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A New Single-Crystal Heater for the Precession Camera and Four-Circle Diffractometer

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Abstract

A new, relatively simple, single-crystal heater for the precession camera and four-circle diffractometer has been designed and tested in a number of experiments on lunar and terrestrial minerals. Only minor modifications to the standard precession camera or four-circle diffractometer are required for installation, and data may be collected in a routine manner with minor restrictions due to the heater geometry on the amount or type of data. The temperature stability is ±5°C at 1000°C with a maximum operating temperature of about 1200°C. Heating is accomplished by means of a ZrO_2 cement-covered Pt(13% Rh) coiled wire yoke with crystals mounted in evacuated and sealed quartz glass capillaries on standard goniometer heads.

Introduction

Recent interest in phase transitions and high-temperature studies of silicates has prompted the development of a number of single-crystal heaters for use with X-ray cameras of Weissenberg and precession geometries. Buerger (1964) reviewed a number of precession camera heaters which had been described up to that time. These included several resistance heaters which can be used to approximately 1000°C plus the flame heater of Gubser, Hoffmann, and Nissen (1963) which can reach 2000°C. Other single-crystal heaters have been described by Young (1960), Lefkowitz and Megaw (1963), Foit and Peacor (1967), Gehlen (1969), Quareni (1969), Hanic, Kučera, and Medveč (1970), Viswamitra, Jayalakshmi, and Kalyani (1970), Czank and Kleber (1971), Lynch and Morosin (1971), and Smyth (1972).

Even though a large number of crystal heaters have been reported, surprisingly few sets of high-temperature X-ray intensity data suitable for crystal structure refinement have been obtained. Some of the studies which have been published are those on tridymite (Dollase, 1967), high chalcocite (Buerger and Wuensch, 1963), nepheline (Foreman and Peacor, 1970), and the anisotropy of Na atoms in albite (Quareni and Taylor, 1971).

We wish to report the development of a new, relatively simple single-crystal heater which can be used routinely and interchangeably on a standard precession camera or four-circle diffractometer without major modifications to either. Its design places minimum restrictions on the amount of data observable, and it has the advantages of allowing either normal or high-temperature operation (up to ~1200°C) without heater removal or recalibration. The heater is attached to the camera or diffractometer, not in contact with the goniometer head, permitting a relatively simple crystal mounting and alignment on any standard goniometer head and placing no restriction on crystal motion. It has been used on both the Buerger precession camera and Picker four-circle diffractometer in a number of applications on terrestrial and lunar minerals.

Heater Description

The heater assembly shown in perspective in Figure 1 and in plan view with dimensions in Figure 2 consists of a telescoping aluminum post with exit slots in the upper half for lead and thermocouple wires which run the length of the lower half. The lead wires are #14 gauge teflon-covered strand copper which have been silver soldered to the ends of a Pt–Rh (13%) heater element. The ends of the heater element are encased and fixed in 1/8″ diameter alumina tubes using ZrO_2 cement. These alumina tubes are held in place by set screws. The thermo-

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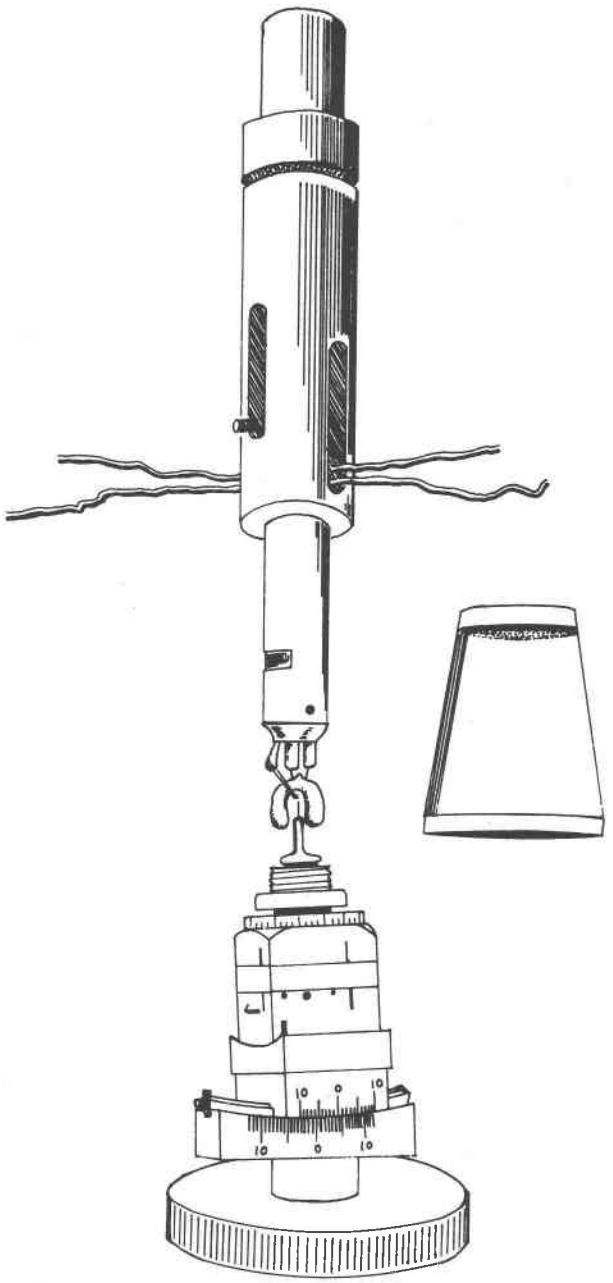

FIG. 1. Perspective view of crystal heater with heater fully extended over crystal. Kapton covered conical frame which covers the heater element and crystal during data collection is shown at right.

couple wire is 0.008″ Pt–Pt (10% Rh) which has been insulated with Teflon. The lower aluminum post can be raised or lowered by means of sliding handles on either side of the upper assembly and locked in place by set screws. An additional translational adjustment is provided by a hollow socket holder which is attached to the chi circle of a standard four-circle diffractometer (Fig. 3) or a horizontal extension arm on a precession camera (Fig. 4).

The heater element consists of a coiled yoke of 0.020″ Pt (13% Rh) wire with two full turns per side which has been covered by a mixture of finely ground ZrO_2 and Zircoa Bond 6.[2] Trial and error have shown that the most effective cover is obtained by at least three separate layers of the ZrO_2-Zircoa Bond 6 coating with 3–5 hour heat treatments of ~200°C between coatings. Such a coating is essential for operation above a crystal temperature of about 1000°C to help prevent evaporating Pt from depositing on the glass capillary holding the crystal and interfering with data collection. The thermal mass of the coating is also useful for reducing temperature fluctuations and minimizing temperature gradients within the furnace. We have found that the two prongs of the heater element should be separated by at least 1.5 mm to allow an essentially unrestricted window to the incident and diffracted X-ray beams. Because the heater assembly is mounted on the chi circle of the four-circle diffractometer, it moves with chi and omega allowing unrestricted phi motion for the crystal, which facilitates crystal alignment (see Figure 3). This also permits use of almost the full useful two theta range for data collection with Mo$K\alpha$ radiation (in practice up to ~75°). The assembly is attached to the precession cradle of the precession camera and precesses with the crystal, maintaining a constant crystal to heater element relationship (Fig. 4).

The measuring thermocouple is supported beyond the base of the lower aluminum post by a two-holed alumina rod with the thermocouple junction centered at the top of the heating yoke. The length of the heater element can be adjusted so that the crystal is about 1.0 mm from the measuring thermocouple junction when the telescoping heater assembly is fully extended. The measured temperature is approximately 150°C different from the crystal temperature at 900°C due to this displacement, so an initial calibration is necessary.

The approximately one-inch translation motion of the lower aluminum post allows the heater to be raised when removing the goniometer head. The upper and lower posts of the telescoping assembly have been machined to a tolerance that permits the

[2] Available from Zirconium Corporation of America, P. O. Box 39217, Solon, Ohio 44139.

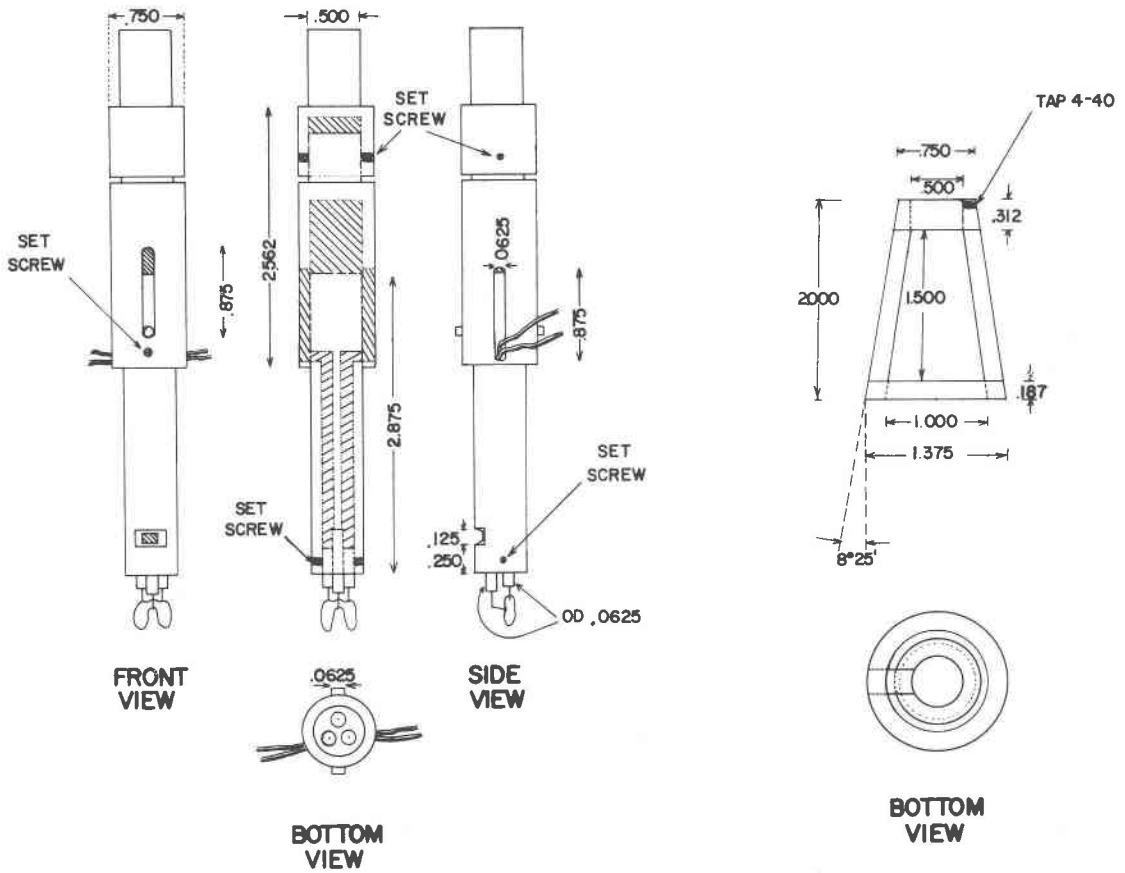

FIG. 2. Plan view of crystal heater and heater cover with dimensions.

heater to be raised and lowered without destroying its centering or changing the crystal to thermocouple or crystal to heater separations, thereby eliminating the need for recalibration or recentering.

During calibration and data collection, the heater element and crystal are surrounded by a cone-shaped frame covered with 0.005″ Kapton[3] film (shown in Figures 1 and 2) to prevent air currents from affecting temperature stability. Kapton is transparent to X-rays and can withstand temperatures up to 400°C. For precession camera use, a cylindrical, rather than conical, heater cover has been found more desirable. The heater cover can be raised or lowered by sliding along the lower aluminum post and is locked in place by a set screw. The diameter of the heater covers necessitates a shortening of collimators on the four-circle diffractometer and precession camera. Stainless steel collimators ~2″ long with inside diameters of 0.5 and 1.5 mm were machined for use with the heater on the Picker diffractometer. A special short collimator (~2″ long) and beam stop are also needed when the heater is mounted on the precession camera.

Power Supply

Our first power supply, rated at approximately 48 watts (at a maximum current of 12 amperes), was adequate for a maximum operating temperature of ~1200°C. This supply consisted of an 8 amp variac controlling the primary of an 18 volt/20 amp step-down transformer, wired in series with a 10 amp variac autotransformer for increased resolution. We are now experimenting with an SCR supply rated at 40 amps and featuring a thermocouple feed-back control for improved stability.

Temperature Calibration

The heater output at the crystal position was calibrated by mounting a 0.0025″ Pt–Pt (10% Rh)

[3] Kapton film is available from E. I. DuPont de Nemours & Co., Inc., Film Department, Wilmington, Delaware 19898.

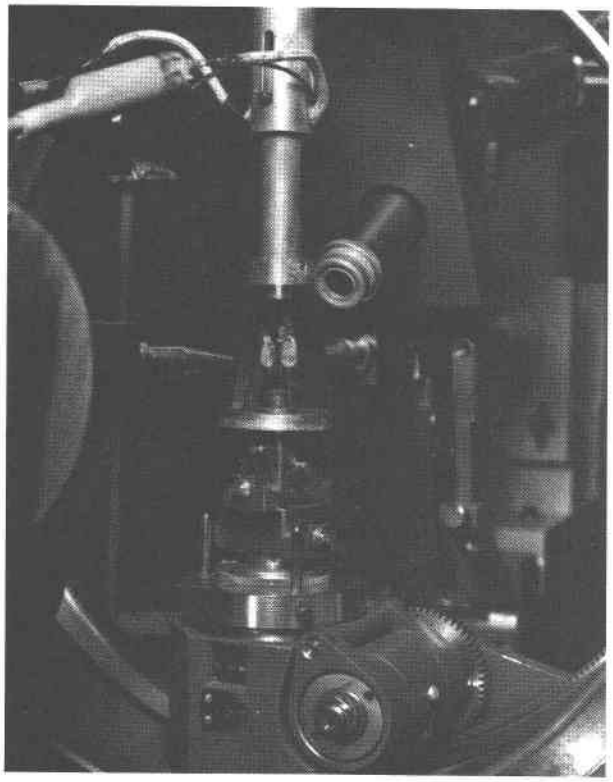

FIG. 3. Photograph of heater assembly attached to the chi circle of a Picker 4-circle diffractometer.

thermocouple in a sealed quartz glass tube on a goniometer head and centering the junction in the same manner as a crystal is centered. The junction was made with a diameter of ~0.15 mm, simulating a crystal in size. The hot spot of the heater was located by translating the sliding assembly until the measured temperature was maximized. Temperature readings at various power settings were recorded for both the calibration thermocouple and the permanently mounted measuring thermocouple discussed earlier. Calibrations were established at various chi settings on the four-circle diffractometer and for the one heater position on the precession camera. Figure 5 is a typical measured mV versus crystal temperature curve for the four-circle diffractometer. The measured mV readings differ by a maximum of 0.3 mV for the two extreme chi settings (0° and 90°) (see Figure 6); however, the temperature at the crystal position remains constant at all chi settings to within ~6°C. The variation in measured mV with chi can be lessened by placing the measuring thermocouple closer to the crystal; however, this distance should be at least 1.5 mm in practice to avoid interference with the incident X-ray beam.

Further calibrations were made using the melting points of Au(1063°C), BaCl(963°C), NaCl(801°C), $Ba(NO_3)_2$(592°C) and $NaNO_3$(307°C) in evacuated, water-free, silica glass capillaries in order to simulate as nearly as possible the conditions under which experiments are performed. The beginning of melting may be observed using the standard telescope mounted on the four-circle diffractometer. In the case of the precession camera, it is necessary to devise a suitable telescope arrangement. The melting of these standard materials was performed several times and is reproducible to 1°C.

The differences between the two calibration curves in Figure 5 illustrate the problems which are associated with using a heater of low thermal mass. When a thermocouple is placed in the crystal position, it acts as a heat sink and more power is required to raise the temperature to a given value than when using a crystal mounted on a silica fiber. Therefore, the melting-point calibration curve is thought to be more representative of our actual diffraction experiments. Because of other difficulties such as in determining the beginning of melting, we cannot be certain about errors in temperature measurement at any given temperature. Optical pyrometry has been suggested as an independent indicator of temperature, but we have found that reflection of light from the heater itself causes these temperature readings

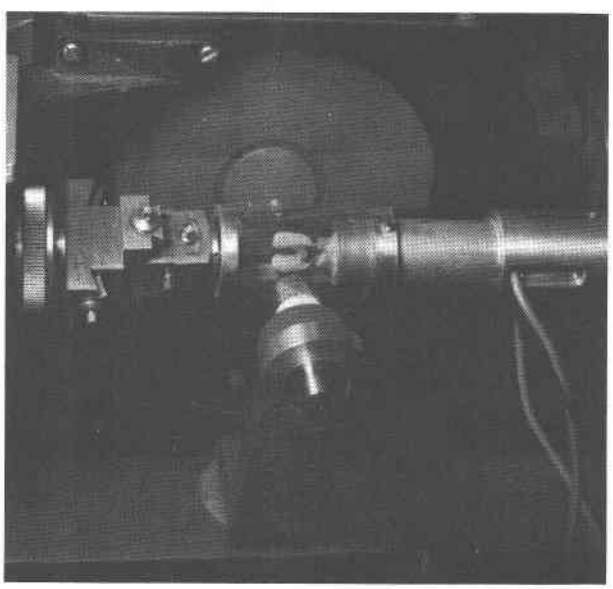

FIG. 4. Photograph of heater assembly attached to a Buerger precession camera. An L-shaped arm connected to the precession cradle holds the heater.

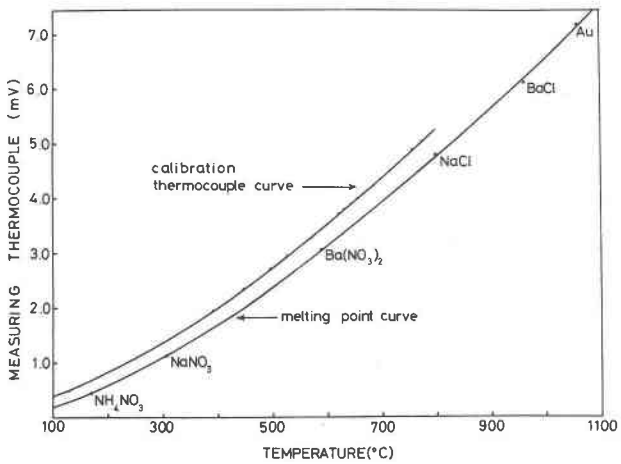

FIG. 5. Typical calibration curves based on melting points of various standard materials and on thermocouple measurement at the crystal position. Measured temperatures are accurate to ±20°C.

to be too large. Calibration with known rapid phase transition in the solid state may be the best way to provide reliable temperatures; thus far, we have been able to determine the alpha to beta quartz transition to within ± 3° of its reported value. However, because of greater heat loss at higher temperatures and flattening of the thermocouple curve at lower temperatures, errors in our temperature measurement may be as much as ± 20°C. The problems mentioned above associated with a thermocouple acting as a heat sink in furnaces of low thermal mass should be considered when mounting crystals directly on a thermocouple.

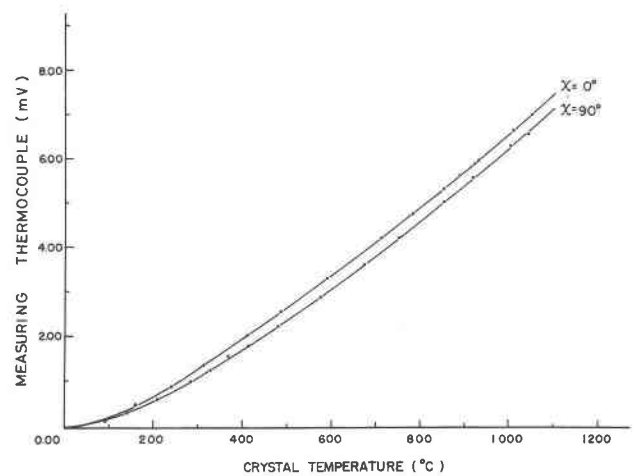

FIG. 6. Plot of measured millivoltage versus crystal temperature (°C) at $\chi = 0°$ and $\chi = 90°$ on the 4-circle diffractometer. These differences reflect change in temperature at the measuring thermocouple with a change in χ. The temperature at the crystal is not affected by changes in χ and is constant to ±6°C as χ varies from 0° to 90°.

Crystal Mounting

Perhaps the most critical part of a high-temperature experiment is the manner in which the crystal is mounted. Because of the 1.5–2 mm opening in the heater element in which the crystal is placed, the goniometer arcs are restricted to ~ ± 5° from the zero settings. We have tried two techniques, both involving silica glass capillaries which are evacuated and sealed. In the first, the crystal is simply wedged into a sufficiently small diameter silica glass capillary with the hope that an axis is not more than 4 or 5° off. This is not critical, if automatic orientation around any vector is possible. One fault with this mounting is that the crystal may move considerably and continually during the experiment, in some cases making high-temperature experiments impossible. The second technique begins by preliminary alignment using a standard crystal mounting medium such as wax. The aligned crystal is remounted on a silica glass or mullite fiber using a mixture of finely ground quartz glass wool or mullite glass wool and Zircoa Bond 6, which is relatively transparent to X-rays and adds little to background. The mounted crystal is then inserted into a small diameter (normally 0.3 mm inside diameter) silica glass capillary[4]. Evacuation is accomplished by attaching the capillary with fast-curing epoxy to a pipette which is connected to a vacuum pump. During evacuation, the capillary containing the mounted crystal is inserted into a small furnace and heated at about 200°C for 6–8 hours to cure the cement and drive off water and other volatiles. The capillary is finally sealed under vacuum using a Tescom oxy-acetylene "Little Torch."[5]

In most cases the crystal can be heated to the maximum limit of the furnace or to the crystal's melting point with only minor crystal movement (~ 1°) during a temperature increase or decrease. Once the temperature has equilibrated, final align-

[4] 0.3, 0.5 and 0.7 mm quartz glass capillaries are available in lots of 25 from the Uni-Mex Co., 1829 North Arborgast Ave.; 1-G, Griffith, Indiana 46319.

[5] The oxy-acetylene "Little Torch" is available from Tescom Corporation, Instrument Division, 2633 S.E. Fourth Street, Minneapolis, Minnesota 55414.

ment can be made and further crystal movement is in the range of the crystal setting error. One possible difficulty with the mounting cement is exchange of Si and Al from the ground wool. This possibility should always be checked by microprobe analysis of the crystal after the heating experiment is completed or by re-collecting room temperature data after high temperature data collection and comparing the refined atomic parameters with those of pre-heating room temperature data.

Applications and Performance

Heater assemblies have been mounted and used on both a Supper precession camera (Fig. 4) and a Picker four-circle automated diffractometer (Fig. 3). A number of experiments have been successfully performed including a study of the $P \rightleftharpoons C$ centered transitions in lunar and terrestrial pigeonites (700–1100°C, Prewitt *et al,* 1971) and in cummingtonite (100°C, Sueno *et al,* 1972); and structural studies of high pigeonite (960°C, Brown *et al,* 1972); lunar hortonolite (24–710°C, Brown and Prewitt, 1973); high cummingtonite (270°C, Sueno *et al,* 1972); tremolite (400°C, 700°C, Sueno *et al,* 1973); acmite (400–800°C), diopside (400–1000°C), hedenbergite (24–1000°C), jadeite (24–800°C), spodumene (300–760°C), and ureyite (400–600°C) (Cameron *et al,* 1973). Collection of intensity data has been done automatically at temperatures up to 1000°C with relative ease, and the data have been successfully refined to *R*-factors ranging from 2 to ~7 percent.

As mentioned earlier, crystal alignment changes by as much as 1° total arc movement when the crystal temperature is raised or lowered. Rather than realigning the crystal in the conventional fashion, we have been using an orientation program similar to that of Busing (1970) written by L. J. Guggenberger (DuPont Central Research Department) and modified for the PDP-15 computer. Three noncoplanar reflections are individually centered using the L/R and T/B shutter assembly. χ, ϕ, ω, and 2θ coordinates of these reflections are input and the direct and reciprocal cell and orientation matrix are computed. High-temperature cell parameters are also easily obtained by measuring approximately twenty reflections in the same manner followed by least-squares refinement.

Temperature equilibration is attained within about five minutes and has remained constant to ±5°C at 960°C over a three-day period. Because of the high resistance to thermal shock of the ZrO_2 cement, the temperature may be raised or lowered rapidly. The thermal gradient surrounding the crystal is relatively high, with a gradient of ~40°/mm along the center line of the approximately 8 mm long heater element and 30°/mm from heater wall to wall. However, this is not critical since the crystal can be precisely centered for each experiment using the centering telescope of the diffractometer or precession camera.

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References

Brown, G. E., and C. T. Prewitt (1973) High-temperature crystal chemistry of hortonolite. *Amer. Mineral.* **58,** 577–587.

———, ———, J. J. Papike, and S. Sueno (1972) Comparison of the structures of high and low pigeonite. *J. Geophys. Res.* **77,** 5778–5789.

Buerger, M. J. (1964) *The Precession Method.* John Wiley and Sons, Inc., New York. 276 pp.

———, and B. J. Wuensch (1963) Distribution of atoms in high chalcocite, Cu_2S. *Science,* **141,** 276–277.

Busing, W. R. (1970) Least-squares refinement of lattice and orientation parameters for use in automatic diffractometry. *In, Crystallographic Computing,* Ed. F. R. Ahmed, Munksgaard Publishers, Copenhagen.

Cameron, M., S. Sueno, C. T. Prewitt, and J. J. Papike (1973) High-temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene and ureyite. *Amer. Mineral.* **58,** 594–618.

Czank, M., and E. Kleber (1971) Ein Hochtemperaturofen für Einkristall-Rontgenkameras. *Z. Kristallogr.* **133,** 168–178.

Dollase, W. A. (1967) The crystal structure at 220°C of orthorhombic high tridymite from the Steinbach meteorite. *Acta Crystallogr.* **23,** 617–624.

Foit, F. F., Jr., and D. R. Peacor (1967) A high temperature furnace for a single crystal x-ray diffractometer. *J. Sci. Instruments* **44,** 183–185.

Foreman, N., and D. R. Peacor (1970) Refinement of the nepheline structure at several temperatures. *Z. Kristallogr.* **132,** 45–70.

Gehlen, P. C. (1969) A 77–1300K single crystal x-ray specimen chamber. *Rev. Sci. Instrum.* **40,** 715–718.

GUBSER, R. A., W. HOFFMAN, AND H. U. NISSEN (1963) Röntgenaufnamen mit der Buergerschen Präzessionskamera bei Temperaturen zwischen 1000°C und 2000°C. *Z. Kristallogr.* **119,** 264–272.

HANIC, F., Z. KUČERA, F. MEDVEČ, AND E. PLUHAR (1970) X-ray single crystal structure analysis technique for high temperatures. *J. Appl. Crystallogr.* **3,** 97–98.

LEFKOWITZ, I., AND H. D. MEGAW (1963) A device for taking x-ray photographs of single crystals at high temperatures. *Acta Crystallogr.* **16,** 453–455.

LYNCH, R. W., AND B. MOROSIN (1971) A hemispherical furnace for high-temperature single crystal x-ray diffraction studies. *J. Appl. Crystallogr.* **4,** 352–356.

PREWITT, C. T., G. E. BROWN, AND J. J. PAPIKE (1971) Apollo 12 clinopyroxenes: high temperature x-ray diffraction studies. *Proc. Second Lunar Sci. Conf.* **1,** 59–68.

QUARENI, S. (1969) A high-temperature apparatus for Weissenberg and precession diffractometers. *Z. Kristallogr.* **128,** 294–299.

———, AND W. H. TAYLOR (1971) Anisotropy of the sodium atom in low albite. *Acta Crystallogr.* **B27,** 281–285.

SMYTH, J. R. (1972) A simple heating stage for single crystal diffraction studies up to 1000°C. *Amer. Mineral.* **57,** 1305–1309.

SUENO, S., C. T. PREWITT, J. J. PAPIKE, AND G. E. BROWN (1972) The crystal structure of high cummingtonite. *J. Geophys. Res.* **77,** 5767–5777.

———, M. CAMERON, J. J. PAPIKE, AND C. T. PREWITT (1973). The high-temperature crystal chemistry of tremolite. *Amer. Mineral.* **58,** 649–664.

VISWAMITRA, M. A., K. JAYALAKSHMI, AND V. KALYANI (1970) A miniature furnace suitable for x-ray Weissenberg photography up to 1000°C. *J. Appl. Crystallogr.* **3,** 227–229.

YOUNG, R. A. (1960) Counter adaptor and furnace for Weissenberg camera. *Adv. X-ray Anal.* **4,** 219–232.

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