A SINGLE CRYSTAL TEMPERATURE CONTROLLED OVEN FOR AN X-RAY SPECTROMETER

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Abstract

An oven was built to heat a single crystal on the end of a goniometer head so that absolute x-ray diffraction intensity measurements of the basal plane reflections could be made at various temperatures. The temperature range is 50° C. to 270° C. and the temperature stability is within ±0.1° C. This stability is accomplished by a main winding and a controlled auxiliary winding outside the circumference of the main winding; these windings radiate energy to a copper block in which the crystal is mounted, and so maintain constant crystal temperature.

Introduction

A high-temperature crystal heater was built for the purpose of obtaining absolute intensity measurements from the basal plane reflections of a crystal. The integrated reflection for a mosaic crystal is determined by either of two methods:[1] the crystal is revolved with angular velocity ω and the total counts summed; or a point-by-point determination of the counts per second for each angular setting through the range of reflection is made, and the area under the curve that represents these data is determined by a planimeter or by graphical integration. The first method is mathematically expressed by $E\omega/I_0$, where E is the total counts from the line reflection, ω the angular velocity in radians per second, and I_0 the direct beam intensity in counts per second. The second method is defined by the expression

$$\int_{\theta_0-\epsilon}^{\theta_0+\epsilon} \frac{R(\theta)}{I_0}\, d\epsilon,$$

where θ_0 is the Bragg angle and $\theta_0+\epsilon$ and $\theta_0-\epsilon$ the angular limits over which the reflection occurs, $R(\theta)$ the reflected beam intensity in counts per second at angle θ, and I_0 is defined as above.

From these absolute intensity measurements the electron density as a function of a particular direction in the crystal may be determined and from the position of the peaks, the atomic parameters determined.

Requirements

The requirements were as follows: (1) The oven must be light in weight to prevent over-loading of the goniometer to which it is attached; (2)

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[1] *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Gebrüder Borntraeger, Berlin, **2**, 560 (1935).

The oven must be thermally insulated to prevent excessive heating of the goniometer head; (3) The temperature to which the oven is set must remain constant within ±0.1° C. for long periods of time and at any temperature setting within the range from 50° C. to 270° C.; (4) The size of the oven must conform to the limited mounting space available in the spectrometer;[2] (5) The crystal face must be on the boundary of the oven to receive the incident *x*-ray beam for diffraction work.

The temperature accuracy is necessary because the oven was built to study ferroelectric barium titanate, the integrated intensity of which changes rather rapidly, i.e., by more than a factor of five for the second order with a change of four degrees of the crystal temperature near the Curie point at 120° C.[3]

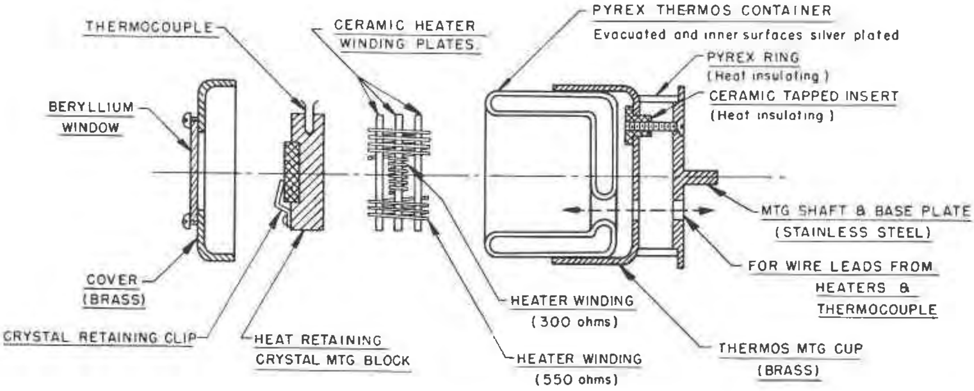

FIG. 1. Exploded cross-sectional view of heater.

MECHANICAL AND ELECTRICAL CHARACTERISTICS

The main body of the oven is a Dewar or "thermos" container, constructed of "pyrex" glass with the space between the inner and outer walls evacuated, and the inner surfaces of the walls silver plated, shown in the exploded drawing (Fig. 1) and the photograph (Fig. 2). This construction satisfies the requirement for a comparatively thin oven wall with high thermal insulating properties, together with the necessity of using a heat-resisting and an electrical non-conducting material.

The "thermos" mounting base consists of a brass cup mounted on a stainless steel base plate. The base plate contains a stud for mounting the assembled oven in the chuck of the goniometer head. The "thermos" container is held in position on the brass mounting cup by a light press

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[2] Baron, M. L., deBretteville, Jr., A., *Rev. Sci. Inst.*, **21,** 458–461 (1948).

[3] Kanzig, W., *Helv. Phys. Acta,* **24,** 184, 186, 187 (1951).

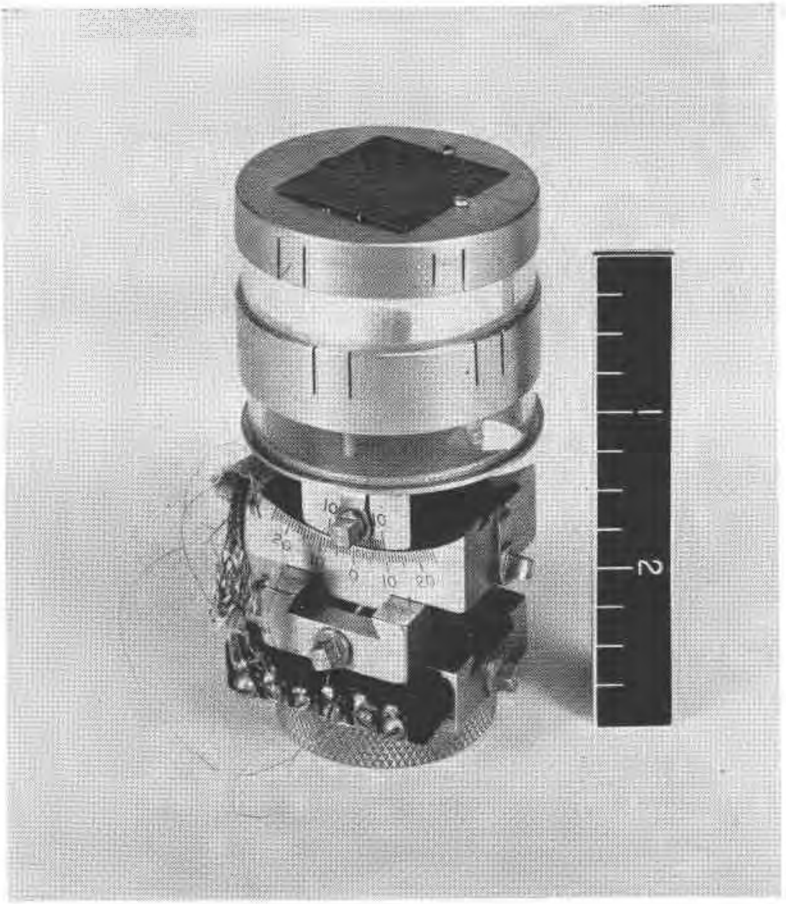

FIG. 2. Single crystal heater on adjustable goniometer head with beryllium cover.

fit. The cup and stainless steel base plate are mounted or coupled together through a "pyrex" stand-off ring; the purpose of the glass ring is to minimize heat conduction between the oven and the oven-mounting stud, and thus to prevent heat absorption by the goniometer head.

Two heater windings of #40 wire are provided. The main winding and the auxiliary one are 300 and 550 ohms, respectively. The main winding is located inside the auxiliary winding. To achieve maximum oven temperature, the main winding uses energy at the rate of some 20 watts. The temperature-stabilizing auxiliary winding operates best when it uses energy at the rate of approximately 7 watts. The concentric arrangement of the windings produces uniform heating of the exposed under-surface of the crystal mounting block. The main winding is connected, directly, to the energy source; the auxiliary winding operates only when needed. The oven may be set at any temperature between 50° and 270° C.; over long periods of time, the oven temperature is maintained within ±0.1° C. of the established value.

The crystal mounting block is made of oxygen-free electrolytic copper and is chromium plated. An iron-constantan thermocouple is inserted into a recess in the mounting block. Two spring clips hold the crystal in position.

The crystal mounting block is attached to a brass cover which slips over the "thermos" container with a light press fit. A beryllium window, 0.016 cm. thick, is mounted on the cover. The beryllium window provides thermal insulation for the crystal under study, and is transparent to iron and copper K radiations.

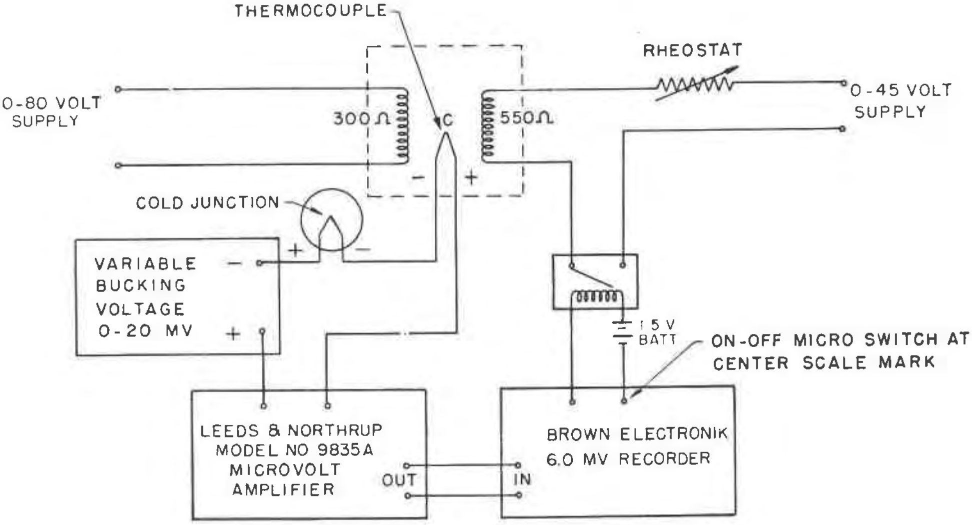

FIG. 3. Block wiring diagram of heater control circuits.

The electrical connections are shown in Fig. 3. The thermocouple is in series with the reference ice (cold) junction; to obtain the variety of possible oven temperatures, a bias voltage of 0–20 mv. is provided. The bias voltage output is applied to a Leeds and Northrup Amplifier No. 985-A; the amplifier output, made positive and set at approximately 150 microvolts, is connected to a 6 millivolt Brown Recorder—one that has a time constant of 1 second. This arrangement adjusts the pen of the recorder to the midscale position; the recorder is provided with a microswitch—one that closes whenever the scale reading is less than 3 milli-

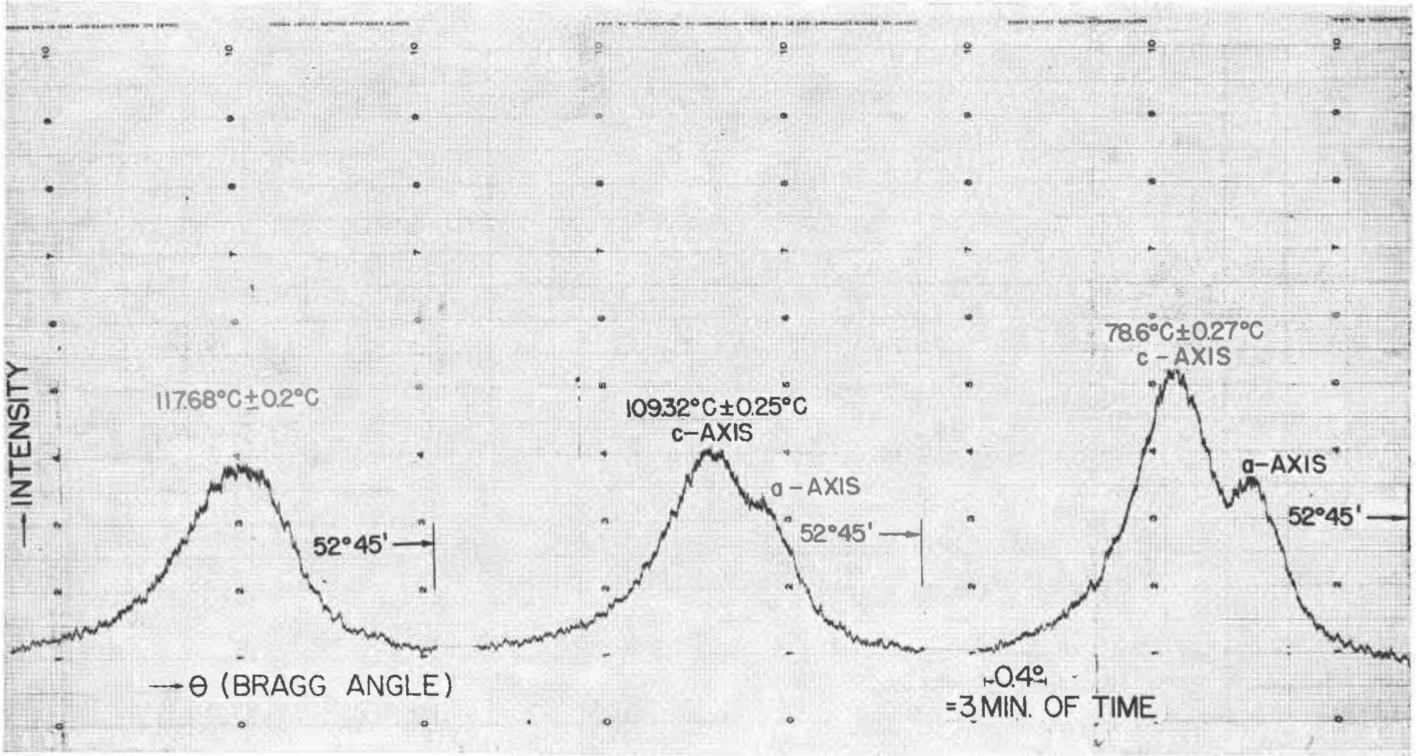

FIG. 4. *X*-ray intensities as a function of angle for single crystal oven. The 4th order reflection of $BaTiO_3$ tetragonal to cubic phase change for Cu K radiation is used to check the crystal vs. thermocouple temperature.

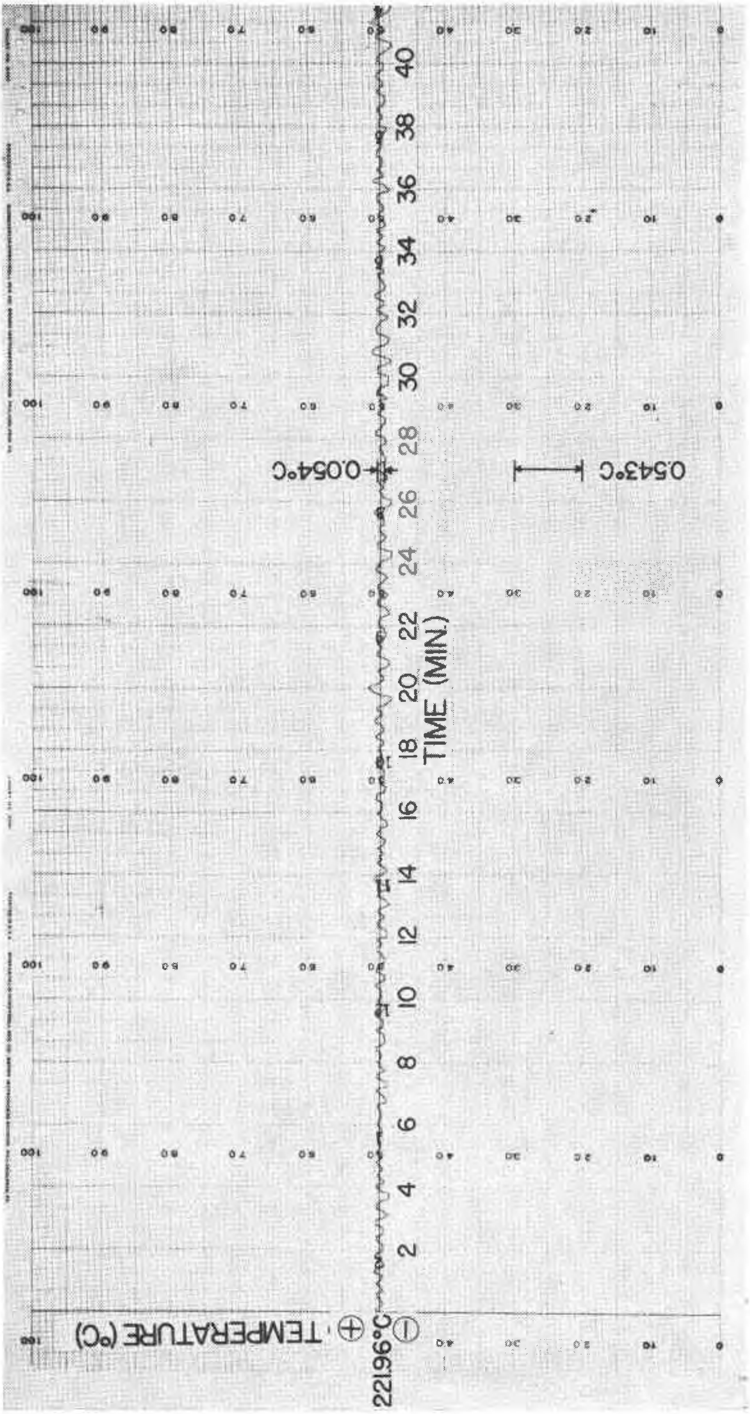

FIG. 5. Temperature vs. time chart for 221.96° C.

volts, and opens when the reading is 3 millivolts or greater. The microswitch actuates a relay that controls the energy supplied to the auxiliary winding of the heater.

The oven here described is intended, primarily, for flat crystal surfaces, 4 millimeters on a side and a few millimeters thick; the oven is not designed for rod-shaped crystals.

X-ray diffraction data are used to check temperature at the crystal; these data show the phase transition, known to occur at approximately 120° C., of a multi-domain single crystal of $BaTiO_3$. Figure 4 shows recordings of these data; above 120° C. (the Curie temperature) the cell structure is cubic, and hence a single reflection peak occurs; below the Curie temperature the cell structure is tetragonal, and so there are two reflection peaks—one corresponding to the *a* and one to the *c* axis. Figure 4 also shows a shift in the reflection peaks; such a shift may be used to calculate the coefficient of thermal expansion of the barium titanate.

Figure 5 is a recording of oven temperature over a 40-minute test period. The inherent stability of the temperature-control system is indicated by the recorded temperature variations—approximately ±0.054° C. during most of the test period.

CONCLUSIONS

The oven described maintains a constant temperature, within the range 50° to 270° C. with an accuracy of ±0.1° C. The particular design of this oven was determined by its use on an *x*-ray spectrometer; the small size and weight were necessary in order to mount the oven on the end of a goniometer head, so that the crystal could be positioned near the outer surface of the oven, thus permitting optical alignment and measurement of the intensity of reflected *x*-rays. Variation in oven design is possible, without impairing the precision control of temperature.

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