developed software, } \]
\[ \text{For silver at } T = 1200°C, \]
\[ \text{this estimate has to be taken as a lower} \]
\[ \text{by BM01, and integrated into the } \]
\[ \text{software to apply calibrations during measurements (Dyadkin} \]
\[ \text{APPENDIX A} \]
\[ \text{A1. Calculation of temperature from thermal expansion} \]
\[ \text{The thermal expansion is defined as} \]
\[ \varepsilon = \frac{a - a_{20}}{a_{20}}, \quad (1) \]
\[ \text{where } a \text{ is a unit-cell dimension of the reference material} \]
\[ \text{measured as a function of temperature, and} \]
\[ \text{at} \]
\[ \text{Temperature dependence of the thermal expansion can be} \]
\[ \varepsilon = a_0 + a_1 T + a_2 T^2 + a_3 T^3. \quad (2) \]
\[ \text{The temperature at the sample position is calculated from the} \]
\[ \text{of a reference material placed at the same} \]
\[ \text{For calibration purposes it is convenient} \]
\[ \text{to use an inverted function,} \]
\[ \text{where coefficients } b_i \text{ are refined from the tabulated data on} \]
\[ \text{thermal expansion of the reference materials (Ag, Pt) and} \]
\[ \text{given in Table 1.} \]
\[ \text{A2. A note on the accuracy of temperature calibration from} \]
\[ \text{Thermal expansion is defined as} \]
\[ \frac{\delta T}{\alpha} = \frac{R}{\alpha} \left( 1 + \frac{\beta T}{\alpha} \right)^{1/2} = \frac{R}{\alpha} \left[ 1 + (\epsilon + 1) \right]^{1/2}. \quad (6) \]
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\[ \text{For silver at } T = 1200°C, \]
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\[ \text{thermal expansion of a reference material placed at the same} \]
\[ \text{position as the sample. For calibration purposes it is convenient} \]
\[ \text{to use an inverted function,} \]
\[ \text{T = } b_0 + b_1 \varepsilon + b_2 \varepsilon^2 + b_3 \varepsilon^3, \quad (3) \]
\[ \text{where coefficients } b_i \text{ are refined from the tabulated data on} \]
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\[ \text{T = } b_0 + b_1 \varepsilon + b_2 \varepsilon^2 + b_3 \varepsilon^3, \quad (3) \]
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\[ \text{Thermal expansion is defined as} \]


