Influence of the concentration and lanthanoide type on the phase transitions in Ln2O3-MO₂ system
(Ln = La, Gd, Y; M = Zr, Hf)

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Abstract. Influence of the concentration and type of rare-earth oxide on the chemical composition and structure of the compounds formed in the “Ln₂O₃-MO₂” system has been investigated by X-ray powder diffraction and Raman spectroscopy. It was found that crystallization temperature of synthesized powders rises with an increase in the concentration of Ln₂O₃. Besides, it was revealed that the efficiency of stabilization of high-temperature phases (tetragonal and cubic) in Ln₂O₃-ZrO₂ systems increases with the introduction of RE cations in the La³⁺ → Gd³⁺ → Y³⁺ series in accordance with the increase in the solubility of Ln₂O₃ in ZrO₂. A similar behavior was also observed for the Ln₂O₃-HfO₂ systems. Finally, we established that the compounds formed in Ln₂O₃-HfO₂ systems have a greater ability to crystallize in the monoclinic phase.

1. Introduction
Complex oxides forming in the Ln₂O₃-MO₂ system (Ln is a lanthanoide and M is a titanium subgroup metal) represent a large group of inorganic materials, that demonstrate a variety of outstanding physical effects, such as order-disorder phase transitions [1-4], geometrically frustrated magnetism [5] and ionic conductivity [6]. These materials have wide technological applications, which include solid electrolytes in high temperature solid oxide fuel cells, neutron absorbing [7], thermal barrier coatings [8], etc.

Despite a large number of investigations concerned with Ln₂O₃-MO₂ compounds, the vast majority of publications are dedicated to the properties of well-crystallized samples [1-3] prepared by the solid-state synthesis method at elevated temperature. In this paper, we use another synthesis methodic, based on the annealing of precursors with highly homogeneous cation distribution, prepared by reverse co-precipitation [9]. This method is more suitable for studying the evolution of crystalline phases and polymorphic transformations during the process of Ln₂O₃-MO₂ calcination.
The aim of the present work is to study the influence of annealing temperature and molar ratio of initial oxides in precursors on structure and phase composition of the powders formed in “Ln$_2$O$_3$-MO$_2$” system by means of X-ray powder diffraction (XRD) and Raman spectroscopy.

2. Experimental
The lanthanide hafnate and zirconate series with composition Ln$_2$O$_3$-MO$_2$ (Ln = La, Gd, Y; M = Zr, Hf) have been synthesized from lanthanide nitrates Ln(NO$_3$)$_3$•6H$_2$O and zirconium (hafnium) oxychloride octahydrate MOCl•8H$_2$O. Initial metal salts were taken in stoichiometric amounts affording samples xLn$_2$O$_3$•(1-x)MO$_2$ with the molar content x = 3, 8, 18, 33 mol. %. Precursor (mixed Ln-M hydroxide) was prepared by co-precipitation of metal salts solution with ammonia NH$_3$•H$_2$O (analytical grade) [9-10]. The final powders of Ln$_2$O$_3$-MO$_2$ were prepared by calcination of precursor in a muffle furnace annealed isothermally in air for 3 h. From each synthesized precursor with a certain content of initial oxides 5 powder samples were annealed at 600, 800, 1000, 1200 and 1400°C.

Crystal structures of synthesized powders were studied by X-ray powder diffraction at “Center for X-ray structural research and diagnostics of materials” MISiS using a Rigaku MiniFlex 600 diffractometer with Cu Kα radiation (λ = 1.54178 Å). Also, XRD experiments for 33Ln$_2$O$_3$•67MO$_2$ series were carried out at “Structural Materials Science” beamline of the Kurchatov synchrotron radiation source. Measurements were performed in the transmission mode at λ = 0.68886 Å, using XY detector Imaging Plate Fuji Film BAS-5000 [10, 11]. The Rietveld full-profile analysis of X-ray diffraction patterns was performed with the Jana2006 software [12].

The Raman spectra were collected on a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific Inc.) with Thermo Scientific iS50 Raman module (λ = 1064 nm) at room temperature [4].

3. Results and discussion
X-ray powder diffraction analysis of precursor demonstrated that, at any molar ratio of the components, all synthesized samples were X-ray amorphous [4, 11]. At calcination temperature 600°C, order of crystallization in sample with certain molar content x in xLn$_2$O$_3$•(1-x)MO$_2$ compound was slightly different for each powder sample, and depended both on the type and concentration of the rare-earth cation.

![Figure 1](image-url)

**Figure 1.** XRD patterns (a) and Raman spectra (b) of xLa$_2$O$_3$•(1-x)ZrO$_2$ powders obtained by calcination of the precursor at 800 and 1200°C: 1 - 3LaSZ (1200°C), 2 - 3LaSZ (800°C), 3 - 18LaSZ (800°C), 4 - 33LaSZ (1200°C).
For example, at molar concentration of Ln$_2$O$_3$ equals 3 and 8 mol. %, we observed weakly crystallized (CSL ~ 20-30 nm) tetragonal structure (space group $P4_2/mnc$ (137)) and $t''$-structure (according to Raman) for each concentration, respectively. Figure 1 (curve No. 2) shows approximate XRD patterns and Raman spectra for structures with these types of ordering. The feature of powders with $t''$-ordering mainly consists in the absence of a clear cubic structure in these compounds with presence an admixture of the tetragonal phase [13]. So, the X-ray diffractograms of such compounds represent analogous to the XRD patterns of the structure with fluorite ordering (space group $Fm\bar{3}m$ (225), shown in Figure 1(a) (curve No. 3). The sample labels are given in the generally accepted abbreviated form: LnSZ = lanthanoid stabilized zirconia. Similarly, an abbreviated form (LnSH) is also accepted for powders based on HfO$_2$.

For higher concentration of Ln$_2$O$_3$, the presence of a crystal structure in a sample strongly depends on the type of the rare-earth cation. At a concentration of the dopant impurity $x = 18$ mol. %, the lanthanum compounds remain X-ray amorphous at 600°C, while the gadolinium and yttrium compounds have a fluorite-type structure with similar values of CSL ~ 20 nm. When the molar ratio of the initial oxides becomes Ln$_2$O$_3$ : MO$_2$ = 1 : 2, only yttrium compounds have a weakly crystallized crystalline structure with very broad peaks (CSL ~ 4-5 nm). Other compounds (with concentration of lanthanum and gadolinium oxides $x = 33$ mol. %) remain X-ray amorphous at an annealing temperature of 600°C. Moreover, in the La$_2$O$_3$-MO$_2$ system at $x = 33$ mol. %, the crystallization begins only at temperatures above 800°C.

Thus, the behavior of the crystallization temperature of studied systems can be described by two common tendencies:

1) An increase in the rare-earth cation radius, used as a dopant in the Ln$_2$O$_3$-MO$_2$ compounds, increases the crystallization temperature.

2) An increase in the content of rare-earth oxide in the Ln$_2$O$_3$-MO$_2$ compound raises the crystallization temperature of the sample as well.

These results well agree with the results of analysis of the DSC data for $x$Y$_2$O$_3$·(1-x)ZrO$_2$ ($x = 0.5$ - 18 mol. %), reported in [14].

At annealing temperatures from 800 to 1000°C, in the Ln$_2$O$_3$-MO$_2$ systems a gradual transition between low-temperature phases was observed. It was found that an increase in the fraction of Ln$_2$O$_3$ in the precursor from 3 to 18 mol. % causes a smooth transition from a tetragonal to a fluorite ordering with an intermediate $t''$-structure. In ref. [14] it was also reported that the compound $x$Y$_2$O$_3$·(1-x)ZrO$_2$ crystallizes in the tetragonal phase at a molar content $x = 2$ mol. %, while at $x < 1.5$ mol. % these compounds crystallizes mainly into the pure monoclinic structure (space group $P2_1/c$ (14)). Summing up we can conclude that at relatively low annealing temperatures < 1000°C a series of polymorphic transformations $P2_1/c \rightarrow P4_2/mnc \rightarrow Fm\bar{3}m$ occur in the Ln$_2$O$_3$-MO$_2$ systems with an increase in the Ln$_2$O$_3$ concentration.

A further increase of annealing temperatures ≥ 1000°C causes more complex polymorphic transformations in the Ln$_2$O$_3$-MO$_2$. An example of a such polymorphic behavior in the studied systems is shown in Figure 2 for the $x$La$_2$O$_3$·(1-x)HfO$_2$ compounds. As can be seen from Figure 2, the specific phase composition of a single sample strongly depends both on the annealing temperature and on the molar concentration of the La$_2$O$_3$. Along with the tetragonal and fluorite phases, the presence of both monoclinic and pyrochlore (space group $Fd\bar{3}m$ (227)) phases was observed in the synthesized at high temperatures samples. XRD patterns and Raman spectra for all observed phases located in the $x$La$_2$O$_3$·(1-x)ZrO$_2$ samples have shown in Figure 1. All the experimental curves are given in order of increasing crystal structure symmetry from monoclinic $P2_1/c$ (curve No. 1) to pyrochlore $Fd\bar{3}m$ structure (curve No. 4). It should be noted that maps of the phase composition for La$_2$O$_3$·ZrO$_2$ compounds are quite similar to those shown in Figure 2. The difference between zirconium and hafnium based La$_2$O$_3$-MO$_2$ complex oxides concludes in the ratio of the tetragonal and monoclinic phases at higher concentrations of rare-earth oxide (at $x > 8$ mol. %).

In contrast to the compounds doped with lanthanum oxide, the systems with Gd$_2$O$_3$ and Y$_2$O$_3$ doping do not have such a large variety of polymorphic phases. This is in particular due to the restriction
on the formation of the pyrochlore structure in gadolinium hafnates [15] and zirconates [16], and absence of this possibility in Y2O3-MO2 system. Thus, for systems based on ZrO2, only the tetragonal and fluorite phases were revealed throughout the annealing temperature range from 600 to 1400°C. It should be noted, that in 8Gd2O3•92ZrO2 samples annealed at 1000 and 1200°C, a higher content of the tetragonal phase (20% and 40%, respectively) was observed in comparison with other ZrO2-based samples.

![Figure 2](image_url)  
**Figure 2.** Maps of the phase composition for multiphase compounds xLa2O3•(1-x)HfO2 (x = 3 - 18 mol. %).

On the other hand, in HfO2 based compounds doped by Gd2O3 and Y2O3 the phases with monoclinic and pyrochlore (only in Gd2O3 containing samples) ordering were also observed in addition to the above-mentioned structures (fluorite and tetragonal). Moreover, the pyrochlore Fd-3m structure was detected only in the xGd2O3•(1-x)HfO2 samples calcinated at 1200°C, which once again indicates the peculiarity of this temperature for Gd2O3-MO2 systems.

So, using the obtained results, we can single out several general rules concerning the behavior of the Ln2O3-MO2 systems. First of all, it should be noted that compounds based on hafnium oxide have a greater ability to form a monoclinic phase at high annealing temperatures in comparison with compounds based on zirconium oxide. Differences in the behavior of systems based on HfO2 and ZrO2 can be seen from Figure 3. It is obvious that the curves for the compounds xLn2O3•(1-x)HfO2 are located...
above the corresponding curves for \( x\text{Ln}_2\text{O}_3 \cdot (1-x)\text{ZrO}_2 \) with the same doping of the \( \text{Ln}^{3+} \) ions. In addition, Figure 3 shows another common trend for all \( \text{Ln}_2\text{O}_3 \cdot \text{MO}_2 \) compounds, which consists in a decrease in the monoclinic phase content with an increase in the concentration of the doped ion.

![Figure 3](image1)

**Figure 3.** The content of the monoclinic phase in \( x\text{Ln}_2\text{O}_3 \cdot (1-x)\text{MO}_2 \) powders with calcination temperature 1200°C as a function of the \( \text{Ln}_2\text{O}_3 \) concentration (1 - YSZ, 2 - GdSZ, 3 - YSH, 4 - LaSZ, 5 - LaSH, 6 - GdSH).

Finally, it is necessary to point out on another remarkable phenomenon that occurs when various rare-earth ions are replaced in the \( \text{Ln}_2\text{O}_3 \cdot \text{MO}_2 \) system, while all other conditions are preserved. It consists in the fact that the efficiency of stabilization of high-temperature phases, namely tetragonal and fluorite, increases in \( \text{Ln}_2\text{O}_3 \cdot \text{MO}_2 \) systems as the radius of the \( \text{Ln}^{3+} \) cation decreases. This effect can be demonstrated by comparing the tetragonal phase content in the \( 3\text{Ln}_2\text{O}_3 \cdot 97\text{HfO}_2 \) samples at the same annealing temperature (Figure 4). It is clearly seen that doping with rare-earth ions in accordance with \( \text{La}^{3+} \rightarrow \text{Gd}^{3+} \rightarrow \text{Y}^{3+} \) shifts the curves to higher annealing temperatures and increases the region of existence of the tetragonal phase. The only exception is the sample \( 3\text{Gd}_2\text{O}_3 \cdot 97\text{HfO}_2 \), for which the tetragonal phase content is higher than that for the \( 3\text{Y}_2\text{O}_3 \cdot 97\text{HfO}_2 \) sample. Perhaps, this is due to the peculiarity of the unusual behavior of the \( \text{Gd}_2\text{O}_3 \cdot \text{HfO}_2 \) system in the temperature range of 1000 - 1200°C, which was noted above.

![Figure 4](image2)

**Figure 4.** The content of the tetragonal phase in \( 3\text{Ln}_2\text{O}_3 \cdot 97\text{HfO}_2 \) (1 - \( \text{Ln} = \text{La}, \) 2 - \( \text{Ln} = \text{Gd}, \) 3 - \( \text{Ln} = \text{Y} \)) samples as a function of annealing temperature.

4. Conclusion

Structure and phase composition of the zirconium and hafnium based complex oxides formed in “\( \text{Ln}_2\text{O}_3 \cdot \text{MO}_2 \)” system has been studied using a combination of X-ray powder diffraction and Raman spectroscopy. As a result, it was found that the crystallization temperature of the synthesized powders increases both with an increase in the \( \text{Ln}_2\text{O}_3 \) concentration and an increase in the radius of the \( \text{Ln}^{3+} \) cation. Also, it was revealed that the formation of polymorphic forms in \( x\text{Ln}_2\text{O}_3 \cdot (1-x)\text{MO}_2 \) compounds depends strongly on both the ratio of initial oxides \( \text{Ln}_2\text{O}_3 \) and \( \text{MO}_2 \), and the annealing temperature of precursor. The observed behavior of the \( \text{Ln}_2\text{O}_3 \cdot \text{MO}_2 \) systems can be reduced into two general rules:

1) Efficiency of stabilization of high-temperature phases (tetragonal and cubic) in \( \text{Ln}_2\text{O}_3 \cdot \text{ZrO}_2 \) systems with the introduction of \( \text{Ln}^{3+} \) cations increases in the \( \text{La}^{3+} \rightarrow \text{Gd}^{3+} \rightarrow \text{Y}^{3+} \) series in accordance with the increase in the solubility of \( \text{Ln}_2\text{O}_3 \) in \( \text{ZrO}_2 \). A similar effect is also valid for the \( \text{Ln}_2\text{O}_3 \cdot \text{HfO}_2 \) systems.
2) Compounds based on HfO$_2$ have a greater ability to form a monoclinic phase at high annealing temperatures in comparison with compounds based on ZrO$_2$.

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