HIGH TEMPERATURE X-RAY CRYSTALLOGRAPHY: DEVICES FOR SINGLE CRYSTAL ANALYSIS

M. A. Viswamitra, A. M. Shaikh and K. Jayalakshmi Ramanuja

(Department of Physics, Indian Institute of Science, Bangalore 560012)

1. Introduction

The beginning of high temperature X-ray crystallography would be traced to as early as 1914, when Bragg (1914) demonstrated, at elevated temperatures, the diminution of X-ray reflection intensities from NaCl and also change in their reflecting positions due to expansion of the lattice. Since then high temperature X-ray techniques have been used for the study of wide range of problems: phase transformation, thermal expansion, stress effects at elevated temperatures, condensation reactions, solid state chemical reactions, molten salts, crystal structure analysis and thermal vibrations. Most of these techniques have been devised for investigating samples in the form of powders, blocks, plates, wires and rods. Some of them have now become well established and have been developed as commercial instruments.

We have been interested, over the last few years, in the application of high temperature X-ray techniques for single crystal studies. With a view to enable routine collection of high temperature X-ray diffraction data we have developed a few simple heating devices which could be adapted to ordinary room temperature cameras (Viswamitra *et al.*, 1970; Viswamitra and Jayalakshmi, 1972; Shaikh and Viswamitra, 1973) and diffractometers (Viswamitra and Jayalakshmi, 1970). X-ray measurements on single crystals can provide more detailed and significant information than those on polycrystalline samples, in several areas related to crystal structure and thermal vibrations of the atoms. Many of the phenomena in high temperature crystal chemistry such as phase transitions and solid solutions would be better explained by precise high temperature structure models than those based on room temperature data.

1

In view of the increasing interest in these studies by single crystal analysis, we have compiled the various single crystal heaters that are now available and have summarised them in this review in the form of a bibliography. Devices developed since 1964 alone have been included as the earlier work can be found in the excellent compilation by Goldschmidt (1964). An attempt has been made to make the bibliography as complete as possible; but it is likely that there might be omissions because of non-availability of relevant journals. Figures have not been given as we have not described any particular apparatus or technique in detail. A general outline, however, of various heating methods, temperature measurement, calibration and control, specimen holders and adhesives is given as a background to the bibliography. Earlier review to deal with this subject are those by Goldschmidt (1955), Campbell (1967) and Schossberger (1967).

2. METHODS OF HEATING

The heating methods that have been employed in high temperature X-ray diffraction instruments are: 1. Resistance heating, 2. Induction heating, 3. Electron or ion bombardment, 4. Radiation focussing, 5. Hot gas blowing, 6. Flame heating and 7. Thermoelectric heating.

1. *Resistance heating*

The simplest in this method is the straight heating of a metallic sample by passing a current through it. If the specimen is non-metallic, it is placed in a suitable metallic block, boat or plate which is current heated. The most common resistance heating, however, makes use of an external furnace surrounding the specimen, in the form of a metallic spiral wound on refractory tubes or hemispherical shells. It is necessary to have a suitable gap between the two halves of the furnace for X-rays incidence and scattering. Hemispherical furnaces provide more effective heating of the sample and minimum temperature gradients compared with coil furnaces. For temperatures in oxidizing atmospheres, below 1100° C, nichrome alloy seems to be the best available resistance material. Pt and Pt alloys are the most desirable heating elements up to 1500° C over long periods and up to 1700° C over short periods only, as these materials evaporate at these temperatures. The evaporation can, however, be minimized by covering the heating element by a thin coating of refractory cement such as Al_2O_3 or ThO_2.

For still higher temperatures, the common heating elements are Mo, **Ta,** W or Re. In these cases it is necessary to employ either neutral or

reducing atmospheres or vacuum. Up to 2000° C, Mo is preferred because of its greater ductility and ease of handling. For extended use beyond 2000° C, W is preferable as Mo becomes too volatile at these temperatures. When suitably coated, some of these metals could also be used in an oxidising atmosphere. Mo windings coated with molybdenum disilicide have been employed in ordinary air up to 2000° C for a period more than 100 hours (Sherwood, 1956).

In some resistance heating devices, the specimen is heated by a current through a thin metallic foil (Ni, Ta, W or Pt) enclosing it. If the foil is nickel, it also serves as a β-fitter when copper radiation is used.

The most commonly used refractory tubes for supporting the heating coil are quartz (1100° C), BeO (1500° C), Al_2O_3 (1700° C) and ThO_2 (2000° C.) BeO is expensive and needs careful handling being a toxic material. ThO_2, which is the most suitable oxide from the point of view of chemical stability, appears to be the best choice, if its slight radioactivity is not a disadvantage.

When a spiral is supported on a tube, the windings can be either on the inside or on the outside of the tube. Externally wound furnaces are more satisfactory from the point of view of temperature uniformity. The internally wound heaters inherently give higher sample temperatures as the sample is subjected to direct radiation heating.

Instead of wire resister furnaces, the specimen can be heated by enclosing it inside suitable resister tubes. A carbon tube furnace has been designed for operating in vacuum up to 1800° C by Matuyama (1955). The tube ends are electroplated for good electrical contact and the tube is provided with suitable holes for X-ray irradiation and scattering. Perri, Banks and Post (1957) have used a silicon carbide heater rod instead of a tube with recess for Pt/Rh sample holder (1700° C).

Sample heating through the thermocouple which, in addition to measuring temperature supports as well as heats the crystal, has also been employed in some devices (Aruja, Welch and Gutt, 1959; Czank and Kleber, 1971). A synchronous switch phased to the supply voltage isolates the thermoelectric current from the heating current which flows only during alternate half-cycles. In the intervening half-cycles, the thermocouple is connected to the temperature measurement circuit. In a recent design by Hanic, Kucera, Medved and Pluhar (1970), both heating and measuring circuits operate over complete cycles. In this method, as the crystal is heated only from one end, there is possibility of large temperature gradients

in the case of non-conducting crystals if no suitable metal shields are employed.

2. *Radio frequency power heating or induction heating*

In this method, the sample, placed in a ceramic tube, is heated by conduction and radiation from surrounding thin walled refractory susceptor (*e.g.*, Pt, W, Ta, Mo, graphite) which is heated by eddy currents induced by an r.f. current (frequency about $0 \cdot 5$ megacycle) flowing in the surrounding work coil (usually copper). The main advantage of induction heating is that it requires no direct electrical connection to the heating element, *i.e.*, the susceptor. The method has been adapted for both cameras and diffractometers (Edwards, Speiser and Johnson, 1949; Land and Franklin, 1962). Though temperatures up to $3000°$ C could be obtained, this method cannot be employed in an ordinary laboratory in view of the expensive peripheral equipment like the r.f. generator. Also the susceptor in the heating element is in the same form as for resistance heating; hence the material problems and the atmospheric requirements are the same as for conventional resister heating devices.

3. *Heating by electron or ion bombardment*

In this method, the sample is bombarded by a stream of high speed electrons emitted from a tungsten filament and accelerated by a suitable potential drop. Hatt, Kent and Williams (1960) have applied this method to a counter-*cum*-camera apparatus and have reported that a specimen of tantalum attained a temperature of $1500°$ C with a filament temperature $2000°$ C and voltage difference of 100 volts. The main restriction on the maximum working temperature obtainable with this method seems to come from the excessive contamination of the specimen by the evaporation of the filament material. These authors suggest that the evaporation could be controlled to some extent by the use of thoriated tungsten as filament material.

Prickett (1965) designed a high temperature single crystal texture camera diffractometer for use with either film or Siemens horizontal diffractometer. The sample is heated in vacuum by an ion beam to temperatures as high as $2500°$ C.

4. *Radiation focusing or thermal imaging techniques*

Crystal temperatures of more than $3000°$ C can be obtained by focusing on the crystal the radiant energy from an incandescent lamp or a carbon

are situated at one focus of a semi-ellipsoidal or double-parabolic reflector. The sample is situated at the second focus, intercepting the maximum radiation flux. The temperature of the heated object can be controlled by switching in and out of a resister in series with the lamp.

Radiation focusing devices have, in principle, a number of advantages over the other methods applicable in the range 1000–3000° C range. One is that, they permit experiments to be carried out under extremely pure conditions, or in strongly oxidizing or deducing atmospheres—chemical conditions not easy to produce with more conventional heater techniques. This particular advantage arises because the sample is completely isolated from the heating source and except for the radiation falling on it, disturbing electric fields and reactive furnace elements are excluded. The utilization of this method for high temperature X-ray diffraction work so far has been very limited (Baron, 1962; Kruh 1959; Hatt, Kent and Williams, 1960; Maust and Warnke, 1962). Recently, Osamu Kamada *et al.* (1971) have made use of solar energy in construction of a high temperature diffractometer, for study of oxides up to 2150° C. Considering the advantages mentioned above the method of radiation focusing merits a more extensive application.

5. *Gas heating*

The sample is heated by passing a continuous stream of hot air or gas, pre-heated in a suitable furnace. If the gas is N_2 or He, in addition to heating, it protects the sample from oxidation effects. This method can be easily adapted to ordinary Weissenberg cameras without any water-cooling problems up to 250° C. Quareni (1969) has employed this method with a Weissenberg diffractometer a maximum working temperature of 900° C. The hot air, heating the crystal is driven back by means of a porcelain crucible mounted on the base of the crystal goniometer head, thus preventing the heating of the goniometer. Smyth (1972) has recently used this technique with a Picker four circle goniostat up to working temperature of 1000° C.

6. *Flame technique*

In this method, the sample is directly heated by a fine flame of oxy-acetylene jet issuing out of a nozzle. It is perhaps the simplest method of obtaining very high sample temperatures (1000–3000° C) in an ordinary laboratory. The crystal temperature is changed by regulating the flow of oxygen with suitable needle valves and pressure regulators. The temperature distribution inside an oxy-acetylene flame is spread over 1000 to

3000° C. Therefore, the temperature of the sample can also be varied by altering its position inside the flame. This method is unsuitable for crystals that are chemically active in oxidizing atmospheres. Flame heating has been adapted for both precession cameras (Gubser, Hoffmann and Nissen, 1963) and Weissenberg photography (Viswamitra and Jayalakshmi 1972).

Modern research in high temperature technology is producing an ever-increasing number of new and interesting refractory materials. Detailed single crystal analysis at high temperatures, which has not been done so far, can contribute significantly to a better understanding of these materials—coordination in crystal structure, thermal vibrations, and electron densities in atoms and hence the ionization state of the atoms and the nature of chemical binding at elevated temperatures. There is, therefore, a particular need for high temperature devices which permit these investigations above the melting point of the platinum. Admittedly, the flame technique does not provide for experimentation under highly controlled conditions of temperature and atmosphere. The paucity of single crystal X-ray data at high temperatures and simplicity and inexpensiveness of the technique, however, make the flame approach for getting these temperatures profitable particularly in ordinary X-ray laboratories, even though the information obtained may be of limited nature.

7. *Thermoelectric heating*

Horne, Croft and Smith (1959) have devised a thermoelectric furnace (maximum temperature about 70° C) for X-ray diffraction work on a Norelco diffractometer. The powdered sample is pasted on to a copper plate having two cavities for a *p*-type semiconductor (BiTe doped with Sb) and an *n*-type thermoelectric element (BiTe), which form the two legs of a single thermoelectric couple. The temperature increase or decrease of the copper plate is affected by passing a current in opposite direction through the couple. The power is supplied from a 6 volt battery. Thermoelectric furnaces have the advantage that they permit studies below and above room temperature without any changes in the experimental set-up. However, the maximum temperature obtainable with the method in practice is highly restricted.

3. TEMPERATURE MEASUREMENT, CALIBRATION AND CONTROL

Temperature measurement

The most common method of measuring the sample temperature involves the use of a thermocouple either in contact with or placed a few mm away

from the sample. The thermocouple wires should be as thin as possible, consistent with the mechanical strength, so as to reduce the heat loss through conduction along the wires. When the thermocouple is mounted only on one side of the sample, it provides an unsymmetrical path for heat withdrawal leading to temperature gradients particularly in low heat capacity furnaces. Ring-shaped thermocouples on either side of the sample have been employed to reduce the gradients to minimum (Basinski, Pearson and Christian, 1952).

The primary factor in the choice of a thermocouple for a given temperature range is the thermoelectric e.m.f. produced in that range. The most satisfactory thermocouples from this viewpoint are chromel-alumel thermocouples up to 900° C, Pt-Pt/13% Rh thermocouples up to 1600° C and Pt 20% Rh *vs* Pt 40% Rh up to 1800° C. Using an alloy on both legs increase the thermocouple strength at high temperatures. The thermocouples for measuring temperatures beyond the platinum point are based on Mo, Re, W and Ir and their alloys. Molybdenum *vs* rhenium can be used in vacuum, reducing or neutral atmospheres up to 1900° C and tungsten *vs* iridium thermocouples up to 2100° C in inert gas atmospheres.

For the measurement of temperatures beyond 2000° C (up to 2800° C) in reducing atmospheres, W and Re thermocouples appear to be the most promising (Harper, 1969). Le Mont Sci. Co. has developed recently a ceramic-refractory metal thermocouple based on W3Re-W25Re for use in oxidising, reducing, inert or corrosive environment. Information on long term reliability and reproducibility of temperatures with these thermocouples is not available. A serious restriction on any extensive use of W-Re thermocouples in the very high temperature range arises from the lack of suitable materials for protection and insulation.

Optical pyrometry

This provides a convenient method for measuring temperatures in the range 1000 to 3000° C. Properly calibrated optical pyrometers can provide an accuracy of 4° C at the gold point, 6° C at 2000° C and 40° C at 4000° C (Kostkowski, 1959). The two major sources of error in visual pyrometry connected with photoelectric matching and the mean effective wavelength can be reduced significantly by the use of photoelectric optical pyrometers as the photomultiplier tube is more sensitive than the eye and can discriminate between smaller differences of radiance. The pyrometer method has a decided advantage in devices where the sensing element cannot be brought to the sample.

Temperatures in the range from room temperature to 300° C could be estimated by using colour crayons and small thermisters (Lefkowitz and Megaw, 1963).

Temperature calibration

The temperature calibration of the high temperature X-ray devices is done using the following methods: 1. Power input, 2. Melting point, 3. Phase transition point and 4. Thermal expansion of internal standards.

1. *Power input.*—In this method, the power input *vs* temperature curve is plotted by noting the temperature of a pre-calibrated thermocouple in the same position, as a function of the power consumed by the furnace. The method is not suitable for very low heat capacity furnaces as the substitution of the thermocouple is likely to alter the experimental conditions. It is preferable, therefore, to draw the power *vs* temperature curve by placing, instead of the thermocouple, standard specimens in the sample position, and observing their melting points. With the prolonged use of a furnace, a recalibration of temperature is necessary because of changes in furnace resistance.

2. *Melting point.*—In this method, the thermocouple is placed in the vicinity of the sample and is calibrated *in situ* by observing the melting of standard specimens located at the sample position. The common melting point standards are: Al (660° C), Ag (960° C), Au (1063° C), Ni (1453° C) and Pt (1769° C). Exact melting points of these are somewhat difficult to decide visually as these materials are opaque and in addition, the melting of some of these can be observed only in selected atmosphere. It has been found more convenient to use transparent substances such as *p*-nitro toluene (54° C), naphthalene (80·2° C, urea (132·7° C), succinic acid (185·2° C), potassium chlorate (368·4° C), cadmium chloride (568° C), sodium tungstate (698° C), potassium bromide (730° C), potassium chloride (776° C), sodium chloride (801° C) and alumina (2045° C). When these substances are transparent and also non-cubic, they have the additional advantage that any temperature gradient in the sample could be accurately assessed by observing their differential melting through crossed polaroids (Viswamitra and Jayalakshmi, 1970).

Above the alumina temperature, the melting point of the following ceramic oxides could perhaps be employed: Y_2O_3 (2376° C), ZrO_2 (2706° C), HfO_2 (2753° C) and ThO_2 (3050° C). As there are differences in the melting

point data of these oxides obtained by different investigators, they could be used only as rough estimates of the temperature.

Thermocouple calibration can also be done by noting down the disappearance of diffraction lines of the standard substances on melting. The method is more suited to diffractometers than for cameras in view of the long exposures needed for photographing the lines at various temperatures. Presence of small temperature gradients cannot also be easily observed in this method.

3. *Calibration using known transition points.*—This method at present is of limited applicability due to lack of materials with reliable transformation temperatures. Mckinstry (1970) has recently suggested the following polymorphic transition points for possible calibration by this method: AgI ($146 \pm 1°$ C), NH_4Cl ($186°$ C), SiO_2-Cristobalite-3C ($268 \pm 2°$ C), $KClO_4$ ($300°$ C), CsCl ($479°$ C), Na_3AlF_6 ($562°$ C), quartz ($573°$ C), K_2SO_4 ($583 \pm 2°$ C), WO_3 ($770°$ C), $PbWO_4$ ($877°$ C), $BaSO_4$ ($1180°$ C), $CaSO_4$ ($1194°$ C).

4. *Calibration by internal standard.*—Next to the melting point method, temperature calibration against the known lattice expansion of materials has been most widely employed. The most suitable substances are MgO ($1400°$ C) and Pt ($1700°$ C). Ag and quartz have also been used up to $800°$ C and $1200°$ C respectively (Wilkinson and Calvert, 1963; Yannaquis Regourd, Ch. Mazieres and Guinier, 1962). The accuracy of the temperature obtainable with the method is mainly limited by the accuracy of the X-ray instrument in the measurement of Bragg angles. In order to obtain an accuracy of $\pm 1°$ C, diffraction angles must be measured to $\pm 0.002°$ in 2θ. In most of high temperature cameras the accuracy at high temperatures is usually $\pm 0.01°$ in 2θ, which limits the high temperature accuracy to about $5°$ C (Campbell, 1967).

Temperature stability and control

The primary factor in temperature stability of a high temperature device is the constancy of power input in case of the resister furnaces. A constancy of $\pm 5°$ C at elevated temperatures can be easily achieved in vacuum furnaces, using electronic stabilizer power supply without any additional automatic control unit (Johnson, 1954). Temperature constancy of $\pm 10°$ C can be maintained by heating the furance in air by direct current supplied from a battery which is kept charged simultaneously, at a slight higher current than the discharge current through the heater (Viswamitra *et al.*, 1970). Brumberger and Alexandropoulos (1967) have reported a constancy of

± 0·05° C with their wire wound furnace, using system of two windings one inside the other with different power consumptions. The outer one is used to maintain the sample at about 5 to 10° C below the desired temperature with a constancy of ± 1° C. The second controls the temperature at desired level to ± 0·05° C.

For automatic temperature control two types of controllers, *viz.*, on-off and proportionate have been used. Simple on-off controllers are controllers not suitable for low heat capacity furnaces on account of the problem of 'hunting the temperature' due to the thermal inertia and thermal lag of the controllers.

In proportionate controllers, used for high temperature work, usually a thermocouple is used as the sensing element. The thermo e.m.f. is held to the set operating point by a proportioning device (usually a reference setting potentiometer circuit) that supplies a corrective signal to the on-line power device supplying power to the heater. If the e.m.f. becomes un-equal, the controller rapidly and continuously restores the equilibrium feeding back the heat-power proportional to the temperature deviation.

Mckinstry (1970) has devised a low-thermal gradient high temperature resistance furnace with a controller modelled after Strong (1938) and Mueller *et al.* (1946). With this controller, the temperature is held constant over-night with changes less than 1/4° C. A control circuit capable of maintaining temperature constant to ± ·01° C indefinitely has been devised by Lynch and Morosin (1971). The voltage corresponding to the desired temperature is set on the potentiometer and difference between this and thermocouple voltage is fed to the null detector. The Current Adjusting Type controller maintains a constant output at null condition, but when input is disturbed, either by resetting the set point or by fluctuations in the thermocouple temperature, the thermocouple voltage creates on-off signal and controller adjust the heater current accordingly. The output of C.A.T. controller is matched to a programmable power supply through an amplifier. This temperature controller has been reported for their furnace which could be used in the range from room temperature to at least 1000° C.

N. Bett and A. M. Glazer (1972) have devised a three-term temperature controller and programme drive unit. With this type of equipment the temperature can be held constant to within ± 1/4° C for long periods of time and can be raised or lowered smoothly at rates between 2·5° C h⁻¹ and 1·6° C S⁻¹. In this controller a voltage corresponding to the thermo-couple e.m.f. is fed to a chopper amplifier of fixed gain, in series with that

from the thermocouple together with a cold junction compensation e.m.f. The derivative and integral stages which are placed parallel and are summed by a DC amplifier of variable gain, by means of which the width of proportional band is adjusted; this is then connected to a controlled dc stabilizer using power transistors. In order to vary the temperature automatically and smoothly, a motor-driven helical potentiometer is used which controls the reference potential.

Resister heating below 1000° C permits accurate control of sample temperature and also a proper assessment of temperature gradient in the sample. In the range 1000–3000° C, however, the same degree of accuracy assessment is difficult, irrespective of the method employed to heat the sample. The problem seems to be not one of accurate instrumentation but of proper understanding of temperature gradients and thermal conditions prevailing at the heated sample.

4. SPECIMEN HOLDERS AND ADHESIVES

The specimen holders have been of various types and shapes depending on the material and its form and on the furnace design adapted. The common specimen holders are: platinum and tantalum dishes, silica capillaries, ceramic embedded platinum foil, rhenium trough or boat. The thermocouple boat itself has been used in the form of tongs for holding small single crystal specimens (Hania, Kucer, Medved and Pluhar, 1970; M. Czank and E. Kleber, 1971).

Recently, the Uranium Carbide Corporation has been marketing boralloy, a pyrolytic boron nitride which is a non-toxic and easily machinable material. Its excellent thermal shook resistance, chemical inertness and insulating property and low X-ray absorption make it a very desirable material for sample holders and also for thermocouple protection and furnace support.

As far as adhesives are concerned, organic adhesives are normally satisfactory only at low temperatures. However, some of the organics like Canada balsam retain sticking property up to as high as 1000° C although they decompose at much lower temperatures (*International Tables*, Vol. III, 1962). The silico-phosphate dental cements, Harvaridid 52 (R. and H. Harvard Detal Ger, Berlin) and Petralit (Dental Fillings Limited, England) have been found good up to 700° C. The autostic ceramic cement of brushing viscosity (Carlton Brown and Partner Ltd., Staffordshire, U.K.) has excellent properties like withstanding severe reverse stresses and chemical inactivity

in the range $-180°$ to $1200°$ C (Viswamitra and Jayalakshmi, 1970). The ceramic cement " 250 " by Haldenwanger Co., has been used up to $1800°$ C and for still higher temperatures the " 1000 F " (very pure alumina) is recommended (Gubser, Hoffman and Nissen, 1963).

5. POSSIBLE DEVELOPMENTS IN THE HIGH TEMPERATURE X-RAY DEVICES

Resistance heating

The main appeal of resistance heating devices is that they can be designed to get highly uniform temperature regions, with temperatures accurately controlled and measured. Extension of this method to much higher temperatures than reached at present is desirable. Many refractory oxides like ZrO_2, ThO_2 and their mixtures, which are insulators at room temperatures, become conducting at elevated tempeatures. Sample holders, made of these materials, could first be heated to about $1500°$ C using supplementary source of heat in the form of external platinum winding, after which their own resistance could be used for ohmic heating. This may perhaps provide most reliable means of reaching temperatures of the order of $2000°$ C in oxidizing atmospheres.

The high temperature investigation of refractory oxides, carbides and nitrides is of theoretical as well as technological importance. X-ray diffraction study of these materials could be done up to their melting points by straight heating of their samples by an internal current as their self-resistance at temperatures close to their melting points is low. As mentioned in last paragraph, a pre-heating of these up to about $1500°$ C, using an auxiliary outer furnace is however necessary.

Resistance furnace devices up to $3500°$ C may become practicable with the use of such extremely high melting carbide resisters as tantalum carbide (m.p. $3800°$ C). This possibility depends on the desired shapes being fabricated and made available through current developments in high temperature materials.

Application of lasers

The laser has, over the conventional radiation sources, the advantage that it can deliver an extremely high flux radiation density to a small localized area. The present limitation in the use of available lasers for heating purposes is due to the fact that power is obtainable mostly on a pulsed basis. This, however, should not be a major problem with the current develop-

ment of high power continuous CO_2 lasers. Use of these lasers for high-temperature X-ray diffraction studies warrants serious consideration as this eliminates the upper temperature limit available at present under controlled conditions and atmospheres.

Plasma devices

Many exotic species of molecules like Ag_2, Na_2Cl_2 and Li_3F_3 have been identified at high temperatures by mass spectrometric methods. There is no information on their interatomic distances and structures. Hot gas plasma devices which permit temperatures of the order of 10000 to 20000° C to be attained are likely to find application for the study of these by X-ray and electron diffraction. It must, however, be mentioned that severe experimental problems have to be encountered in the application of this method.

High temperature X-ray diffraction techniques are being increasingly applied for following the kinetics and the intermediate states in chemical reactions. These studies call for very accurate temperature measurement and control. There is virtually unlimited scope for developing these control systems.

REFERENCES

1. Aruja, E., Welch, J. H. and Gutt, W.   *J. Sci. Instr.*, 1959, **36**, 16.

2. Baron, J. L.   ..   Metaux Corrosion-Industries No. 446, 1962, 349.

3. Basinski, Z. S., Pearson, W. B. and Christian, J. W.   *J. Sci. Instr.*, 1952, **29**, 154.

4. Bett, N. and Glazer, A. M.   *J. Phys. E.*, 1972, **5**, 1178.

5. Bragg, W. H.   ..   *Phil. Mag.*, 1914, **27**, 881.

6. Brumberger, H. and Alexandro-poulos, N. G.   *Rev. Sci. Instr.*, 1967, **38**, 1579.

7. Campbell, W. J.   *Hand Book of X-rays.* Edited by E. M. Kaelble, Chapter 13, New York, McGraw-Hill, 1967.

8. Czank, E. and Kleber, E.   *Zeit. Fur. Krist.*, 1971, **133**, S 168-178.

9. Edwards, J. W., Speiser, R. and Johnston, H. L.   *Rev. Sci. Instr.*, 1949, **20**, 343.

10. Goldschmidt, H. J.   *X-ray Diffraction by Polycrystalline Materials*, 1955, Ch. 9, London: The Institute of Physics.

11. Goldschmidt, H. J.   *High Temperature X-ray Diffraction Techniques*, International Union of Crystallography, Commission on Crystallographic Apparatus, 1964.

12. Gubser, R. A., Hoffman, W. and Nissen, H. U.   *Z. Krist.*, 1963, **119**, S 264.

13. Hani, F., Kucera, Z., Medved, F. and Pluhar, E.   *J. Appl. Cryst.*, 1970, 3, 97.

14. Harper, E. A.   ..   *J. Sci. Instr.*, 1969, **2** (2), 807.

15. Hatt, B. A., Kent, P. J. C. and Williams, G. I.   *J. Sci. Instr.*, 1960, **37**, 273.

16. Horne, R. A., Croft, W. J. and Smith, J. B.   *Rev. Sci. Instr.*, 1959, **30**, 1132.

17.   ..   *International Tables for X-ray Crystallography* Kynoch Press, Birmingham, England, 1962, Vol. III.

18. Johnson, J. R,   ..   *J. Am. Cer. Soc.*, 1954, 37, 360.

19. Kamada, O., Takizawa, T. and Sakurai, T.   *Jap. J. Appl. Phys.*, 1971, **10** (4), 485.

20. Kostowski, H. J.   The Accuracy and Precision of Measuring Temperature above $1000°$ K. *Proceedings of an International Symposium on High Temperature Technology*, California, Oct. 6–9, McGraw-Hill, 1959, p. 38.

21. Kruh, R. F.   ..   Private communication referred to by Campbell in *Advances in X-ray Analysis*, 1961, 5.

22. Lang, S. M. and Franklin, E. W.   *Report ARL* 1962, 62–315 (Owens-Ill. Techn. Ctr., Toledo, Ohio), AD 277190.

23. Lefkowitz, I. and Megaw, H. D.   *Acta Cryst.*, 1963, **16**, 453.

24. Lynch, R. W. and Morosin, B.   *J. Appl. Cryst.*, 1971, **4** (5), 352.

25. Matuyama, E.   ..   *J. Sci. Instr.*, 1955, **32**, 229.

26. Maust, E. E. and Warnke, W. E.   *U.S. Bureau of Mines Report*, 1962, **RI 5946**.

27. McKinstry, H. A.   *J. Appl. Phys.*, 1970, **41**, 5074.

28. Mueller, R. H., Garman, R. L. and Droz, M. E.   *Experimental Electronics*, Prentice-Hall, New York, 1946.

29. Perri, J. A., Banks,   *J. Appl. Phys.*, 1957, **28**, 1272.
    E. and Post, B.

30. Prickett, R. L. ..   *Advances in X-ray Analysis*, 1965, **8**, 86.

31. Quareni, S.   ..   *Z. Krist.*, 1969, Bd. 128, S. 294.

32. Schossberger, F. V.   *Hand Book of X-rays*, Edited by E M. Kaelble, New York: McGraw
                          Hill, Chap. 14, 1967.

33. Shaikh, A. M.   *Pramāṇa*, 1973, **1** (4), 204.
    and Viswamitra,
    M. A.

34. Sherwood, E. M.   Metals, Chapter in *High Temperature Technology*, I. E. Campbe
                         (ed.), John Wiley and Sons, Inc., New York, 1956, pp. 17–28.

35. Smyth, J. R.   ..   *Am. Mineral*, 1972, **57**, 1305.

36 Strong, J.   ..   *Procedures in Experimental Physics*, Prentice-Hall, New York, 1938.

37. Viswamitra, M. A.,   *J. Appl. Cryst.*, 1970, **3**, 227.
    Jayalakshmi, K.
    and Kalyani, V.

38. Viswamitra, M. A.   *J. Phys.*, 1970, B 3, 656.
    and Jayalakshmi, K.

39. Viswamitra, M. A.   *Advances in X-ray Analysis*, New York: Plenum Press, 1972, **15**, 548.
    and Jayalakshmi, K.

40. Wilkinson, J. E.   *Rev. Sci. Instr.*, 1963, **34**, 545.
    and Calvert, L. D.

41. Yannaquis, N.,   *Bull. Soc. Franc. Miner Crit.*, 1962, **85**, 271.
    Regourd, M., Ch.
    Mazieres and
    Guinier, A.

BIBLIOGRAPHY OF HIGH TEMPERATURE
SINGLE CRYSTAL X–RAY DIFFRACTION TECHNIQUES

Goldschmidt (1964) has reviewed the high temperature X–ray diffraction devices developed till 1964. This bibliography includes, therefore, mainly those papers which have appeared since then. A few papers published in 1963 have also been included as they were not referred to the earlier review. The present review is confined to only those heating devices which are meant for single crystal X–ray analysis. It follows general pattern of Goldschmidt's review. The order is chronological and data given are: authors, reference, title and brief details. Information has been taken from *Chemical Abstracts* wherever original papers were not accessible.

Symbols:

MT	—	Maximum temperature in °C
TC	—	Thermocouple
OP	—	Optical pyrometer
V	—	Vacuum
G	—	Gas filling
A	—	Application
*	—	Details not accessible; information taken from *Chemical Abstracts*.

BIBLIOGRAPHY

Authors and Reference	*Title of the article and brief details*

1. Robinson, J. M. M. and Flörke, O. W., 1963, *Zeit. Krist.*, **119**, S. 257.

A simple heating attachment for the precession camera. Kanthal, also Pt-(20%) Rh band heating *MT* 1200. Sample cemented on the Pt/Pt–10% Rh *TC*. Air.

2. Gubser, R. A., Hoffmann W. and Nissen, H. U., *Zeit. Krist.*, 1963, **119**, S. 264.

X-ray crystal photographs with Buerger's precession camera at temperatures between 1000 and 2000° C. Extend stemperature of device (1) by replacing resistance heating by butane oxygen open flame. *MT* depends on combustion gas mixture. Sample mounting similar to (1). *A*.: Anorthite ($CaAl_2SiO_8$).

*3. Goldak, G. R. and Goldak, J. A., *Can. Wet. Quart.*, 1964, **3**, 27.

An improved high temperature X-ray diffractometer apparatus with a new type of specimen oscillator. *MT* 450. Oscillating specimen optical alignment. *V* or *G* (He). High precision in lattice spacings of the order of 1 part in 20,000.

4. Prickett, R. L., *Advances in X-ray Analysis*, 1965, **8**, 86.

An ultra high temperature, single crystal texture camera diffractometer. Ion bombardment heating *MT* 2500. Sample in the form of powder, single crystal, wire or rod. *TC. V.* Water cooling.

5. Zubenko, V. V., Krants, B. G. and Umanskii, M. M., *Kristallografiya*, 1966, **11**, 280.

A high temperature camera attachment for an X-ray diffractometer. MO spiral heater. *MT* 1400. Powder or single crystal specimen on a ceramic rod. TC: Pt/Pt-Rh for temperature measurement and control. *V* or *G* (He) ; water cooling.

*6. Ebel, H. and Novak, W., *Acta Phys. Austriaca*, 1966, **24**, 161.

High temperature attachment of X-ray diffractometer. Band heating device. *MT* 1200? TC: Pt/Pt 10% Rh. *V*.

7. Foi, F. F. Jr. and Peacor D. R., *J. Sci. Instr.*, 1967, **44**, 183.

A high temperature furnace for a single crystal X-ray diffractometer. Pt wire wound inside the innermost tube of three concentric alumina tubes. *MT* 1200 to 1300. Specimen mounted in sealed silica capillary. TC: Pt/Pt-13% Rh. Stability $\pm 2°$ C at 1000° C over 24 hours. Air, water cooling. *A*: study of anorthite.

*8. Kuzel, Hans, J. and Kiehne, H., *Neues Jahrb. Mineral Montash*, 1969, 235.

Heating furnace for X-ray diffractometer upto 8000° C. Can be operated in *V* or *G*.

9. Quareni, S., *Zelt. Krist* 1969, Bd. **128**, S. 294.

A high temperature apparatus for Weissenberg and precision diffractometers. Hot air blowing *MT* 900. Temperature control $\pm 3°$ C. Single crystal sintered on to a platinum wire on the Pt/Pt: Rh *TC* ; water cooling.

10. Hanic, F., Kucera, Z., Medved, F. and Pluhar, E., *J. Appl. Cryst.*, 1970, **3**, 97.

X-ray single crystal analysis technique for high temperatures. TC: Pt/Rh in the form of tongs for heating, supporting and temperature measurement. *MT* 1750. Temperature fluctuation about 0·5% ; water cooling.

11. Viswamitra, M. A.,
    Jayalakshmi, K and
    Kalyani, V., *J. Appl.
    Cryst.*, 1970, 3, 227.

    A miniature furnace suitable for X-ray Weissenberg photography up to 1000° C. Split platinum coil mounted on a quartz bracket. Camera mounted vertically. *MT* 1000. Sample in sealed silica capillary. *TC*: Pt/Pt-13% Rh. Thermal gradient 5 to 10° C at 800° C, along the sample, 1 mm long. Air. No water cooling for vertical mounting. *A*: Single crystal structure analysis.

12. Viswamitra, M. A. and
    Jayalakshmi, K., *J. Phys.
    E. (J. Sci. Instr.)*, 1970,
    3, 656.

    A simple miniature furnace for routine collection of intensity data on the Hilger and Watts 190 linear diffractometer. Split platinum coil wound on quartz bracket *MT* 1000. Sample in sealed silica capillary, mounted on goniometer head. Furnace independent of crystal movements. *TC*: two Pt/Pt-Rh 13% on either side across the X-ray gap. Thermal gradient is 5 to 10° C at 800° C, along a sample, 1 mm long. Air. No water cooling or radiation shield, except for covering with mylar. *A*: Single crystal structure analysis.

13. Mckinstry, H. A., *J.
    Appl. Phys.*, 1970, 41,
    5074.

    Low thermal gradient high temperature furnace for X-ray diffractometers. Pt wire internally wound on to two hemispheres. *MT* 1400. Fused silica sample support up to 1000° C and Mullite above 1000 C. Temperature control 0·5° C over 24 hours. *TC*: Pt/Pt-10% Rh. Air or *G*. Forced air cooling. *A*: study of NaCl, SiO_2, GeO_2, $FeAsO_4$.

14. Viswamitra, M. A. and
    Jayalakshmi, K.,
    *Advances in X-ray
    Analysis* (New York:
    Plenum Press), 1972, 15,
    548.

    Flame technique for high temperature single crystal Weissenberg photography (1000–3000° C). Sample heating by oxyacetylene flame. *MT* 3000. Sample fixed on to the goniometer head by high temperature cement. OP. Air. No water cooling or radiation shield. *A*: Single crystal structure analysis.

15. Ulrich Keppler, *Zeit.
    Krist.* 1969, B.d. 130
    S 234–235.

    A heating attachment for Buerger's precession camera. *MT* 500° C. Crystal mounted on a platinum wire using mixture of Al_2O_3 powder and silicate of soda (water glass).

16. Czank, M. and Kleber, E.,
    Zeit. Krist., 1971, Bd.
    133, S 168–178.

    A high temperature furnace for single crystal X-ray cameras. Thermocouple as heating element crystal holder and temperature measuring probe. Supplementary furnace for diffractometry employing Pt-Pt/Rh-10% band heating. MT 1500° C. Temp. fluctuation 20–21° C for 1 mm diameter *TC* and 5–6° C. for 4 mm *TC* at 1500° C. Water cooling to goniometer and supplementary furnace. *A*: Anorthite, eucryptite.

17. Lynch, R. W. and Morosin, B., *J. Appl. Cryst.*,
    1971, 4, 352.

    A hemispherical furnace for high temperature single crystal X-ray diffraction studies. Rhenium wire heater potted in ceramic cement. Furnace employs three concentric beryllium hemispheres to provide vacuum environment and to act as heat reflecting shields. *MT* 1000° C *TC*: Pt-Pt/Rh 13% Temp. control: ± 0·1° C. *V*

    A: Thermal expansion data for eucryptite (Li Al SiO_4), Beryl ($Al_2Be_3S_6O_{18}$) and Aluminium Titanate (Al_2TiO_5).

18. Smyth, J. R., *Am. Mineral,* 1972, 57, 1305.

A simple heating stage for single crystal diffraction studies upto 1000° C. Platinum wire would pyrophyllite furnace. Nitrogen gas heating. *MT* 1000° C. *TC*: Pt-Pt/Rh 10%. Crystal in evacuated silica gas capillary. Temperature constancy ± 10° C. Water cooling, Kapton film covering to the heater assembly. *A*: X-ray intensity data of ferrous-iron pyroxene minerals upto 1000° C.

19. Bett, N. and Glazer, A.M., *J. Phys. E.,* 1972, 5, 1178.

A high temperature apparatus for accurate single crystal and powder X-ray studies. Furnace made of two nichrome coil placed inside a pyrophyllite cylinders. *MT*: 1000° C.

TC: Chromel-alumel mounted on goniometer head. Specimen sealed capillary attached to TC tip. Three term temperature controller and programme drive unit. Temp. constancy ± 1/4° C. Cooling of film cassette by blowing air above 300–400° C. Aluminium foil on inside surface of film cassette. *A*: Phase transition in NaNbO₃. High precision lattice constant and structure determination.

20. Brown, G. E., Shigeho, S. and Prewitt, C. T., *Am. Mineral,* 1973, 58, 698–704.

A new single crystal heater for the precession camera and four circle diffractometer. Heating element is a ZrO₂ cement covered Pt-13% Rh coiled yoke. *MT* 1200° C. *TC*: Pt/Pt Rh 10%. Temp. constancy ± 5° C at 1000° C. Crystal in evacuated and sealed quartz capillary. Kapton film frame to prevent air currents. *A*: Phase transition in lunar and terrestrial pigeonites, structural studies of high pigeonites. Lunar hortonolite, high cummingtonite, tremolite, acmite, diopside, hendenbergite, jadeite, spodumene, ureyite.

21. Shaikh, A. M. and Viswamitra, M. A. *Pramāna,* 1973, 1(4), 204.

A simple heater attachment to precession camera for high temperature X-ray diffraction studies upto 1000° C. Platinum wire wound heater split in the middle for sample insertion and X-irradiation. *MT*: 1000° C. *TC*: Pt/Pt-Rh 13%. Temp. constancy ± 2° C at 550° C. Mylar film covering to film. No water cooling. *A*: Sodium meta-vanadate.

22. Shaikh, A. M. and Viswamitra, M. A., National Conference on Crystallography and Symposium on the structure and conformation of Biological molecules, I.I.Sc., Bangalore, Dec. 26–29, 1974, G1, p. 54.

A High temperature Weissenberg camera for single crystal X-ray diffraction studies. Different types of heating attachments such as platinum wire wound heater, hot air probe. M. T. 1000° C. TC; Pt/Pt-Rh 13% Air, V. or G. Forced air cooling. Aluminium coated mylar covering to film. *A*: Single crystal structure analysis and phase transition.