UNCLASSIFIED

AD ____________

DEFENSE DOCUMENTATION CENTER
FOR
SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION ALEXANDRIA, VIRGINIA

DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DOD DIR 5200.10

UNCLASSIFIED

AD No. 4803
ASTIA FILE COPY

ET
RMC

The Growing of Lead Titanate Crystals and Some of Their Properties

Technical Report 56
Laboratory for Insulation Research
Massachusetts Institute of Technology

December, 1952

2/27/53

THIS REPORT HAS BEEN DECLASSIFIED
AND CLEARED FOR PUBLIC RELEASE.

DISTRIBUTION A
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

THE GROWING OF LEAD TITANATE CRYSTALS AND SOME OF THEIR PROPERTIES

by

H. H. Rogers

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

O. N. R. Contracts N5ori-07801
N5ori-07858

December, 1952

THE GROWING OF LEAD TITANATE CRYSTALS AND SOME OF THEIR PROPERTIES

by

H.H.Rogers

Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

Abstract: Small, high-purity, single crystals of lead titanate were grown from a melt consisting of TiO_2 and an excess of PbO. The preparation of a large single crystal by the Bridgman-Stockbarger method is described. Its subsequent fracturing on cooling is interpreted by visual observation and by X-ray measurements. $PbTiO_2$. The chemical reactivity of $PbTiO_3$ is discussed and data on the thermal dissociation into PbO vapor and by X-ray measurements. $PbTiO_3$ appears to be the only stable compound in the system PbO-TiO_2. The chemical reactivity of $PbTiO_3$ is discussed and data on the thermal dissociation into PbO vapor and solid TiO_2 are given. $PbTiO_3$, as expected, is piezoelectric at room temperature, has the domains characteristic of a ferroelectric substance, and, in addition, undergoes a reversible color change from red to yellow when cooled through the Curie point (ca. 490°C). The density of a cracked crystal, measured at 25°C, proved to be 7.96 g/ml, or 99.2 percent of X-ray density. The birefringence at 25°C has been measured as a function of wavelength (at 5800A, $n_{max.} - n_{min.} = 0.011$).

Introduction

As part of a broad program of research on ferroelectricity,[1)] the present work has been concerned with lead titanate, $PbTiO_3$, a compound analogous in structure to $BaTiO_3$. Particular interest is centered on $PbTiO_3$ because the transition[2, 3)] from the tetragonal to cubic form occurs at 490°C, in contrast to

---

1) A.von Hippel, Rev. Mod. Phys., 22, 221 (1950).

2) G.Shirane, S.Hoshino, and K.Suzuki, J.Phys.Soc. Japan, 5, 453 (1950).

3) G.Shirane and S.Hoshino, ibid., 6, 265 (1951).

the 120°C transition point of $BaTiO_3$. Consequently, $PbTiO_3$ is important for high-temperature applications and small additions are used to raise the transition point of barium titanate ceramics. A difficulty in preparing these ceramics is caused by the high volatility of PbO from the mixture. This is the reason that pure $PbTiO_3$ ceramics are reported as porous and fragile,[3)] and that the permittivity values reported for the $PbTiO_3$ ceramic (50[2)] and 250[4)] at 250°C) do not agree.

Finely powdered $PbTiO_3$ has been prepared by sintering an equimolar mixture of PbO and TiO_2 at 680° - 700°C for 5 to 10 minutes;[5, 9)] the reaction[6)] begins at 360°C and is complete in 40 hours at 375°C. Cole and Espenshied[6)] found that $PbTiO_3$ crystallizes from a melt of PbO and TiO_2 (mole ratio 2 : 1) on cooling.

The phase transition in lead titanate at 490°C has been determined by X-ray,[2, 3)] specific heat,[3, 5)] and dilatometric[3)] measurements. This transition is stated[2)] to be the only one found in the range –170° to 550°C, as determined by permittivity measurements.

X-ray diffraction powder patterns have shown $PbTiO_3$ not to be orthorhombic[6)] at room temperature, but tetragonal[2, 3, 7, 8)] with a = 3.894A, c = 4.140A, and c/a = 1.063.[8)]

The object of the present research was to investigate the growing of $PbTiO_3$ crystals and to study some of their chemical and physical properties.

Preparation of Lead Titanate Crystals

It was decided to investigate the method of Cole and Espenshied[6)] for the preparation of small crystals of $PbTiO_3$. In order to grow crystals from

---

[4)] G.H. Jonker and J.H. Van Santen, Chem. Weekblad 43, 672 (1947).

[5)] G. Shirane and E. Sawaguchi, Phys. Rev. 81, 458 (1951).

[6)] S.S. Cole and H. Espenshied, J. Phys. Chem. 41, 445 (1937).

[7)] St. V. Naray-Szabb, Naturwissen. 31, 466 (1943).

[8)] H.D. Megaw, Proc. Phys. Soc. 58, 133 (1946).

solution, it is necessary either to allow the solvent to evaporate or to cool the solution very slowly. Since PbO is very destructive of ceramics and furnace windings, the latter course is preferable. To restrict the loss of PbO the crucibles were covered. A Cenco electric crucible furnace was modified by the addition of a platinum heater. The temperature of this furnace could be lowered gradually either by a motor-driven Variac which decreased the voltage across the furnace in a linear manner, or better, by a temperature controller which lowered the temperature linearly.

Because of the reactivity of PbO at the melting point (886°C) and above, ceramic materials were found to be unsuitable as a crucible material. Platinum alloy (3.5 percent Rh) crucibles held the melt without apparent deterioration, but unfortunately colored the $PbTiO_3$ black, probably due to the absorption of Rh, while the PbO crystals were unaffected. Pure platinum crucibles did not color the $PbTiO_3$ and appeared resistant to attack from the melt. Although platinum is embrittled[10)] by heating in contact with oxides of lead above 1250°C it was used as a crucible material in the present research.

The most satisfactory method for preparing $PbTiO_3$ crystals from a PbO-TiO_2 melt with PbO in excess, was found to consist of cooling it rapidly from ca. 1300°C to 1040°, (within the crystallizing range) holding it there for 4 hr. and then cooling slowly (ca. 50°/hr) to room temperature. Crystals were obtained as large as 3 x 1.5 x 0.2 mm with all faces at right angles and containing some clear areas. Some clear cubes, which were so small as to appear as specks to the naked eye, were apparently "single domain" crystals, as examination under the polarizing microscope indicated. Crystals above 0.5 mm in any dimension invariably appeared cracked, in addition to having domains.

The addition of 0.5 percent of B_2O_3 to the melt, which had proved useful

---

10) "Notes on the Care and Use of Platinum Crucibles and Dishes," J. Bishop and Co., Malvern, Pa., 1949, p.5.

when growing $BaTiO_3$ from ternary melts,1) resulted in crystals with few domains, less cracks, and larger clear areas, but less regular in external shape. The mixture of PbO and TiO_2 was used in the mole ratio of 3 : 1. However, experiments with a 2 : 1 mixture gave no appreciable difference in results.

The use of the temperature controller in growing $PbTiO_3$ crystals by this procedure resulted in crystals of somewhat poorer quality (cooling rate, 53°C/hr.). It is possible that the slower cooling rate produced by the motor-driven Variac near the Curie point (490°C) was the cause of the better crystals obtained above. Both the PbO and TiO_2 used in these experiments were of Baker's reagent grade. Substitution of higher-purity chemicals did not appear to affect the quality of the crystals.

The $PbTiO_3$ crystals were separated from the excess PbO by boiling them with 10 - 20 percent acetic acid and rinsing with 10 - 20 percent nitric acid to remove a white deposit, probably a basic lead acetate. The yellow crystals were rinsed in distilled water and dried at 110°C. X-ray powder patterns of the product agreed with those given in the literature.6, 8, 11) Chemical analysis showed that the compound was of stoichiometric proportions (anal. found for $PbTiO_3$: PbO, 73.75%; TiO_2, 26.31%; mole ratio, 1.003; calcd. for $PbTiO_3$: PbO, 73.64%; TiO_2, 26.36%; precision, ± 0.3%).

In the preparation of a large crystal of $PbTiO_3$ by the Bridgman-Stockbarger method12) the $PbTiO_3$, used as the starting material, was synthesized from a melt containing PbO in excess, as described above. The PbO and TiO_2 were found by spectroscopic analyses to contain a total of less than 0.1 percent and was no doubt much purer than this, while the $PbTiO_3$ prepared from them was found to be unchanged in impurity content.

A cylindrical platinum crucible, 0.6 dia. x 10.0 cm with a 90° conical

---

11) ASTM Index of X-ray Diffraction Patterns, American Society for Testing Materials, Philadelphia, Pa., June, 1945, p. 44.

12) H. E. Buckley, "Crystal Growth," John Wiley and Son, New York, 1951, p. 77.

end and 0.015 mm walls, was thoroughly cleaned, filled with about 12 g of $PbTiO_3$ and the open end flattened, leaving a hole 0.02 inches. The crucible was inserted in a vertical tube furnace to about 4 mm of the open end. The temperature of the furnace was then raised to 1050°C, the 0.02 inch hole closed by pinching, and a bead fused along the end with a torch for final sealing.

The crucible was lowered into a platinum-wound vertical tube furnace so that it would be in a temperature gradient (Fig. 1) that caused the lead titanate to melt from the tip upward, preventing the entrapment of gas bubbles. After allowing the furnace to come to equilibrium at 1330° overnight, the crucible was lowered at the rate of 1.56 mm/hr. through a temperature gradient of 60°/cm from 1330°, through the melting point at 1280°, and through the Curie point at 490°C. The furnace was then cooled to room temperature, so that the crystal was cooled at a rate not exceeding 12°/hr.

After the platinum crucible was peeled from the crystal, the latter was found to be yellow and nearly opaque, 30 mm long, and in the shape of the crucible. A 3 mm section at the top, separated by a sharp line of demarcation, consisted of dark unoriented grains, presumably containing impurities. The top of the crystal was slightly concave, indicative of a satisfactory temperature gradient. The crystal shows striations (Fig. 2) on two opposite faces, indicating that the crystal had been single before passing through the Curie point and fractured afterward. This is not surprising in view of the 6.3 percent change in axial ratio from 490°C to room temperature, as compared with 1.0 percent for $BaTiO_3$.

Attack of the platinum crucible occurred, causing about 40 percent of the $PbTiO_3$ to be lost. In a second attempt to grow a $PbTiO_3$ crystal, the platinum was attacked to an even greater extent making it necessary to stop the experiment. After peeling the platinum from the crystal, the latter was

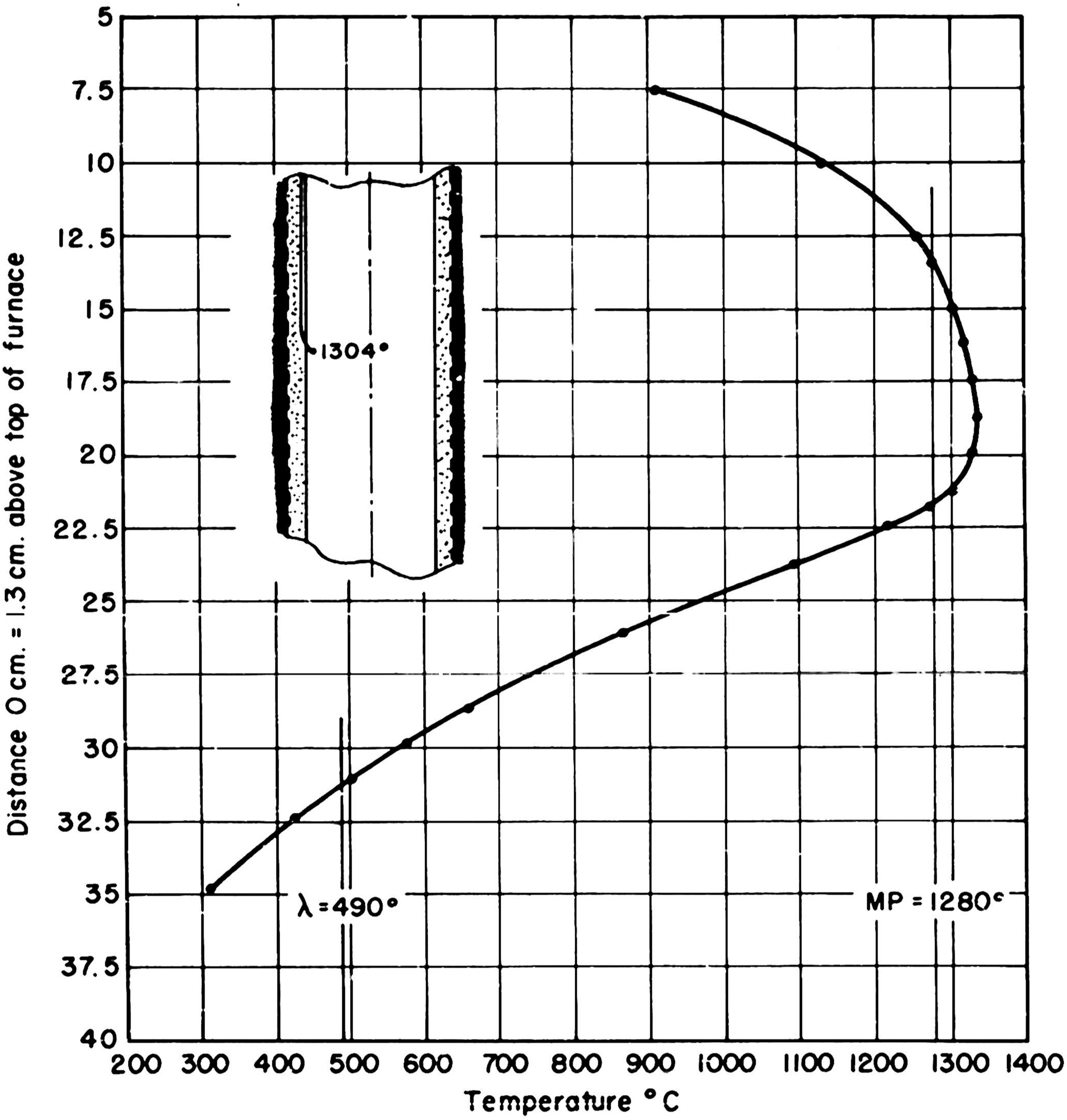


Fig. 1. Thermal gradient of crystal-growing furnace.

analyzed both spectroscopically and chemically, showing it to be identical in composition to the starting material.

Fig. 2. Striations in lead titanate crystal. Mag. 4X.

Chemical Properties

Phase studies

Nicholson,[9)] sintering various mixtures of PbO and TiO_2 at 680 – 700°C for 5 – 10 minutes obtained, by the use of X-ray diffraction patterns, evidence of three compounds only: PbO, TiO_2, and $PbTiO_3$. The preceding crystal growing experiments show that there are no stable compounds of PbO and TiO_2 other than $PbTiO_3$ (in PbO-rich mixtures) at temperatures up to 1400°. By fusing, above 1400°, mixtures of TiO_2 and PbO in mole ratios of 1.4, 2, 3, 4, 5, and 8 to 1, it was shown by X-ray analysis that no stable compounds were formed in TiO_2-rich mixtures. Clear, colorless crystals (up to 5 x 3 x 0.2mm) of the rutile form of TiO_2(identified by X-ray analysis) were obtained by cooling slowly a mixture of TiO_2 and PbO (molar ratio 1.5 : 1) from 1400°C.

A paper by Belyaev and Nesterova[13)] reports the melting diagram of the system PbO-TiO_2, and states that a transition point exists at 19 mole percent TiO_2 at 1024°C. This transition, not apparent in their plot, is ascribed to Pb_2TiO_4, which the authors claim to have crystallized from ternary melts (with V_2O_5) while the compound is said to be difficult to detect in binary melt. No evidence, analytical or X-ray, is given to prove that the crystals are Pb_2TiO_4 instead of $PbTiO_3$ or some compound resulting from a 0.5 percent

---

13) I. N. Belyaev and A. K. Nesterova, Zhur. Obshchei Khim. 22, 396 (1952).

CaO impurity present in their TiO_2.

Reaction with various reagents

Pamifilov et al.[14] found that $PbTiO_3$ is stable in cold H_2SO_4 and in concentrated alkali, is attacked by HNO_3 and by HCl, and decomposed by hot H_2SO_4.

It was found that, at room temperature, the $PbTiO_3$ is stable for at least six days in concentrated alkali, as demonstrated by the lack of a precipitate upon neutralization of the supernatant liquid. However, both concentrated and 20 percent H_2SO_4 attacked $PbTiO_3$. This was indicated by the formation of a white precipitate upon neutralization with aqueous NaOH, the same general method used to detect attack with the following acids. Concentrated HCl attacked $PbTiO_3$ to about the same extent as H_2SO_4 while both concentrated and 20 percent HNO_3 attacked it only very slightly, as indicated by a much smaller precipitate than had been obtained in the case of H_2SO_4 and HCl. Glacial and 20 percent acetic acids were without effect, while fused $KHSO_4$ dissolved it completely.

Thermal decomposition

On heating, $PbTiO_3$ was found to decompose into PbO vapor and solid TiO_2. For a semiquantitative study of the rate of decomposition, the bottom of a carefully weighed 15-ml platinum crucible was covered with approximately 1 g finely powdered $PbTiO_3$. After reweighing, it was placed inside a loosely covered porcelain crucible, heated to a specified temperature for one hour, and cooled. The crucible was weighed and the loss of PbO calculated to be ca. 20% at 1320°C, 5% at 1250°C, 1% at 1170°C, 0.1% at 1060°C, and 0.01% at 950°C (Fig.3).

Melting point

The melting point of $PbTiO_3$ has been reported[15] as 1280°C. This temperature was found to be correct (1281 ± 3°C) by means of a cooling curve; the effect of vaporization of PbO was within the 3°C error.

---

14) A. V. Pamifilov, E. G. Ivancheva, and M. A. Rabkin, Zhur. Priklad. Khim. 11, 398(1938).

15) E. Rudzitis, private communication.

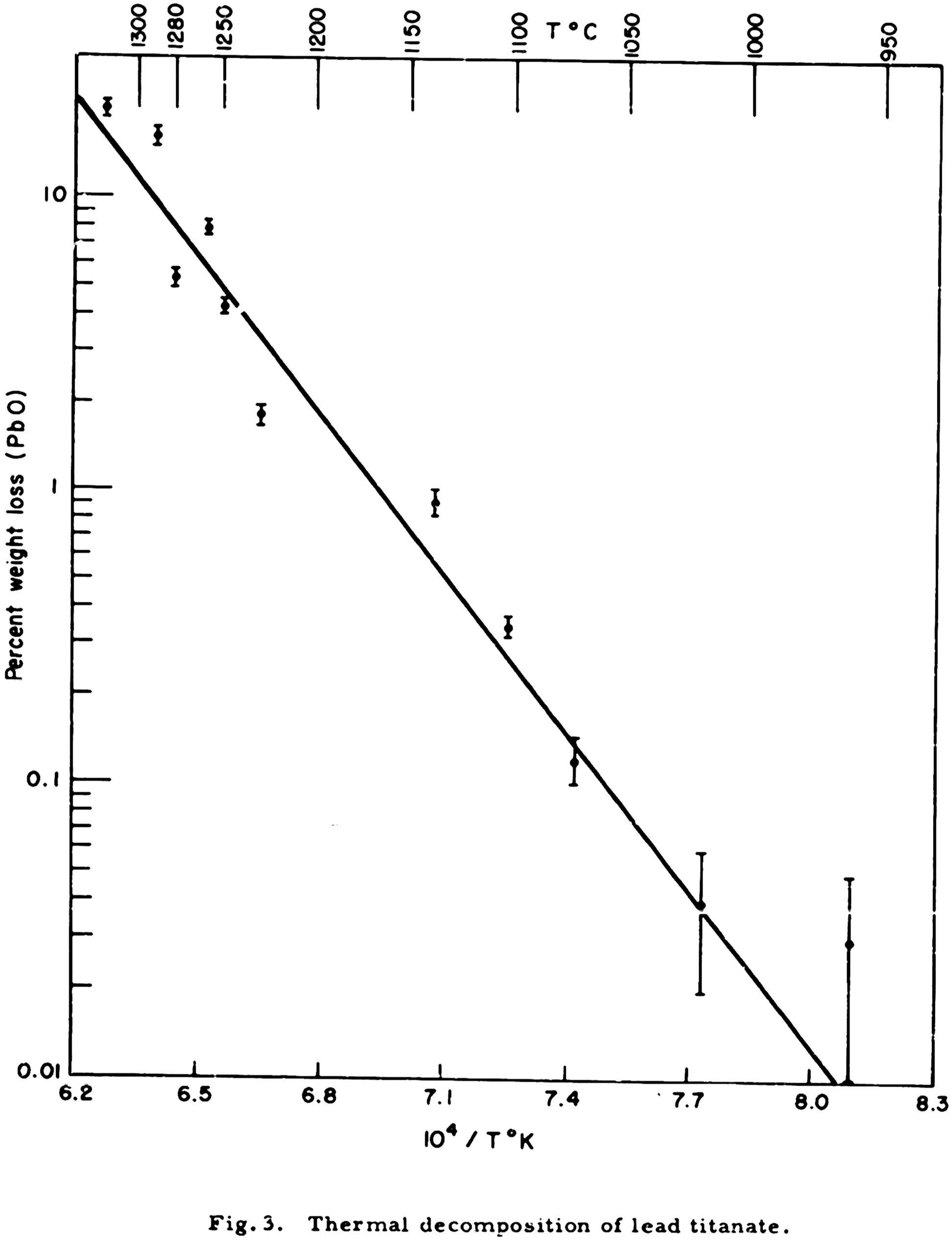


Fig. 3. Thermal decomposition of lead titanate.

Color Change at the Transition Point

A reversible color change from yellow to red was observed in $PbTiO_3$ crystals when heated through the region of the Curie point, a second-order transition at 490°C. The temperature at which the color changed was found to be 491° ± 2°C as indicated by a thermocouple calibrated against the boiling point of sulfur (444.6°C). The uncertainty may be caused by the transition occurring over a small temperature range rather than abruptly. The equivalent color change can also be seen in finely powdered $PbTiO_3$ (yellow to orange), although with more difficulty. It is interesting to note that a similar color change accompanies the first-order transition of PbO at 488.4°C.16)

Piezoelectricity

Examination of a crystal of $PbTiO_3$ with a Giebe-Scheibe piezoelectric detector17) indicates that $PbTiO_3$ is piezoelectric below the Curie point, as expected.

Domains

From microscopic examination, the domain structures of $PbTiO_3$ appear to be similar to those observed in $BaTiO_3$ crystals.1, 18)

Birefringence

By illumination with monochromatic light, interference fringes were produced in a wedge-shaped domain, the distance between the fringes measured, the thickness of the crystal equivalent to a given path difference calculated, and

---

16) J. Barksdale, "Titanium: its Occurrence, Chemistry and Technology," Ronald Press Co., New York, 1949, p. 101.

17) Cf. Prog. Rep. No. X, p. 10.

18) B. Matthais and A. von Hippel, Phys. Rev. 73, 1378 (1948); P.W. Forsbergh, Jr., ibid. 76, 1187 (1949).

the birefringence obtained from a chart.19) The following values of the birefringence were obtained at 25°C: 5800A, 0.011; 5500A, 0.013;, 5150A, 0.014; 4300A, 0.024. The monochromatic illumination was obtained by combinations of Corning glass filters, with a tungsten lamp as the light source.

Studies on the temperature dependence of the birefringence of lead titanate have been made by Forsbergh20) on crystals grown in the present research. He found the birefringence to decrease gradually to one half of the room-temperature value at liquid-air temperature and of the order of one third at liquid-helium temperature. The fact that the decrease in birefringence is gradual indicates that the phase transition at 490°C is the only one that occurs. $BaTiO_3$, in contrast, shows the transition18) from cubic to tetragonal at 120° and, in addition, a transition to orthorhombic at 5° and finally to trigonal at -70°C.

Density

The literature values6, 21) for the density of lead titanate vary from 7.3 to 7.5 g/cm^3. From the unit cell dimensions,7) the theoretical (or X-ray) density22) was calculated as 8.02 ± 0.02 g/cm^3.

The second crystal grown by the Stockbarger-Bridgman method was used, before being analyzed, or a density determination by immersion.23) This experimental density proved to be 7.96 ± 0.01 g/ml^3, or approximately 99.2 percent of theoretical density. The 0.8 percent difference may have

---

19) E.E.Wahlstrom, "Optical Crystallography," Ed. 2, John Wiley and Sons, New York, 1951, p. 104.

20) Cf. Prog. Rep. XI, p. 51.

21) D.W.Robertson, Ind. Eng. Chem. 28, 216 (1936).

22) Annual Conf. of X-Ray Analysis Group, Institute of Physics (England), July, 1946; J.Sci.Instr., 24, 27 (1947).

23) J.Reilly and W.N.Rae, "Physico-Chemical Methods," Ed. 3, Vol. I, Methuen and Co., Ltd., London, 1940, p. 482.

been caused by cracks formed when the crystal cooled through the transition point.

X-Ray Studies on Lead Titanate

The large crystal of $PbTiO_3$ (Fig. 2) was examined by means of the back-reflection Laue method. The crystal was oriented so that the cylindrical axis of the rod-shaped sample was normal to the X-ray beam, and the area of maximum serration exposed to it. It was observed that a corresponding serrated area existed on the opposite side of the crystal. Laue photographs taken of these two areas, 180° apart, bear a mirror-image relationship to each other, indicating that a continuous periodic crystal lattice connects both areas. However, the Laue "spots" are fragmented, showing that the crystal is no longer single, but consists of a large number of small crystals, closely but not precisely oriented. A similar conclusion was drawn from the visual observations, — that the crystal was indeed single above the Curie point, but that it had fractured on passing through the transition.

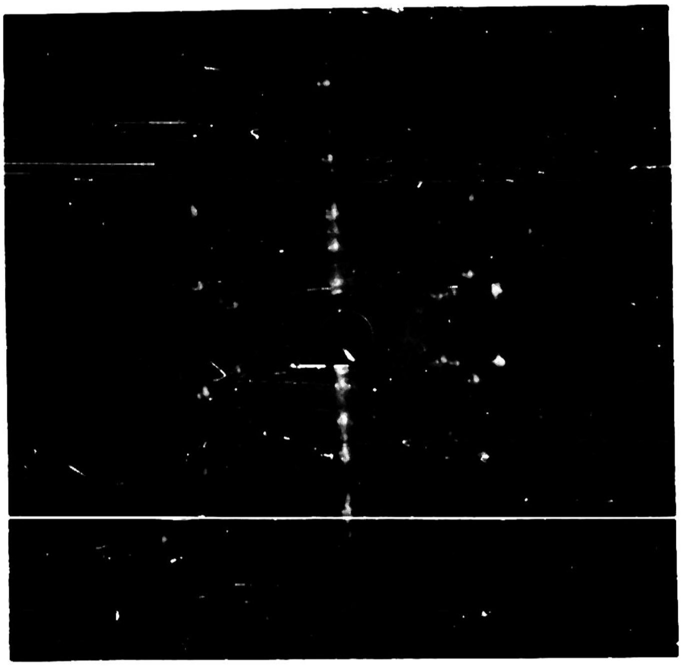


Fig. 4. Laue photograph of lead titanate crystal showing twinning.

The serrated areas are obviously caused by the existence of twinning planes. The crystal was cut along such a plane, polished, and etched. A Laue photograph (Fig. 4) with the beam normal to this surface, identified the plane as (101). The crucial feature of this photograph is the presence of two distinct, identical patterns, displaced 10.3 mm* from each other.** A similar, although smaller, effect was observed[24] in $BaTiO_3$.

The angle between the twins is dependent on the c/a ratio, and in the case of $BaTiO_3$ where c/a = 1.010, the angle is 1.1°. For $PbTiO_3$, where c/a = 1.063, the twinning angle is 7.0°. The observed displacement corresponds to an angle of 6.9°, in satisfactory agreement with this model (Fig. 5).

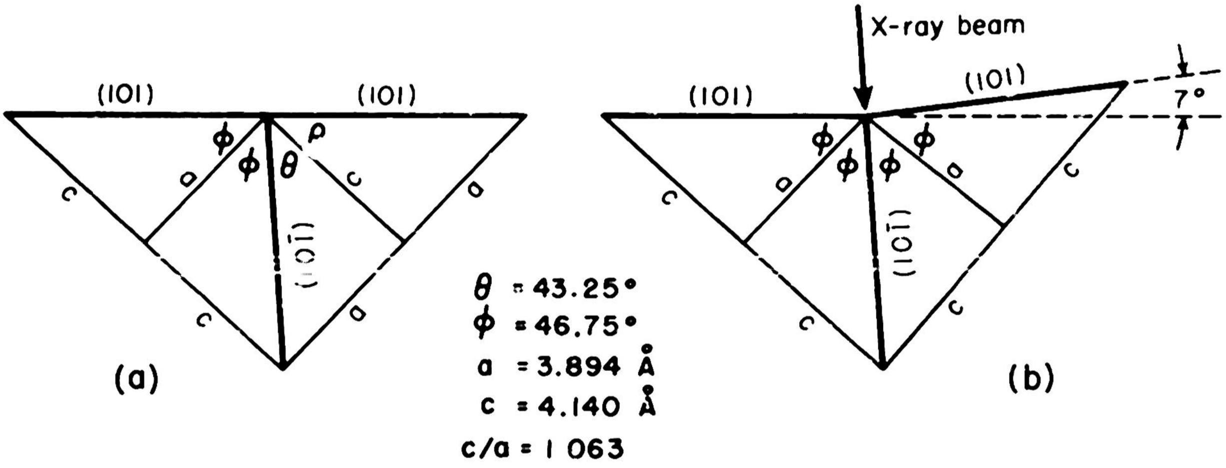


Fig. 5. Schematic view of several lead titanate unit cells, seen normal to the (010) plane. (a) Normal crystal. (b) Twinned crystal.

The Crystal-Growing Furnace

This furnace was designed to allow crystals of $PbTiO_3$ to be grown by the Bridgman-Stockbarger method[11] by lowering a melt of the substance through a thermal gradient. Provision was made for lowering the crucible a great enough distance from the thermal center so that a crucible could pass through the transition point of $PbTiO_3$ at 490°C in a thermal gradient.

The furnace was designed to be taken apart readily in the event that

---

24) E. A. Wood, Bell System Tech. J. 30, 945 (1951).

[*] Crystal to film distance, 43 mm.

[**] We are indebted to Dr. Elizabeth A. Wood, Bell Telephone Laboratories, for giving us her opinion about the X-ray photographs of $PbTiO_3$.

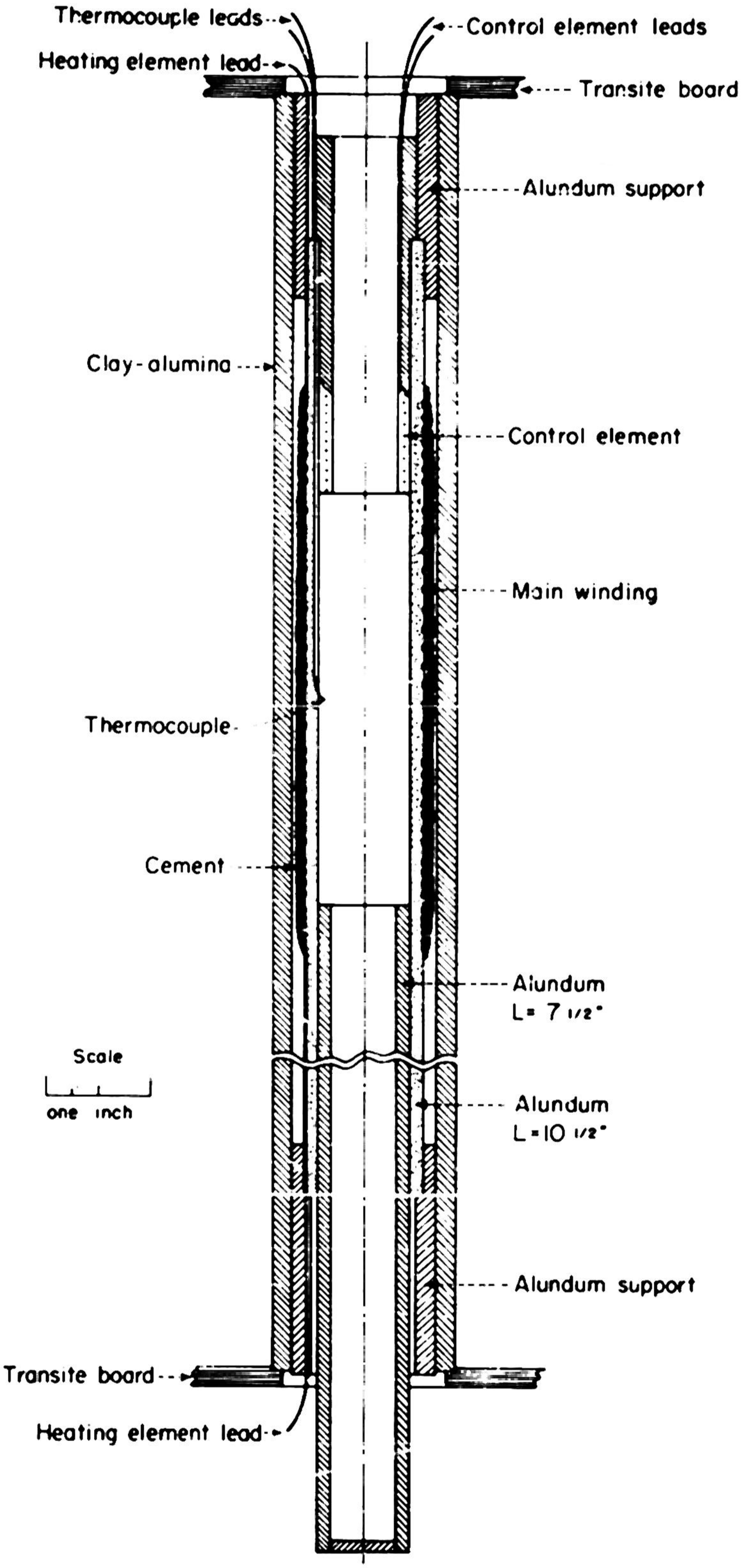


Fig. 6. Details of crystal-growing furnace.

either the winding burned out or lead oxide escaped and damaged the refractory. The parts shown in Fig. 6 were assembled in the 1 3/8 in. i.d., 13 1/4 in. long, clay-alumina tube contained in a firebrick-insulated shell.

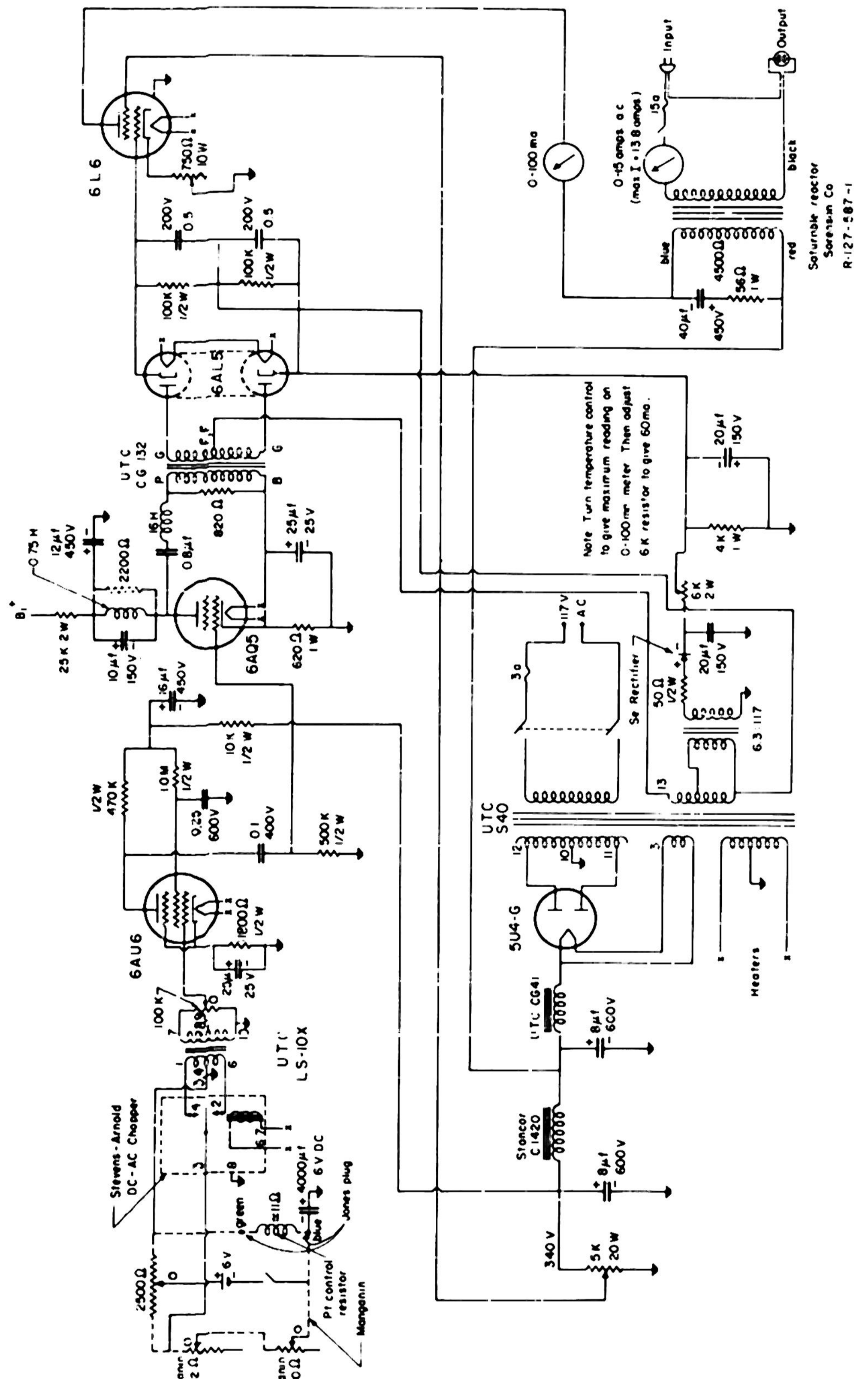
At 58 v and 6.5 amp. the imbedded thermocouple read 1304°C while a thermocouple probe inserted from the top of the furnace gave the readings plotted in Fig. 1.

Temperature Controller

The temperature controller (Fig. 7) controls a maximum of 1500 watts at 230 v a.c. with a load of 15 ohms, or a maximum of 900 watts at 115 v a.c. with a load of 9 ohms. With other than these optimum loads, proportionately less power can be controlled. Tests show the temperature of the crystal-growing furnace was kept constant to better than 0.5° at 1300°C. A motor-driven control lowers the temperature slowly and linearly from the highest temperature of the furnace to the point where the natural cooling rate of the furnace becomes slower than the controller cooling rate (usually 50 - 200°C).

Equilibrium is established between the furnace and the controller in a time dependent on the size of the furnace and the closeness of the sensitive resistor to the winding. It is of course desirable to have the sensitive resistor as near as possible to the furnace winding, but this was not done at a sacrifice in insulation. Any a.c. pickup by the resistor is detrimental to the action of the controller. A tendency towards hunting is minimized by close proximity of the sensitive resistor to the furnace winding.

A platinum resistor was chosen as a temperature-sensitive element because of its greater inherent sensitivity compared with a thermocouple, even though the latter would have been much more convenient in size and simplicity of construction, and would have had freedom from the drift caused



Note Turn temperature control to give maximum reading on 0-100ma meter Then adjust 6K resistor to give 60ma.

FIG 7 CIRCUIT OF TEMPERATURE CONTROLLER

by vaporization of platinum.

The temperature-sensitive resistor is one arm of a d.c. Wheatstone-bridge circuit. A large electrolytic capacitor shunts the resistor in order to short out a.c. pickup which was found to be troublesome. The output of the bridge is chopped to 60 cycle a.c., amplified, and fed into a phase-sensitive rectifier so that the polarity of the original d.c. signal from the bridge may be reproduced. This d.c. signal is amplified and, by means of a saturable reactor, proportionately controls a.c. to the furnace.

Acknowledgment

The author sincerely wishes to thank Professor Arthur R. von Hippel for his advice and generous help, and the staff of the Laboratory for assistance with various phases of the work.