

ADVANCES IN CERAMICS • VOLUME 3

SCIENCE AND TECHNOLOGY OF ZIRCONIA

Edited by A. H. Heuer
and L. W. Hobbs



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**Edited by A. H. Heuer
and L. W. Hobbs
Case Institute of Technology
Case Western Reserve University
Cleveland, Ohio**



**The American Ceramic Society, Inc.
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Foreword

The First International Conference on the Science and Technology of Zirconia (ZrO_2) was held on 16–18 June 1980 in Cleveland, Ohio. The present volume, number three of the series *Advances in Ceramics*, published by the American Ceramic Society, comprises the Conference Proceedings.

The meeting, sponsored and organized by the Ceramics Group of the Department of Metallurgy and Materials Science, Case Institute of Technology, Case Western Reserve University, was held in conjunction with the Centennial Celebration of Case Institute of Technology. The Organizing Committee, in addition to A. H. Heuer and L. W. Hobbs of Case, included R. J. Bratton of Westinghouse, R. J. Brook of the University of Leeds (United Kingdom), R. C. Garvie of CSIRO (Australia), and E. C. Subbarao of IIT, Kanpur (India).

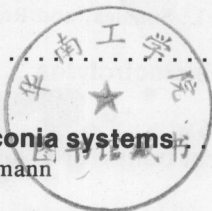
As reflected in these Proceedings, the Conference provided a state-of-the-art picture of the rapidly-growing field of ceramic science and technology based on ZrO_2 -containing ceramics. Interest in the field is evident from the attendance at the Conference, 175 in total, including representatives from all parts of the United States and 8 other countries. A second international conference has been tentatively scheduled for 1983 in Stuttgart.

The meeting organizers are grateful to the following organizations for their financial support: The National Science Foundation; Army Research Office; Norton Company, Worcester, Massachusetts; Corning Glass Foundation, Corning, New York; Magnesium Elektron, Ltd., Twickenham, United Kingdom, and Magnesium Elektron, Inc., Flemington, New Jersey; Singh Industries, Inc., Randolph, New Jersey; NL Industries, Inc., Niagara Falls, New York, and especially to the Department of Metallurgy and Materials Science, Case Institute of Technology for financial underpinning. Ms. Phyllis Witriol is thanked for her untiring efforts as Conference Secretary, and Ms. Gerry Smith of the American Ceramic Society for her yeoman editorial efforts which permitted publication of these Proceedings in a timely fashion.

A. H. Heuer
L. W. Hobbs

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Zirconia—an overview

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Intense investigations of the science and technology of zirconia over the last half century have propelled it into an outstanding, versatile material. A historical perspective is provided through bench marks in the development of zirconia. The crystal structures of the three polymorphs—cubic, tetragonal, and monoclinic—are reviewed. The martensitic nature of the monoclinic-tetragonal transformation is substantiated. Enhancement of strength and toughness through the phase transformation in partially stabilized zirconia, which led to important applications as extrusion dies and tool bits, is discussed. The process of stabilization, which enabled refractory applications of zirconia, is covered, followed by a discussion of the defect structure and consequent ionic conductivity of doped zirconia. The use of stabilized zirconia in oxygen sensors, fuel cells, etc., is based on its high oxygen ion conduction. Cubic zirconia, because of its high refractive index, is widely used as jewelry. The state of knowledge in each area is reviewed, and gaps in present understanding are highlighted for future studies.

Zirconia (ZrO_2) is a remarkable material, which has attracted a great deal of attention from scientists, technologists, and users. The progress in our understanding of this material and in exploiting it has been substantial. Pedagogically, ZrO_2 is a case study in materials science, since structure-property correlations have been very extensively examined. Atomic structure and microstructure, defects, phase transformations, and processing on the one hand and properties (thermal, mechanical, electrical, and optical) on the other, are intimately connected in zirconia. In this overview, a historical perspective is presented, followed by a brief mention of the sources of zirconia. The major aspects (crystal structure, phase transitions in zirconia, mechanical behavior of partially stabilized zirconia, and stabilization, ionic conductivity, and optical properties of fully stabilized zirconia) are reviewed, including the important applications of zirconia as well as the significant outstanding problems.

Historical Perspective

Ten major bench marks in the field of zirconia are listed in Table I. The discovery of baddeleyite in 1892 in Brazil, by Hussak, was followed soon thereafter by attempts at its exploitation for refractory applications. Ruff and Ebert,¹ in a classic study, used X-ray diffraction (XRD) to establish the monoclinic symmetry of zirconia at room temperature. They also studied the monoclinic-tetragonal transformation at $>1000^\circ\text{C}$ by high temperature

XRD. Ruff and coworkers² demonstrated, in the same year, the disruptive phase change in zirconia as well as the stabilization of the material by the addition of metal oxides. Related to this is the determination of binary phase equilibria of ZrO_2 with RO and R_2O_3 by Duwez and coworkers.^{3,4} Both these aspects were later studied more extensively.

While refractory applications represent the tonnage usage of stabilized zirconia, Nernst,⁵ as early as 1900, used zirconia as a glower for incandescent lighting; Wagner⁶ elucidated the defect structure of stabilized zirconia, and Kiukkola and Wagner⁷ determined its electrolytic nature and used it as an oxygen concentration cell in thermodynamic measurements. Kingery *et al.*⁸ confirmed the oxygen ion conduction through diffusion and conductivity measurements.

By high temperature XRD ($> 2370^\circ\text{C}$), Smith and Cline⁹ found the expected cubic phase of zirconia, though doubts¹⁰ have been raised about the possible contamination or reduction of zirconia at such high temperatures. Careful studies of the tetragonal—monoclinic transition in ZrO_2 prompted Wolten¹¹ to liken this transformation to that of martensite. Many elaborate studies which have since been undertaken support the martensitic nature of the transition.¹²⁻¹⁴ These studies have led to the development of transformation strengthening in partially stabilized zirconia by appropriate heat treatment.¹⁵⁻¹⁷

The ionic conductivity and transformation toughening of zirconia have opened up such nonrefractory uses of zirconia as oxygen sensors, heaters, and extrusion dies. Much progress regarding transformations and processing is due to the detailed crystal structure analyses of the various phases of zirconia, using powder as well as single crystal diffraction methods.¹⁸⁻²⁰ The conference, totally devoted to zirconia, organized in 1962 at Wright-Patterson Air Force Base must be recognized as a significant landmark.

The chapters on zirconia by Ryshkewitch²¹ in 1960 and by Garvie²² in 1970 are excellent reviews on the subject. The present proceedings represents the most up-to-date and exhaustive state of our understanding of zirconia.

Occurrence

The two main sources of zirconia are: (1) baddeleyite in Brazil, which contains 80–90% ZrO_2 , with TiO_2 , SiO_2 , Fe_2O_3 , etc. as major impurities and (2) zircon, ZrSiO_4 , which occurs as secondary deposits in Kerala (India), New South Wales (Australia), and Florida (U.S.A.). With its presence of 0.02 to 0.03% in the earth's crust, zirconia is more abundant than many metallic ores.

Crystal Structure

Cubic

The cubic phase, which is stable from 2370°C to the melting point ($2680 \pm 15^\circ\text{C}$), was detected by Smith and Cline⁹ by high temperature XRD. It has a fluorite-type crystal structure, in which each Zr is coordinated by eight equidistant oxygens and each oxygen is tetrahedrally coordinated by four zirconiums (Fig. 1(a)).

Tetragonal

This phase is stable between about 1170°C and 2370°C . Teufer²⁰ has shown that Zr is surrounded by eight oxygens, four at a distance of 0.2455

nm and the other four at a distance of 0.2065 nm (Fig. 1(b)).

Monoclinic

This phase is stable at all temperatures below 1170°C. The crystal structure of monoclinic ZrO_2 was determined by XRD by McCullough and Trueblood,¹⁸ Smith and Newkirk,¹⁹ and others. The main features of the structure are: (1) sevenfold coordination of Zr with a range of bond lengths and bond angles (Fig. 1(c)), (2) layers of triangularly coordinated O_I -Zr, and (distorted) tetrahedrally coordinated O_II -Zr, (Fig. 1(d)), (3) Zr atoms are located in layers parallel to the (100) planes, separated by O_I and O_II atoms on either side (Fig. 1(d)) and (4) the layer thickness is wider when the Zr atoms are separated by O_I atoms than when they are separated by O_II atoms (Fig. 1(d)). These interlayer distances become equal in the tetragonal phase.

Some outstanding tasks: The following list is only suggestive, but not exhaustive: (1) AX_2 compounds with a radius ratio of cation to anion between 0.414 and 0.732 have the rutile structure. However, ZrO_2 with an $r_{\text{Zr}^{4+}}/r_{\text{O}^{2-}}$ of 0.57 has the distorted fluorite structure. Why? (2) The sevenfold coordination of Zr (Fig. 1(c)) suggests a certain degree of covalency. Is this the reason for ZrO_2 to assume the fluorite structure? The covalency may be explored with X-ray absorption spectra and Moessbauer spectra (preferably with an Sn probe). (3) The electronic structure of ZrO_2 may be studied by photoelectron spectroscopy.

Phase Transformations

Zirconia exhibits the following transformations:

monoclinic $\xrightleftharpoons{1170^\circ\text{C}}$ tetragonal $\xrightleftharpoons{2370^\circ\text{C}}$ cubic $\xrightleftharpoons{2680^\circ\text{C}}$ liquid

Monoclinic \rightleftharpoons Tetragonal

This transformation was first detected by Ruff and Ebert¹ in 1929 using high temperature XRD. Since then, and particularly in the last 35 years, this transformation has been intensely studied using a variety of techniques (DTA, X-ray and electron diffraction, optical and electron microscopy, electrical resistivity, spectroscopy, etc.) due to the theoretical interest in understanding this important transition and due to the practical importance of the large, disruptive volume change associated with this phase change. The extensive literature in this field was reviewed by Subbarao *et al.*¹² in 1974 and by Subbarao more recently.¹⁴ Only the salient features are mentioned here.

Wolten¹¹ was the first to suggest that this transformation is martensitic. The main experimental results are:

(1) The high temperature tetragonal phase cannot be quenched to room temperature.

(2) The thermal expansion of monoclinic ZrO_2 is strongly anisotropic, with the b axis exhibiting negligible expansion while the expansion is substantial for the a and c axes (Fig. 2).²³ There is an abrupt change in the lattice parameters at the phase transition (Fig. 2). Zirconia ceramics undergo substantial contraction on heating and a corresponding expansion on cooling through the monoclinic \rightleftharpoons tetragonal transformation²⁴⁻²⁶ (Fig. 3), leading to a crumbling of the ceramic.

(3) The transformation is athermal, as established by XRD, metallography, and DTA. Thus, the transformation does not take place at a

fixed temperature but over a range, i.e. the amount of transformed phase changes by varying the temperature but not as a function of time at a fixed temperature. For example, no changes in XRD intensities are observed with time under isothermal conditions.¹¹ High temperature metallography shows the appearance of new plates with change of temperature but not growth of existing plates.²⁷ In successive, interrupted DTA runs, the transformation starts each time only at the temperature to which the sample was heated in the previous cycle (Fig. 4).²⁷ However, fine-grained (≈ 100 nm) ZrO_2 appears to exhibit an isothermal component in the transformation kinetics.^{28,29} This is attributed to the contribution of the surface energy.

(4) The transition takes place with a velocity approaching that of sound in solids, as evidenced by the growth of platelets during high temperature metallographic observations.²⁷ The transformation exhibits a burst-like behavior in DTA during cooling (Fig. 5).²⁹ Annealing out the imperfections, including strains induced at the monoclinic \rightarrow tetragonal transition by heating at high temperatures for short times or at lower temperatures for longer times, enhances the burst phenomena.²⁹ The bursts were observed only in the reverse direction, never in the forward direction. This may be due to the different strain energy contribution and the deformation mechanisms in the two directions.

(5) The transformation exhibits a large thermal hysteresis (Fig. 6).¹¹ The forward transition occurs at 1170°C and the reverse one between 850° and 1000°C , depending on the surface and strain energies associated with the forward transformation. The hysteresis is decreased by annealing at high temperatures (1550°C) for short times or at lower temperatures (e.g. 1260°C) for longer times.²⁹

(6) Optical and electron microscopic observations of the transformed materials reveal surface distortions due to the sudden appearance of the acicular tetragonal phase through shear-like atomic movements (Fig. 7).¹³ Transformation twins are also observed.^{13,30}

(7) Single crystal XRD showed a diffusionless, shear transformation in which the atoms retain their neighbors in either phase.³¹ Atomic movements of less than one interatomic distance, mainly of the oxygen atoms with only minor shifts of Zr atoms, are inferred.^{32,33}

(8) An orientation relationship is established between the parent (monoclinic) and product (face centered tetragonal) phases.^{33,13}

$$\begin{aligned}(100)_m &\parallel (110)_{fct} \\ [010]_m &\parallel [001]_{fct}\end{aligned}$$

At temperatures below 1000°C , Bansal and Heuer,¹³ Bailey,³⁴ and Smith and Newkirk¹⁹ have also found

$$\begin{aligned}(100)_m &\parallel \approx (100)_{fct} \\ [001]_m &\parallel \approx [001]_{fct}\end{aligned}$$

(9) The following habit planes and lattice invariant deformation have been suggested¹³:

	Habit plane normals	Lattice invariant deformation
Lenticular-type product	$(671)_m, (761)_m$	$(1\bar{1}0) [001]$
Plate-shaped product	$(100)_m$	$(1\bar{1}0) [110]$

While the above experimental results generally support the martensitic nature of the monoclinic-tetragonal transformation, there are many aspects which are unclear and deserve further study. These include:

(a) Detailed crystallography of the transformation, including atomic movements, orientation relationships, habit, and twinning planes. The experimental studies are made difficult by the high temperature of the transition.

(b) Thermodynamics of the transformation, including free energy changes, possibly incorporating strain and surface energy terms and effects of alloying elements.

(c) The role of imperfections, including point defects, impurities, dislocations, stacking faults, etc., on the nature of the transformation.

Tetragonal = Cubic

The transformation temperature (2370 °C) has been established, but little else is known about this phase change. While the high temperatures make experiments very difficult, a study of this transformation may throw light on the phenomenon of stabilization of the cubic phase in ZrO₂-based alloys.

Partially Stabilized Zirconia (PSZ)

Early studies on zirconia alloyed with CaO, MgO, Y₂O₃, and rare earth oxides showed that the two transition temperatures (monoclinic-tetragonal and tetragonal-cubic) are lowered. The phase diagrams of the binary oxide systems, reviewed in detail by Stubican,³⁵ show that a PSZ [i.e. a mixture of cubic and monoclinic (or tetragonal) zirconia] occurs (a) when the dopant is present in a concentration less than that needed for complete stabilization (i.e. for the formation of cubic, fluorite-type zirconia phase) or (b) when the fully stabilized, cubic zirconia with a suitable solute content is heat-treated under appropriate conditions of temperature and time.

The incorporation of alloying elements not only decreases the transition temperatures, but decreases the linear thermal expansion coefficient of the two-phase material as also the volume change associated with the monoclinic-tetragonal phase change (Fig. 3). The lower linear thermal expansion coefficient of PSZ than that of pure as well as fully stabilized zirconia²⁴⁻²⁶ contributes to the better thermal shock resistance of the PSZ³⁶ than that of cubic (stabilized) and monoclinic (pure) zirconia.

King and Yavorsky³⁷ were the first to draw attention to the interesting mechanical properties of PSZ. Based on microstructural and microhardness studies, they argued that the material consists of single grains containing monoclinic and cubic domains. As the original tetragonal domain converts to the stable monoclinic form on cooling, the stresses resulting from the accompanying volume increase (over and above the stresses due to the difference in the thermal expansion coefficients of the monoclinic particles and cubic matrix), instead of rupturing the ceramic, are believed to be relieved by the plastic deformation of the cubic grains around pores and inclusions in the monoclinic-cubic hybrid phase by a slip mechanism. Fully stabilized zirconia did not show slip bands or plastic deformation and exhibited grain boundary strain.

Since then, there has been an intense interest in the mechanical behavior of PSZ. Thermal processing of PSZ to achieve maximum strength and

toughness was studied by Garvie and Nicholson³⁸ and by Green *et al.*³⁹ for Ca-PSZ and by Bansal and Heuer¹⁶ and Porter and Heuer⁴⁰ for Mg-PSZ. For example, Porter and Heuer subjected commercial 8.1 mol% Mg-PSZ (which seems to have been sintered at $<1800^{\circ}\text{C}$) to a solution anneal at 1850°C for 4 h. While optical microscopy of the as-received material shows a single phase material (Fig. 8(A)), transmission electron microscopy reveals inter- and intragranular monoclinic particles (Fig. 8(B) and 8(C)), both of which are formed with tetragonal symmetry and transformed to the monoclinic form during cooling below the M_S (start of martensite) temperature. The intergranular particles (Fig. 8(B)) are believed to have been present during sintering, while the intragranular particles are probably formed by precipitation during the postsintering cooling (Figs. 8(C) and (D)). Solution-annealed samples essentially consist of cubic ZrO_2 solid solution, though a small amount ($\approx 3\%$) of a second phase occurs as small plate-like precipitates ($\approx 5\text{ nm}$) (Fig. 8(E)). The authors aged the solution-annealed samples at $1400\text{--}1500^{\circ}$, $1200\text{--}1300^{\circ}$, 1000° , and $<1000^{\circ}\text{C}$.

Enhanced mechanical properties (strength and fracture toughness) were obtained by aging at 1400°C for $\approx 4\text{ h}$ (Fig. 9). Under these conditions, tetragonal ZrO_2 solid solution, precipitated in a matrix of cubic ZrO_2 solid solution, is retained metastably during cooling. If the tetragonal particles were converted to the stable monoclinic phase during cooling, the mechanical properties of the material were found to be poorer. The phase assemblages resulting from the various heat treatments can be understood in terms of the phase diagram for the $\text{ZrO}_2\text{--MgO}$ system (Fig. 10.)

Microstructural evolution of PSZ was investigated in Mg-PSZ by Bansal and Heuer¹⁶ and by Porter and Heuer⁴⁰ and in Ca-PSZ by King and Yavorsky,³⁷ Garvie and Nicholson,³⁸ and Green *et al.*³⁹ The microstructure of PSZ generally consists of cubic ZrO_2 solid solution as the major phase with monoclinic or tetragonal ZrO_2 solid solution as the minor precipitate phase. The second phase may exist at grain boundaries either from the sintering process or by precipitation during postsintering heat treatment or during cooling, or within the cubic matrix grains. The intragranular precipitates are ellipsoidal, are oriented along $\{100\}$ of the cubic phase, and have an optimum size of $\approx 0.2\text{ }\mu\text{m}$. Particles of this size range retain the tetragonal symmetry on cooling, whereas larger particles convert spontaneously to the monoclinic form which involves a volume increase leading to microcracking. The monoclinic particles are often heavily twinned. The largest coherent tetragonal ZrO_2 solid solution precipitate particles appear to be smaller ($\approx 0.1\text{ }\mu\text{m}$) in Ca-PSZ. At optimum aging, the precipitate accounts for 25 to 30% of the volume.

Various mechanisms have been suggested to account for the strengthening and toughening of PSZ ceramics. As already mentioned, King and Yavorsky³⁷ proposed that the plastic deformation of the cubic matrix is responsible for the stress relief. Garvie and Nicholson³⁸ refer to the subgrain structure of PSZ ceramics in which 100 nm domains of pure ZrO_2 are distributed in a cubic stabilized ZrO_2 . These domains undergo the tetragonal \rightarrow monoclinic transformation on cooling. The volume increase associated with this phase change (which may take place at subtransformation temperatures also) produces extensive microcracking. Because of the large number of cracks, they propagate only quasi-statically and the sample retains most of its strength.

Green *et al.*⁴¹ studied the fracture toughness of Ca-PSZ, in conjunction with the microstructure,³⁹ and drew attention to the formation of a microcrack zone at the tip of the propagating crack. The stresses developed during the transformation of the pure ZrO_2 grain present at the grain boundaries lead to separation and weakening of the grain boundaries and consequent strength degradation. The initial stable crack propagation is attributed to the increase in microcrack zone size. This zone absorbs energy by processes such as secondary crack formation, surface roughening, and crack branching. Bansal and Heuer¹⁶ argued that the fine monoclinic precipitates dispersed coherently in the cubic grains impede crack propagation. This has been questioned by Claussen⁴² and Rice,⁴³ who prefer to consider that the microcracks produced within or between the cubic grains by the transformation of large monoclinic particles cause subcritical propagation of the cracks, similar to the ideas of Green *et al.*^{39,41} and based on results of ZrO_2 -containing Al_2O_3 . Porter *et al.*^{44,45} refuted the above questions involving microcracking as the strengthening mechanism.

The importance of metastable tetragonal phase precipitated in a cubic stabilized zirconia for toughening PSZ was first noted by Garvie *et al.*¹⁵ and elucidated by Porter *et al.*^{40,46,47} Porter *et al.* have shown that all the precipitate particles within several micrometers of a crack had monoclinic symmetry (Fig. 8(F)), whereas all other particles were tetragonal (Fig. 8(G)). This suggests that the stresses near the crack tip had caused the particles to transform to the monoclinic symmetry by making the particles lose their coherency; additional stress is then required for crack extension. Thus, the stress-induced martensitic transformation of the metastable tetragonal particles to the stable monoclinic phase is the mechanism which absorbs energy and inhibits crack propagation, thereby strengthening and toughening PSZ. These authors have estimated the large strain energy difference between the tetragonal and monoclinic particles within a cubic matrix. This large energy difference prevents the martensitic transformation on cooling below M_s , at least for small particles. They also estimated the difference in chemical free energy, ΔG_0 , as 228 MPa, in close agreement with the 226 MPa determined by DTA. Porter *et al.*⁴⁷ also mapped the crack tip transformation zones. Strength decrease due to overaging results from precipitate coarsening, since large particles spontaneously transform to the monoclinic form and hence are not available for energy absorption processes.

On the basis of the above, these materials are now more appropriately termed transformation-toughened zirconia ceramics (rather than precipitation-strengthened ceramics) and likened to TRIP steels.¹⁵ Table II shows that the coexistence of tetragonal and cubic zirconia results in strength and fracture toughness values approximately three times those of a mixture of monoclinic and cubic phases or only cubic zirconia.

The importance of the metastable tetragonal phase in toughening PSZ was forcefully illustrated by Gupta and coworkers.¹⁷ They showed that a nearly fully tetragonal material, prepared of $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solution by fine particle technology,^{48,49} exhibits high strength at room temperatures,^{17,50} whereas a $\text{ZrO}_2\text{-CeO}_2$ solid solution, in which the tetragonal phase is stable at room temperature, is relatively weak, though the same composition exhibits enhanced strength and toughness at liquid nitrogen temperature, where the tetragonal phase is only metastable.⁵¹

Unlike most ceramic materials, the PSZ has enhanced strength when the surface is abraded, due to the transformation strengthening.^{52,53}

The strong, tough PSZ components exhibit outstanding performance as extrusion dies for nonferrous metals, as tool bits, as thread guides, etc.

Transformation-toughened PSZ ceramics is likely to be an important area of investigation in the next decade, just as the ionic conductivity of zirconia electrolytes was in the last two decades. Processing technology, detailed mechanisms, *T-T-T* diagrams, and alloying additions are some of the areas which need attention.

Stabilized Zirconia

Stabilization

Zirconia is stabilized in the fluorite-type cubic phase when it is alloyed with an appropriate amount of di- or trivalent oxides of cubic symmetry. According to earlier binary oxide phase diagrams,^{3,4} the cubic phase exists over a wide range of composition and temperature, though more recent equilibrium studies over extended times indicate that the cubic phase is not truly stable at room temperature in many cases³⁵ (see Fig. 10). The slow rate of the destabilization process as well as the formation of intermediate phases (e.g. CaZr_4O_6 ^{22,54-57} and $\text{Y}_4\text{Zr}_3\text{O}_{12}$ ^{56,58}) is due to the very low cation diffusion coefficients⁵⁹ which are a millionfold smaller than the diffusion coefficient of oxygen.^{8,60} As a consequence, the cubic phase remains metastable for long periods at temperatures sufficiently below the decomposition temperatures. The topotactic relationship of the decomposition products to the parent phase has also been investigated.¹⁶

The high melting point and chemical inertness of stabilized zirconia are the basis for its extensive use as a refractory material.

In spite of its importance, the phenomenon of stabilization is not well understood. Some of the factors which may influence stabilization deserve attention: the role of anion vacancies, minimum number of vacancies, size, charge and concentration of dopant ions, crystal structure of the dopant oxide (e.g. cubic), and the role of electronic energy levels.

Defect Structure and Crystal Structure

In 1943, Wagner⁶ established that stabilized zirconia contains oxygen ion vacancies. By comparing measured and calculated densities of CaO-stabilized ZrO_2 , Hund⁶¹ established that the Ca^{2+} and Zr^{4+} ions are statistically distributed over the cation sites and the electrical neutrality is achieved by the creation of oxygen ion vacancies, equal in concentration to the Ca^{2+} ions. Similar studies have since been done on ZrO_2 stabilized by Y_2O_3 and rare earth oxides. Direct evidence for this defect structure has been obtained, using XRD methods, by Tien and Subbarao⁶² among others. The defect structure and defect concentration of stabilized zirconia are essentially fixed by dopant content and are independent of temperature and surrounding atmosphere.⁶³⁻⁶⁷

The crystal structure of stabilized zirconia is of the cubic fluorite type. The cubic phase extends over a wide range of dopant concentration with a correspondingly large anion vacancy concentration. Electrostatic attraction between the two oppositely charged species (Ca_{Zr}'' and V_{O}' or Y_{Zr}' and V_{O}'), together with the large concentration of anion vacancies, interferes with a

random distribution of dopant cations over cation sites and vacancies over anion sites. Defect ordering in stabilized zirconia has been examined by X-ray, electron, and neutron diffraction methods by several workers.^{54-58,68-72}

The diffuse scattering and forbidden reflections observed in neutron diffraction of CaO-stabilized zirconia prompted Carter and Roth⁶⁸ to propose that the high temperature disordered state of CaO-stabilized zirconia has a cubic fluorite structure with oxygen ions displaced from the ideal fluorite lattice sites and the low temperature (<1300 K) ordered state involved cooperative ordering of the oxygen ions on the oxygen sublattice (Fig. 11). Electron diffraction studies of CaO-stabilized zirconia by Allpress and Rossell⁵⁵ were interpreted in terms of domains of ordered arrangement, ≈ 3 nm in diameter, embedded coherently in a cubic matrix. Similar work by Hudson and Moseley⁶⁹ demonstrated that the intensity of diffuse scattering increases with CaO content, while the intensity of extra (forbidden) reflections decreases with CaO content. The anion vacancies become aligned along $<111>$ directions. They report the presence of coherent microdomains of CaZr_4O_9 and intragranular precipitates of monoclinic ZrO_2 in a cubic matrix, as a result of aging.

Based on a neutron diffraction study of yttria-stabilized zirconia, Steele and Fender⁷⁰ indicated that the six oxygens surrounding an oxygen vacancy relax by 0.036 nm and probably the four neighboring cations (which include Y^{3+} ions) by a smaller relaxation. Faber *et al.*⁷¹ refined the neutron diffraction studies on CaO- and Y_2O_3 -stabilized zirconia. They found that the oxygen ions are shifted from the ideal fluorite positions (by ≈ 0.023 nm) by an internal shear deformation of the oxygen sublattice (Fig. 12). This may (as in CaO-doped ZrO_2) or may not (as in Y_2O_3 -doped ZrO_2) be accompanied by external strain. The internal rearrangement appears to be dominated by the cation-anion (and indirectly anion-anion) interactions.

Ionic Conductivity

As early as the turn of the century, Nernst recognized the electrolytic properties of yttria-doped zirconia and used it as a Nernst glower.⁵ As discussed above, Wagner⁶ established the defect character of doped zirconia as being composed of oxygen ion vacancies. The galvanic cell measurements of Kiukkola and Wagner⁷ in 1957 and the oxygen diffusion and ionic conductivity study of Kingery *et al.*⁸ in 1959 confirmed the defect structure of doped cubic zirconia. In the following two decades, more detailed studies of defect equilibria and ionic conductivity of these materials have been conducted as a function of composition, concentration of dopant, temperature, oxygen partial pressure, and frequency of measuring electric field. Several recent reviews of this topic are available.⁶³⁻⁶⁷ A few salient features of the ionic conductivity of doped zirconia are:

(1) It follows an Arrhenius behavior over a wide temperature range with an activation energy of ≈ 1 eV (Fig. 13).

(2) Over a wide temperature range, the electrical conductivity is independent of oxygen partial pressure (P_{O_2}) over several orders of magnitude (Fig. 14). Under these conditions, the conduction is truly electrolytic, with the transport number for oxygen ions nearly unity and the transport number for electrons $\ll 1\%$.

(3) The variation of the isothermal electrical conductivity (with dopant content) of a binary oxide system based on zirconia exhibits a maximum at or near the lowest dopant concentration required to stabilize the cubic phase and decreases with increasing dopant concentration. This trend is accompanied by an increase in activation energy for conduction (Fig. 15). The decrease in conductivity with increasing dopant concentration is contrary to the dilute solution model and has not been fully accounted for in a quantitative way, though defect ordering,⁶⁸ clustering,^{69,78} electrostatic interactions,^{79,80} precipitation of a second phase,⁶⁹ etc. have been invoked.

The ionic conductivity of stabilized zirconia is utilized in a variety of devices as discussed in some recent reviews.⁸¹⁻⁸³ The major applications include (a) an oxygen sensor for control of automotive emissions, deoxidation of steel, combustion control of furnaces (for glassmelting, heat treatment, thermal power plants, etc.), (b) electrochemical oxygen pump, (c) high temperature fuel cell, (d) susceptor for induction heating, (e) resistance heating element, (f) electrodes for power generation by magnetohydrodynamics, etc.

The oxygen sensor and fuel cell are based on the relation between the electromotive force (E) generated by an oxygen concentration cell and the difference in the oxygen partial pressure (P_{O_2}) on the two sides of the cell:

$$E = \frac{RT}{4F} \ln (P_{O_2}/P'_{O_2}) \quad (1)$$

The measured emf indicates the unknown P_{O_2} if the reference P'_{O_2} is known for a sensor operating at a temperature T (K). The same equation, when it is used to describe the functioning of the oxygen pump, prescribes the potential to be applied for achieving a required P_{O_2} in a flowing stream relative to a reference P'_{O_2} (e.g. air with $P'_{O_2}=0.21$).

Some of the unresolved problems regarding the ionic conductivity of doped zirconia are: (a) a quantitative explanation of the variation of conductivity with dopant concentration; (b) is it coincidental that the composition corresponding to the maximum conductivity occurs at the minimum dopant needed to stabilize the cubic form? (c) clear evidence for clustering, ordering, or other structural features; (d) relationship between the ionic conductivity and ionic size of the dopant, for a given defect concentration, though the conductivity appears to be higher when the cation size of the dopant is smaller.

Optical Properties

ZrO_2 , in pure as well as in the stabilized forms, has high refractive index,⁸⁴ as shown in Table III. One of the largest users of zirconia is in ceramic glazes as an opacifier; this is based on the high refractive index of zirconia. In recent years it has been possible to grow large, clear, transparent crystals of stabilized zirconia by skull melting,⁸⁴ using zirconia itself as the susceptor in a radio frequency induction furnace (Fig. 16).

Since stabilized zirconia has adequate electrical conductivity to couple to the rf field only when it is at a high temperature ($>1000^\circ\text{C}$), a few chips of zirconium metal or metal of the stabilizing oxide are introduced into the feed material to melt first. The mixed oxide powder dissolves in the melt and then the melting operation of the feed continues. The melt is contained in an