

Diffusionless Phase Transformations in Zirconia and Hafnia

by G. M. WOLTEN

Materials Sciences Laboratory, Aerospace Corporation, El Segundo, California

A study, by high-temperature diffractometry, of the monoclinic-tetragonal phase changes in pure ZrO_2 and HfO_2 disclosed that the hysteresis loops associated with the transformations have similar shapes which are typical of many martensitic phase changes, but that the widths of the loops differ greatly for the two materials, being about 200°C for zirconia and only 20° to 30°C for hafnia. The temperature-induced transformations are predominantly athermal. The nature of these and similar transformations is discussed. The reversible formation of a cubic form of ZrO_2 above 2200°C was confirmed.

I. Introduction

THE nonquenchable transformation¹ of pure zirconium dioxide from a monoclinic to a tetragonal phase occurs with hysteresis over a temperature interval in the neighborhood of 1000°C , and at any constant temperature within the transformation range the relative proportions of the two phases do not change with time.² In 1958, it was pointed out by the writer³ that this behavior, far from being strange, as often claimed, is typical of the majority of martensite transformations. Although the zirconia transformation may not be martensitic in the strict sense, the kinetic and thermodynamic aspects of martensite transformations seem to hold for many other diffusionless phase changes. From a consideration of the crystal structures involved^{4,5} it is quite clear that the transformation is indeed diffusionless, i.e., all atoms have the same neighbors in either phase.

Apart from some transitions of the paramagnetic-ferromagnetic type, typical martensitelike transformation behavior has been clearly established for very few nonmetallic systems. An investigation of the transformation kinetics in zirconia and in the very similar hafnia should add to the knowledge of this phenomenon in ceramics. A high-temperature diffractometer was chosen for this investigation because this device permits each phase to be unambiguously identified and its concentration to be measured as a function of temperature. Electrical resistivity versus temperature measurements, often employed in the case of metals, do not readily lend themselves to ceramic systems, and the desirable high-temperature petrographic investigation of the transformation behavior of single crystals is best preceded by the mapping of the hysteresis loop as carried out in this investigation.

II. Experimental

(1) Diffractometer

A Materials Research Corporation's high-temperature diffractometer attachment, model X86-G, was used in conjunction with a conventional 4-in. vacuum system and a General Electric XRD-5 diffractometer. Nickel-filtered

copper radiation was used. The combination heating element and specimen support used in the diffractometer furnace was a ribbon of platinum-rhodium alloy for the zirconia transformation study. For studying the hafnia transformation and for observing the tetragonal-cubic transformation of zirconia, some of the heaters were made of tungsten foil 0.0015 in. thick and some were of rhenium foil 0.002 in. thick.

(2) Temperature Measurement

A noble metal thermocouple was welded to the rear surface of the heater ribbon and the heater's edge and front surface were observed with an optical pyrometer through a window and prism. Optical pyrometer readings of a fold at the heater's edge agreed with the readings of the thermocouple. Since the window and prism transmitted only 84% of the radiant energy, the thermocouple temperatures must also have been too low. This observation is not surprising in view of the steep temperature gradient along the thermocouple wires immediately behind the hot junction. At all temperatures in the red heat range, the surface of the specimen was visibly darker than the heater itself, apparently to a greater degree than the difference in emissivities would have justified, and optical pyrometer measurements of the front surface of the specimen confirmed the existence of a temperature gradient through the thickness of the specimen. Since the diffracted X-ray beams arise in the top layer of the specimen at an average depth of 0.05 mm or less, the temperatures measured optically on the specimen surface were taken to be most representative of the true temperatures associated with the observed diffraction patterns. Because optical temperature measurements tend to show more scatter than thermocouple measurements, the optical pyrometer temperatures of the specimen surface were plotted against the thermocouple temperatures and a smooth curve drawn through the points. This curve provided cor-

¹ W. A. Lambertson and M. H. Mueller, "Uranium Oxide Phase Equilibrium Systems: III, $\text{UO}_2\text{-ZrO}_2$," *J. Am. Ceram. Soc.*, **36** [11] 365-68 (1953).

² (a) A. Dietzel and H. Tober, "Über Zirkonoxyd und Zweistoffsysteme mit Zirkonoxyd" (Zirconium Dioxide and Binary Systems with Zirconia as Component), *Ber. Deut. Keram. Ges.*, **30** [3] 47-61; [4] 71-82 (1953); *Ceram. Abstr.*, **1954**, January, p. 23a.

(b) H. J. Goldschmidt, "Selected Applications of High-Temperature X-Ray Studies in the Metallurgical Field," pp. 191-211 in *Advances in X-Ray Analysis: Vol. 5—Proceedings of the Tenth Annual Conference on Applications of X-Ray Analysis*, August 1961. Edited by W. M. Mueller. Plenum Press, New York, 1962. 564 pp.; *Ceram. Abstr.*, **1963**, February, p. 60j.

³ G. M. Wolten, "Solid-Phase Transitions in the $\text{UO}_2\text{-ZrO}_2$ System," *J. Am. Chem. Soc.*, **80** [18] 4772-75 (1958).

⁴ Otto Ruff and Fritz Ebert, "Beiträge zur Keramik hochfeuerfester Stoffe: I, Die Formen des Zirkondioxyds" (Ceramics of Highly Refractory Materials: I, Forms of Zirconium Dioxide), *Z. Anorg. Allgem. Chem.*, **180** [1] 19-41 (1929); *Ceram. Abstr.*, **8** [9] 660 (1929).

⁵ (a) J. D. McCullough and K. N. Trueblood, "Crystal Structure of Baddeleyite (Monoclinic ZrO_2)," *Acta Cryst.*, **12** [7] 507-11 (1959).

(b) G. Teufer, "Crystal Structure of Tetragonal ZrO_2 ," *Acta Cryst.*, **15** [11] 1187 (1962).

rections to the thermocouple measurements allowing, after correction for window and prism transmittance and the emissivity of ZrO_2 ,⁶ calculation of true surface temperatures. This procedure also made it possible, by extrapolation, to obtain surface temperatures below the range of the optical pyrometer. Ordinarily, such an extrapolation would be of low accuracy, but two factors probably made it acceptable. Although the plot of corrections versus the thermocouple temperatures had considerable curvature at the higher temperatures, it became almost linear at the lower temperatures and its slope was such that the corrections changed very slowly with temperature. As would be expected, the corrections appeared to be a function of specimen thickness. A precision of $\pm 10^\circ$ and an accuracy of $\pm 20^\circ$ are estimated for the temperature measurements.

The procedures just described were employed to study the monoclinic-tetragonal inversion of zirconia. The thermocouple was omitted when tungsten and rhenium heaters were substituted for the study of the corresponding hafnia transformation and the tetragonal-cubic zirconia transformation. The hafnia transformation and the tetragonal-cubic zirconia transformation did not require extrapolation to temperatures below the optical range and the optical pyrometer was used exclusively. Corrections for window and prism absorption and for emissivity were calculated as before, the emissivity of HfO_2 being assumed equal to that of ZrO_2 .

(3) Phase Equilibrium Measurements

The relative proportions of the monoclinic and tetragonal phases present, at any particular temperature, were measured by scanning over suitable diffraction peaks and measuring their integrated intensities. This was done by drawing a smooth outline of the peak and tracing it with a planimeter. For the monoclinic phase, the sum of the intensities of the 11 $\bar{1}$ and 111 lines was used, and for the tetragonal phase, the 101* line was employed. The intensity of the tetragonal 101 line, when the tetragonal phase alone was present (1160°C in the case of ZrO_2), was taken to represent 100% tetragonal phase and the monoclinic 11 $\bar{1}$ and 111 line intensities were taken to represent 100% monoclinic at temperatures low enough to show this phase exclusively. At intermediate temperatures, when both phases were present, the intensities of the respective peaks were divided by the 100% values, yielding the fraction of each phase present in the mixture. The two fractions usually added up to between 97 and 103% and in the majority of cases between 98 and 102%. The factors that limited the precision to the indicated level were probably grain growth, slight temperature fluctuations, and the Debye-Waller factor (which describes the dependence of intensities on temperature). Because of these factors, it was thought that no significant gain in precision would result from substituting the normally more accurate scaled count of intensities for the recording method used.

(4) Procedure

Measurements of the relative proportions of the monoclinic and tetragonal phases were made during both rising and falling temperatures. Since transition temperatures in diffusionless transformations often show a dependence on the thermal history of the specimen, the specimen was cycled nine times between room temperature and 1200°C (in the case of ZrO_2), with measurements taken during each cycle. Usually the temperature was raised slightly as soon as a reading was completed and the diffraction peaks were scanned at once. In about one out of three such determinations, however, the temperature was held constant for periods from $1/2$ to 2 hours and additional readings were taken before raising the temperature again. This was done to detect a possible isothermal component of the reaction. The analogous procedure was followed at falling temperatures. Between the heating and the cooling portions of the eighth cycle, the specimen was annealed for 3 hours at 1400°C.

Table I. Spectrographic Analysis of Materials

Element	ZrO ₂ * (ppm)	HfO ₂ † Hf 99.5%, Zr 0.47 % (ppm)
Hf	47	
Al	<20	<20
B		‡
Co	<10	<10
Cr	<20	<20
Cu	<20	<20
Fe	<50	<40
Mg	<20	<20
Mn	<20	<20
Mo	<20	‡
Na		<10
Ni	<20	<20
Pb	<20	<20
Si	30	<30
Sn		‡
Ti	<20	<40
V	<20	<20

* Lot No. 4968, The Carborundum Metals Company, Akron, N. Y.

† Lot No. 5072, The Carborundum Metals Company, Akron, N. Y.

‡ Not detected.

(5) Materials

The Carborundum Metals Company's spectrographic grade of zirconia, lot No. 4968, was used. The manufacturer's spectrographic analysis is shown in Table I.

Two grades of hafnia were used. One was the Carborundum Metals Company's spectrographic grade, lot No. 5072, the supplier's analysis for which is also given in Table I. It was of very high purity except for its zirconium content which may have been as high as 0.5%. The other grade of hafnia contained less than 30 ppm of zirconium but was probably not quite as free of other impurities as the first grade.†

III. Results

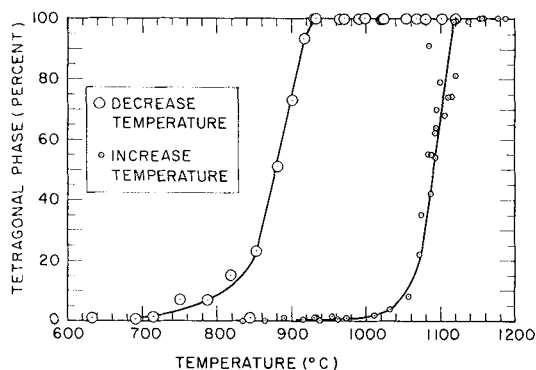
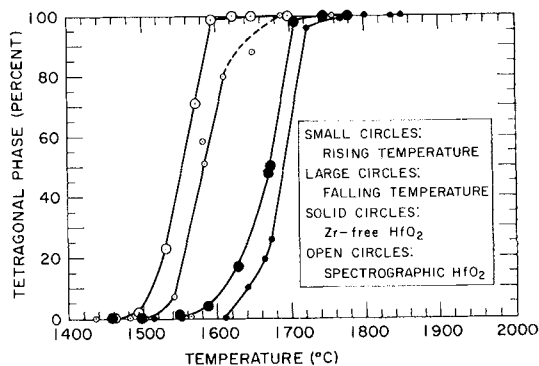
(1) Zirconia

Figure 1 summarizes the results graphically; percentage of tetragonal phase is plotted as a function of temperature. A wide hysteresis loop was observed. The influence of thermal history was observed when the second cycle showed the entire loop shifted about 15°C toward higher temperatures as compared with the first cycle. The subsequent 7 cycles reproduced the second one and disclosed no further changes. The anneal at 1400°C, before the last $1\frac{1}{2}$ cycles, had no effect. Figure 1 is a composite of cycles 2 through 9. Table II summarizes the results and gives the exact numerical values.

⁶ J. L. Margrave, "Data for Radiation Pyrometry," Appendix VII, pp. 372-74 in *Physico-Chemical Measurements at High Temperatures*. Edited by J. O'M. Bockris, J. L. White, and J. D. Mackenzie. Academic Press, Inc., New York, 1959. 394 pp.; *Ceram. Abstr.*, 1960, October, p. 247i.

* This line is usually designated 111 in the literature. Tetragonal zirconia has a quasifluorite structure, slightly stretched in the c_0 direction. Because of this resemblance to the fluorite structure, and because the monoclinic cell can be obtained by distorting a face-centered tetragonal cell, the structure of tetragonal zirconia has generally been discussed in terms of a face-centered cell, on the basis of which the foregoing diffraction line would be indexed as 111. However, any face-centered tetragonal cell can also be indexed as an alternate and smaller body-centered cell, and it is standard crystallographic practice to do so. On this basis, the index becomes 101. The same applies to hafnia.

† This material was prepared some time ago at Iowa State University by H. A. Wilhelm and was made available through the cooperation of F. H. Spedding, director of the Ames Laboratory, at Iowa State University.

Fig. 1. Monoclinic-tetragonal transformation in ZrO_2 .Fig. 2. Monoclinic-tetragonal transformation in HfO_2 .Table II. Monoclinic-Tetragonal Phase Transformation in ZrO_2

Conversion (%)	Forward reaction, monoclinic to tetragonal, with increasing temp. (°C)	Reverse reaction, tetragonal to monoclinic, with decreasing temp. (°C)
10	1055	910
50	1086	878
90	1110	804
Width of hysteresis loop at midpoint: 208°C		

Table III. Monoclinic-Tetragonal Phase Transformation in HfO_2

	Conversion (%)	Increasing temp. monoclinic to tetragonal (°C)	Decreasing temp. tetragonal to monoclinic (°C)
Zr-free HfO_2	10	1642	1701
	50	1690	1672
	90	1718	1610
Spectrographic HfO_2	10	1547	1588
	50	1583	1554
	90	1636	1512

When the temperature was held constant, intensities either did not change or changed so slightly that the effect was ascribed to recrystallization or slight temperature fluctuations. The effect of time at constant temperature was checked both with the X rays on and off to check for a possible effect of irradiation on the transformation. None was observed. It was observed that a trace of the tetragonal phase was retained at room temperature when the specimen was cooled from within the transformation range, but no tetragonal phase was found at room temperature when the cooling started from above the transformation range.

(2) Hafnia

The hysteresis loops for the two grades of hafnia employed in this work are shown in Fig. 2 and summarized in Table III.

There is a considerable difference between the mean transformation temperatures of the two grades of hafnia. The higher of the two, found for the low-zirconium hafnia, agrees quite well with rather qualitatively stated inversion temperatures in the literature.⁷ The lower inversion temperature for the spectrographic hafnia is less likely to be connected with its zirconium content than with its high purity with respect to other constituents. The difference in the widths of the hysteresis loops at midpoint, 18° and 29° respectively, is probably within experimental error and also within the variability usually encountered because of differences in thermal history and purity.

IV. Discussion

(1) Background

A diffusionless transformation is, by definition, one in which atoms do not move past their neighbors, i.e., the displacement of atoms due to the transformation is less than an interatomic distance. The new crystal structure is a distorted version of the old one.

One important consequence of the diffusionless character of a phase transformation is the fact that compositional changes cannot occur. The material undergoing the transformation need not be a single compound but may be a solid solution, and yet it will behave as a single material. In the phase rule sense, the diffusionless transformation is always a unary phase reaction regardless of the number of components that would be counted for more conventional phase equilibria. Conventional phase equilibria give rise, in binary systems, to two-phase regions filled with horizontal tie-lines which connect two phases of differing compositions in equilibrium. This type of two-phase region is absent from a binary phase diagram if the reaction is diffusionless, for then the system is unary for purposes of this transformation. This point has been overlooked in many published phase diagrams and discussions of binary systems of zirconia.

At least three distinct classes of diffusionless transformations are known. The high-low type, e.g. the α - β transformation in quartz,⁸ involves only small volume changes and is not associated with the large strains that are important to the interpretation of the other two classes, which alone are relevant to this discussion.

By far the better known of the two remaining classes is the martensite transformation. In this, a martensite nucleus is a plastically deformed region of the parent grain, initially coherent with the latter. By coherent it is meant that the two crystal structures are connected at the boundary by a crystallographic plane which is common to both and remains undistorted. Since the transformation involves a change of shape

⁷ C. E. Curtis, L. M. Doney, and J. R. Johnson, "Some Properties of Hafnium Oxide, Hafnium Silicate, Calcium Hafnate, and Hafnium Carbide," *J. Am. Ceram. Soc.*, **37** [10] 458-65 (1954).

⁸ R. A. Young, "Mechanism of the Phase Transition in Quartz," Final Report, AFOSR-2569, ASTIA Document Service Center, Arlington, Va., April 30, 1962.

and of volume inside of a solid matrix, large strains are set up which, in a diffusionless transformation, are not relieved by the migration of atoms. Usually this strain opposes the progress of the reaction, stopping while it is still incomplete. A further change of temperature is required to advance the reaction further, until a new balance is reached, and so on, step by step. Thus, the equation of state of the material contains the strain energy as a determinative variable in addition to the conventional variables of temperature and pressure. In terms of the phase rule, $F = C - P + n$, n is now three instead of two. This additional variable explains why the transformation has that extra degree of freedom which is evidenced by the fact that the transformation occurs over a range of temperatures instead of at a single temperature as normally expected for a pure compound.

The plastic deformation is generally followed by slip and shear at the boundary plane, and quite often by twinning. Since this relieves some of the strain, the energy balance is sufficiently upset that the reaction is no longer reversible at the same temperature. This can explain the hysteresis which generally is a very characteristic feature of the large majority of diffusionless transformations. Among the martensite transformations proper, two limiting types have been distinguished⁹: (1) those that have large hysteresis loops, such as in iron-nickel alloys, progress primarily by additional nucleation of martensite plates, that essentially spring into existence fully grown, and (2) those that have small hysteresis loops, as in the system gold-cadmium in which further growth of already formed plates is important. Many transformations behave in a fashion that is intermediate between these two extremes.

In addition to hysteresis, martensite transformations are conspicuous by their predominantly athermal character, which comes about in the following way. The interplay of chemical (temperature, pressure) and mechanical (strain) forces has already been shown to cause the reaction to progress stepwise over a range of temperatures. It must now be stated that whenever a step occurs during the transformation, it is extremely fast. In the absence of diffusion, the transformation is essentially a cooperative movement of many atoms at once and such a motion propagates through the crystal with the properties of an elastic wave. Where it has been possible to measure the speed of a martensite transformation, values of the order of one third the speed of sound in the material have been found.⁹ In practical terms, this means that the reaction keeps pace with the temperature and cannot be observed to proceed isothermally but only while the temperature is changing. This is what is meant by athermal characteristics. Some martensite transformations do have an isothermal component, but the athermal aspect is usually dominant and often exclusive. If an isothermal component is present, it can sometimes be suppressed by quenching, but the athermal reaction is not suppressible with the quenching rates normally available.

The martensite transformation has been discussed in some detail for the following reasons: (1) It is by far the best studied of the diffusionless transformations, (2) nonmetallurgists are not generally familiar with it, and (3) the data on zirconia will be examined in the light of what is known about martensite transformations.

For further information concerning martensite transformations, reference is made to the excellent review article by Kaufman and Cohen⁹ which emphasizes the thermodynamic aspects of the problem. A review by Bilby and Christian¹⁰ deals with the crystallographic aspects.

The last type of diffusionless transformation relevant to this discussion was recognized as a distinct type by Basinski and Pearson when they found an example of it in manganese arsenide.¹¹ They called it "nonmartensitic diffusionless," but this writer prefers the terms quasi-martensitic or brittle martensitic, because apparently it occurs in materials that are too brittle to sustain plastic deformation. Instead of

plastic deformation producing slip and shear, the parent crystal cracks into a number of parallel pencil-like grains. Thus, this is a different type of phase change from the martensitic one, and yet it seems from the meager information presently available, that the kinetics and thermodynamics of brittle martensite reactions are quite the same as those of conventional martensite transformations. Although there is at present no evidence on this point, it would seem likely, simply because zirconia is a brittle ceramic and not a metal, that the zirconia transformation is of the brittle type rather than of the truly martensitic type with which it is to be compared here. One should, however, maintain some reservation concerning this assumption.

(2) Discussion of Results

The large size of the hysteresis loop found for the monoclinic to tetragonal transformation of zirconia immediately leads to the conclusion that, if analogies between brittle and true martensite transformations are permissible, the zirconia transformation resembles the iron-nickel type rather than the cadmium-gold type, whereas the reverse is true for the hafnia transformation, where the hysteresis loop was found to be 20° to 30°C wide in marked contrast to the 200°C loop of zirconia.

In metals the hysteresis loop of a martensite transformation can often be narrowed by cold work. It is thought by some⁹ that cold work facilitates nucleation, and so the width of the loop would be connected with the relative ease of nucleation. Since zirconia and hafnia are very similar, but the hafnia transformation occurs at a considerably higher temperature, it is certainly conceivable that nucleation is easier in hafnia and causes a narrower loop. This hypothesis, however, is by no means firmly established. The lattice strain energy is a thermodynamic variable in solid-state transformations, and cold work and plastic deformation, indeed any kind of mechanical energy, would alter the strain energy and thus affect the course of the transformation. It may well be that the difference in the size of the hysteresis loops is due to the smaller volume change of the hafnia transformation compared with the zirconia transformation. A smaller volume change would lessen the strain and this could combine with easier strain relief at the higher temperature to produce a much narrower hysteresis loop.

Examination of the graphs shows the curvature at the high temperature end to be much sharper than at the low temperature end, where it is quite gradual, for both rising and falling temperatures. This property is shared by martensite transformations often enough to be called typical, but the writer does not know of any explanation for it.

Although an isothermal component was not observed in this study (see, however, Section IV (3)), it is known that, at least at low temperatures, the zirconia transformation can take place isothermally, but the rate of the isothermal reaction is very slow. When ZrO_2 is prepared by the thermal decomposition of certain salts at relatively low temperatures, it is a mixture of monoclinic and metastable tetragonal phases. This was first clarified by Ruff and Ebert⁴ and can easily be observed in samples of many currently commercially

⁹ Larry Kaufman and Morris Cohen, "Thermodynamics and Kinetics of Martensitic Transformations"; pp. 165-245 in *Progress in Metal Physics*: Vol. 7. Edited by Bruce Chalmers and R. King. Pergamon Press, Ltd., London, 1958. 408 pp.

¹⁰ B. A. Bilby and J. W. Christian, "Martensitic Transformations"; pp. 121-72 in *Symposium on Mechanism of Phase Transformations in Metals*, The Institute of Metals, London, 1955. 346 pp.

¹¹ Z. S. Basinski and W. B. Pearson, "The Non-Martensitic Diffusionless Transition in Manganese Arsenide at About 40°C," *Can. J. Phys.*, **36** [8] 1017-21 (1958).

available grades of zirconia. Over a period of months, the tetragonal content diminishes slowly. The tetragonal phase can also be eliminated by prolonged heating (12 to 24 hours) at temperatures between 600° and 800°C, and in either case, the reaction must be primarily an isothermal one.* If the temperature is high enough, however, to intrude into the transformation range where additional tetragonal phase is formed and then cooled rapidly, some tetragonal phase will be retained as the writer has observed. The reason is that if the cooling time is less than several hours, the athermal reaction, which occurs only with changing temperature, controls. Unless cooling starts at the top of the transformation range, the temperature drop is insufficient for complete elimination of the tetragonal phase. Failure to observe the isothermal component in heating times of up to 2 hours illustrates the slowness of the isothermal component.

The effect of thermal history on transformation temperatures was shown by the difference between the first and subsequent cycles. This difference was fairly small, as described. Repeating the same temperature cycle over and over, and in one instance going slightly above the previous limit, apparently did not constitute a new thermal history.

(3) Comparison with Recent Russian Work

After this paper had been submitted for publication, the writer's attention was drawn to a recent Russian publication¹² in which the authors described an investigation of the same phase transformation by methods very similar to those employed here. They found a marked dependence of the transition temperatures and of the width of the hysteresis loop on the origin and hafnium content of the specimens. They also claim to have measured very clearly an isothermal component of the transformation, which was fastest during the first heating and steadily slowed with each subsequent cycle. If these results are confirmed in the future it would mean that in the present work the specimens already had reached the final slow stage of the isothermal component during the first cycle. This could be accounted for partly by the lesser purity of the Russians' specimens but especially by the difference in their specimen preparation. Their specimens were cylindrical compacts prepared under 1000 kg per cm² pressure compared with the uncompacted powders used in the present

work. The sensitivity of martensite transformations to mechanical energy has been mentioned, so perhaps these results are not surprising.

V. Tetragonal-Cubic Transformation of Zirconia

Smith and Cline recently reported¹³ that ZrO₂ transforms reversibly to a cubic fluorite structure at 2285°C. Attempts were made to map the hysteresis loop of this transition in the same fashion in which the monoclinic-tetragonal transformations of ZrO₂ and HfO₂ were successfully investigated. The existence of the transformation and its reversibility were verified, but the relative proportions of tetragonal and cubic material as a function of temperature could not be measured. Whenever an appreciable amount of cubic phase was present, there was a rapid loss of material and in most cases this led to almost complete disappearance of the specimen in a short time. The cause for this loss of specimen has not been determined, but a clue can be found in the fact that such a difficulty was not reported by Smith and Cline. They employed a vertical goniometer where the specimen rests on a heater which, at low diffraction angles, is nearly horizontal. In the present work, a horizontal goniometer was used where the heater and specimen are vertical at all angles. One would surmise that the transformation to the cubic phase destroys the adhesion of the specimen to the heater. It is remarkable that no such difficulty was encountered for the other two phase changes, at lower temperatures, that have been investigated by the writer. Although the development of the cubic phase with increasing temperature was observed in many separate runs, generally it could not be followed to completion because of the loss of the specimen. In one instance, however, the well-developed 111 and 200 peaks of the cubic phase were observed in the complete absence of any tetragonal peaks. The temperature for this observation was 2342°C. In another instance, a very clean pattern was obtained at 2280°C in which the cubic 111 and the tetragonal 101 peaks were of almost equal intensity. This is in excellent agreement with the conversion temperature of 2285°C reported by Smith and Cline. In only a single case was enough specimen retained on the heater to follow the transformation at decreasing temperatures, and it was evident that the cubic material returned first to the tetragonal and then to the monoclinic form. This reversibility, also reported by Smith and Cline, should help to dispel doubts advanced by Weber¹⁴ who suggested that the cubic phase might arise from contamination.

* Adam and Cox investigated a number of factors involved in the elimination of the tetragonal phase by heating (J. Adam and B. Cox, "The Irradiation-Induced Phase Transformation in Zirconia Solid Solutions," *J. Nuclear Energy: Pt. A, Reactor Sci.*, **11** [1] 31-33 (1959)) but their conclusions should be reinterpreted, taking into account the existence of both isothermal and athermal components of the phase transformation.

¹² B. Ya. Sukharevskii and I. I. Vishnevskii, "Polymorphic Transition Kinetics of ZrO₂," *Dokl. Akad. Nauk SSSR*, **147** [4] 882-85 (1962).

¹³ D. K. Smith and C. F. Cline, "Verification of Existence of Cubic Zirconia at High Temperature," *J. Am. Ceram. Soc.*, **45** [5] 249-50 (1962).

¹⁴ B. C. Weber, "Inconsistencies in Zirconia Literature," *J. Am. Ceram. Soc.*, **45** [12] 614-15 (1962).