

Phase Distribution in the $\text{HfO}_2\text{-Er}_2\text{O}_3\text{-Ta}_2\text{O}_5$ System*

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Phase relationships obtained by heating coprecipitated oxide powders in the $\text{HfO}_2\text{-Er}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system were investigated by X-ray diffractometry. Partial isothermal sections at 1100 and 1500°C are presented. © 1985 Academic Press, Inc.

Literature Review

Although phase equilibria studies of ternary compositions in the $\text{HfO}_2\text{-Er}_2\text{O}_3\text{-Ta}_2\text{O}_5$ system have not been reported, the bounding binary systems and several related systems have been partially investigated.

Considerable work has been devoted to investigation of phase equilibria in the $\text{HfO}_2\text{-Er}_2\text{O}_3$ system. In 1970, Johnstone (1) and Spiridonov and Komissarova (2) independently suggested phase diagrams for this system. The major point of disagreement between these authors concerned the report of Spiridonov and Komissarova of an ordered hexagonal phase, nominally $\text{Er}_6\text{HfO}_{11}$, occurring within the boundaries of the rare-earth oxide type C (REOC) solid solution region. The existence of this hexagonal phase was refuted by Johnstone. More recently, Duran *et al.* (3) verified the existence of the $\text{Er}_6\text{HfO}_{11}$ compound and

also reported two other hexagonal compounds, $\text{Er}_4\text{Hf}_3\text{O}_{12}$ and $\text{Er}_3\text{Hf}_2\text{O}_{11.5}$. Furthermore, they proposed the existence of a peritectic which would produce changes in the shape of the liquidus and thereby account for the noncontinuous transition from fluorite to REOC phase at high temperature. Shevchenko and Lopato (4) published results for the equilibrium relationships for REO-rich compositions which are consistent with the existence of a peritectic near 2400°C. Shevchenko *et al.* (5) have also investigated the liquidus for HfO_2 -rich compositions.

The $\text{Er}_2\text{O}_3\text{-Ta}_2\text{O}_5$ binary system has been studied in detail. Isupova *et al.* (6) reported a distorted fluorite structure solid solution phase based on the compound Er_3TaO_7 and three other line compounds: ErTaO_4 , ErTa_3O_9 , and $\text{ErTa}_7\text{O}_{19}$. Wirkus *et al.* (7) reported much wider compositional limits of the fluorite phase than those observed by Isupova *et al.*

Only one investigation of the $\text{HfO}_2\text{-Ta}_2\text{O}_5$ system has been reported. Spiridonov *et al.* (8) reported formation of a series of orthorhombic phases:

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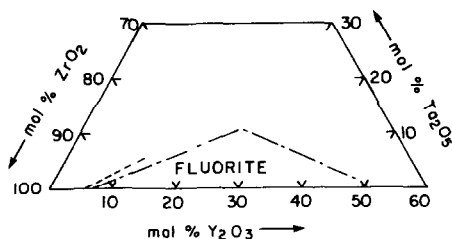


FIG. 1. Limits of fluorite phase in the ZrO_2 - Y_2O_3 - Ta_2O_5 system. ---, Ref. (13), ----, Ref. (14).

$5HfO_2 \cdot Ta_2O_5$, $6HfO_2 \cdot Ta_2O_5$, and $7HfO_2 \cdot Ta_2O_5$. Phase equilibria in the related ZrO_2 - Nb_2O_5 (9, 10) and ZrO_2 - Ta_2O_5 (11, 12) systems have been more thoroughly investigated.

While phase equilibria in the ternary HfO_2 - Er_2O_3 - Ta_2O_5 system have not been investigated, two studies of phase equilibria in the analogous ternary system ZrO_2 - $YO_{1.5}$ - $TaO_{2.5}$ have been reported. Figure 1 shows the extent of the single-phase fluorite region in the ternary system as determined by Caillet *et al.* (13) and by Choudhary and Subbarao (14). (Note that compositions in the figure have been converted to the ZrO_2 - Y_2O_3 - Ta_2O_5 basis before plotting to facilitate comparison with the present work.) Only ZrO_2 -rich compositions were investigated. Caillet *et al.* determined the fluorite phase boundary corresponding to the limit of Ta_2O_5 solubility for only a very limited range of compositions. Although Choudhary and Subbarao studied a broader range of compositions and indicated that the fluorite phase boundary was triangular or dome-shaped, their data were actually insufficient to describe the boundary corresponding to the limit of Y_2O_3 solubility. (Twelve of thirteen ternary compositions investigated were found to be single phase.)

Prietzl *et al.* (15) investigated isothermal sections at 1500 and 1650°C in the related ZrO_2 - MgO - Ta_2O_5 system. (Electrical conductivity measurements were interpreted to indicate that Ta_2O_5 additions suppressed vacancy formation as has been sug-

gested for fully stabilized ZrO_2 (13, 14) and also HfO_2 (16).) Subsequently, Michel and Perez y Jorba (17) identified M_7O_{12} phases having fluorite superstructures in the ternary ZrO_2 (HfO_2)- MgO - Nb_2O_5 (Ta_2O_5) systems. Similar M_7O_{12} ordered phases have been reported for numerous related stabilized ZrO_2 and HfO_2 binary systems (3, 18-21) and one other ternary system (22).

The literature for these and other related systems for which at least partial phase equilibrium diagrams are available are summarized in the tables in the Appendix.

Procedure

Thirty-nine (39) compositions in the HfO_2 - Er_2O_3 - Ta_2O_5 system were prepared for examination. Powders were prepared by calcination of coprecipitated hydroxide precursors. Precipitation was accomplished by adding aqueous ammonia (2.5 N) to blends of cation stock solutions. The stock solutions were prepared by dissolving reactor grade hafnium oxychloride¹ in distilled water (50 g HfO_2 /liter), 99.9% Er_2O_3 ² in 2.35 N HNO_3 (50 g Er_2O_3 /liter), and 99.9% $TaCl_5$ ³ in absolute ethanol (25 g Ta_2O_5 /liter). Final pH of all precipitations was approximately 10.5. To improve the reactivity and sinterability of the powders, the gelatinous hydroxide precursors were dewatered using a series of organic washes (23) prior to calcination at 1100°C in air for 2 hr. A portion of each powder was reheated in an Er_2O_3 crucible in air at 1500°C for 1 hr, followed by fairly rapid cooling (250°C/min). The compositions of the powders prepared are included in Table I.

Lattice parameters for the cubic phases present were determined for all powders treated at 1100 and 1500°C using an automated Picker θ - θ diffractometer with a Mo tube operated at 50 kV and 16 mA. A 1° slit

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³ Alfa Products.

TABLE IA
LATTICE PARAMETER SUMMARY

Composition, mole% HfO ₂ -Er ₂ O ₃ -Ta ₂ O ₅			Phases present ^a	After 1100°C heat treatment Fluorite (or REOC) a ₀ , Å	
				Observed	Calculated
0	85	15	C+F	5.2541	5.2539
0	82	18	F	5.2507	5.2522
0	80	20	F	5.2457	5.2462
0	76½	23½	F	5.2345	5.2362
0	75	25	F	5.2345	5.2313
0	70	30	F	5.2200	5.2163
0	65	35	F	5.1980	5.2014
10	90	0	C	(10.5294) ^b	(10.5362)
10	88	2	C	(10.5242)	(10.5242)
10	86	4	C	(10.5122)	(10.5122)
10	85	5	C+F	5.2531(10.5062)	5.2539(10.5078)
10	80	10	C+F	5.2546(10.5092)	5.2539(10.5078)
10	75	15	F	5.2469	5.2468
10	70	20	F	5.2304	5.2307
10	65	25	F	5.2150	5.2147
10	60	30	F	5.1984	5.1986
10	55	35	F+M	5.1914	5.1895
10	50	40	F+M	5.1877	5.1895
25	75	0	C	(10.5175) ^c	(10.5175)
25	74	1	C	(10.5135) ^c	(10.5135)
25	70	5	C+F	5.2403 ^d (10.5095) ^c	5.2402(10.5045)
25	65	10	F	5.2377	5.2380
25	60	15	F	5.2217	5.2208
25	55	20	F	5.2031	5.2036
25	50	25	F	5.1866	5.1865
25	45	30	F+M	5.1746	5.1761
25	40	35	F+M	5.1777	5.1761
40	60	0	C+F	5.2413 ^d	5.2414
40	55	5	F	5.2211 ^b	5.2293
40	50	10	F	5.2132	5.2122
40	45	15	F	5.1932	5.1952
40	40	20	F	5.1791	5.1781
40	30	30	F+M	5.1648	5.1649
70	30	0	F	5.1733	5.1693
70	27	3	F	5.1627	5.1621
70	24	6	F	5.1481	5.1549
70	21	9	F	5.1432	5.1476
70	18	12	F	5.1471	5.1404
70	15	15	F	5.1331	5.1332

^a F = fluorite phase; C = REOC phase; M = monoclinic phase.

^b Data not used in linear regression.

^c a₀ from minor "non-fluorite" reflections only.

^d Mean of two runs.

TABLE IB
LATTICE PARAMETER SUMMARY

Composition, mole% HfO ₂ -Er ₂ O ₃ -Ta ₂ O ₅			After 1500°C heat treatment		
			Phases present ^a	Fluorite (or REOC) a ₀ , Å	
				Observed	Calculated
0	85	15	C+F	5.2478	5.2456
0	82	18	C+F	5.2451	5.2456
0	80	20	C+F	5.2460	5.2456
0	76 [‡]	23 [‡]	F	5.2342	5.2360
0	75	25	F	5.2334	5.2310
0	70	30	F	5.2153	5.2159
0	65	35	F+M	5.2158	5.2150
10	90	0	C	(10.5221)	(10.5224)
10	88	2	C	(10.5218)	(10.5212)
10	86	4	C+F	5.2601(10.5196) ^e	5.2475(10.5200)
10	85	5	C+F	— ^e	5.2475(10.5200)
10	80	10	C+F	5.2414(10.5204) ^e	5.2475(10.5200)
10	75	15	C+F	5.2410(10.5200) ^e	5.2475(10.5200)
10	70	20	F	5.2346	5.2346
10	65	25	F	5.2177	5.2177
10	60	30	F+M	5.2101	5.2101
10	55	35	F+M	— ^e	5.2101
10	50	40	F+M	— ^e	5.2101
25	75	0	C	(10.5024)	(10.5024)
25	74	1	C	(10.4902)	(10.4902)
25	70	5	C+F	5.2418(10.4836)	5.2418(10.4834)
25	65	10	F	5.2343	5.2358
25	60	15	F	5.2239	5.2210
25	55	20	F	5.2046	5.2061
25	50	25	F+M	5.1968	5.1941
25	45	30	F+M	5.1914	5.1941
25	40	35	— ^f	— ^f	— ^f
40	60	0	C+F	5.2389	5.2389
40	55	5	F	5.2214	5.2275
40	50	10	F	5.2229	5.2108
40	45	15	F	5.1881	5.1942
40	40	20	F+M	5.1825	5.1825
40	30	30	— ^f	— ^f	— ^f
70	30	0	F	5.1701	5.1723
70	27	3	F	5.1644	5.1612
70	24	6	F	5.1505	5.1501
70	21	9	F	5.1377	5.1390
70	18	12	F+M	5.1340	5.1335
70	15	15	F+M	5.1339	5.1335

^a F = fluorite phase; C = REOC phase; M = monoclinic phase.^e a₀ from minor "non-fluorite" reflections only.^e Data not included since alignment poor.^f No fluorite phase.

system was used with a 0.005° slit in front of a graphite monochromer set to select Mo $K\alpha$ radiation. Step scanning in 0.04° increments was performed over the 2θ range $7-41^\circ$ using a 1-sec counting time for each step. Internal standardization using 5 wt% W metal powder assured that alignment was maintained within one step increment. (No extrapolation function was necessary since (i) internal standardization virtually eliminated systematic errors due to instrument misalignment and (ii) use of short wavelength Mo radiation assured that all reflections of interest occurred at low angles.) The scanned range contained nine fluorite phase peaks, approximately twelve minor REOC peaks (intensity $>4\%$), and four W peaks. The estimated uncertainty in lattice parameters determined in this way was $\pm 0.0003 \text{ \AA}$.

Boundaries of single-phase regions were determined by extrapolating the composition dependence of these precision lattice parameters to the invariant parameter values found in two-phase regions. This was done along composition lines of constant HfO_2 concentration at 0, 10, 25, 40, and 70 mole%. More direct methods (See, e.g., Cullity (32)) for determination of these phase boundaries were not practical because of the large amount of overlap of peaks between the fluorite and the REOC phases; the REOC phase is, in effect, a modified fluorite phase with a lattice parameter approximately two times that of the fluorite phase. The direct comparison method is not practical because the fluorite phase has no reference line that is independent of any REOC phase reflection. The "single-line" method and internal standards method fail because neither phase coexisting at a boundary is pure; i.e., neither mass absorption coefficients (in the "single-line" method) nor calibration curves (in the internal standards method) can be determined, except perhaps by an iterative method.

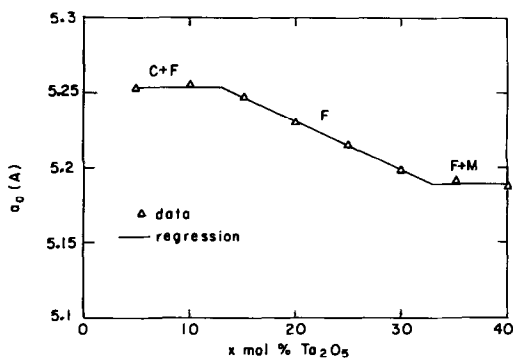


FIG. 2. Lattice parameters of 10 mole% $\text{HfO}_2-(90-x)$ mole% Er_2O_3-x mole% Ta_2O_5 at 1100°C .

Results and Discussion

The lattice parameters measured for fluorite and REOC phases as a function of composition and temperature are given as "observed" values in Table I. The designation M in the table represents detection of one or more unidentified phases which are probably monoclinic in structure. Parameters within parentheses are for the REOC phase; those without parentheses are for the fluorite phase.

At a constant HfO_2 content, the lattice parameters in the ternary fluorite and REOC solid solution phases were found to vary linearly with Ta_2O_5 content, or in other words, with Ta_2O_5 : Er_2O_3 molar ratio; see, e.g., Fig. 2. Therefore, for purposes of extrapolation in order to determine phase boundaries, linear least-squares regressions of lattice parameter on Ta_2O_5 content (at constant HfO_2) were determined of the form

$$a_0(\text{\AA}) = C_1(\text{mole\% Ta}_2\text{O}_5) + C_2$$

The fitting parameters for the regressions for the two phases are given in Tables II and III. Lattice parameters calculated from these linear regression relationships are indicated in Table I as "calculated" values

TABLE II
LATTICE PARAMETER EQUATIONS
IN THE FLUORITE SINGLE-PHASE REGIONS
 $a_0(\text{\AA}) = C_1(\text{mole\% Ta}_2\text{O}_5) + C_2$

Constant HfO ₂ content (mole%)	After 1100°C heat treatment		After 1500°C heat treatment	
	C ₁	C ₂	C ₁	C ₂
0	-.002986	5.3059	-.003010	5.3062
10	-.003218	5.2951	-.00338	5.3022
25	-.003438	5.2724	-.00297	5.2655
40	-.003410	5.2463	-.00333	5.2441
70	-.002407	5.1693	-.003703	5.1723

TABLE III
LATTICE PARAMETER EQUATIONS
IN THE REOC SINGLE-PHASE REGIONS
 $a_0(\text{\AA}) = C_1(\text{mole\% Ta}_2\text{O}_5) + C_2$

Constant HfO ₂ content (mole%)	After 1100°C heat treatment		After 1500°C heat treatment	
	C ₁	C ₂	C ₁	C ₂
10	-.00600	10.5362	-.000625	10.5224
25	-.00400	10.5175	-.01220	10.5024

for comparison with the "observed" values. The phase boundary compositions established by extrapolation of these lattice parameter regressions to the fixed value for compositions in a two-phase region are summarized in Tables IV and V.

The results of these investigations were used to construct partial isothermal sections representing the possibly metastable extent of solid solutions found for the HfO₂-Er₂O₃-Ta₂O₅ system heated at 1100°

for 2 hr and 1500°C for 1 hr. These partial sections are shown in Figs. 3 and 4. The phase boundaries are those obtained by extrapolation of lattice parameters with the following exceptions: those in the HfO₂-Er₂O₃ binary system were established by Johnstone (1); those for the REOC single phase region in the Er₂O₃-Ta₂O₅ binary system were established by Isupova *et al.* (6). The width of the fluorite phase region at 1500°C in the Er₂O₃-Ta₂O₅ system established in the present study (20.1 to 30.3 mole% Ta₂O₅) is slightly greater than that

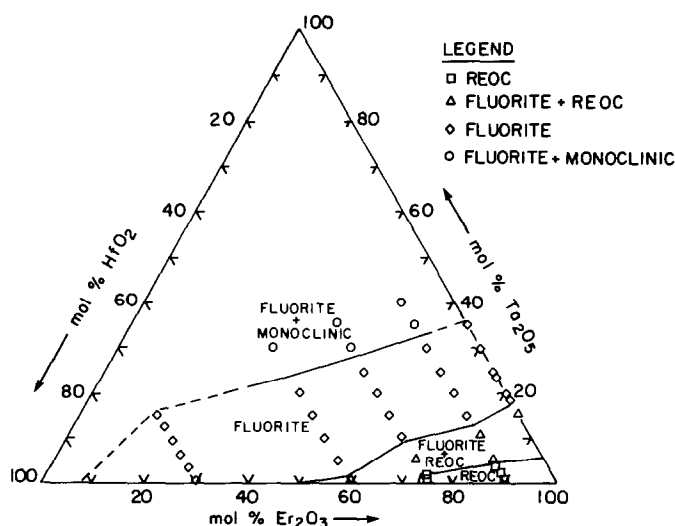


FIG. 3. HfO₂-Er₂O₃-Ta₂O₅ system partial 1100°C isothermal section. ---, Boundary uncertain. The region labeled (fluorite + monoclinic) contains one or more monoclinic phases along with the fluorite phase.

TABLE IV
LIMITS OF THE FLUORITE SINGLE-PHASE REGION

Constant HfO ₂ content (mole%)	After 1100°C heat treatment		After 1500°C heat treatment	
	Lower limit (mole% Ta ₂ O ₅)	Upper limit (mole% Ta ₂ O ₅)	Lower limit (mole% Ta ₂ O ₅)	Upper limit (mole% Ta ₂ O ₅)
0	17.4	U.D.(>35)	20.1	30.3
10	12.8	32.8	16.2	27.2
25	9.4	28.0	8.0	24.0
40	1.5	23.9	1.6	18.5
70	0	U.D.(>15)	0	10.5

TABLE V
LIMITS OF THE REOC SINGLE-PHASE REGION

Constant HfO ₂ content (mole%)	After 1100°C heat treatment		After 1500°C heat treatment	
	Lower limit (mole% Ta ₂ O ₅)	Upper limit (mole% Ta ₂ O ₅)	Lower limit (mole% Ta ₂ O ₅)	Upper limit (mole% Ta ₂ O ₅)
10	0	4.7	0	3.8
25	0	2.0	0	1.6

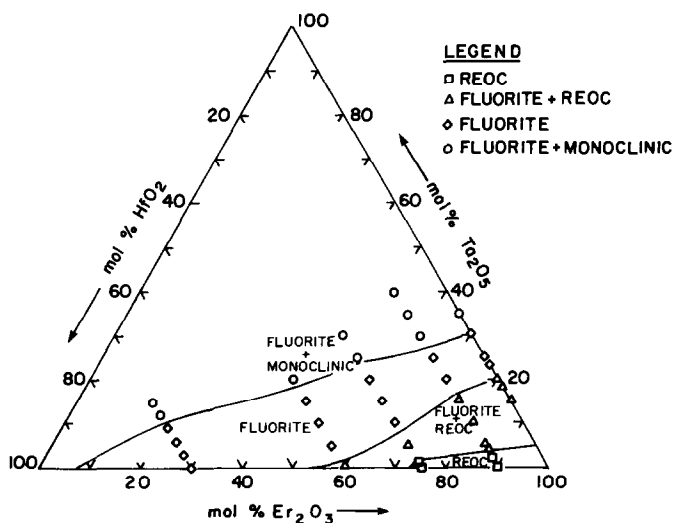


FIG. 4. HfO₂-Er₂O₃-Ta₂O₅ system partial 1500°C isothermal section. The region labeled (fluorite + monoclinic) contains one or more monoclinic phases along with the fluorite phase.

determined by Isupova *et al.* (6) (20 to 28 mole% Ta₂O₅), but is much narrower than that reported by Wirkus *et al.* (7) (18 to 34 mole% Ta₂O₅). In the ternary region, the fluorite phase appears to be about one-third broader at 1100 than at 1500°C.

Michel and Perez y Jorba (17) have reported M₇O₁₂ ordered phases in the ZrO₂(HfO₂)-MgO-Nb₂O₅(Ta₂O₅) ternary systems, and numerous reports have been made of compounds and ordered phases in the bounding and related binary systems. No compounds or ordered phases were observed at any of the compositions in the HfO₂-Er₂O₃-Ta₂O₅ system for the short heat treatments studied in the present work. The sluggish nature of the ordering reactions in the previously reported studies implies that ordered phases, even though they represent true equilibrium, may not appear except after long anneals at temperatures just below the order-disorder transition temperature. Long-time anneals of 60 mole% HfO₂-40 mole% Er₂O₃ (the M₇O₁₂ composition) at a series of temperatures between 1330 and 1480°C did not produce any evidence of ordering.

Appendix

TABLE AI
HfO₂-RARE-EARTH OXIDE PHASE DIAGRAMS

System	Phase Diagrams for Ceramists (24-27) Figure (year compiled)	Other references
HfO ₂ -Sc ₂ O ₃	4428(1975), 5242(1981)	
HfO ₂ -Y ₂ O ₃	4436(1975)	
HfO ₂ -La ₂ O ₃	2371(1969)	
HfO ₂ -Sm ₂ O ₃	4432(1975)	
HfO ₂ -Gd ₂ O ₃	4414(1975)	
HfO ₂ -Dy ₂ O ₃	5208(1981)	
HfO ₂ -Er ₂ O ₃		This review (1-3)
HfO ₂ -Yb ₂ O ₃	5255(1981)	

TABLE AII
ZrO₂-RARE-EARTH OXIDE PHASE DIAGRAMS

System	Phase Diagrams for Ceramists (24-27) Figure (year compiled)	Other references
ZrO ₂ -Sc ₂ O ₃	2385(1969), 4430(1975)	
ZrO ₂ -Y ₂ O ₃	354(1964), 2390(1969), 4437(1975)	This review (19, 21)
ZrO ₂ -La ₂ O ₃	346(1964), 2374-75(1969), 5232(1981)	
ZrO ₂ -Ce ₂ O ₃	355(1964)	
ZrO ₂ -Nd ₂ O ₃	350(1964), 2382-83(1969), 4426(1975), 5239(1981)	
ZrO ₂ -Sm ₂ O ₃	2387(1969), 4433(1975), 5245(1981)	
ZrO ₂ -Gd ₂ O ₃	2370(1969), 4417(1975), 5224(1981)	
ZrO ₂ -Dy ₂ O ₃	2363(1969), 5211(1981)	
ZrO ₂ -Ho ₂ O ₃	5228(1981)	
ZrO ₂ -Er ₂ O ₃	4404-05(1975), 5217(1981)	This review (20)
ZrO ₂ -Yb ₂ O ₃	2392(1969), 4440(1975), 5257(1981)	
ZrO ₂ -RE ₂ O ₃	5241(1981)	

TABLE AIII
HfO₂(ZrO₂)-Ta₂O₅(Nb₂O₅) PHASE DIAGRAMS

System	Phase Diagrams for Ceramists (24-27) Figure (year compiled)	Other references
HfO ₂ -Ta ₂ O ₅ (Nb ₂ O ₅)	None	None
ZrO ₂ -Nb ₂ O ₅	373(1964), 4457(1975)	
ZrO ₂ -Ta ₂ O ₅	374(1964), 4458(1975)	

TABLE AIV
RARE-EARTH OXIDE-Ta₂O₅(Nb₂O₅) PHASE DIAGRAMS

System	Phase Diagrams for Ceramists (24-27) Figure (year compiled)	Other references
Sc ₂ O ₃ -Ta ₂ O ₅	4431(1975)	
Y ₂ O ₃ -Nb ₂ O ₅	5253(1981)	
Y ₂ O ₃ -Ta ₂ O ₅	None	This review (28, 29)
La ₂ O ₃ -Nb ₂ O ₅	4421(1975)	
La ₂ O ₃ -Ta ₂ O ₅	4422(1975)	
Eu ₂ O ₃ -Ta ₂ O ₅	4409(1975)	
Gd ₂ O ₃ -Nb ₂ O ₅	343(1964)	
Gd ₂ O ₃ -Ta ₂ O ₅	None	This review (30)
Er ₂ O ₃ -Ta ₂ O ₅	None	This review (6, 7)
Lu ₂ O ₃ -Ta ₂ O ₅	4425(1975)	

TABLE AV
HfO₂ or ZrO₂ CONTAINING TERNARY PHASE
DIAGRAMS

System	Phase Diagrams for Ceramists (24-27) Figure (year compiled)	Other references
ZrO ₂ -Y ₂ O ₃ -Ta ₂ O ₅	None	This review (13, 14)
ZrO ₂ -Y ₂ O ₃ -MgO	None	This review (22)
HfO ₂ -Y ₂ O ₃ -SiO ₂	5440-41(1981)	
ZrO ₂ -La ₂ O ₃ -MgO	716(1964), 4572(1975)	
ZrO ₂ -CeO ₂ -Ce ₂ O ₃	5042(1981)	
ZrO ₂ -CeO ₂ -CoO	5403(1981)	
ZrO ₂ -CeO ₂ -CaO	5390(1981)	
ZrO ₂ -CeO ₂ -MgO	5418(1981)	
HfO ₂ -PrO _{1.5} -DyO _{1.5}	None	This review (31)
ZrO ₂ -MgO-Ta ₂ O ₅	None	This review (15)

TABLE AVI
RARE-EARTH OXIDE AND Nb₂O₅(Ta₂O₅) CONTAINING
TERNARY PHASE DIAGRAMS

System	Phase Diagrams for Ceramists (24-27) Figure (year compiled)	Other references
La ₂ O ₃ -Nb ₂ O ₅ -CaO	5389(1981)	
Gd ₂ O ₃ -Nb ₂ O ₅ -BaO	563(1964)	
Gd ₂ O ₃ -Nb ₂ O ₅ -Fe ₂ O ₃	779(1964)	
RE ₂ O ₃ -Ta ₂ O ₅	None	None

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