RESEARCH

PHASE FORMATION IN THE ZrO_2 – HfO_2 – Gd_2O_3 AND ZrO_2 – HfO_2 – Yb_2O_3 SYSTEMS

A. G. Karaulov[1] and E. I. Zoz[1]

The formation of phases and properties of solid solutions and $Gd_2Zr_2O_7$ and $Yb_4Zr_3O_{12}$ chemical compounds in the ZrO_2 – Gd_2O_3 and ZrO_2 – Yb_2O_3 systems are studied. The compounds undergo a phase transformation of the type "order – disorder" and melt incongruently. The data on the parameters of the elementary cells, the melting temperatures, and the TCLE of phases in the ZrO_2 – Gd_2O_3 and ZrO_2 – Yb_2O_3 systems are presented. These data are compared with similar data for phases based on HfO_2. The considered solid solutions are shown to be promising for the production of high-temperature. heat-insulating ceramics for growing single crystals.

The creation of new high-temperature materials with special properties leads us to a study of systems based on ZrO_2 and HfO_2 stabilized by oxides of rare-earth elements. High-temperature ceramics based on ZrO_2 stabilized by oxides of rare earth elements are used, in particular, for insulating installations for growing single crystals whose purity determines their quality and applicability in optical quantum generators (OQG) [1]. The high refractoriness (2700°C) and the low pressure of ZrO_2 vapors at 2000 – 2300°C diminish the possibility of contamination of the medium of the installation by impurity ions, which is a decisive factor for growing single crystals for OQG.

The structure and properties of phases in systems based on HfO_2 have been studied much less than the structure and properties of solid solutions and chemical compounds in systems based on ZrO_2, because an intense study of HfO_2 as a base for high-temperature ceramics with special properties began only 10 – 15 years ago.

The position of Gd and Yb in the yttrium subgroup of the lanthanide row of the Periodic System has attracted the attention of researchers to systems based on ZrO_2 and HfO_2 that include Gd_2O_3 and Yb_2O_3. At the present time, the phase diagrams of the $ZrO_2 (HfO_2)$ – Gd_2O_3 and $ZrO_2 (HfO_2)$ – Yb_2O_3 systems have not been plotted in their final form [2, 3]. No data on the ternary ZrO_2 – HfO_2 – Ln_2O_3 systems (where Ln = Gd, Yb) can be found in the literature.

The formation of phases in the limiting ZrO_2 – Gd_2O_3 system has been studied earlier in [4, 5]. An important result of this work consisted of obtaining a 100% fluorite-like cubic solid solution in specimens fabricated at 1750°C for 1 h in a concentration range of 6.0 – 6.5 mole % Gd_2O_3. The optimum composition has been shown to bear 6.5 mole % Gd_2O_3 and was used for fabricating a heat-resistant ceramics for installations for growing single crystals. The single crystals were not contaminated because the stabilizing additive evaporated.

Increasing the isothermal hold of specimens containing 6.5 mole % Gd_2O_3 in ZrO_2 to 6 h and subjecting them to subsequent quenching, we decreased the content of the cubic phase to 86% and observed the appearance of a tetragonal phase. An x-ray study has shown that 1850°C is the limiting temperature of the existence of the tetragonal phase in the composition containing 6.5 mole % Gd_2O_3. Above 1900°C we observed a domain of cubic solid solutions. By the data of [2, Fig. 756] the limiting temperature of the existence of the tetragonal phase for a concentration of 4 mole % Gd_2O_3 in ZrO_2 is 1900°C.

In the present work, we studied the phase transformation and some properties of phases in the systems ZrO_2 – HfO_2 – Gd_2O_3 and ZrO_2 – HfO_2 – Yb_2O_3 by the methods of x-ray diffraction analysis and dilatometry, crystal optics,[2] and measurement of the melting temperatures[3] and

---

[1] A. S. Berezhnoi Ukrainian Research Institute of Refractories. Kharkov, Ukraine.

[2] The refractive indexes were measured by N. V. Gul'ko.
[3] Measured by a refined method of [6].

TABLE 1. Crystallochemical and Thermophysical Characteristics of the $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$ Compounds

Compound	Elementary cell parameter a, nm	X-ray density ρ, 10^{-3} kg/m^3	Refractive index N	Temperature of the order – disorder transformation T_t, °C	α, 10^{-6} K^{-1}	T_{melt}, °C
$Gd_2Zr_2O_7$	1.0530	6.926	2.90	1543[*1]; 1530[*3]	12.48	2570 ± 14[*2]
$Gd_2Hf_2O_7$	1.0507	10.110	2.05	2475 ± 20[*3]	10.40	2720 ± 20[*2]

[*1] High-temperature radiography.

[*2] T_{melt} of the cubic solid solution of $Gd_2O_3 \cdot 2ZrO_2$ and $Gd_2O_3 \cdot 2HfO_2$ [6].

[*3] High-temperature diffractometry and thermal analysis [7].

the temperatures of phase transformations.[4] The initial materials were ZrO_2 of grade TsrO-I with 97.79% ZrO_2 and 1.75% HfO_2, HfO_2 of grade GfO-2 with 98.4% HfO_2 and 1.2% ZrO_2, Gd_2O_3 of grade Gd-3 with 99.9% Gd_2O_3, and Yb_2O_3 of grade It-1 with 99.9% Yb_2O_3. The materials were preliminarily milled for a grain size below 3 μm, which promoted the processes of diffusion and intensified substantially the interaction between zirconia and hafnia and the oxides of the rare earth elements in fabrication of highly refractory materials by solid-phase synthesis.

In order to obtain solid solutions and chemical compounds in the systems studied, we synthesized solid solutions in the ZrO_2 – HfO_2 system with compositions $(Hf_{0.1}, Zr_{0.9})O_2$ and $(Hf_{0.3}, Zr_{0.7})O_2$ at 1300°C. These solid solutions were then enriched with Gd_2O_3 and Yb_2O_3 stabilizing additives in specified concentrations. The specimens were synthesized at various temperatures in the range 1200 – 1900°C in air with subsequent water quenching. The quality of the synthesis was controlled by the methods of x-ray diffraction and crystal optics.

We determined the existence of a narrow (≤ 1 mole % Gd_2O_3) region of monoclinic (β-tetragonal at a high temperature) solutions and a region of fluorite-like solid solutions in the limiting HfO_2 – Gd_2O_3 system by radiography. In between, we found a region of a mixture of solid solutions with monoclinic and cubic structures or a region of cubic and tetragonal solid solutions at a high temperature. Quenching from high temperatures did not provide solid solutions with a tetragonal structure, which was determined by the higher temperature of the monoclinic-tetragonal transformation (over 1900°C) in HfO_2 than in ZrO_2 [3], where the formation of the tetragonal phase occurs at a temperature below 1200°C, i.e., below the temperature at which the specimens are fired.

In the limiting systems of $ZrO_2(HfO_2)$ – Gd_2O_3, we studied the $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$ compounds. They are crystallographic analogs and crystallize in a pyrochlore-like structure with a spatial group O_h^7 – $Fd3m$. The crystallo-

graphic and thermophysical characteristics of gadolinium zirconate and hafnate are presented in Table 1. The compounds undergo a phase transformation of the type "order – disorder" and melt congruently. The melting temperature of gadolinium hafnate is 150°C higher than that of gadolinium zirconate.

We established radiographically that regions of nonstoichiometry lie on both sides of the compounds and constitute 23.5 – 33.3 mole % Gd_2O_3 on the side rich with ZrO_2 and 33.3 – 37.5 mole % on the side rich with gadolinium oxide, as well as 24.5 – 33.3 mole % Gd_2O_3 on the side rich with HfO_2 and 33.3 mole % Gd_2O_3 on the side rich with Gd_2O_3. In the ZrO_2 (HfO_2) – Gd_2O_3 systems the radiography did not show regions of a mixture of solid solutions of the fluorite type based on zirconia and hafnium oxide with solid solutions of a pyrochlore type based on chemical compounds. This seems to be connected with the fact the region of the mixture is very narrow and has a low intensity of the superstructural lines.

In addition to the limiting systems, we studied the structure of phases based on ray sections $(Hf_{0.1}, Zr_{0.9})O_2$ – Gd_2O_3 and $(Hf_{0.3}, Zr_{0.7})O_2$ – Gd_2O_3 in the ZrO_2 – HfO_2 – Gd_2O_3 system and solid solutions of the $Gd_2Zr_2O_7$ – $Gd_2Hf_2O_7$ system obtained from gadolinium zirconate and hafnate as the initial materials.

The method of high-temperature radiography has shown that the introduction of 10 and 30 mole % HfO_2 increases the temperature of the monoclinic-tetragonal transformation. For example, for ZrO_2 + 1 mole % Gd_2O_3 the temperature is 1090°C, and for $(Hf_{0.1}, Zr_{0.9})O_2$ + 1 mole % Gd_2O_3 and $(Hf_{0.3}, Zr_{0.7})O_2$ + 1 mole % Gd_2O_3 the respective temperatures are 1152 and 1285°C. In the ZrO_2 – HfO_2 – Gd_2O_3 sys-

[4] Measured by the method of high-temperature diffraction and thermal analysis [7].

TABLE 2. Elementary Cell Parameters, Refractive Indexes, and X-Ray Density of $Gd_2Zr_2O_7$ – $Gd_2Hf_2O_7$ Solid Solutions

Composition	a, nm	N	ρ, 10^{-3} kg/m^3
$Gd(Hf_{0.25}, Zr_{0.75})_2O_7$	1.0532	2.08	7.781
$Gd(Hf_{0.5}, Zr_{0.5})_2O_7$	1.0520	2.07	8.500
$Gd(Hf_{0.75}, Zr_{0.25})_2O_7$	1.0512	2.06	9.345

tem, the radiography showed the existence of a narrow region of monoclinic (β-tetragonal at high temperatures) solid solutions, a region of mixed tetragonal and cubic solid solutions, a single-phase region of fluorite-like cubic solid solutions, and regions of nonstoichiometry based on chemical compounds. The linear variation of the crystallochemical and thermophysical characteristics of the solid-solution crystals (Table 2) in the $Gd_2Zr_2O_7$ – $Gd_2Hf_2O_7$ system indicates that the system possesses an unlimited series of solid solutions of the pyrochlore type.

A radiographic study [5, 8, 9] of phase formation in the limiting systems ZrO_2 – Yb_2O_3 and HfO_2 – Yb_2O_3 has shown that there exist regions of monoclinic (β-tetragonal at high temperatures) solid solutions that include 1.0 – 1.5 mole % Yb_2O_3 and a wide field of cubic solid solutions of fluorite type. Between the regions of homogeneity lies a region of a mixture of monoclinic and cubic solid solutions. By the data of [10], stabilization of ZrO_2 by Yb_2O_3 with subsequent firing at 1730°C provides a 100% cubic solid solution based on zirconia.

In the limiting systems considered above, compositions $Yb_2O_3 \cdot 2ZrO_2$ and $Yb_2O_3 \cdot 2HfO_2$ crystallize in a cubic lattice of fluorite type. The microstructure of the solid solution based on ZrO_2 is represented by isotropic grains 3 – 30 μm in size and that based on HfO_2 is represented by isotropic grains 2 – 12 μm in size. The electron-microscopic structure of the cubic solid solution of composition $Yb_2O_3 \cdot 2ZrO_2$ is characterized by a grain size of 3 – 5 mm; for the composition $Yb_2O_3 \cdot 2HfO_2$ the mean size of the grains is 3 – 3.5 mm. In both structures we encounter individual grains 15 – 25 μm in size (Fig. 1a and b). The crystallochemical characteristics of the compositions are presented in Table 3.

Taken in a specified proportion, $Yb_2O_3 \cdot 2ZrO_2$ and $Yb_2O_3 \cdot 2HfO_2$ were used as the initial substances for synthesizing solid solutions in the system $Yb_2O_3 \cdot 2ZrO_2$ – $Yb_2O_3 \cdot 2HfO_2$. It was established radiographically and crystallographically that the obtained solid solutions crystallize in a fluorite-like cubic lattice. The parameters of the elementary cell and the refractive indexes decrease linearly with in-
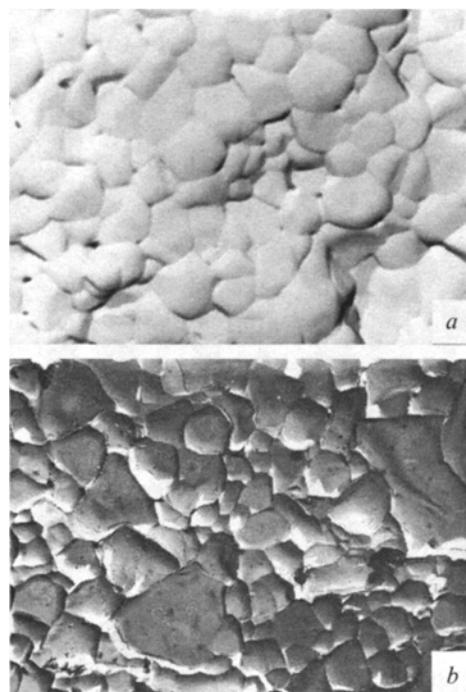

Fig. 1. Microstructures of solid solutions with a cubic structure: a) $Yb_2O_3 \cdot 2ZrO_2$; b) $Yb_2O_3 \cdot 2HfO_2$. × 6000.

crease in the concentration of hafnium ions in the solid solution (see Table 3). The linear dependence indicates that this system possesses an unbounded series of fluorite-type solid solutions [9]. The method of x-ray dilatometry has been used to measure the temperature coefficients of expansion of cubic solid solutions in the $Yb_2O_3 \cdot 2ZrO_2$ – $Yb_2O_3 \cdot 2HfO_2$ system, the values of which decrease linearly with increase in the concentration of hafnium ions in the solid solution (Fig. 2).

$Yb_4Zr_3O_{12}$ and Yb_4HfO_{12} chemical compounds that crystallize in a rhombohedral lattice with a spatial group $R\bar{3}$

TABLE 3. Crystallochemical Characteristics of Solid Solutions in the $Yb_2O_3 \cdot 2ZrO_2$ – $Yb_2O_3 \cdot 2HfO_2$ System

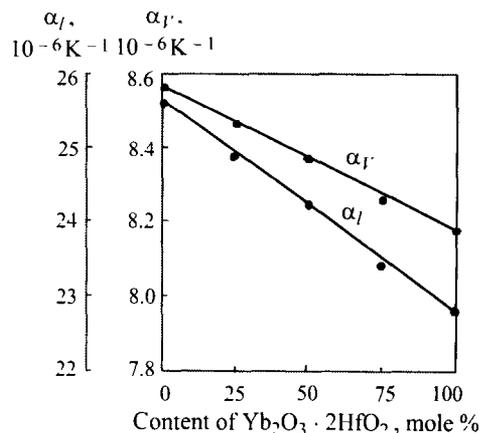| Composition: $Yb_2O_3 \cdot 2HfO_2$ in $Yb_2O_3 \cdot 2ZrO_2$, mole %	a, nm	ρ, 10^{-3} kg/m³	N	T_{melt}, °C
0	0.5171	15.382	2.06	2697 ± 11
25	0.5167	16.645	2.05	2745 ± 7
50	0.5163	17.510	2.04	2780 ± 10
75	0.5159	18.652	2.02	2800 ± 15
100	0.5161	19.688	2.01	2820 ± 20

Fig. 2. Concentration dependence of the coefficients of linear α_l and volume α_V thermal expansion of the elementary cell of fluorite-like solid solutions in the $Yb_2O_3 \cdot 2ZrO_2$ – $Yb_2O_3 \cdot 2HfO_2$ system.
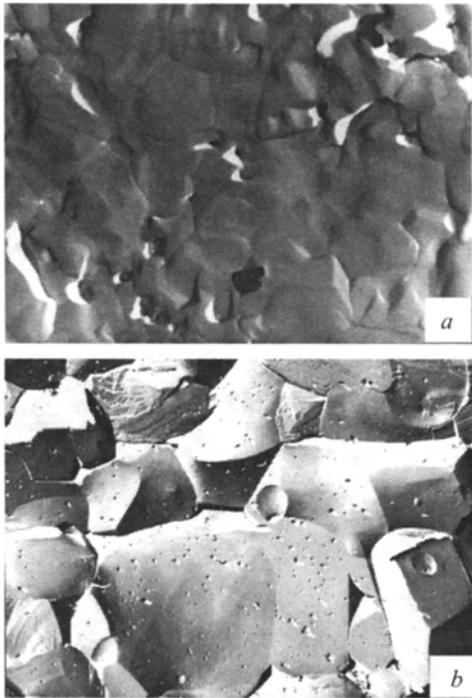
Fig. 3. Microstructure of compounds: *a*) $Yb_4Zr_3O_{12}$; *b*) $Yb_4Hf_3O_{12}$. × 12,000.

have been synthesized in the $ZrO_2 - Yb_2O_3$ and $HfO_2 - Yb_2O_3$ systems. Crystallographic analogs of these compounds, i.e., scandium and magnesium zirconates and hafnates, have been synthesized in [3]. The parameters of the elementary cells of these compounds are presented in Table 4.

In the field of the microscope, ytterbium zirconate and hafnate are represented by isotropic grains and aggregates with a fine disperse structure. The weak double refraction did not allow us to measure both refractive indexes (Fig. 3). We studied compositions lying close to the $Yb_4Zr_3O_{12}$ and $Yb_4Hf_3O_{12}$ compounds in the range 1200 – 1900°C with various holds (from 200 h at 1200°C to 5 h at 1900°C). It has

been shown that there is a region of nonstoichiometry based on the mentioned compounds. The boundaries of the regions of nonstoichiometry are 37 – 40 mole % Yb_2O_3 on the side of the region rich with ZrO_2 and 40 – 45 mole % Yb_2O_3 on the side of the region rich with Yb_2O_3. For the compound based on HfO_2 these regions occupy 38 – 40 and 40 – 42 mole % Yb_2O_3, respectively. Firing of the compounds at a high temperature causes the formation of fluorite-like cubic solid solutions. This indicates the existence of an order–disorder phase transformation. The temperature of the transition of the low-temperature form of the compounds into a high-temperature form with a fluorite-like cubic lattice is 1630 and 1710°C for ytterbium zirconate and hafnate, respectively.

It follows from Tables 1 – 3 that the increase in the concentration of hafnium ions in solid solutions of the $ZrO_2 - HfO_2 - Gd_2O_3$ and $ZrO_2 - HfO_2 - Yb_2O_3$ systems causes a decrease in the parameters of the elementary cell and the refractive indexes, decreases the temperature coefficients of expansion, shifts the temperatures of the phase transformations to higher values, and increases the melting temperature. The existence of quite wide regions of homogeneity with a fluorite-like cubic structure and regions with unlimited solubility in the systems considered, as well as the rules of variation of the crystallooptical properties with increase in the concentration of ions in the solid solution allow us to state that the solid solutions of these systems are promising for manufacturing highly refractory ceramics with elevated thermal strength and controllable properties for various fields of advanced engineering. For example, solid solutions of the $ZrO_2 - HfO_2 - Gd_2O_3$ system are interesting materials for installations for growing single crystals. The introduction of HfO_2 and fabrication of ternary solid solutions should decrease the vapor pressure relative to the solid solutions in the $Zr_2O_3 - Gd_2O_3$ system, which should, in turn, improve the quality of the grown single crystals.

REFERENCES

1. A. A. Kamenskii and V. V. Osiko, "Inorganic laser materials with fine structure," *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **3**(3), 417 – 463 (1967).
2. *Minerals. Diagrams of Phase Transformations. A Handbook, Issue 2* [in Russian], Nauka, Moscow (1974).
3. V. B. Glushkova et al., *Hafnia and Its Compounds with Oxides of Rare Earth Elements* [in Russian], Nauka, Leningrad (1984).
4. A. G. Karaulov, E. I. Zoz, and T. M. Shlyakhova, "Structure and properties of refractories based on zirconia stabilized by gadolinium oxide," *Ogneup. Tekh. Keram.*, No. 3, 12 – 16 (1996).
5. A. G. Karaulov and E. I. Zoz, "Phase formation and properties of solid solutions in the $ZrO_2 - Gd_2O_3$ and $ZrO_2 - Yb_2O_3$ systems," in: *Abs. Rep VIIth Int. Conf. "High-Temperature Chemistry of Silicates and Oxides"* [in Russian], Ross. Akad. Nauk, St. Petersburg (1988), p. 101.
6. E. N. Fomichev, A. A. Kalashnik, E. I. Zoz, and G. G. Eliseeva, "Some data on the melting diagram of the $ZrO_2 - HfO_2 - CaO$ system," *Zh. Neorg. Khim.*, **23**(5), 1417 (1990).

TABLE 4. Crystallochemical Characteristics of Compounds of the Type M_7O_{12}

Compound	Characteristics of rhombohedral elementary cell			N
	a, nm	α	V, nm³	
$Yb_4Zr_3O_{12}$	0.6174	99°38'	0.22372	2.14
$Yb_4Hf_3O_{12}$	0.6157	99°38'	0.22220	2.08
$Sc_4Zr_3O_{12}$	0.6165	99°37'	0.22231	$n_g = 2.10$; $n_p = 2.09$
$Sc_4Hf_3O_{12}$	0.6152	99°37'	0.22212	2.09
$Mg_2Zr_3O_{12}$	0.6186	99°36'	0.22652	2.125
$Mg_2Hf_3O_{12}$	0.6148	99°36'	0.22188	2.06

7. E. I. Zoz, G. G. Eliseeva, and L. M. Lopato, "Methods of high-temperature diffractometry and thermal analysis in studying phase transformations in solid solutions based on ZrO_2," in: *Coll. Works VIIth All-Union Conf. on Thermal Analysis* [in Russian], Kuibyshev (1983), pp. 144 – 149.

8. E. I. Zoz. E. N. Fomichev, A. A. Kalashnik, and G. G. Eliseeva, "On the structure and properties of zirconates and hafnates of rare earth elements," *Izv. Akad. Nauk SSSR, Zh Neorg. Khim.*, **27**(1), 95 – 99 (1982).

9. E. I. Zoz and N. G. Yakovenko, "Structure and properties of solid solutions of the $Yb_2O_3 \cdot 2ZrO_2 - Y_2O_3 \cdot 2HfO_2$ system." *Izv. Vuzov Ser. Fiz. Zh., Fizika*, No. 5, (1980).

10. L. N. Popov and R. Ya. Popil'skii, "On the phase proportions and some properties of zirconium ceramics in the $ZrO_2 - Yb_2O_3$ system," in: *Silicates, Proc. Moscow Chemical Technological Institute. Issue 63* [in Russian], MKhTI, Moscow (1964), pp. 120 – 131.