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Y-1913

**SURVEY STUDY OF LOW-EXPANDING,
HIGH-MELTING, MIXED OXIDES**

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**UNION
CARBIDE**

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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ABSTRACT

Approximately 40 mixed oxide materials were prepared and characterized primarily as to their thermal expansion and melting-point behavior. Of particular interest were those materials which were stable, had melting points in excess of 1,400° C, and had low thermal expansions.

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SUMMARY

A survey of the preparation and characterization of mixed oxides revealed twenty intermediate, ten low, and eight very low expanding compositions with melting points in excess of $1,400^{\circ}\text{C}$. Zirconium oxide and aluminium oxide additions to the HfTiO_4 system were studied. Several compositions over a wide range in the $\text{WO}_3 \cdot \text{Ta}_2\text{O}_5$ system revealed thermal contraction to $1,000^{\circ}\text{C}$. Two other compositions ($\text{HfO}_2 \cdot \text{Nb}_2\text{O}_5$ and $\text{HfO}_2 \cdot \text{WO}_3 \cdot \text{Ta}_2\text{O}_5$) were also found to exhibit very low expansive behavior.

INTRODUCTION

There is a general industrial need for low-expanding, refractory ceramics with high thermal shock resistance. Extensive uses for such materials include turbine blades, flame tube liners, refractory coatings and other elements of combustion systems (liners, calcining trays, saggars, quenching crucibles, furnace structures, and supports), high-temperature requirements for aircraft, high-speed abrasives, and electrical insulators.

Thus, a study was undertaken at the Oak Ridge Y-12 Plant^(a) to prepare and characterize a broad range of mixed oxides which have the characteristics of stability, high melting points (arbitrarily $> 1,400^{\circ}\text{C}$), and low thermal expansion (preferably with $\alpha < 1 \times 10^{-6}/^{\circ}\text{C}$). The investigated mixed oxide compositions were chosen by considering the single oxides which have low expansion properties (including systems with TiO_2 , Nb_2O_5 , Ta_2O_5 , SnO_2 , and WO_3) in conjunction with high-melting-point oxides (such as HfO_2 , ZrO_2 , Al_2O_3 , Y_2O_3 , and NiO). The binary systems were chosen to include low-expanding compounds which had been reported in the literature. Since compounds having orthorhombic or lower-symmetry structures usually have lower expansion than compounds with higher symmetry,⁽¹⁾ lower-symmetry compounds were those generally selected for this study. The two highest melting mixed oxide compounds with low expansion properties are $\beta\text{-Al}_2\text{TiO}_5$ (mp, $1,860^{\circ}\text{C}$)^(2,3) and HfTiO_4 (mp, $> 2,000^{\circ}\text{C}$)^(4,5). Also included were solid solutions of high-melting-point oxides with these two materials.

In order to obtain specimens with optimum homogeneity, organometallic coprecipitation techniques were used. Isostatic pressing of the calcined mixed oxides was used to insure minimum preferred orientation effects in the thermal expansion measurements.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

A SURVEY OF MIXED OXIDES

EXPERIMENTAL WORK

Material Preparation

Syntheses of Organometallic Precursors - The basic method employed in preparing the various mixed-oxide systems examined consisted of the cohydrolysis to the mixed metal hydroxides from solutions of the respective metal alkoxides. Metal alkoxides are compounds of the general type $M(OR)_x$ where x represents the valence of the metal (M) and R represents an alkyl group. Upon hydrolysis, a majority of the metal alkoxides exhibit cleavage of the $M-OR$ bonds, and a hydrated metal hydroxide is formed.

Several of the metal alkoxides used during this study were obtained commercially, namely: the aluminum and titanium isopropylates $[Al(OC_3H_7)_3]$ and $Ti(OC_3H_7)_4]$ and tetraethyl orthosilicate $[Si(OC_2H_5)_4]$. The remaining alkoxides used were prepared at Y-12 by employing standard metal alkoxide preparative procedures.⁽⁶⁾ The materials needed for the various syntheses were of a nominal 99 percent purity. All syntheses were carried out in an argon atmosphere.

There were two basic preparative methods used: (1) synthesis from the free metal, and (2) synthesis from the metal chloride. Preparation of the majority of the mixed-oxide systems was based on the syntheses of the metal ethylates or isopropylates from the metal chlorides and either absolute ethanol or isopropanol. These syntheses followed the general reaction:

where x represents the valence of the metal (M). (M is either Ta, Nb, Hf, Zr, Sn, or Ni.)

In the case of tungsten, the oxychloride was used rather than the chloride, thus:

Since the tungsten alkoxide was photosensitive, it was prepared immediately before use.

The free metal reaction with the alcohol was employed in the preparation of the yttrium isopropylate $[Y(OC_3H_7)_3]$.⁽⁷⁾ The reaction consisted of the addition of yttrium metal turnings to isopropanol, with mercuric chloride present as a catalyst, and then refluxing the mixture for 48 hours. The reaction is described by the following equation:

Several of the metal isopropylates were converted to their respective tert-amylates by an ester exchange between the individual metal isopropylates and an excess of tert-amyl alcohol, according to the general reaction:

The ester exchange permitted the use of compounds that exhibit very similar hydrolysis rates.

Due to the limited solubility of the magnesium alkoxides, a Grignard compound was utilized.

Cohydrolysis of Mixed Oxides - To prepare the various mixed metal hydroxides, the metal tert-amylates, isopropylates, or ethylates were refluxed for three hours in quantities calculated to produce the desired molar ratios of the mixed oxides. After refluxing, the cooled solutions were hydrolyzed by the dropwise addition of distilled water with vigorous stirring. The general equation for the hydrolysis was:

where "A" and "B" were either Ta, Nb, Ti, Zr, Hf, Sn, W, Ni, or Al and "R" was C_2H_5 , C_3H_7 , or C_5H_{11} .

There was one exception to the procedure just described for producing the mixed hydroxides. In preparing the systems containing magnesium oxide (namely, $MgO \cdot Ta_2O_5$ and $2 MgO \cdot 2 Al_2O_3 \cdot 5 SiO_2$), a freshly prepared Grignard reagent (phenyl magnesium bromide) was added to the metal alkoxides of the other components in a dry box. Upon the addition of the Grignard, a precipitate began to form and the reflux step before hydrolysis was omitted. In the case of $2 MgO \cdot 2 Al_2O_3 \cdot 5 SiO_2$, the aluminum and silicon alkoxides were refluxed for three hours before adding the calculated amount of the Grignard reagent and subsequent hydrolysis.

The main problem encountered by using this cohydrolysis technique is to obtain component alkoxides that have the same or nearly the same rate of hydrolysis. If sufficient matchup of these rates is not obtained, the final chemical compositions will depart significantly from the calculated values. The metal alkoxides that presented the greatest problem in this area were those of tungsten and silicon. These problems are reflected in the low weight percentages measured by chemical analysis. The tetraethyl orthosilicate $[Si(OC_2H_5)_4]$ appeared to be only slightly hydrolyzed and, hence, only provided an extremely low silicon content in the attempt to prepare $2 MgO \cdot 2 Al_2O_3 \cdot 5 SiO_2$.

Fabrication of Samples - All products of the coprecipitation reactions were vacuum dried at $50^\circ C$ for 24 hours and then calcined at temperatures of $800 - 1,000^\circ C$ for 40 hours in an air environment. The resultant fine powders were then isostatically pressed into rods at 30,000 psi. These rods were sintered in a flowing argon atmosphere in alumina or boron nitride containers at temperatures about 20 percent below the melting temperatures (in $^\circ C$) determined previously by a differential thermal analysis-thermal gravimetric analysis study

(DTA-TGA) of the calcined powders. Soaking times were for two to four hours at the sintering temperatures. Heatup time was about four hours, and the specimens were furnace cooled after sintering (about two hours). The rod specimens were nominally 1 1/2 inches long and 1/2 inch in diameter.

Methods of Property Determinations

Chemical Analyses - Chemical analyses were made by either X-ray fluorescence or atomic absorption methods, depending on the particular species in question.

Densities - Densities were obtained using either mercury intrusion porosimetry or kerosene absorption (ASTM C-373-56) on the specimens after their thermal expansions were measured. Theoretical (X-ray) densities were calculated or taken from the literature for compounds for which the crystal structure was known.

Phase Identification - Qualitative phase identification was by X-ray diffraction using $\text{CuK}\alpha$ radiation with the Debye-Scherrer film or diffractometer techniques.

Thermal Analyses - Thermal analyses (DTA-TGA) were obtained to determine melting points and other behavior. Instrumentation (thermoanalyzer Model TA1, Mettler Instrument Corp) had a temperature capability of 2,400° C. Samples were run in tungsten containers in a flowing helium-2% hydrogen atmosphere. Temperatures were measured with a tungsten/tungsten-25 percent rhenium thermocouple using aluminum oxide (SRM 742) as a melting point standard. Heating rates of from 5 to 25° C per minute were used.

Electrical Resistivities - Room-temperature electrical resistivities were performed on most of the specimens; some appeared to be too friable to test. Resistivities were made both before and after the thermal-expansion tests to determine whether significant variations as a function of testing could be found. A John Fluke Model 8100 A digital multimeter and a Keithly Model 500 megohmmeter were used with appropriate standard resistances.

Thermal Expansion - Thermal expansive behavior was determined from 20 to 1,000° C, using a quartz pushrod dilatometer. Samples were tested in argon using heating rates of 5 - 10° C per minute. Data acquisition was by digital multiplexed signals from a LVDT and platinum/platinum-10 percent rhodium thermocouple. A computer program was used to reduce the data and to plot expansion versus temperature. National Bureau of Standards fused silica and platinum were used as expansion standards. Error is estimated to be within ± 3 percent of the given values.

RESULTS AND DISCUSSION

The results of the study are summarized in Tables 1 and 2. The compositions tested had melting points in excess of 1,400° C and exhibited coefficient of thermal expansion (CTE) values from -3 to $9 \times 10^{-6}/^{\circ}\text{C}$ over the temperature range from 20 to 1,000° C. Calcined materials, in general, were amorphous (with broad, diffuse X-ray diffraction patterns); incompletely reacted; or, in some cases, well crystallized. The amorphous nature of some coprecipitated powders had previously been observed in the literature⁽³⁴⁾ and depends on

Table 1
BINARY COMPOSITIONS

Batch Reference Number	Composition	Calcined Material			Sintered Material																		Coefficient of Thermal Expansion (̑ x 10 ⁶)	Electrical Resistivity (ohm-cm)			Literature Reference(1)	Comments(2)
		DTA-TGA			Melting Point (° C) Measured Literature	Anomalous Points	Weight Loss Before Melting (%)	Sintering Conditions		Chemical Analysis			Density		Apparent Specific Gravity	Porosity (%)	X-Ray Diffraction			Reported Crystal System								
		X-Ray Diffraction						Temperature (° C)	Time (hr)	Oxide Component	Theoretical (%)	Measured (%)	Theoretical (g/cm ³)	Bulk (g/cm ³)			Major	Intermediate	Minor									
		Major	Intermediate	Minor																								
		Major	Intermediate	Minor																								
With Hafnium Oxide																												
5C-72-72	HfO ₂ · Al ₂ O ₃	HfO ₂		Al ₂ O ₃ , Unidentified Lines	1880	1745 EN(3)	None	1500	4	HfO ₂ Al ₂ O ₃	67.96 32.63	64.96 34.58	4.15	6.61	37.2	HfO ₂	Al ₂ O ₃			7.43	1.5 · x 10 ⁸	6.2 · x 10 ⁷	8	No compounds form in this system.(8)				
5C-38B-72	HfO ₂ · Nb ₂ O ₅				1425	None	None	1400	3	HfO ₂ Nb ₂ O ₅	44.2 55.8	43.00 55.08	3.92	6.29	37.7	Nb ₂ Hf ₆ O ₁₇ (ss)	Nb ₂ O ₅ (ss)			< 1.0 (with phase change)	7.1 · x 10 ²	2.8 · x 10 ¹	9-12					
6M-8-72	HfO ₂ · 3Nb ₂ O ₅				1425	None	None	1400	2	HfO ₂ Nb ₂ O ₅	20.88 79.12	20.20 79.30	3.31	5.09	34.8	Hf ₂ Nb ₁₀ O ₂₉		̢-Nb ₁₂ O ₂₉ (w)		3.2	3.0 · x 10 ⁰		9-12					
5C-36-72	HfO ₂ · Ta ₂ O ₅	̢-Ta ₂ O ₅	Ta ₂ Hf ₆ O ₁₇		1760	None	None	1450	3	HfO ₂ Ta ₂ O ₅	32.26 67.74	32.36 67.59	5.74	9.17	37.5	Ta ₂ O ₅ (tricl ss) Ta ₂ Hf ₆ O ₁₇ (ss)				4.82	5.0 · x 10 ⁹	3.5 · x 10 ⁸	9-12					
6M-11-72	HfO ₂ · 3Ta ₂ O ₅	Ta ₂ O ₅	Ta ₂ Hf ₆ O ₁₇		1840	None	None	1450	2	HfO ₂ Ta ₂ O ₅	13.70 86.30	12.24 87.33	4.23	8.69	51.3	Ta ₂ O ₅ (tricl ss)	Ta ₂ Hf ₆ O ₁₇ (ss)			3.36	~ 10 ¹⁰	~10 ¹⁰	9-12					
With Tantalum Oxide																												
5C-69-72	Al ₂ O ₃ · Ta ₂ O ₅	AlTaO ₄ , ̢-Ta ₂ O ₅		Unidentified Lines	1663	1693	None	None	1350	5	Al ₂ O ₃ Ta ₂ O ₅	18.75 81.25	18.10 81.96	6.86	5.17	6.55	21.1	AlTaO ₄ (hex)	̢-Ta ₂ O ₅	Unidentified Lines	Orthorhombic	4.96	9.0 · x 10 ⁷	1.3 · x 10 ⁸	9, 10, 12-14			
6C-13A-72	MgO · Ta ₂ O ₅	MgTa ₂ O ₆			1725	1770	1012-1070 EN	None	1380	4	MgO Ta ₂ O ₅	8.40 91.60	8.27 92.41	7.85	4.92	7.91	37.8	MgTa ₂ O ₆		̢-Ta ₂ O ₅	Tetragonal	6.79	5.1 · x 10 ⁷	6.0 · x 10 ⁷	12, 15	Congruent melting behavior.(15) Rapid weight loss began at melting.		
5C-86-72	NiO · Ta ₂ O ₅	NiTa ₂ O ₆		̢-Ta ₂ O ₅	1690	None		17.1	1350	4	NiO Ta ₂ O ₅	14.50 85.50	12.42 88.01	8.44	6.95	8.47	17.9	NiTa ₂ O ₆	̢-Ta ₂ O ₅		Tetragonal	4.10	1.9 · x 10 ⁸	3.8 · x 10 ⁷	16	Rapid weight loss began at melting.		
5C-79-72-1	SnO ₂ · Ta ₂ O ₅	̢-Ta ₂ O ₅	SnO ₂		1518	1875 EN		40.8	1500	4	SnO ₂ Ta ₂ O ₅	23.40 76.60	23.49 74.62	8.52	4.26	8.08	47.3	SnO ₂ , Ta ₂ O ₅			Monoclinic	1.68	2.9 · x 10 ⁷	2.1 · x 10 ⁷	17	Severe weight loss began at ~ 1250° C.		
6C-31-72	WO ₃ · Ta ₂ O ₅	3WO ₃ · Ta ₂ O ₅			1593	1580	1318 EX(4)	16.9	1550	4	WO ₃ Ta ₂ O ₅	34.41 65.59	17.95 81.81	7.79	6.28	7.77	19.2	Ta ₂ WO ₈			Orthorhombic	-3.34	1.1 · x 10 ⁶		18-21	Incongruent melting behavior.(21) Rapid weight loss began at ~ 1540° C.		
6C-47-72	45WO ₃ · 55Ta ₂ O ₅	̢-Ta ₂ O ₅			1620		800-1190 EX	None	1500	3	WO ₃ Ta ₂ O ₅	30.03 69.97	26.96 73.20		5.88	7.42	20.7	11Ta ₂ O ₅ · 4WO ₃ (similar to ̢-Ta ₂ O ₅), W				-0.6	1.4 · x 10 ⁴	1.01 x 10 ⁵	18-21			
6C-46A-72	55WO ₃ · 45Ta ₂ O ₅	̢-Ta ₂ O ₅			1529		780-1140 EX	None	1500	3	WO ₃ Ta ₂ O ₅	39.07 60.93	33.75 66.38		5.90	8.14	27.5	Ta ₂ WO ₈				-2.0			18-21			
6C-46B-72	63WO ₃ · 37Ta ₂ O ₅	̢-Ta ₂ O ₅			1550		1160-1280 EX	None	1500	3	WO ₃ Ta ₂ O ₅	47.18 52.82	36.95 63.30		5.01	6.70	25.3	Ta ₂ WO ₈				-0.7	3.7 · x 10 ²	1.1 · x 10 ³	18-21			

Table 1 (Continued)

Batch Reference Number	Composition	Calcined Material						Sintered Material										Coefficient of Thermal Expansion ($\alpha \times 10^6$)	Electrical Resistivity (ohm-cm)			Literature Reference(1)	Comments(2)				
		DTA-TGA			Weight Loss Before Melting (%)	Sintering Conditions		Chemical Analysis			Density		Apparent Specific Gravity	Porosity (%)	X-Ray Diffraction				Reported Crystal System								
		X-Ray Diffraction				Melting Point (° C)		Anomalous Points	Oxide Component	Theoretical (%)	Measured (%)	Theoretical (g/cm ³)			Bulk (g/cm ³)	Major	Intermediate			Minor							
		Major	Intermediate	Minor		Measured	Literature														Temperature (° C)			Time (hr)			
5M-88-71	Al ₂ O ₃ · TiO ₂				1785	1860	None	None	1650	2	Al ₂ O ₃ TiO ₂	56.04 43.95	52.00 43.30	3.70	3.16	3.61	12.4	Al ₂ TiO ₅	TiO ₂	α -Al ₂ O ₃	Orthorhombic	0.8	9.1 × 10 ⁵	3	Incongruent melting behavior; $\bar{a} < 1$.(3)		
5M-2-72	HfO ₂ · TiO ₂	HfTiO ₄ (broad)			2180	~ 2200	755 EN	None	1675	2	HfO ₂ TiO ₂	72.49 27.51	66.82 30.18	7.27	4.82	6.81	29.0	HfTiO ₄		TiO ₂	Orthorhombic	3.59	1.5 × 10 ⁵	22			
5M-92-72	Nb ₂ O ₅ · TiO ₂	Nb ₂ TiO ₇			1880	1498	618-730 EN 1463 EN	~1	1350	2	Nb ₂ O ₅ TiO ₂	76.89 23.11	75.80 24.40	4.29	4.08	4.17	2.2	Nb ₂ TiO ₇		Nb ₂ O ₅ (w)	Monoclinic	2.3	6.25 × 10 ⁰	9-11, 23, 24	Congruent melting behavior;(11, 24) $\bar{a} = 2.3 \times 10^{-6}$.(9)		
6M-6-72	Ta ₂ O ₅ · TiO ₂	Ta ₂ TiO ₇ (broad)			1645	1662	765-916 EX	None	1400	2	Ta ₂ O ₅ TiO ₂	84.69 16.31	84.50 15.20	6.55	4.23	6.56	35.5	Ta ₂ TiO ₇		3TiO ₂ · 97Ta ₂ O ₅ (w)	Monoclinic	3.4	~ 1 × 10 ³	25	Congruent melting behavior.		
5C-27-72	Y ₂ O ₃ · TiO ₂	Y ₂ TiO ₅ (broad)			1842	> 1500	None	None	1400	4	Y ₂ O ₃ TiO ₂	73.84 26.16	73.36 26.66	4.73	3.81	4.90	22.2	Y ₂ TiO ₅ , Unidentified Lines			Orthorhombic	8.77	4.0 × 10 ⁹	1.7 × 10 ⁶	26		
With Zirconium Oxide																											
5C-37-72	ZrO ₂ · Nb ₂ O ₅				1432		1655 EN	None	1400	2	ZrO ₂ Nb ₂ O ₅	31.67 68.33	31.59 65.57		4.36	5.13	15.1	Nb ₂ Zr ₆ O ₁₇ (ss)	HT-Nb ₂ O ₅ (ss)			2.71	2.9 × 10 ²	3.7 × 10 ¹	9-12	Nb ₂ Zr ₆ O ₁₇ is isostructural with HfTiO ₄ .(11)	
6M-5-72	ZrO ₂ · 3Nb ₂ O ₅				1405	1440	None	None	1400	2	ZrO ₂ Nb ₂ O ₅	13.38 86.62	13.20 86.20		3.19	4.67	31.6	Zr ₂ Nb ₁₀ O ₂₉		β -Nb ₁₂ O ₂₉ (w)		2.5	5.0 × 10 ⁰		9-12	Twenty-five mole percent ZrO ₂ is reported;(9) eutectic composition;(11) $\bar{a} = 1 \times 10^{-6}$.	
5C-39-72	ZrO ₂ · Ta ₂ O ₅	δ -Ta ₂ O ₅	Ta ₂ Zr ₆ O ₁₇	Unidentified Lines	1718	1732	825-1080 EX	None	1450	3	ZrO ₂ Ta ₂ O ₅	21.80 78.20	21.80 78.49		5.21	8.25	36.9	δ -Ta ₂ O ₅ (ss)	Ta ₂ Zr ₆ O ₁₇ (ss)	Unidentified Lines Lines		5.72	5.8 × 10 ⁶	1.5 × 10 ⁷	9-12	Ta ₂ Zr ₆ O ₁₇ is isostructural with HfTiO ₄ .(11)	
6M-9-72	ZrO ₂ · 3Ta ₂ O ₅	δ -Ta ₂ O ₅		Ta ₂ Zr ₆ O ₁₇	1725	1749	1785 EN	2.5	1450	2	ZrO ₂ Ta ₂ O ₅	8.50 91.50	10.12 89.38		5.25	8.26	38.4	δ -Ta ₂ O ₅ (ss)		Ta ₂ Zr ₆ O ₁₇ (ss), Unidentified Phase		4.20	4.3 × 10 ⁸	4.3 × 10 ⁷	9-12		

(1) See References at end of report.
(2) Elevated numbers in parentheses are reference numbers.
(3) Endotherm.
(4) Exotherm.

Table 2
HAFNIUM TITANATE SOLID SOLUTIONS AND TERNARY COMPOSITIONS

Batch Reference Number	Composition	Calcined Material			DTA-TGA		Anomalous Points	Weight Loss Before Melting (%)	Sintered Material										Coefficient of Thermal Expansion ($\bar{\alpha} \times 10^6$)	Electrical Resistivity (ohm-cm)		Literature Reference ⁽¹⁾	Comments ⁽²⁾			
		X-Ray Diffraction			Melting Point (° C)				Sintering Conditions		Chemical Analyses			Density		X-Ray Diffraction				Reported Crystal System	Before CTE Measurement			After CTE Measurement		
		Major	Intermediate	Minor	Measured	Literature			Temperature (° C)	Time (hr)	Oxide Component	Theoretical (%)	Measured (%)	Theoretical (g/cm ³)	Bulk (g/cm ³)	Apparent Specific Gravity	Porosity (%)	Major							Intermediate	Minor
Solid Solutions with Aluminum Oxide																										
5M-67-72	63(HfO ₂ ·) · 37TiO ₂	HfTiO ₄ (broad)			> 2200 (not observed)	420-600 EN ⁽³⁾ 1438 EN	None	1650	2	HfO ₂ TiO ₂	81.75 18.25	83.8 15.9	8.43	6.74	8.04	16.1	HfTiO ₄		HfO ₂ (w)	~ 0	7.0 x 10 ⁶		4	Moderate weight loss; > 1800° C; $\bar{\alpha} < 1$. ⁽⁴⁾		
5C-80-72-II	63(75HfO ₂ , 25Al ₂ O ₃) · 37TiO ₂	HfTiO ₄	HfO ₂	Al ₂ O ₃ , TiO ₂	1720	800-1200 EX ⁽⁴⁾	None	1450	4	HfO ₂ Al ₂ O ₃ TiO ₂	68.5 11.9 20.4	67.27 12.36 19.97		5.04	6.93	27.3	HfTiO ₄ (ss)	HfO ₂		5.53	1.8 x 10 ⁵	9.4 x 10 ⁴				
5C-80-72-I	63(50HfO ₂ , 50Al ₂ O ₃) · 37TiO ₂	HfTiO ₄	HfO ₂	Al ₂ O ₃ , TiO ₂	1710	770-1060 EX	None	1370	4	HfO ₂ Al ₂ O ₃ TiO ₂	51.8 25.2 23.1	51.66 24.85 23.24		4.17	5.84	28.6	HfTiO ₄ (ss)	Al ₂ O ₃ , TiO ₂	HfO ₂	6.45	6.1 x 10 ⁴	4.0 x 10 ⁴				
5C-80-72-III	63(25HfO ₂ , 75Al ₂ O ₃) · 37TiO ₂	HfTiO ₄		TiO ₂ , Al ₂ O ₃	1710	None	None	1425	4	HfO ₂ Al ₂ O ₃ TiO ₂	29.89 43.42 26.69	30.79 42.74 26.46		3.72	4.74	21.6	HfTiO ₄ (ss)	Al ₂ O ₃ , Al ₂ O ₅ , TiO ₂		5.31	4.2 x 10 ⁶	2.9 x 10 ⁸				
5C-79-72-II	63(·, Al ₂ O ₃) · 37TiO ₂	TiO ₂	Al ₂ O ₃		1828	928-1170 EX	None	1450	4	Al ₂ O ₃ TiO ₂	68.4 31.6	67.76 32.68		3.37	3.70	8.8	Al ₂ TiO ₅	Al ₂ O ₃	TiO ₂	1.47	5.6 x 10 ⁷	7.3 x 10 ⁷				
Solid Solutions with Zirconium Oxide																										
5M-67-72	63(HfO ₂ ·) · 37TiO ₂	HfTiO ₄ (broad)			> 2200 (not observed)	420-600 EN 1438 EN	None	1650	2	HfO ₂ TiO ₂	81.75 18.25	83.8 15.9	8.43	6.74	8.04	16.1	HfTiO ₄		HfO ₂ (w)	~ 0	7.0 x 10 ⁶		4	$\bar{\alpha} < 1$. ⁽⁴⁾		
5C-68C-72	63(75HfO ₂ , 25ZrO ₂) · 37TiO ₂	HfTiO ₄	(Hf, Zr)O ₂	TiO ₂	1860	990-1650 EX	None	1500	3.5	HfO ₂ ZrO ₂ TiO ₂	66.9 13.1 20.0	64.39 14.66 20.62		6.31	7.13	11.6	HfTiO ₄ (ss)			2.24	2.5 x 10 ⁶	7 x 10 ⁵				
6C-50-72	63(50HfO ₂ , 50ZrO ₂) · 37TiO ₂	(Hf, Zr)O ₂		TiO ₂ (w)	>2350 (not observed)	None	None	1500	3	HfO ₂ ZrO ₂ TiO ₂	49.22 28.78 22.0	62.16 35.28 2.57		7.32	7.72	5.1	(Hf, Zr)O ₂		TiO ₂ (w)	5.9	2.6 x 10 ⁸	6.1 x 10 ⁸				
6C-12-72	63(25HfO ₂ , 75ZrO ₂) · 37TiO ₂	HfTiO ₄ , (Hf, Zr)O ₂		TiO ₂	1800	997-1215 EX	None	1450	4	HfO ₂ ZrO ₂ TiO ₂	27.41 48.12 24.47	28.43 48.60 23.90		4.81	6.00	19.8	ZrTiO ₄ (ss)	ZrO ₂ (ss)		6.67	1.2 x 10 ⁵	2.4 x 10 ⁶				
6M-12-72	63(·, ZrO ₂) · 37TiO ₂	ZrO ₂ (tet), ZrO ₂ (mono)		ZrTiO ₄	1810	800-1240 EX	None	1450	2	ZrO ₂ TiO ₂	72.39 27.61	70.42 28.11		3.29	5.35	38.4	ZrTiO ₄ (ss)	ZrO ₂ (ss)		< 7.2 (with phase change)	1.3 x 10 ⁷	6.7 x 10 ⁷	27-30			

Table 2 (Continued)

Batch Reference Number	Composition	Calcined Material							Sintered Material										Coefficient of Thermal Expansion ($\alpha \times 10^6$)	Electrical Resistivity (ohm-cm)			Literature Reference(1)	Comments(2)	
		DTA-TGA						Weight Loss Before Melting (%)	Sintering Conditions Temperature (° C) Time (hr)		Chemical Analyses			Density		Apparent Specific Gravity	Porosity (%)	X-Ray Diffraction			Reported Crystal System				
		X-Ray Diffraction			Melting Point (° C)		Anomalous Points				Oxide Component	Theoretical (%)	Measured (%)	Theoretical (g/cm ³)	Bulk (g/cm ³)			Major		Intermediate		Minor			
		Major	Intermediate	Minor	Measured	Literature																			
																									Before CTE Measurement
Solid Solution with Aluminum Oxide and Zirconium Oxide																									
6M-23-72	63(33Al ₂ O ₃ · 33HfO ₂ · 33ZrO ₂) · 37TiO ₂	HfTiO ₄		Al ₂ O ₃ , TiO ₂	1050	995-1465 EX 1168-1250 EX		None	1350	5	Al ₂ O ₃ HfO ₂ ZrO ₂ TiO ₂	18.3 27.2 23.1 32.0	18.99 29.25 19.74 32.09	3.41	5.37	36.4	HfTiO ₄ (ss)		Al ₂ TiO ₅ , TiO ₂		6.45	2.3 x 10 ⁵	8.2 x 10 ⁴		
Ternaries with Tantalum Oxide																									
5C-73-72	Al ₂ O ₃ · 2TiO ₂ · Ta ₂ O ₅	AlTaO ₄ (tet)	TiO ₂	β-Ta ₂ O ₅	1698	> 1500 970-1350 EX 1200 EX		None	1400	5	Al ₂ O ₃ TiO ₂ Ta ₂ O ₅	14.5 22.7 62.8	14.22 22.47 63.37	6.30	4.51	6.26	28.0	AlTaO ₄ Type (AlTiTaO ₆)			7.09	3.7 x 10 ⁴	3.2 x 10 ⁴	31	Rutile (TiO ₂) type structure, same as AlTaO ₄ (tet). (31)
6C-8-72	Al ₂ O ₃ · 2HfO ₂ · Ta ₂ O ₅	HfTiO ₄ Type (AlHfTaO ₆)		HfO ₂	2160	1000-1090 EX 1105-1200 EX 1715-1850 EN		None	1650	4	Al ₂ O ₃ HfO ₂ Ta ₂ O ₅	10.6 43.6 45.8	10.83 44.96 44.72	5.78	8.27	30.1	HfTiO ₄ Type (AlHfTaO ₆)				4.43				
6C-41-72	HfO ₂ · WO ₃ · Ta ₂ O ₅	δ-Ta ₂ O ₅ (ss)	Ta ₂ Hf ₆ O ₁₇ or HfO ₂ (tet)	HfTiO ₄ Type	1418	1000-1180 EX		None	1300	3	HfO ₂ WO ₃ Ta ₂ O ₅	23.81 26.22 49.98	23.24 28.49 48.82	4.93	8.38	41.1	Ta ₂ WO ₈ Type (ss)		Ta ₂ Hf ₆ O ₁₇ or HfO ₂ (tet)	HfTiO ₄ Type	~ 0 (with phase change)				Rapid weight loss began at 1400° C.
5C-84-72	Y ₂ O ₃ · 2TiO ₂ · Ta ₂ O ₅	YNbTiO ₆ Type (YTiTaO ₆)		Unidentified Lines	1750	> 1500 1015-1200 EX		None	1400	4	Y ₂ O ₃ TiO ₂ Ta ₂ O ₅	27.2 19.4 53.4	27.13 19.40 53.85	6.52	4.51	6.28	28.2	YNbTiO ₆ Type (YTiTaO ₆)	Orthorhombic		7.49	1.1 x 10 ⁸	4.4 x 10 ⁸	31,32	HfTiO ₄ structure type. (31)
5C-85-72	Y ₂ O ₃ · 2HfO ₂ · Ta ₂ O ₅	Cubic ZrO ₂ Type (YHfTaO ₆)			1910	1630 EN		None	1350	18	Y ₂ O ₃ HfO ₂ Ta ₂ O ₅	20.74 38.67 40.59	20.78 37.03 41.70	7.09	8.17	13.2	Unidentified				6.56	3.6 x 10 ⁷	6.0 x 10 ⁹		
	2HfO ₂ · 2WO ₃ · Ta ₂ O ₅	Ta ₂ Hf ₆ O ₁₇ Type	δ-Ta ₂ O ₅ (ss)		1445	None		9.04	1480	3								Ta ₂ Hf ₆ O ₁₇ Type	δ-Ta ₂ O ₅ (ss); 3WO ₃ · Ta ₂ O ₅						Sample melted.
Ternaries with Silicon Dioxide																									
6C-49-72	2MgO · 2Al ₂ O ₃ · 5 SiO ₂	MgAl ₂ O ₄ (broad)			1750-2100 (broad EN)	1470 800-1250 EX		8.4	1300	3	MgO Al ₂ O ₃ SiO ₂	13.78 34.86 51.35	21.40 74.76 9.31	2.82	3.45	18.3	MgAl ₂ O ₄	Mg ₂ Al ₄ SiO ₁₀			8.1	~ 10 ¹⁰	~ 10 ¹⁰	33	$\bar{a} < 2$. (33)

(1) See References at end of report.
(2) Elevated numbers in parentheses are reference numbers.
(3) Endotherm.
(4) Exotherm.

the rates of crystallization and growth of the very fine (~ 50 Å) particles initially precipitated. Lower-melting compositions had a greater crystallinity after calcining than the higher-melting ones.

The DTA results for the calcined materials indicated the melting temperatures and, in several cases, broad endotherms or exotherms in the range from 800 to 1,200° C which have been observed for other systems.⁽³⁴⁾ These, generally, are believed to be related to second-order transitions (disordering of metal atoms), crystallization, and/or rapid grain growth. Sharp energy transitions which occurred in some compositions below the melting point could be caused by phase transformations or decompositions. Weight losses from TGA results were less than five percent for most of the materials when heated to the melting temperatures. However, for the $\text{NiO} \cdot \text{Ta}_2\text{O}_5$, $\text{SnO}_2 \cdot \text{Ta}_2\text{O}_5$, $\text{WO}_3 \cdot \text{Ta}_2\text{O}_5$, and $\text{MgO} \cdot 2 \text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2$ compositions, 8 to 40 percent weight losses resulted. Originally, two other SnO_2 compositions were to be investigated but were eliminated from the study. They were: $\text{HfO}_2 \cdot \text{SnO}_2$, which had a 59.3 percent weight loss before melting at about 1,150° C and $\text{Y}_2\text{O}_3 \cdot 2 \text{SnO}_2$, which had a 44.8 percent weight loss before melting at 1,540° C. Also, $\text{WO}_3 \cdot \text{TiO}_2$ was not studied since it melted at 1,260° C.

Under the conditions employed for sintering, the materials had porosities generally in the range from 20 to 40 percent. The measured chemical analyses agreed well with the desired compositions with the exceptions of 63 (50 HfO_2 , 50 ZrO_2) $\cdot$ 37 TiO_2 , $\text{MgO} \cdot 2 \text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2$, and the WO_3 - Ta_2O_5 materials. The HfO_2 -containing material had very little TiO_2 present (2.6 vs 22 wt %), and two attempts to prepare the silicate material were unsuccessful with the SiO_2 content being less than 10 percent (9.3 vs 51.4 wt %). The WO_3 - Ta_2O_5 compositions resulted in WO_3 contents lower than those calculated by 3 to 16 weight percent.

X-ray diffraction analyses showed that the actual phase analyses were in moderate agreement with the desired compositions. In many cases the patterns were quite complicated, particularly the ZrO_2 (or HfO_2)- Nb_2O_5 (or Ta_2O_5) systems which had not been well substantiated. The compound $\text{Nb}_2\text{Zr}_6\text{O}_{17}$ and its tantalum and hafnium counterparts are isostructural with HfTiO_4 , and it was a predominant phase in these systems. Also, $\text{Zr}_2\text{Nb}_{10}\text{O}_{29}$ and $\text{Hf}_2\text{Nb}_{10}\text{O}_{29}$ (analogous to $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$)⁽³⁵⁾ may occur; however, these compositions could possibly be mixtures of the Nb_2O_5 phases and $\text{Nb}_2\text{Zr}_6\text{O}_{17}$. Single-crystal analyses would be necessary to resolve the true phase identifications.

The sample 2 $\text{HfO}_2 \cdot 2 \text{WO}_3 \cdot \text{Ta}_2\text{O}_5$ melted when sintered at 1,480° C. The X-ray and DTA-TGA data are shown since the phase analysis showed the $\text{Nb}_2\text{Zr}_6\text{O}_{17}$ -type (HfTiO_4 -type) structure to occur. The composition $\text{HfO}_2 \cdot \text{WO}_3 \cdot \text{Ta}_2\text{O}_5$ gave the Ta_2WO_8 -type structure.

HfTiO_4 solid-solution samples showed that Al_2O_3 and ZrO_2 form nearly complete to partial solid solutions (depending on the composition and sintering temperature). With

respect to HfO_2 , ZrO_2 , Al_2O_3 , and TiO_2 , an almost complete solid solution with the HfTiO_4 structure type occurred.

Room-temperature electrical resistivities were performed on the specimens before and after the CTE measurements. In some cases, resistivities were not made because of the friable nature of the specimens. Although wide variations in resistivities existed among the specimens (ranging from conductors to insulators), with resistivities from a few ohm-cm to about 10^{10} ohm-cm, only a few specimens were found to vary in pre-test and post-test resistivity by an order of magnitude or more. In particular, compounds containing Nb_2O_5 had the lowest resistivities ($3 - 7 \times 10^2$ ohm-cm); whereas, most of the samples containing Al_2O_3 , TiO_2 , ZrO_2 , HfO_2 and Ta_2O_5 , or combinations therein, were high-resistivity ($10^6 - 10^{10}$ ohm-cm) insulators.

Resistivity and thermal-expansion tests were performed on some air-sintered or reoxidized specimens (not given in the table). Of particular interest were the increases in resistivity noted in those containing Nb_2O_5 . These substances had as much as a seven-orders-of-magnitude increase, yielding an electrical insulator instead of a conductor. From reoxidation studies, very little weight gain (0.01 to 0.1%) was noted, indicating that a small but definite oxygen deficiency existed in the argon-sintered samples. This oxygen deficiency caused the observable darkening of the samples sintered in argon, decreased (to some extent depending on the composition) the electrical resistivities, and affected the thermal expansion behavior (increases or decreases of up to about 20%). As previously mentioned, all data in Tables 1 and 2 are for argon-sintered specimens.

Coefficients of thermal expansion (CTE) for the materials are also reported in Tables 1 and 2, with expansive behavior given in Figures 1 through 8. CTE values assume linear expansion from 20 to $1,000^\circ\text{C}$, although some specimens exhibited cyclic behavior. Thus, for those materials having nonlinear expansion, CTEs are of a somewhat qualified nature.

In order to correlate the expansion behaviors of the materials, CTEs were considered to be intermediate, low, and very low if their values were in the ranges: $4 - 9 \times 10^{-6}/^\circ\text{C}$, $1 - 4 \times 10^{-6}/^\circ\text{C}$, and $< 1 \times 10^{-6}/^\circ\text{C}$, respectively. Of the samples studied, eight were found to have very low expansions, ten low, and twenty intermediate expansions.

Figure 1 provides a plot of the expansion of binary oxides containing HfO_2 . Samples of $\text{HfO}_2 \cdot \text{Al}_2\text{O}_3$ and $\text{HfO}_2 \cdot \text{Ta}_2\text{O}_5$ yielded intermediate expansions while the $\text{HfO}_2 \cdot 3\text{Ta}_2\text{O}_5$ and $\text{HfO}_2 \cdot 3\text{Nb}_2\text{O}_5$ behavior was low. Only $\text{HfO}_2 \cdot \text{Nb}_2\text{O}_5$ gave cyclic and very low expansion. This specimen yielded an X-ray diffraction pattern which showed the major phase ($\text{Nb}_2\text{Hf}_6\text{O}_{17}$) to be isostructural with that of HfTiO_4 (orthorhombic).⁽¹¹⁾ This type of structure may be an indicator of other low-expanding materials.

The graph of Figure 2 covers the binary mixed oxides containing Ta_2O_5 . The $\text{MgO} \cdot \text{Ta}_2\text{O}_5$, $\text{Al}_2\text{O}_3 \cdot \text{Ta}_2\text{O}_5$, and $\text{NiO}_2 \cdot \text{Ta}_2\text{O}_5$ compositions yielded intermediate expansions, with only $\text{SnO}_2 \cdot \text{Ta}_2\text{O}_5$ yielding a low value. Since TGA measurements indicated significant weight loss above $1,200^\circ\text{C}$ (41% up to the melting point of $1,518^\circ\text{C}$), this material is not very well suited for high-temperature applications due to SnO_2 volatilization.

Figure 1. LINEAR THERMAL EXPANSION OF BINARY OXIDES CONTAINING HAFNIUM DIOXIDE.

Figure 2. LINEAR THERMAL EXPANSION OF BINARY OXIDES CONTAINING TANTALUM PENTOXIDE.

Figure 3. LINEAR THERMAL EXPANSION OF OXIDES CONTAINING TUNGSTEN TRIOXIDE AND TANTALUM PENTOXIDE.

Figure 4. LINEAR THERMAL EXPANSION OF BINARY OXIDES CONTAINING TITANIUM DIOXIDE.

Figure 5. LINEAR THERMAL EXPANSION OF BINARY OXIDES CONTAINING ZIRCONIUM DIOXIDE.

Figure 6. LINEAR THERMAL EXPANSION OF HAFNIUM TITANATE SOLID SOLUTIONS CONTAINING ALUMINUM OXIDE.

Figure 7. LINEAR THERMAL EXPANSION OF HAFNIUM TITANATE SOLID SOLUTIONS CONTAINING ZIRCONIUM DIOXIDE.

Figure 8. LINEAR THERMAL EXPANSION OF THE TERNARY OXIDES.

Behavior of the mixed oxides containing WO_3 is indicated in Figure 3. Compositions (mol % WO_3) were lower than those desired, probably because of the volatilization of WO_3 at the sintering temperatures ($\sim 1,500^\circ\text{C}$) and also possibly due to poor control of the coprecipitation parameters. Actual compositions relative to the nominal compositions of WO_3 were: 29.5, 41.4, 50.5, and 52.8 mole percent for the desired 50, 45, 55, and 63 mole percent, the remainders being Ta_2O_5 . The actual ternary composition $\text{HfO}_2 \cdot \text{WO}_3 \cdot \text{Ta}_2\text{O}_5$ agreed well with the desired (nominal) composition.

All compositions were found to have zero-to-negative expansions over the temperature range, with a mole percent variation in WO_3 from 29.5 to 52.8—a 23 mole percent (19 wt %) range. The negative expansion behavior of the WO_3 - Ta_2O_5 compositions must be related to the atomic configuration within the three reported⁽¹⁸⁻²¹⁾ orthorhombic compounds in the range investigated— $11 \text{ Ta}_2\text{O}_5 \cdot 4 \text{ WO}_3$ ($\text{Ta}_{22}\text{W}_4\text{O}_{67}$), Ta_2WO_8 , and $\text{Ta}_2\text{O}_5 \cdot 2.25 \text{ WO}_3$ ($\text{Ta}_{16}\text{W}_{18}\text{O}_{94}$), occurring at 27, 50, and 69 mole percent WO_3 , respectively. Expansion behavior of the nominal 55 $\text{WO}_3 \cdot 45 \text{ Ta}_2\text{O}_5$ should be representative of nearly single-phased Ta_2WO_8 . Although it is beyond the scope of this survey to elucidate the cause of this thermal contraction characteristic of these tungsten tantalates, a range of compositions having this behavior was demonstrated. The actual range may be much wider than that shown here, but further work would be necessary to substantiate this. Also, each of the three orthorhombic compounds just mentioned should be studied further to show the effects of their structures on the negative expansion (contraction) behaviors observed.

The $\text{WO}_3 \cdot \text{HfO}_2 \cdot \text{Ta}_2\text{O}_5$ composition yielded a cyclic behavior that gave almost no overall expansion. This material had the Ta_2WO_8 orthorhombic structure as a major X-ray diffraction phase. Apparently, the HfO_2 was in solid solution with the Ta_2WO_8 .

Binary oxides containing TiO_2 are given in Figure 4. All gave smooth and positive expansions, with the $\text{Y}_2\text{O}_3 \cdot \text{TiO}_2$ yielding an intermediate expansion, while $\text{Ta}_2\text{O}_5 \cdot \text{TiO}_2$, $\text{HfO}_2 \cdot \text{TiO}_2$, and $\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ yielded low expansions. Only $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ gave an expansion value less than $1 \times 10^{-6}/^\circ\text{C}$. An analogue (63 $\text{HfO}_2 \cdot 37 \text{ TiO}_2$), which was included with the HfTiO_4 solid solutions, gave a lower expansion (Figures 6 and 7), although both were the single-phase solid solution of HfTiO_4 and HfO_2 .

Binary mixed oxides containing ZrO_2 (Figure 5) show that compositions with Ta_2O_5 (1:1 and 1:3 mole ratios) gave intermediate expansions whereas those with Nb_2O_5 (1:1 and 1:3) gave low expansions. In particular, the lower expansion was from $\text{ZrO}_2 \cdot 3 \text{ Nb}_2\text{O}_5$. The $\text{ZrO}_2 \cdot \text{Nb}_2\text{O}_5$ exhibited the cyclic behavior characteristic of Nb_2O_5 -containing compounds, although the expansion at $1,000^\circ\text{C}$ was about the same.

Thermal-expansion behaviors for HfTiO_4 solid solutions with Al_2O_3 and ZrO_2 are: given in Figures 6 and 7, respectively. The composition 63 $\text{MeO}_x \cdot 37 \text{ TiO}_2$ was chosen for the solid-solution study since Simpson⁽⁴⁾ and Lynch and Morosin⁽⁵⁾ found 63 $\text{HfO}_2 \cdot 37 \text{ TiO}_2$ to be a very-low-expanding composition in the HfO_2 - TiO_2 system. The effect of Al_2O_3 in solid solution with HfTiO_4 was to increase the thermal expansions to an intermediate level—by a factor of four over the 63 $\text{Al}_2\text{O}_3 \cdot 37 \text{ TiO}_2$ composition. Both endpoints (63 $\text{HfO}_2 \cdot 37 \text{ TiO}_2$ and 63 $\text{Al}_2\text{O}_3 \cdot 37 \text{ TiO}_2$) expanded very little. Low ZrO_2 percentages

appear to have much less effect than low Al_2O_3 additions on the $63 \text{ HfO}_2 \cdot 37 \text{ TiO}_2$ composition, since the $63 (75 \text{ HfO}_2, 25 \text{ ZrO}_2) \cdot 37 \text{ TiO}_2$ material had a low ($2.24 \times 10^{-6}/^\circ\text{C}$) CTE value. Greater amounts of ZrO_2 than in the composition $63 (75 \text{ HfO}_2, 25 \text{ ZrO}_2) \cdot 37 \text{ TiO}_2$ were quite detrimental to the very-low-expansion properties of the $63 \text{ HfO}_2 \cdot 37 \text{ TiO}_2$ end member. The $63 \text{ ZrO}_2 \cdot 37 \text{ TiO}_2$ end member exhibited a cyclic thermal expansion behavior ($600 - 700^\circ\text{C}$), which has been attributed⁽²⁹⁾ to the phase inversion from monoclinic to tetragonal crystal systems for ZrO_2 solid solutions containing TiO_2 mixed with ZrTiO_4 . The decrease in expansion from $900 - 1,000^\circ\text{C}$ for the $63 (25 \text{ HfO}_2, 75 \text{ ZrO}_2) \cdot 37 \text{ TiO}_2$ material was reproducible and probably results from the same type of phase inversion.

The composition $63 (33 \text{ Al}_2\text{O}_3, 33 \text{ HfO}_2, 33 \text{ ZrO}_2) \cdot 37 \text{ TiO}_2$, seen in Figure 6, exhibited the highest linear (not cyclic) expansion, having a CTE in the intermediate range ($6.45 \times 10^{-6}/^\circ\text{C}$).

Ternary compositions had the expansion behavior indicated in Figure 8. All of these materials had intermediate CTE values except $\text{HfO}_2 \cdot \text{WO}_3 \cdot \text{Ta}_2\text{O}_5$ (~ 0 expansion, included on Figure 3) and $\text{Al}_2\text{O}_3 \cdot 2 \text{ HfO}_2 \cdot \text{Ta}_2\text{O}_5$ (AlHfTaO_6) which had a low-to-intermediate expansion (CTE of $4.43 \times 10^{-6}/^\circ\text{C}$). The AlHfTaO_6 and YTiTaO_6 materials have the HfTiO_4 (or $\alpha\text{-PbO}_2$) structure type and were expected to have lower expansions than those measured. Since HfTiO_4 has a much higher expansion than $63 \text{ HfO}_2 \cdot 37 \text{ TiO}_2$ (also single-phased $\alpha\text{-PbO}_2$) there may be some variation in the metal contents of the $\text{ABCO}_6^{(b)}$ materials which would result in a much lower expansion behavior.

The cordierite composition,⁽³³⁾ nominally $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5 \text{ SiO}_2$, was actually very low in SiO_2 (due to the problems in simultaneous precipitation of the three components). Therefore, the reported expansion behavior is essentially that of an $\text{Al}_2\text{O}_3\text{-MgO}$ composition, accounting for the $8.1 \times 10^{-6}/^\circ\text{C}$ value of the CTE.

CONCLUSIONS

This survey of low-expanding oxide materials showed the expansion behavior of twenty intermediate-expanding (with CTE values in the range of 4 to $9 \times 10^{-6}/^\circ\text{C}$), ten low-expanding (with CTE values in the range of 1 to $4 \times 10^{-6}/^\circ\text{C}$), and eight very-low-expanding (with CTE values $< 1 \times 10^{-6}/^\circ\text{C}$) compositions. All the materials investigated had melting temperatures in excess of $1,400^\circ\text{C}$. The following is an enumeration of the main findings concerning the very-low-expanding compositions:

1. A $\text{HfO}_2 \cdot \text{Nb}_2\text{O}_5$ material (mp, $1,425^\circ\text{C}$) with a CTE $< 1 \times 10^{-6}/^\circ\text{C}$ was found which contains the $\text{Nb}_2\text{Hf}_6\text{O}_{17}$ phase isostructural to HfTiO_4 .

(b) "A", "B", and "C" designate metals of +3, +4, and +5 valences, respectively.

2. Negative-expanding (contracting) specimens in the $\text{WO}_3\text{-Ta}_2\text{O}_5$ system in the range from 29.5 to 52.8 mole percent WO_3 (18 - 37 wt % WO_3) were discovered.
3. A ternary composition ($\text{HfO}_2 \cdot \text{WO}_3 \cdot \text{Ta}_2\text{O}_5$; mp, $1,418^\circ\text{C}$) had essentially a zero expansion over the temperature range from 20 to $1,000^\circ\text{C}$.
4. Additions of Al_2O_3 in solid solution in the HfTiO_4 (or $\alpha\text{-PbO}_2$) structure of the composition $63 \text{ MeO}_x \cdot 37 \text{ TiO}_2$ were detrimental to the very-low-expansion characteristics of the parent material.
5. ZrO_2 additions, in the same manner as the Al_2O_3 with respect to HfTiO_4 , caused the expansive behavior of the system to remain relatively low with the composition $63(75 \text{ HfO}_2, 25 \text{ ZrO}_2) \cdot 37 \text{ TiO}_2$, but increasing amounts of ZrO_2 further increased the expansion.

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