the mirrorlike properties of the outer hot surface of the window. The oscillatory dependence upon thickness suggests that one could observe, at 10 GHz, a series of transmissivity peaks as the ablation process proceeds. We consider the peak values as the maximum obtainable transmissions, for if the window were coupled to a continuously tuned cavity the interference cancellation could be removed.

The conclusion to be drawn from these calculations is that, at the considered reentry conditions, the transmissivity of intrinsic boron nitride windows at 10 GHz will have an upper limit of 10%; i.e., the one-way loss will be 10 dB or greater. By preparing composite mixtures of BN with a more transparent material such as SiO_2 , the average transmissivity can be increased while retaining some of the ablation resistance of the BN.

ing the use of operational amplifiers.

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Metastability of Tetragonal Zirconia Powders

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The formation of metastable t-ZrO₂ by thermal treatment was studied in a systematic way on two different samples: a gel (G) and zirconyl acetate (A). The results show that initially nucleation of t-ZrO₂ is favored by creation of anionic vacancies with trapped electrons. At higher temperatures the electronic defects disappear, the crystallites grow, and the *m*-phase can nucleate. This evolution is observed perfectly on sample A because of its special morphological characteristics.

I. Introduction

UE to the great technological interest of the modern zirconia ceramics¹ much attention has recently been devoted in the literature to the metastable phase transformation of this oxide.¹⁻¹

It is well-known that thermal decomposition of amorphous hydrous zirconia, zirconium alkoxides, and zirconium salts, ball milling of monoclinic zirconia, and vapor-phase reactions produce metastable tetragonal zirconia at room temperature. However, the mechanism of stabilization of this tetragonal zirconia at low temperature is still a matter of controversy. Several explanations have been given in the literature.

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(1) Influence of the Particle Size

On the basis of the lower value of the surface energy in the tetragonal phase (γ_i) in relation to the monoclinic one (γ_m) , Garvie² considers that in order to stabilize the tetragonal phase at low temperature the following equation must be satisfied:

$$(G_t - G_m) + S_t \gamma_t - S_m \gamma_m \leq 0$$

Where G is the molar free energy in single crystals, γ the surface energy, and S the surface area. Garvie determined that the particle size for stabilizing the tetragonal phase must be ≤ 30 nm.

Bailey et al.³ carried out intensive milling experiments in m-ZrO₂ powders observing a progressive transformation to tetragonal phase when the milling time increased. Recently, Murase and Kato⁴ have studied the influence of water vapor atmosphere on the $t \rightarrow m$ transformation of ZrO₂. They observed that the H₂O vapor increased the crystal size and reduced the critical size for transformation. These effects are explained in terms of reduction in the differences between the corresponding surface energy of both phases.

(2) Influence of the Structural Similarities

Other authors attribute the t-ZrO₂ metastability to structural similarities between the precursor amorphous phase and the tetragonal phase. Livage et al.,⁵ after a complete study by X-ray and neutron diffraction on amorphous ZrO₂, found that the interatomic

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Fig. 1. DTA and TGA of ZrO₂ gel (G) and of zirconyl acetate (A).

Zr-Zr and Zr-O distances were similar to the corresponding ones in the tetragonal structure. Tani et al.⁶ working on ZrO₂ powders under hydrothermal conditions proposed a mechanism of topotactic crystallization of t-ZrO₂ on nuclei in the amorphous ZrO₂.

Stabilization Produced by Lattice Strain (3)

Mitshuashi et al.⁷ claim that domain boundaries inhibit the $t \rightarrow m$ transformation; the existence of a single-domain t-ZrO₂ is explained by the absence of an active nucleation site. Recently, Torralvo *et al.*⁸ have shown a certain parallelism

between the t-phase crystallization and the formation of paramagnetic defect centers in ZrO_2 . In the present work, on the basis of a systematic study of the thermal evolution of two ZrO₂ powders obtained by two different methods (precipitation and thermal decomposition) further evidence on the influence of defect centers on the stability of the *t*-phase is presented.

II. Experimental Procedure

Two kinds of ZrO₂ powders have been used as starting materials: (a) zirconia gel obtained by precipitation with ammonia (pH = 10) from a solution of zirconyl oxychloride,* which is labeled sample G, and (b) zirconium oxide obtained by thermal decomposition of zirconyl acetate (99.99% purity),* which is labeled sample A. Both samples were analyzed by DTA and TGA[‡] at a heating rate of 10°C/min. In addition, the samples (\approx 1 g) were introduced slowly (≈ 1 min) into a tubular furnace at selected temperatures (450° to 1100°C) in air atmosphere, held for 10 min, and subsequently quenched.



Fig. 2. (a) Relative t-ZrO₂ content vs temperature for samples A and G. (b) thermal evolution of crystallite size for tetragonal (L_r) and monoclinic (L_M) phases.

The surface, microstructure, phases, and defect structure evolution vs temperature have been studied by the following techniques: BET, scanning electron microscopy (SEM),[§] X-ray diffraction (XRD) with Ni-filtered Cu radiation,[¶] and electron paramagnetic resonance (EPR) working in X-band.^{**} A solid solution of Mn(II) in magnesium oxide was used as a standard. BET determinations were conducted by nitrogen adsorption at liquid nitrogen temperature in a conventional volumetric apparatus.

The relative content of t-ZrO₂ has been determined by considering the intensity relationship: $I(111)_t/I(111)_t + I(11\overline{1})_m +$ $I(111)_m$. The crystallite size was calculated by using the $(111)_m$ and (111), diffraction peaks from the Scherrer formula⁹ D = $0.9\lambda(\beta \cos \theta)^{-1}$, where D is the crystallite size, λ is the radiation wavelength (Cu K_{α}), β is the corrected half-width obtained by using the $(11\overline{1})_m$ peak of sample A treated at 1100°C as the standard peak in Warren's formula,⁹ and θ is the diffraction peak angle.

III. Results

(1) Thermal Behavior of the Samples

The DTA and TGA curves corresponding to both samples (G and A) are shown in Fig. 1. Sample G shows the thermal behavior typical of a gel: a fast initial loss of H₂O at \approx 150°C (\approx 17% of the

^{*}E. Merck AG., Darmstadt, Federal Republic of Germany. Impurity levels: $SO_4^{2-} < 10 \text{ ppm}$, Pb < 10 ppm, Fe < 10 ppm, and Ti < 50 ppm. *Orion Chemical Co., Glendale, CA.

^{*}Mettler Instrument Corp., Princeton, NJ.

 ⁸Model DS 130, ISI, Santa Clara, CA.
 ⁹Model P. W. 1050, Philips Electronic Instruments, Inc., Mount Vernon, NY.
 **Model JESPE-3X, JEOL U.S.A., Inc., Medford, MA.

Table I. Specific Surface Areas of ZrO₂ Samples

Sample	<i>T</i> (°C)	$S_{\rm BET} (m^2/g)$
G	No thermal treatment	124
G	450	63
G	900	10
G	1100	12
А	450	<4
Α	900	<4
А	950	<4
A	1100	<4



Fig. 3. Scanning electron micrographs of sample G heat-treated at 800°C for 10 min in air.

weight) ending at about 900° C (20% of the weight) and a sharp exothermal effect in the DTA at 412°C corresponding to the crystallization of a pseudotetragonal phase.

The DTA of sample A shows a more complex pattern. Following an initial weight loss of $\approx 22\%$, which takes place in successive steps between 150° and 300°C because of the decomposition of the acetate, at 344°C a strong exothermal effect due to crystallization of *t*-ZrO₂ accompanied by an important weight loss ($\approx 13\%$) is observed. At higher temperature (508°, 800°, and 930°C) three additional exothermal effects are also present.

(2) XRD Analysis

The relative content of t-ZrO₂ vs temperature, for samples G and A, is plotted in Fig. 2(*a*). As can be observed, in sample G, the transformation $t \rightarrow m$ begins at $\approx 700^{\circ}$ C and is completed at 1100°C. However, in sample A this transformation occurs suddenly at $\approx 950^{\circ}$ C.

The crystallite size evolution with temperature, for both samples, is shown in Fig. 2(b). From this figure, it is clear that the behavior of both samples is quite different. In sample G, the tetragonal crystallite size does not significantly change with increasing temperature (≈ 25 nm); but the monoclinic crystallite size, which at 800°C is slightly smaller than the tetragonal, increases slowly with increasing temperature. In the case of sample A, the tetragonal crystal grows from ≈ 5 nm at 450°C to ≈ 50 nm at 1000°C. A faster growth is observed in the case of monoclinic crystallites, which at 950°C reach a size of ≈ 120 nm.

In both cases, when the average size of the tetragonal crystallite reaches values close to the critical crystallite size determined by Garvie² (\approx 30 nm), the monoclinic phase is observed.

(3) Specific Surface Area Measurements

The BET values for both samples at different temperatures are shown in Table I. It is clear that the value of the specific surface area is always higher in sample G than in sample A, which is under the detectability limit of the equipment ($\approx 4 \text{ m}^2/\text{g}$).

(4) SEM Study

The microstructural aspects of samples G and A are shown in Figs. 3 and 4, respectively. The morphology of sample G (Fig. 3)









Fig. 4. Scanning electron micrographs of sample A treated at (A) 450°, (B) 900°, (C) 1000°, and (D) 1100°C for 10 min in air.



Fig. 5. EPR spectra of sample A treated at 300° C in air for (a) 3 h, (b) 48 h, and (c) 96 h and (d) expanded spectrum.

does not differ with the temperature of heat treatment; soft agglomerates formed by particles <0.1 μ m in size are found in all cases. The morphology and microstructural evolution of sample A are completely different. At 450°C the sample consists of spheres $\approx 5 \ \mu$ m in diameter (Fig. 4(A)); no crystals are observed (either because of their small size, <5 nm according to XRD, or because they are surrounded by amorphous material). At 900°C single crystals \approx 40 nm in size can be clearly observed on the surfaces of the spheres (Fig. 4(B)). These crystallites drastically grow, reaching a size of $\approx 3 \ \mu$ m at 1100°C (Figs. 4(C) and 4(D)), but during the whole process the same spherical configuration is maintained. These results explain the differences observed in the surface area values for both samples (Table I).

(5) EPR Spectroscopy

Samples G and A have been studied after thermal treatments in the temperature ranges where the initial crystal transitions take place. The samples were heated for several periods of time at a temperature $\approx 50^{\circ}$ C lower than that corresponding to the crystallization peak as follows: sample G was heated at 380°C for 0.75, 2, and 3 h and the final color of the sample was white; sample A was heated at 300°C for 3, 48, and 96 h and the final color was dark. In all cases, the XRD indicated that after these thermal treatments the tetragonal phase had always been nucleated.

Sample A (3 h at 300°C) presents an EPR signal (Fig. 5(*a*)) with g = 2.0023 and $\Delta H = 5$ G. After 48 h of heating, the signal became narrower, was less symmetric ($g_{\parallel} = 2.0035$, $g_{\perp} = 2.0017$), and had higher intensity (Fig. 5(*b*)). After 96 h, the signal was clearly axial (Figs. 5(*c*) and 5(*d*)), with $g_{\parallel} = 2.0035$ and $g_{\perp} = 2.0020$.

Sample G (3 h at 380°C) shows a slightly asymmetric signal, with $g \simeq g_e$, and has low intensity. This signal is more intense if the thermal treatment is conducted under vacuum.^{8b}

The samples have also been studied after heating in air at temperatures close to that of the $t \rightarrow m$ transition. In both cases the samples presented a white color and no significant EPR signal was observed.

IV. Discussion

A general feature of ZrO_2 preparation by the different experimental methods is the transitory formation of the pseudotetragonal phase, which is independent of the compounds used. Livage *et al.*⁵ have indicated that this crystalline phase presents the same Zr-Zr and Zr-O distances as the amorphous ZrO_2 prepared by zirconium oxychloride precipitated with ammonia. The constancy of these distances during the transformation and the generality of the pseudotetragonal phase formation seem to indicate the following: the amorphous ZrO_2 is similar in all preparations; the observed differences in crystallization temperature and intensity of the corresponding exothermic effect are due to the influence of the impurity molecules left over from the preparation method that evolved to the gas phase at that temperature.

The results obtained in the present investigation show that the studied samples have a different behavior with temperature. The fact that sample G shows larger surface area and smaller particle size than sample A does indicate that sample G has higher porosity. This characteristic favors gas evolution and when sample G crystallizes into tetragonal phase the single particle is completely transformed as it is observed by SEM and XRD. The sharpening of the ZrO₂ peaks along with the morphological evolution observed by SEM (Fig. 4), where the crystallites (Fig. 4(B)) grow isolated becoming finally in complete contact (Fig. 4(C) and (D)), suggests that when sample A is heated at $T \leq 900^{\circ}$ C, the tetragonal crystallites grow surrounded by an amorphous phase (Fig. 4(B)). In this stereographic situation, the EPR signal of sample A is not affected by dipolar interactions with the atmospheric oxygen, indicating that the paramagnetic centers are placed in the crystalline phase. Conversely, the signal in sample G is very small because it is affected by oxygen (through broadening or reaction), indicating that in this case the crystalline phase is mostly in contact with the gas phase. To explain the behavior of the EPR spectra of sample A with increasing periods of heating at 300°C, we must consider the preparation method. At 300°C, the acetate decomposition has generated carbonaceous impurities that produce the symmetric signal shown in Fig. 5(a). By keeping the sample at this temperature in air for long periods of time, the carbonaceous material is burned, as indicated by the weight loss; however, the signal does not show a drop in intensity. The lineshape change (the signal now presents axial symmetry, Fig. 5(d)) and the signal intensity increase, indicating that a new species has been generated.

Considering that the thermal treatment had been done in air, it could be thought that the new species was due to adsorbed oxygen. However, this species should be placed on the surface and then the signal would be broadened by dipolar interactions with gaseous oxygen.

The absence of signal broadening indicates that unpaired electrons which originate the EPR signal are stabilized in the bulk. The observation of these electrons, when the sample has been treated at temperatures close to those at which the exothermal effect is observed, indicates that the ZrO_2 has been reduced and a certain amount of lattice oxygen has been lost. The unpaired electrons can be stabilized in Zr^{4+} ions to produce Zr^{3+} , oxygen vacancies, or

impurities (transition-metal ions or gaseous molecules). The transition-metal ions (Zr^{3+} or impurities) should show a broader signal with g values separated from g_e because of spin-orbit coupling effects. Taking into account that gas molecules evolve at the exothermal effect temperatures, we consider that the unpaired electrons are trapped by oxygen vacancies formed under the same conditions. Signals with characteristics similar to those of the signal observed in this work have been observed by other authors.¹⁰

Consequently the EPR spectra of sample A indicates that initially a certain amount of carbon is formed, which produces the dark coloration of the sample. When the sample is fired at 300°C for a long period, this carbon is burned using gaseous oxygen at the surface and probably lattice oxygen or gaseous molecules impurities at the bulk.

This combustion, which is responsible at least partially for the intense exothermal effect and the strong weight loss at 344°C, will help cause the formation of anionic vacancies, which will become trapping centers for electrons. These centers can trap one or two electrons, producing paramagnetic centers, which give EPR signals, or diamagnetic centers, which are not detectable by EPR, respectively. Some of these centers (color centers) can also produce dark coloration in the sample. If the loss of carbon and lattice oxygen is associated with weight loss at 344°C, the observed exothermal effects at 508° and 800°C in the DTA curve can be tentatively associated with the elimination of these two kinds of defects by oxygen adsorption. This process would also justify the slight weight increase (Fig. 1(A)) observed at those temperatures. The elimination of these defects, therefore, seems to be a previous step in the transformation of the tetragonal phase to the monoclinic one.

The thermal behavior of sample G shows less indicative details of structural transformation. Due to the preparation method this sample will contain smaller amounts of volatile as well as reducing elements, which coupled with a more porous structure will cause a sharp crystallization peak with less intensity and at higher temperature than in the case of sample A.

In summary, the experimental data indicate that the formation of lattice defects by the evolution of impurities during crystallization can be associated with the nucleation of the tetragonal phase. The similarity between the Zr-Zr and Zr-O distances in the amorphous

and tetragonal phases⁵ opens the way to the possibility of considering the process of crystallization only as an elimination of impurity molecules, thus allowing the growth of the ZrO₂ nuclei which now can be seen as tetragonal crystals. The presence of lattice defects instead of impurity molecules kept in the tetragonal phase represents a situation equivalent to the amorphous one, allowing the distances of the ions to be maintained. When by thermal treatment the defects have been eliminated, as observed by the loss of the EPR signal and whitening of the sample, those distances will tend to change to reach values that give a lower energy to the lattice, and the $t \rightarrow m$ transformation is produced. The elimination of the defects will also favor crystal growth, and in this way the critical crystal size proposed by Garvie can be understood.

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Critical Review of the Thermophysical Properties of Fast-Reactor Fuel

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This paper identifies the fuel properties for which more data are needed for fast-reactor safety analysis. In addition, a brief review is given of current research on the vapor pressure over liquid UO_2 and $(U,Pu)O_{2-x}$, the solid-solid phase transition in actinide oxides, and the thermal conductivity of molten urania.

I. Property Needs

HE most crucial thermophysical property needs for fast-reactor safety analyses have been identified in sensitivity studies on various safety codes. For fuel, these include the following: density

of the liquid, heat capacity, electrical conductivity, vapor pressure, and thermal conductivity. Table I summarizes the current status of research on these five properties.

Extensive measurements have been made on the thermodynamic properties of UO₂, but additional experiments are still needed for $(U,Pu)O_{2-x}$. The most recent and precise measurements of the density of liquid UO₂ are the experiments by Drotning.¹ Heat

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