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# Chemistry

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Fig. 1. Thermograms of mixtures of hafnium, lanthanum, and neodymium hydroxides of composition  $\text{Me}_2\text{O}_3 : \text{HfO}_2 = 1 : 2$  (mean heating rate 8-10 deg/min, sample weight 0.8 g); *a*—mechanical mixture of hafnium and lanthanum hydroxides; —coprecipitated mixture of hafnium and lanthanum hydroxides; —mechanical mixture of hafnium and neodymium hydroxides; —coprecipitated mixture of hafnium and neodymium hydroxides

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## Abstract

## Full Text

## Chemistry

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### Lanthanum and Neodymium Hafnates

Despite the closeness of the ionic radii of  $\text{Zr}^{4+}$  and  $\text{Hf}^{4+}$ , hafnium dioxide has somewhat more basic properties than zirconium dioxide. The amphoteric character of  $\text{HfO}_2$  has been studied very little. Recently, hafnates of alkali and alkaline-earth elements have been obtained (<sup>1-5</sup>). The interaction of hafnium dioxide with elements of group III of the periodic system has not yet been studied. It is known that the stability of such salts of weak acids decreases with decreasing radius and increasing charge of the cation.

The present work is devoted to the synthesis of lanthanum and neodymium hafnates and to the study of some of their properties. To obtain the compounds, hafnium dioxide was used with an  $\text{HfO}_2$  content of 99.24% (impurities, wt. %:  $\text{ZrO}_2$  0.65;  $\text{SiO}_2$  0.05;  $\text{CaO}$  0.05;  $\sum \text{MgO, Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{TiO}_2 < 0.01$ ), lanthanum oxide of high purity (99.99%), and neodymium oxide containing less than 0.5 wt. % oxides of other rare-earth elements.

**Fig. 1.** Thermograms of mixtures of hafnium, lanthanum, and neodymium hydroxides of composition  $\text{Me}_2\text{O}_3 : \text{HfO}_2 = 1 : 2$  (mean heating rate 8-10 deg/min, sample weight 0.8 g);

*a*—mechanical mixture of hafnium and lanthanum hydroxides;  
 —coprecipitated mixture of hafnium and lanthanum hydroxides;  
 —mechanical mixture of hafnium and neodymium hydroxides;  
 —coprecipitated mixture of hafnium and neodymium hydroxides.

Fig. 2. Phase diagram of the La<sub>2</sub>O<sub>3</sub>–HfO<sub>2</sub> systemFigure 2: Fig. 2. Phase diagram of the La<sub>2</sub>O<sub>3</sub>–HfO<sub>2</sub> system

To study the interaction of HfO<sub>2</sub> with lanthanum and neodymium oxides, the necessary mixtures were prepared by two methods: by mechanical mixing of the initial oxides or by coprecipitation of the corresponding hydroxides. In the first case, the mixtures were carefully ground with the addition of alcohol for 30–40 min, dried at 100–110°, and sieved. The particle size was < 100μ. After this they were calcined for 8–20 h at 1300° and, to obtain well-formed crystals, annealed for 30 min in a high-temperature quenching furnace with a tungsten spiral in an argon atmosphere at 2000°, and again ground to a particle size < 100μ.

Coprecipitation of the hydroxides was carried out with ammonia from hydrochloric-acid solutions with an initial-compound concentration of ~ 0.04 mg-equiv/ml at pH 9 and a temperature of 30–40°. The precipitates were thoroughly washed until NH<sub>4</sub>Cl was completely removed, dried (100–110°), and, for X-ray study, calcined for 8 h at 900° and 20 min at 1300°. The samples were then ground to a grain size < 100μ. The same particle size was possessed by mixtures of coprecipitated hydroxides that had been dried in the range 100–110°.

The principal methods of investigation were thermal and X-ray phase-

analysis. In a number of cases phase chemical analysis was used, and the electrical resistance of some samples was measured. X-ray patterns were recorded under identical conditions with a copper anode in an RKD-57 camera. For more accurate determination and indexing of weak lines characterizing the formation of a new phase, the sensitivity of the X-ray recording was increased by using a germanium monochromator (planes III). The X-ray patterns were measured on a comparator; the accuracy of measurement was  $\pm 0.05$  and  $\pm 0.02$  mm. The specific electrical resistance was determined with an MOM – 3ohmmeter in the temperature range 400–800°. For this purpose samples were used in the form of pellets (diameter 1 and annealed at 1500–1600°. Thin layers of metallic silver deposited on the upper and lower surfaces of the pellet served as electrodes.

### Fig. 2. Phase diagram of the La<sub>2</sub>O<sub>3</sub>–HfO<sub>2</sub> system

The conditions of interaction of lanthanum and hafnium hydroxides were investigated by differential thermal analysis using mixtures of coprecipitated hydroxides of composition La<sub>2</sub>O<sub>3</sub> : HfO<sub>2</sub> = 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5. For comparison, thermograms were recorded for a mechanical mixture of dried hydroxides with the ratio La<sub>2</sub>O<sub>3</sub> : HfO<sub>2</sub> = 1 : 2 and for the initial hafnium and lanthanum hydroxides. X-ray patterns were taken for the samples studied after calcination at 900 and 1300°; these showed that in all cases a new crystalline phase with the pyrochlore structure is detected. No other lines corresponding to the initial HfO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> were observed. Formation of the new phase in

Fig. 3. Schemes of X-ray patterns of  $\text{La}_2\text{Hf}_2\text{O}_7$  and  $\text{Nd}_2\text{Hf}_2\text{O}_7$

Figure 3: Fig. 3. Schemes of X-ray patterns of  $\text{La}_2\text{Hf}_2\text{O}_7$  and  $\text{Nd}_2\text{Hf}_2\text{O}_7$

Fig. 4. Dependence of the specific electrical resistance of  $\text{La}_2\text{Hf}_2\text{O}_7$  on temperature

Figure 4: Fig. 4. Dependence of the specific electrical resistance of  $\text{La}_2\text{Hf}_2\text{O}_7$  on temperature

the case of coprecipitated hydroxides proceeds at low temperatures. It may be assumed that their interaction occurs during dehydration, after which a change in the thermal properties of the mixture is observed (Fig. 1a, b). Meanwhile, in a mechanical mixture of hydroxides or oxides of hafnium and lanthanum, the new phase arises only after prolonged calcination at a temperature of  $1300^\circ$  and above. Study of the phase diagram of the  $\text{La}_2\text{O}_3\text{--HfO}_2$  system by methods of thermal and X-ray phase analysis and by determination of electrical resistance made it possible to establish that the interaction of  $\text{HfO}_2$  with  $\text{La}_2\text{O}_3$  is characterized by the formation of the compound  $\text{La}_2\text{Hf}_2\text{O}_7$  with a cubic structure of the pyrochlore type, on the basis of which solid solutions exist (Fig. 2)\*.

**Fig. 3. Schemes of X-ray patterns of  $\text{La}_2\text{Hf}_2\text{O}_7$  (1, 2) and  $\text{Nd}_2\text{Hf}_2\text{O}_7$  (3, 4): 1, 3 –samples obtained by calcination of coprecipitated hydroxides at  $1300^\circ$ ; 2, 4 –samples obtained after melting**

The analogous neodymium compound  $\text{Nd}_2\text{Hf}_2\text{O}_7$  forms under the same conditions—

\* Yu. P. Simanov took part in the study of the phase diagram of  $\text{La}_2\text{O}_3\text{--HfO}_2$  and in the determination of the lattice parameters of lanthanum and neodymium hafnates.

ways. Thermograms of coprecipitated and mechanical mixtures of hafnium and neodymium hydroxides are presented in Figs. 1c, 2.

In structure and in some physical properties, lanthanum and neodymium hafnates are analogous to the corresponding zirconates (<sup>6, 7</sup>). The lattice parameters of  $\text{La}_2\text{Hf}_2\text{O}_7$  and  $\text{Nd}_2\text{Hf}_2\text{O}_7$ , determined by the Rayleigh–Nilson extrapolation method, are respectively  $10.749 \pm 0.001$  and  $10.627 \pm 0.001$  kX.

**Fig. 4.** Dependence of the specific electrical resistance of  $\text{La}_2\text{Hf}_2\text{O}_7$  on temperature

The synthesized compounds have fairly high density values ( $8 \text{ g/cm}^3$ ). The values\*, calculated from X-ray structural analysis data, agree well with the experimental results, which were determined by the pycnometric method at  $20^\circ$  using carbon tetrachloride (Table 1).

Lanthanum and neodymium hafnates are very refractory compounds; they melt at about  $2300\text{--}2400^\circ$  without decomposition. Their melting points were deter-

mined in an argon atmosphere in a high-temperature thermal-analysis apparatus with a tungsten–molybdenum thermocouple designed by P. P. Budnikov and S. G. Tretyatskii<sup>(8)</sup>. X-ray patterns of the compounds, taken before and after melting, confirm their high thermal stability (Fig. 3).

**Table 1**

**Physical properties of lanthanum and neodymium hafnates and zirconates**

	La <sub>2</sub> Hf <sub>2</sub> O <sub>7</sub>	La <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> (6)	Nd <sub>2</sub> Hf <sub>2</sub> O <sub>7</sub>	Nd <sub>2</sub> Zr <sub>2</sub> O <sub>7</sub> (6)
Lattice parameters, kX	10.749±0.001	10.815 10.627±0.001	10.669 10.662	10.669 10.662
Density, calculated from X-ray structural analysis data, g/cm <sup>3</sup>	7.987	6.047	8.384	6.415
Melting, °C	2300±30	2180 2400±30	2280	2280

For the compound La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> the electrical resistance was measured at temperatures of 400–800° (Table 2). In the temperature range investigated, lanthanum hafnate has a high specific electrical resistance, which decreases rectilinearly with increasing temperature (Fig. 4). The coefficient of electrical resistance has a negative value, which is characteristic of semiconductors. The width of the forbidden band ( $\Delta E$ ) of lanthanum hafnate, calculated from the equation  $\rho = \rho_0 e^{-\Delta E/kT}$ , is 1.28 eV.

**Table 2**

**Specific volume electrical resistance ( $\rho$ ) of La<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>, sintered at 1550°**

T-ra, °C	$\rho$ , ohm · cm	T-ra, °C	$\rho$ , ohm · cm
400	$8.58 \cdot 10^{10}$	650	$2.12 \cdot 10^8$
450	$1.96 \cdot 10^{10}$	700	$0.82 \cdot 10^8$
500	$5.85 \cdot 10^9$	750	$3.29 \cdot 10^7$
550	$1.74 \cdot 10^9$	800	$1.57 \cdot 10^7$
600	$0.62 \cdot 10^9$		

To characterize the chemical stability of lanthanum hafnate, its interaction with

$\text{CCl}_4$  vapors was investigated in the temperature range 600–800° and with solutions of various acids and alkalis at 65–67°. The results obtained are the averages of 2–3 determinations. Below are data characterizing the loss in weight (%) during chlorination of lanthanum hafnate and a mixture of the initial oxides  $\text{La}_2\text{O}_3 : \text{HfO}_2 = 1 : 2$  with carbon tetrachloride (sample

\* In calculating the density, the number of  $\text{Me}_2\text{Hf}_2\text{O}_7$  molecules in the unit cell was taken as 8, by analogy with the crystal structure of the pyrochlore type.

0.2 g; grain size < 100  $\mu$ ; rate of supply of  $\text{CCl}_4$ , 0.47 g/cm<sup>2</sup> h; chlorination time, 30 min.)

Temperature, °C	$\text{La}_2\text{Hf}_2\text{O}_7$	Mixture of $\text{HfO}_2$ and $\text{La}_2\text{O}_3$ (2:1)
600	1.3	9.5
700	3.1	16.8
800	5.5	21.5

The behavior of lanthanum hafnate toward solutions of various acids and alkalis is presented in comparison with the reactivity of  $\text{HfO}_2$ , which was determined under the same conditions (sample 0.3 g; grain size < 100  $\mu$ ; reagent volume 50 ml; temperature 65–70°; treatment time 3 h):

Amount of dissolved substance, wt. % of the initial sample	Substance					
	HCl, 36%	$\text{H}_2\text{SO}_4$ , 96%	$\text{H}_2\text{F}_2$ , 38%	NaOH, 40%	$\text{NH}_4\text{OH}$ , 25%	
Amount of dissolved substance, wt. % of the initial sample	$\text{La}_2\text{Hf}_2\text{O}_7$	4.1	7.9	10.8	6.8	1.4

Amount of dis- solved sub- stance, wt. % of the initial sample	Substance	HCl, 36%	H <sub>2</sub> SO <sub>4</sub> , 96%	H <sub>2</sub> F <sub>2</sub> , 38%	NaOH, 40%	NH <sub>4</sub> OH, 25%
	Amount of dis- solved sub- stance, wt. % of the initial sample	HfO <sub>2</sub>	5.4	11.0	81.5	8.9

The investigations carried out showed that lanthanum hafnate has increased resistance to the reagents tested, especially toward concentrated hydrofluoric acid solution and the chlorinating agent.

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