244
10-20-77

15-06

LA-6918-MS

Informal Report

UC-25

Issued: September 1977

MAS

Zero and Low Coefficient of Thermal Expansion Polycrystalline Oxides

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UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

ZERO AND LOW COEFFICIENT OF THERMAL EXPANSION POLYCRYSTALLINE OXIDES

by

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ABSTRACT

Polycrystalline oxide systems with zero to low coefficient of thermal expansion (CTE) investigated by the author include hafnia-titania and hafnia. The CTE for 30-40 mol% TiO_2 in HfO_2 is $\leq 1 \times 10^{-6}/^\circ\text{C}$, while for other compositions in the range 25-60 mol% it is $\sim 4 \times 10^{-6}/^\circ\text{C}$. An investigation of the CTE of 99.999% HfO_2 yielded a value of $4.6 \times 10^{-6}/^\circ\text{C}$ from room temperature to 1000°C . Correlation with data on HfO_2 by other investigators shows a definite relationship between the CTE and the amount of ZrO_2 present. Data are listed for comparison of the CTE of several other polycrystalline oxides investigated by Holcombe at Oak Ridge.

RESUME

COEFFICIENT ZERO ET BAS D'OXYDES POLYCRYSTALLINS DE DILATATION THERMIQUE

Les systemes d'oxydes polycrystallins avec le coefficient zero à bas de dilatation thermique (CDT) étudiés par l'auteur comprennent les oxydes d'hafnium-dioxydes de titane et les oxydes d'hafnium. Le CDT pour 30-40 moles% TiO_2 en HfO_2 est $\leq 1 \times 10^{-6}/^\circ\text{C}$, tandis que pour d'autres compositions dans le domaine de 25-60 moles% il est $\sim 4 \times 10^{-6}/^\circ\text{C}$. Une étude du CDT de 99,999% HfO_2 a donné une valeur de $4,6 \times 10^{-6}/^\circ\text{C}$ de la température ambiante jusqu'à 1000°C . Une corrélation avec les données sur HfO_2 par d'autres chercheurs montre un rapport défini entre le CDT et la quantité de ZrO_2 présente. Les données sont portées sur une liste pour comparer le CDT de quelques autres oxydes polycrystallins étudiés par Holcombe à Oak Ridge.

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Hafnia—Titania

Considerable interest has been expressed in hafnia-titania compounds for use in flame tube liners in manufacturing processes and steam generators, and for ducts and heat exchangers in MHD systems. The $\text{HfO}_2\text{--TiO}_2$ system is one of the first polycrystalline oxide systems to be studied extensively because of the unusual property of low coefficient of thermal expansion (CTE). In 1960 Goćina et al¹ observed the low CTE in their study in the USSR. In the U.S. during the same year Simpson² reported that compositions from 30- to 40-mol% TiO_2 have zero or slightly negative CTEs.

Ten years later Lynch and Morosin³ in their study of the expansion, compressibility, and polymorphism of 37- and 50-mol% TiO_2 identified the b-axis in the orthorhombic system as having a strongly negative CTE while the other two axes remained positive. A more extensive investigation was conducted by Ruh et al⁴ who studied the CTE of 0- to 60-mol% TiO_2 in HfO_2 in 2.5-mol% increments. They determined that single-phase orthorhombic hafnium titanate exists in the range 36- to 53-mol% TiO_2 . Thermal expansion was measured as a function of composition, and very low coefficients of $\leq 1 \times 10^{-6}/^\circ\text{C}$ were found in the 30- to 40-mol% TiO_2 range. Moderate coefficients of $\approx 4 \times 10^{-6}/^\circ\text{C}$ were found for the 25-, 45-, 50-, and 60-mol% TiO_2 compositions. They attributed the low expansion behavior to microcracking. They also presented a phase diagram for the $\text{HfO}_2\text{--TiO}_2$ system, shown in Fig. 1. It is interesting to note from the phase diagram that this oxide can be heated from room temperature (RT) to over 2000°C across a broad range of compositions and not undergo a single polymorphic transformation. At about 48 mol% the material can be heated to $\sim 2800^\circ\text{C}$ with no crystallographic change.

Discontinuities in other properties were found by other investigators in the same composition range. For example, Hoagland et al⁵ reported that the strength and the modulus were nearly constant in the 30- to 40-mol% TiO_2 range and increased by a factor of 2 in the 45- to 50-mol% TiO_2 range.

Anderson et al⁶ began a study* of 25- to 60-mol% TiO_2 in HfO_2 to determine as a function of composi-

Fig. 1.
Hafnia-titania phase diagram as proposed by
Ruh et al.⁴ (with permission).

tion 1) the coefficient of thermal expansion, 2) the dynamic response to pulsed energy deposition, and 3) the Grüneisen parameter determined independently using the thermal expansion data (static) and the pulsed deposition data (dynamic).

The CTE was determined from room temperature to 800°C using a Fizeau interferometer* on hot-pressed samples 1.5 mm square by 5 mm long. Several thermal cycles were imposed on the samples of each composition of 25-, 30-, 36.75-, 40-, 45-, 50-, and 60-mol% TiO_2 . The CTE data fall into two groups. The data for 30-, 36.75-, and 40-mol% TiO_2 have values $\approx 1 \times 10^{-6}/^\circ\text{C}$ or less and increase very slightly with increasing TiO_2 content. The data for 25-, 45-, 50-, and 60-mol% TiO_2 have values of $\geq 4 \times 10^{-6}/^\circ\text{C}$, see Fig. 2.

Thermal cycling of the samples yielded interesting results. On the second thermal cycle the CTE for the 25-mol% TiO_2 sample duplicated the

*The author was a coinvestigator in this study.

*Model 118, Gaertner Scientific Co., Chicago, Ill.

Fig. 2.

Thermal expansion of $\text{HfO}_2\text{-TiO}_2$ compositions vs temperature. The curves are an average of at least five thermal cycles with exception of those mentioned above.

first curve. On the third cycle the CTE did not repeat but doubled in value and the sample disintegrated. A second sample was cycled and it disintegrated on the third thermal cycle also. In contrast, the 30- and 36.75-mol% TiO_2 samples were cycled several more times and retained their integrity throughout the thermal cycling. This same contrast in behavior was noted in the earlier work by Ruh et al.⁴

For the dynamic response experiments, pulsed electron beam energy deposition was used to generate stress waves in hot-pressed disks of the same material. The Nereus generator was described in the report by Anderson et al.⁶ The sample configuration used in this study is a 12.7-mm-diam, 0.4-mm-thick $\text{HfO}_2\text{-TiO}_2$ disk epoxied to a 25.4-mm-diam, 1.5-mm-thick, fused- SiO_2 disk with a silvered (mirror) rear surface. The electron beam is incident

on and totally absorbed by the $\text{HfO}_2\text{-TiO}_2$ disk. The velocity-time history is measured with a displacement interferometer focused on the mirrored surface of the fused- SiO_2 disk.

Experiments were run on the 30-, 36.75-, 40-, 45-, and 50-mol% TiO_2 compositions at incident fluences of 330 and 710 kJ/m^2 . These fluences correspond to peak deposited energies of 0.58 and 1.25 MGy ,* or peak temperatures of about 1100 and 2200°C (using approximate heat capacities). One or two experiments were conducted on each material at each fluence.

Figure 3 shows the peak free-surface velocities obtained for all five materials. It can be seen that the

*1 $\text{J/g} = 1 \text{ kGy}$.

1 MGy (megagray) = 1000 J/g .

Fig. 3.

Peak free-surface velocities of $\text{HfO}_2\text{-TiO}_2$ samples bombarded with electrons of $\langle E \rangle = 225$ keV.

trends in peak free-surface velocity are similar to the CTE data, i.e., the three compositions with 30-40% TiO_2 have lower U_{fs} than the 45-50% TiO_2 compositions. In the high-fluence experiments the peak deposited energy (1.25 MGy) was approaching the melt energy of the materials (1.42 MGy). This, coupled with the higher amplitude of the stress waves, resulted in a front-surface spallation of an ~ 0.03 -mm layer of the sample materials in every experiment.

The measured peak free-surface velocity can be related to an average Grüneisen parameter, Γ , through the wave velocity, U_s , and the peak deposited energy, E , for the dynamic case.

$$\Gamma = \frac{U_s U_{fs}}{E}$$

A one-dimensional wave propagation computer code⁷ is used to account for finite deposition time and the impedance mismatch, and thus obtain values for Γ from our experimental U_{fs} data.

For the static case the Grüneisen parameter can be calculated from other material properties,

$$\Gamma = 3 \frac{\alpha K_s}{\rho C_p}$$

with α the coefficient of linear expansion, K_s the isentropic bulk modulus, and C_p the heat capacity at constant pressure. The values of α up to 800°C are given in Fig. 2, and K_s and C_p are known approximately from other sources.⁸ With these data, an average Γ was calculated for the temperature range 23-800°C. The values of Γ calculated from CTE data and from the lower fluence dynamic response data (representing Γ from 23-1100°C) are plotted in Fig. 4.

There is fairly good agreement between the two methods for calculating the Grüneisen parameter. The discontinuous jump at 45 mol% TiO_2 is a confirmation of the change in the materials noted in other properties already described. Disagreement between the two methods for the data in Fig. 4 may appear large on a relative basis ($>50\%$); however, on an absolute basis, when compared with normal materials, the agreement is quite good. For example, in a fully dense material of normal CTE the value of Γ ranges from 1-3. Although the low value for this material is primarily related to the low CTE of the $\text{HfO}_2\text{-TiO}_2$ mixtures, a small portion can be attributed to porosity, for it takes some energy to close the pores as the stress wave passes through the material. Stress in the dynamic experiments of 0.1-0.3 GPa

Fig. 4.

Grüneisen parameter as calculated from the static data (black dots) and from the dynamic response data (open circles).

was sufficient to cause some pore collapse, but the material was not treated as fully dense even after the energy deposition.

Hafnia and Zirconia Systems

After the investigations on the hafnia-titania system by Ruh et al.⁴ and Anderson et al.,⁶ it was apparent that the end members of the system needed better understanding. Reed⁹ has worked with TiO₂ quite extensively and has shown that it is difficult to obtain pure stoichiometric TiO₂, although he has obtained many compositions between Ti metal and TiO₂. Because of his extensive work on the Ti-O system we decided to concentrate our investigations on the other end member, HfO₂, which initially appeared to be a neglected area of study. A separate investigation was conducted on pure ZrO₂ because it is isomorphous with HfO₂ and it has been studied quite extensively.

Several measurements on zirconia were performed after the initial measurement was made on hafnia and were prompted by the large disagreement between our results and those of other investigators. Using two separate techniques, a Fizeau interferometer and a quartz dilatometer, we found the average value of the CTE of fairly pure ZrO₂ to be $7.3 \times 10^{-6}/^{\circ}\text{C}$ in good agreement with the measurements of others.

Geller and Yavorsky,¹⁰ the first to study relatively pure ZrO₂, found a CTE value of $7.3 \times 10^{-6}/^{\circ}\text{C}$ in heating and cooling over a range of 80-900°C. Burdick and Hoskyns¹¹ obtained a value of $7.24 \times$

$10^{-6}/^{\circ}\text{C}$ over the temperature range from room temperature to 1075°C (the monoclinic-tetragonal transformation). Grain and Campbell measured a value of $7.37 \times 10^{-6}/^{\circ}\text{C}$ over the temperature range of room temperature to 964°C.

Several more measurements were made on the very pure (99.999%) HfO₂ samples.* The average bulk CTE was $4.6 \times 10^{-6}/^{\circ}\text{C}$ for several samples cycled as many as 10 times between room temperature and 1000°C. Values for the axial expansion coefficients are shown in Table I. Note that there is a considerable disparity, about 30%, between the axial expansion coefficient and the bulk CTE. We attribute this to microcracking because of the sigmoid behavior of the coefficient of thermal expansion when plotted as a function of thermal cycles.

A scanning electron microscope (SEM) was used to try to view the microcracks in a similar fashion to those observed in the hafnia-titania system. We were unable to see the microcracks in the pure hafnia; however, the limits of resolution of the SEM were $\sim 0.03 \mu\text{m}$.

In a review of the literature we found the CTE for HfO₂ has been investigated by several groups. Curtis et al.,¹² Grain and Campbell,¹³ Ohynsty and Rose,¹⁴ Patil and Subbarao,¹⁵ Filatov and Frank-Kamanetskii,¹⁶ and Stacy et al.,¹⁷ have studied a range of compositions of HfO₂. There is a variation of about a factor of 2 in the values of CTE quoted by each of the investigators. The study in which the

*Cerac-Pure, Menominee Falls, Wisconsin, USA.

TABLE I

HfO₂ LATTICE EXPANSION COEFFICIENTS, $\times 10^{-6}/^{\circ}\text{C}$

T (°C)	α_a	α_b	α_c	$1/3(\alpha_a + \alpha_b + \alpha_c)$
27	---	---	---	
250	6.397	-1.471	11.866	5.597
500	7.841	0.653	13.998	7.497
750	7.607	0.294	12.093	6.665
1000	7.510	0.059	12.355	6.641
1250	7.338	-1.347	12.363	6.451

author participated showed still a different value for the CTE of 99.999% HfO_2 , $4.6 \times 10^{-6}/^\circ\text{C}$.

Examination of all of the data available from each sample including this study showed quite a wide variation in the zirconia content. The CTE for each sample was plotted against zirconia content in the sample and the result is shown in Fig. 5. With the exception of the value obtained by Patil and Subbarao, all of the data lie on the same line on semilogarithmic paper with the material in this study being the purest and therefore the lowest in CTE. Apparently there is a strong influence exerted on the CTE of HfO_2 by Zr substituted in specific lattice sites for Hf. The relationship shown in Fig. 3 also suggests that the thermal expansion of HfO_2 can be tailored to a specific value by doping the material with ZrO_2 in a controlled way.

Other Systems

Simultaneously with the work at LASL and Air Force Materials Laboratory (AFML), there was a study conducted by Holcombe and his coworkers¹⁸ at the Union Carbide Corporation (UCC) in Oak Ridge. This group surveyed the various combinations of oxides that might exhibit low or zero CTE behavior. They first explored the HfO_2 - TiO_2 system

as we did, and then progressed to the Al_2O_3 - TiO_2 system. Finally they extended their investigation to other systems which might possibly contain low expanding materials. The choice of the new systems was made using the following considerations. They listed the single oxides which have low expansions: TiO_2 , Nb_2O_5 , Ta_2O_5 , SnO_2 , and WO_3 . They combined these oxides with those that had a history of a low CTE by themselves or in combination with the first group of oxides. These are HfO_2 , ZrO_2 , Al_2O_3 , Y_2O_3 , and NiO . All of this latter group have high melting points, and were chosen because low expanding systems had been reported elsewhere in the literature.

Holcombe attempted first to identify the materials or combinations that had characteristic low expansions, and then to identify the mechanisms that cause the low expansions. Table II lists the oxides that he investigated and reported in four categories; 1) negative or zero CTE, 2) very low CTE ($\leq 1 \times 10^{-6}/^\circ\text{C}$), 3) low CTE ($1.4 \times 10^{-6}/^\circ\text{C}$), and 4) intermediate CTE ($4.8 \times 10^{-6}/^\circ\text{C}$). He also noted in passing but did not investigate several other materials, most of which are naturally occurring minerals such as quartz and β -eucryptite, which have near zero or very low CTE.

Sample Preparation

A presentation of this kind would not be complete without some discussion of the methods of preparation and fabrication. Holcombe prepared his own powders by the technique described by Masdiyasi et al.¹⁹ LASL purchased powders prepared commercially. The distinguishing difference between the two is that the commercially prepared powders are typically ~ 325 mesh, whereas those prepared in the laboratory are $200\text{--}400 \mu\text{m}$. This may have some influence on the characteristic behavior of the final sample.

Holcombe pressed the fine powders into rods isostatically at 200 MPa (300 000 psi). The rods were sintered in flowing argon at $80\% T_m$ for 4 h using alumina or boron nitride crucibles. Several steps were taken to characterize the material after fabrication into rods. Chemical analysis was done

Fig. 5.

Bulk coefficient of thermal expansion of hafnia as a function of the impurity content of zirconia.

TABLE II

LIST OF COMPOUNDS INVESTIGATED BY HOLCOMBE AND
THEIR COEFFICIENT OF THERMAL EXPANSION

Compound	Binary/ Ternary	Crystal System	CTE $\times 10^{-6}$
Negative or Zero			
Ta ₂ O ₅ ·WO ₃	B	ortho	-3.34
55Ta ₂ O ₅ ·45WO ₃	B	incongruent melt-	-0.6
45Ta ₂ O ₅ ·55WO ₃	B	ing behavior in	-2.0
37Ta ₂ O ₅ ·63WO ₃	B	this region of the phase diagram	-0.7
63HfO ₂ ·37TiO ₂	B	ortho	~0
HfO ₂ ·WO ₃ ·Ta ₂ O ₅	T	ortho	~0
(Very low $\leq 1 \times 10^{-6}/^{\circ}\text{C}$)			
HfO ₂ ·Nb ₂ O ₅	B	---	<1
Al ₂ O ₃ ·TiO ₂	B	ortho	0.8
(Low $1-4 \times 10^{-6}/^{\circ}\text{C}$)			
HfO ₂ ·3Nb ₂ O ₅	B	---	3.2
HfO ₂ ·3Ta ₂ O ₅	B	---	3.36
SnO ₂ ·Ta ₂ O ₅	B	monoclinic	1.68
HfO ₂ ·TiO ₂	B	ortho	3.59
Nb ₂ O ₅ ·TiO ₂	B	monoclinic	2.3
Ta ₂ O ₅ ·TiO ₂	B	monoclinic	3.4
ZrO ₂ ·Nb ₂ O ₅	B	---	2.71
ZrO ₂ ·3Nb ₂ O ₅	B	---	2.5
63Al ₂ O ₃ ·37TiO ₂	B	---	1.47
63(75HfO ₂ ·25ZrO ₂)37TiO ₂	T	---	2.24
Negative or Zero			
(Intermediate $4-8 \times 10^{-6}$)			
HfO ₂ ·Al ₂ O ₃	B	---	7.43
HfO ₂ ·Ta ₂ O ₅	B	---	4.82
Al ₂ O ₃ ·Ta ₂ O ₅	B	ortho	4.96
MgO·Ta ₂ O ₅	B	tetra	6.79
NiO·Ta ₂ O ₅	B	tetra	4.10
Y ₂ O ₃ ·TiO ₂	B	ortho	8.77
ZrO ₂ ·Ta ₂ O ₅	B	---	5.72
63(50HfO ₂ ·50Al ₂ O ₃)· 37TiO ₂	T	---	6.45

TABLE II (cont)

Compound	Binary/ Ternary	Crystal System	CTE $\times 10^{-6}$
63(25HfO ₂ , 75Ta ₂ O ₅) · 37TiO ₂	T	---	5.31
63(50HfO ₂ , 50ZrO ₂) · 37TiO ₂	T	..	5.9
63(25HfO ₂ , 75ZrO ₂) · 37TiO ₂	T	---	6.67
63ZrO ₂ · 37TiO ₂	B	---	<7.2
63(33Al ₂ O ₃ , 33HfO ₂ , 33ZrO ₂) · 37TiO ₂	Q	---	6.45
Al ₂ O ₃ · 2TiO ₂ · Ta ₂ O ₅	T	---	7.09
Al ₂ O ₃ · 2HfO ₂ · Ta ₂ O ₅	T	---	4.43
Y ₂ O ₃ · 2TiO ₂ · Ta ₂ O ₅	T	ortho	7.49
Y ₂ O ₃ · 2HfO ₂ · Ta ₂ O ₅	T	---	6.56
2MgO · 2Al ₂ O ₃ · 5SiO ₂	T	---	8.1

by atomic absorption or x-ray fluorescence depending on the particle size. Densities were measured on the specimens after thermal expansion data were taken. The melting points and phase changes were observed by DTA-TGA against alumina standards. Electrical resistivity was measured before and after each thermal expansion measurement. Thermal expansion was determined using a quartz push rod dilatometer over the range from room temperature to 1000°C. Data from the measurements were fed to a small computer which plotted the expansion curve vs temperature. Fused silica and platinum from the NBS were used as standards. The error was estimated to be $\pm 3\%$ of any given value.

Both UCC and LASL have experimented with plasma spraying both the commercial and laboratory prepared powders. The plasma flame partially melts the fine particles which are then propelled toward the work piece and fuse to it in a granular covering. If the sprayed material is examined microscopically a considerable amount of connected porosity is visible. The particle shape, rather than being angular, is now a pancake shape with smooth edges and a depressed or flattened center. In addition, the material is definitely not the same stoichiometry as the powder before spraying. This may pose a problem in that the altered

stoichiometry does not have the same expansion characteristics as the initial powder.

Methods for compensating for the altered compositions are 1) to spray a composition that, when it passes through the gun, will have been altered to the desired expansion characteristics, and 2) to reoxidize the sprayed powder by heat treating it. The former is more desirable because very often the substrate will not tolerate the oxidizing environment necessary to achieve the presprayed CTE conditions.

Adhesion of the materials to the substrate is improved by grit blasting the metal prior to plasma spraying. LASL has prepared free-standing pipes, tubes, and crucibles by spraying onto copper and dissolving the copper later with acid. UCC has developed a production technique for plasma-spraying a high-temperature crucible by spraying oxides on the inside of W-Ni-Fe mandrels. The large difference in thermal expansion allows the crucible to be removed when the part cools to room temperature. UCC also discovered that when Y₂O₃ was sprayed on the same metal substrate, it bonded very tightly.

Plasma spraying has been used at LASL to make most shapes of rotation. Figure 6 shows a combined cylinder and hemisphere shape which is being

Fig. 6.
A typical shape being plasma-sprayed with alumina at Los Alamos.

sprayed with a uniform coat of Al_2O_3 . A small section of a spray coating like this was removed for CTE measurements.

Common Factors Observed in Low CTE Materials

If one looks carefully at these compounds for common properties in order to predict what may be causing the low CTE, the following things are noted. The symmetry of the unit cell is never cubic, very infrequently tetragonal, and in the large majority of cases it is orthorhombic. In some cases it might even be monoclinic. Allied with this property of low symmetry are strong axial expansions and contractions. For instance, the axial expansion in the hafnia-titania system for orthorhombic HfTiO_4 is very

strongly negative along the b axis, while it is moderately positive along the a axis.

The compounds that exhibit the low expansion properties are in large majority ternary or higher order combinations indicating there is probably an influence from the electronic configuration of the metal atoms on an atomic scale, just as there is an influence from the atom positions in the lattice on a molecular scale. The structures however are not complicated. They contain lots of open space similar to glasses. All of the compounds investigated by us and most of the ones investigated by others have melting points $\geq 1400^\circ\text{C}$. The hafnia-titania system contains a composition at about 45% TiO_2 that is single-phase material from room temperature to $\sim 2800^\circ\text{C}$. This is a greater range than any other known compound.

Many people have attributed the curious expansion behavior to microcracking of the grains in these materials. In our very pure HfO_2 study, we were unable to detect any microcracks,²⁰ and Holcombe has had difficulty observing microcracks in the material he has studied. In contrast, however, the hysteresis behavior that is characteristic of the CTE with successive thermal cycles is present in most of these

samples. Holcombe²¹ has speculated on possible mechanisms of "plastic flow" that might cause this behavior to occur and without exhibiting microcracks. (See Appendix.) Blendell and Coble²² while studying Al_2O_3 have described a stress relaxation phenomenon related to grain size. The two hypotheses are related and are of interest to others but will not be elaborated on here.

APPENDIX

HOLCOMBE'S "PRINCIPLES"²¹

1) The structure contains chains or spirals of corner-bonded polyhedra in the lowest expanding or contracting direction. This direction may not coincide with a principal axis of the unit cell, therefore the contraction may be vectorally divided along axial directions.

2) Channels (tunnels or structural voids) must exist in the structure. The open structure permits stuffing of the lattice with small cations without affecting the CTE appreciably. When the lattice becomes filled, the CTE will increase. This behavior has been observed in $\text{Ba}_{-4}\text{Na}_{-2}\text{Nb}_{10}\text{O}_{30}$, a stuffed analog of tungsten bronze manifested in nature by the pyroxenes and zeolites.

3) Tilting of polyhedra is restricted to the direction of channels by a "symmetry clamping" effect. The more restricted the tilt is in the direction of the channel, the smaller the thermal expansion.

4) Polyhedra are distorted and tend to reduce the distortion when heated thus tending to equalize the bond length. The degree of distortion depends on a) cation-anion bond length, b) substitution of differing size cations in specific sites of neighboring polyhedra, c) edge bonding, and d) anion deficiency. This implies that the polyhedral distortion, thus CTE, can be controlled by solid solution as has been demonstrated by Merz et al²³ and by Holcombe with HfO_2 in Ta_2WO_6 .

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