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CRYSTAL GROWTH, ELECTRICAL RESISTIVITY AND LATTICE PARAMETERS OF RuO_2 AND IrO_2

S. R. Butler* and J. L. Gillson
Central Research Department**
Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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ABSTRACT

Chemical vapor transport methods have been used to grow single crystals of IrO_2 and RuO_2 in all silica systems. The morphology of the crystals was generally rod-like; extensive twinning was often observed. The twin plane found in RuO_2 was (301) and in IrO_2 was (101). Lattice parameters were determined at room temperature. Residual (electrical) resistivity ratios ($\rho(300°)/\rho(4.2°)$) from 180 to > 4000 were obtained for RuO_2 and values of ~ 1200 for IrO_2. No simple correlation was found between growth conditions (temperature and atmosphere) and the variations in lattice parameters and/or resistivity ratios.

Introduction

There have been several recent reports (1-4) of the physical properties of RuO_2 and IrO_2. The original discussion of crystal growth was presented by Schäfer et al. (5,6). We report here a study of crystal growth procedures and observed variations in lattice parameters and electrical resistivity of single crystals of these dioxides.

Crystal Growth

The techniques used for crystal growth were elaborations of the methods indicated by Schäfer et al. (5,6). All growth containers were

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* Present address: Materials Research Center, Lehigh University, Bethlehem, Pennsylvania 18015

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fabricated from silica glass, were carefully washed with distilled water, and finally, were dried under vacuum ($< 10\ \mu$ m) at $\gtrsim$ 100°C. The starting materials were oxidized metal "sponge" obtained from Engelhard, (stated $>$ 99.9% pure Ru) and United Mineral and Chemical Co. (stated $>$ 99.9% pure Ir). (See analysis below.)

In one modification of the growth procedure, sealed tubes 10 mm in diameter by 13 cm long, were charged with the powdered oxides, evacuated, back-filled to pressures from 10 torr to 3 atm with oxygen, and sealed. (For pressures above $\sim$ .1 atm liquid nitrogen cooling was employed.) Crystal growth by vapor transport was effected by placing the sealed tubes in a gradient furnace at average temperatures of 950° to 1100°C in temperature gradients from 20° to 60°C. The resulting crystals were generally striated and extensively intergrown, and therefore this method was abandoned.

In a second modification, flowing oxygen was used in a flow system fabricated from silica glass. The system consisted of an 18 mm tube, 130 cm long, with a 15 mm-by 60 cm-long insert (in the hot zone) split into two semi-cylindrical halves along its length. The function of the split inner tube was to facilitate removal of the product crystals, which grow on the inner walls of this tube. The source powder was contained in a morganite Δ RR Al_2O_3 boat. Baffles were inserted in the ends of the tube to suppress convection. The 18 mm tube was equipped at the ends with standard taper joints that connected the inlet end to a monitored source of dry oxygen and on the exit end to a bubbler and final ventilation in a fume hood. The furnace was a 3 zone, 36" long, platinum-wound furnace. The oxides transported from "hot" (source) to "cooler" (growth) zones. The most favorable conditions for producing large crystals ($\sim$1 x 1 x 3 mm) were T_{source} = 1190°C, T_{growth} = 1090°C, and an oxygen flow rate of 17 cc/min, as monitored at room temperature. The temperature distribution in the furnace was such that the axial temperature gradient decreased smoothly from $\sim$5°C/cm in the source region to $\lesssim$ 1° C/cm in the region of optimum growth. The shallow ($\sim$1°C/cm) gradient in the growth region was followed by a rapid temperature drop that occurred beyond the split insert in the area of the convection baffles. Some of the transported material passed into this region, where many small crystals grew in intergrown masses. The duration of the crystal growth runs was 10 to 20 days. Termination was achieved by cutting the flow rate to $\sim$ 2 cc/min and turning off the furnace power to allow natural cooling (overnight). As much as 2 gm of material were transported in $\sim$15 days. The crystals adhered tightly to the glass, but could generally be removed from the insert by tapping. RuO_2 crystals generally grew isolated, and often with a rod-like morphology. Some surface striation and terraced defects were observed. Growth on seeds was nonuniform and resulted in faulted crystals. IrO_2 was often heavily inter-grown and showed less development of clean surface facets.

X-Ray Measurements

Lattice parameters of crystals from nearly all experimental conditions were determined in an effort to establish a characterization of the effects of growth conditions. Crystals were crushed to powder, mixed with a KCl standard (a_o = 6.2931 Å) and patterns were taken with a Guinier-de Wolf camera with CuK_{α_1} radiation (λ = 1.54051 Å). The resulting patterns were computer refined to give the lattice parameters. The parameters so determined are precise to < 1 in 10^4. The results did not show any consistent variation with growth conditions. For RuO_2 the average values at 25°C were found to be

$$a_o = 4.4910 \pm .0003 \text{ Å}$$
$$c_o = 3.1064 \pm .0002 \text{ Å}$$

The spread of values determined was

$$4.4905 \leqslant a_o \leqslant 4.4914 \text{ Å}$$
$$3.1061 \leqslant c_o \leqslant 3.1069 \text{ Å}$$

For IrO_2 average values were

$$a_o = 4.4980 \pm .0003 \text{ Å}$$
$$c_o = 3.1543 \pm .0002 \text{ Å}$$

Back reflection Laue photographs did not show any evidence of streaking even in "crystals" with extensive surface striations. However, crystals were often found with a blade (and/or "Vee", for RuO_2) morphology and were shown to be twinned. For the case of RuO_2 the twin plane was always (301), while for IrO_2 it was (101). The orientation of the major axis of these crystals is shown in Figure 1. The difference in orientation of the twin plane relative to the largest area face of blade crystals is striking, i.e., (301) plane perpendicular to the major "(100)" plane of RuO_2, Figure 1a and the (101) lying in major area plane for IrO_2, Figure 1b. No "Vee" twin crystals of IrO_2 were found, although they frequently occurred for RuO_2 (Figure 1c). However, the characteristic "69 1/2° angle" (between the c axes) was often observed in the morphology of the intergrown masses of IrO_2 whereas the intergrown RuO_2 crystals taken from the baffle region (large temperature gradient) often showed the characteristic "55 1/2° angle".

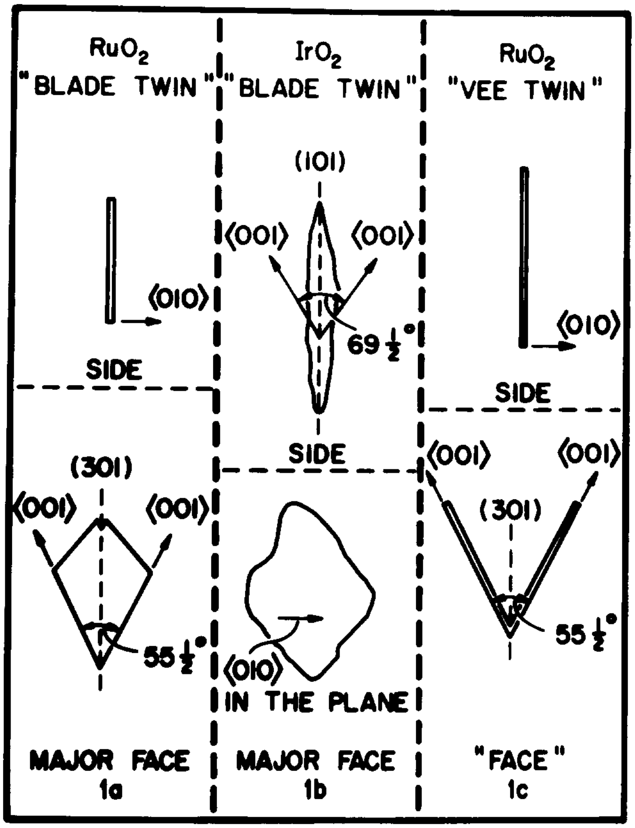

FIG. 1

Morphology and crystallography of growth twins observed for RuO_2 and IrO_2. Twin planes and major axes in the crystals are indicated.

Electrical Resistivity

The electrical resistivity was measured from 4.2 to 300°K by standard D.C. four-probe methods. Indium or indium alloy contacts were ultrasonically soldered to the crystals. Crystals were usually measured in the as-grown condition to avoid effects of damage due to cutting. Since in all cases where an X-ray orientation check was made (RuO_2 only) the rod axis was (001), and since all resistivity measurements were made parallel to the long axis of the rods, it is assumed that all results correspond to resistivity in the c direction. However, this may not be true for IrO_2 due to different growth habit (see below). Some typical results are presented in Figures 2 and 3. The much larger ρ (4.2°K) of the crystal grown in the sealed tube is typical of all crystals grown by this method. The largest residual resistivity ratio (defined as $\rho^{(300°)}/\rho^{(4.2°)}$) obtained for such crystals was 250. For crystals grown in the flowing system, resistivity ratios from 180 to at least 4000* were obtained. Crystals that were grown in sealed systems at low oxygen pressures and subsequently annealed for 27 hours at 1000°C in $>$ 1 atm oxygen showed no significant change in the resistivity ratio. The only correlation

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* Crystals grown by this method and studied in reference 3 exhibited ratios as high as ~10,000.

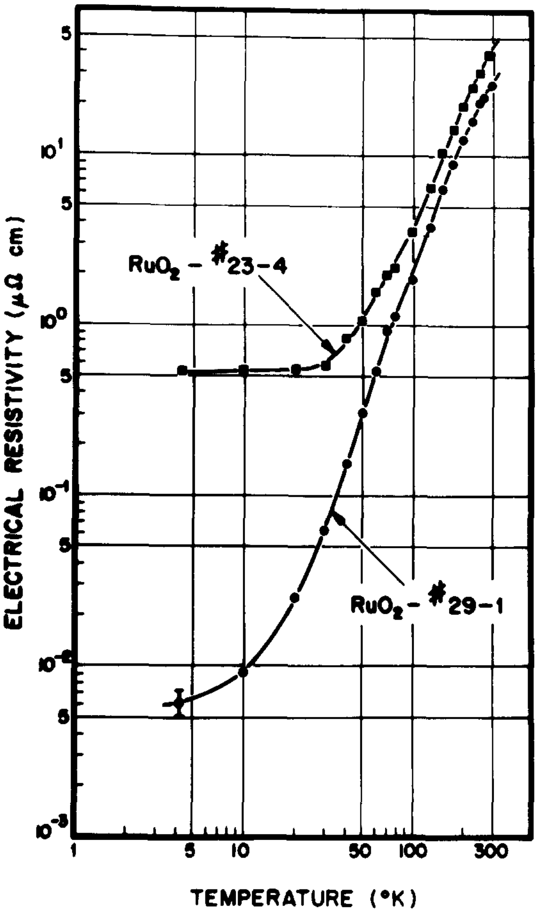

FIG. 2

Electrical resistivity of typical RuO_2 crystals grown in a sealed tube (#23-4, P_{O_2} = 10 torr) and in a flowing system (#29-1, P_{O_2} = 1 atm).

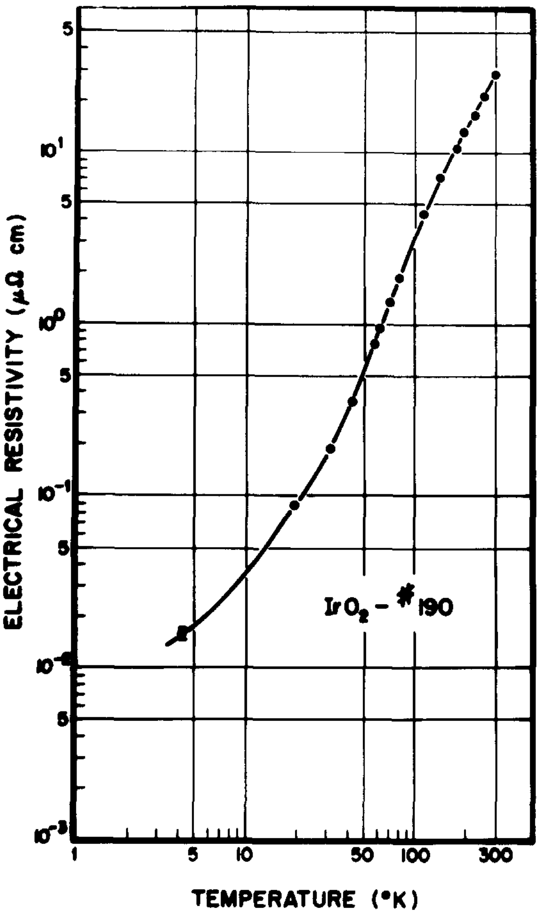

FIG. 3

Electrical resistivity of a typical IrO_2 crystal grown in a flowing system (P_{O_2} = 1 atm).

found between resisitivity ratio and growth conditions was the tendency for crystals grown at high temperatures (~1100°), in low gradients ($\lesssim$2°C/cm), at 1 atm O_2*, and with low flow rates to have higher ratios.

Representing the intrinsic resistivity as in reference 4 by the expression

$$\rho_i(T) \equiv \rho(T) - \rho(4.2°) = \rho_2 T^2 + \rho_3 T^3 \left[J_3^{**}\left(\frac{\Theta_D}{T}\right) - J_3\left(\frac{\Theta_E}{T}\right) \right]$$

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* One growth run in a 10% O_2-in-argon atmosphere resulted in crystals with resistivity ratios in the range 300 to 900.

** $J_3\left(\frac{\Theta}{T}\right)$ is a standard transport integral and tables of values are given in references 10 and 12.

appears to agree with the experimental results for the IrO_2 data (Figure 3) and the high resistivity ratio RuO_2 data (Figure 2). However, the values of the constants ρ_2, ρ_3 must be adjusted even through the values of effective Debye parameter (θ_D) and interband scattering parameter (θ_E) given in reference 4 are satisfactory. Insufficient data were obtained between 1 and 10°K to carefully check for the T^2 temperature dependence.

Chemical Analysis

In order to estimate the effect of impurities on the value of the low-temperature resistivity, semiquantitative, emission spectrographic analyses were made of the starting materials and of a number of the grown crystals. Some typical results are summarized in the table.

TABLE 1

Results of Chemical Analysis (ppm weight)

	RuO_2 Starting Material*	RuO_2 Sealed Tube	RuO_2 Flowing System	IrO_2 Flowing System
Mg	2-10	20-100	10-50	2-10
Al	10-50	25-150	50-150	20-100
Si	100-500	50-250	100-500	50-250
Fe	10-50	20-100	20-100	20-100
Cr	15-74	25-125	25-150	20
Ni	10	100-500	100-500	20

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* No analysis was made of IrO_2 starting material.

From these results the two major elements of concern are silicon and nickel. It seems likely that some small pieces of the silica glass may have adhered to the crystals at its original point of growth from the tube and thus been analyzed with the crystal. However, we have no rationalization for the high nickel values. There does not appear to be a local source for this contamination and the analysis gave the same range for all RuO_2 crystals analyzed.

Another way to consider these results is to compare the relative vapor pressures of oxides of the metals in question under the experimental growth conditions (1100°C, $P_{O_2} = 1$ atm). Schäfer et al. (5) gave the total $RuO_4 + RuO_3$ pressure as 6.8×10^{-4} atm for these conditions. Using the data (7) that can be found for the oxides of the "impurity" metals, it would appear that their vapor pressures are all $\lesssim 10^{-11}$ atm. Since this is about seven orders of magnitude less than the pressure of volatile RuO_x species, it is difficult to rationalize contamination by coevaporation to the levels indicated by the analysis.

The resistivity ratios determined for analyzed RuO_2 crystals were very different depending on their method of preparation, i.e., the sealed-tube sample had a ratio $\sim$200, while the flowing-system sample had a value of $\gtrsim$4000. Since the analyses were very similar it would appear that we cannot use resistivity ratio as an indication of crystal purity. Since no experimental evaluation of structural perfection was carried out, it is possible that "defect" scattering is a significant factor in determining the low-temperature resistivity (currently studies are underway to evaluate possible imperfections present in these crystals).

Discussion

The growth of RuO_2 and IrO_2 crystals suitable for physical property studies is reasonably straight forward using flowing-system methods. The amount of material transport is consistent with the vapor pressure data of Schäfer et al. (5), assuming that all the material vaporized is transported. It would appear that the largest RuO_2 crystals that can be grown without a preferential substrate to suppress random nucleation is $\sim$2 x 2 x 5 mm. Our results for IrO_2 are much more limited, and excessive intergrowth made it difficult to obtain crystals even $\sim$1 x 1 x 3 mm. The frequent occurrence of twins and the layered surface defects suggests layer-spreading as the growth mechanism, with re-entrant twin planes as an important layer source (8). Since limited attempts to find a more suitable single crystal substrate (MgO, Al_2O_3, TiO_2) proved fruitless, control of nucleation would appear to be the most important next step in any experimental attempt to control the growth of these materials. Measurements of crystal lattice parameters were not found to be sufficiently sensitive to be useful in characterizing the variations in crystals produced by different growth conditions (at least to a precision of 1 in 10^4). Electrical resistivity at low temperatures appears to be sensitive to growth conditions, even though we have not been able to show an unambiguous correlation with any one growth parameter. It should be pointed out that the high resistivity ratios are not inconsistent with impurity levels of several hundred ppm. The important quantity is the value of the low-temperature resistivity. Using available data (9) on effects of impurities on the low temperature resistivities of metals, a typical value of $\Delta\rho/\Delta c \sim 1\,\mu\Omega$-cm/% (atomic) seems reasonable. Therefore, with a $\rho^{(4.2)}$ of $10^{-2}\,\mu\Omega$-cm the sample could have 100 ppm impurities and still exhibit a resistivity ratio of $\sim$3000. The effect of interstitials or vacancies is generally much larger (9), so that small deviations from stoichiometry may be important for high resistivity ratios.

The electrical resistivity results presented agree with those of reference 4 insofar as the major temperature dependence is concerned. However, the dependence of the parameters ρ_2 and ρ_3 on residual resistivity ratio and therefore presumably on purity or perfection would imply a violation of Matthiessen's rule (10). The critical test for the appearance of a T^2 temperature dependence (4) between 1 and 10°K should be carried out with crystals with high resistivity ratios such as those prepared by the methods presented here.

The simple band structure suggested for these compounds in a recent paper (11) can not be verified by the results presented here. The agreement with the resistivity expression given above would imply (see reference 4) the data is consistent with a single d-type band. However, the results of the DeHaas-Van Alphen study (3) clearly shows at least two sheets of the Fermi surface with high effective masses.

It appears that further work involving careful characterization of non-obvious defects needs to be carried out before correlations between varying growth conditions and resistivity characteristics can be adequately understood and further fundamental Fermi surface studies undertaken.

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References

1. W. D. Ryden, A. W. Lawson and C. C. Sartain, Phys. Rev. Ltrs. 26A, 209 (1968).
2. C. M. Osburn and R. W. Vest, Bull. Am. Cer. Soc. 47, 354 (1968).
3. S. M. Marcus and S. R. Butler, Phys. Rev. Ltrs. 26A, 518 (1968).
4. W. D. Ryden, A. W. Lawson and C. C. Sartain, Phys. Rev. B1, 1494 (1970).
5. H. Schäfer, G. Schneidereit and W. Gerhardt, Z. Anorg. U. Allgem. Chem. 319, 41 and 327 (1963).
6. H. Schäfer, Chemical Transport Reactions, p. 48. Academic Press, New York (1964).
7. J. P. Elliott and M. Gleiser, Thermochemistry for Steelmaking, Vol. 1. Addesion-Wesley (1960).

8. D. R. Hamilton and R. S. Seidensticker, J. Appl. Phys. 31, 1165 (1960).

9. J. M. Ziman, Electrons and Phonons, p. 335. Clarendon Press, Oxford (1960).

10. F. J. Blatt, Physics of Electronic Conduction in Solids, p. 196. McGraw-Hill, New York (1968).

11. D. B. Rogers, R. D. Shannon, A. W. Sleight and J. L. Gillson, Inorg. Chem. 8, 841 (1969).

12. L. Colquitt, J. Appl. Phys. 36, 2454 (1965).