The combined study of Dy$_2$O$_3$-HfO$_2$ nanocrystallites formation by means of EXAFS, PDF, XRD and SAXS

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Abstract. The process of double oxide Dy$_2$O$_3$-HfO$_2$ nanocrystallites formation upon annealing to 1600$^\circ$C was investigated with the combination of few X-ray and synchrotron methods. XRD and PDF show the mean crystal structure to be fluorite typical for the compounds of Ln$_2$O$_3$-MeO$_2$ type. The ordering of structure and the growth of nanocrystallites upon annealing was estimated independently from XRD patterns, PDF functions and SAXS scattering curves. Neither transition to pyrochlore phase, nor signs of recently shown in related Gd$_2$O$_3$-HfO$_2$ compounds pyrochlore-type superstructure is observed. However, EXAFS and the short range order of PDF clearly indicate the discrepancy between Dy and Hf local environment. Such a disorder of local crystal structure can not be described by the fluorite model.

1. Introduction
The binary compounds Ln$_{2+x}$Me$_{2-x}$O$_7$-$x$/2 forming in the two-component Ln$_2$O$_3$-MeO$_2$ systems (Ln - rare-earth cation, Me - IVB subgroup cation: Ti, Zr, Hf) are attractive from the both scientific (fluorite-pyrochlore phase transition [1, 2, 3]; spin-glass, spin-ice and spin-fluid behavior [4, 5]) and practical point of view (thermal barrier coatings [6], neutron-absorbing materials [7], oxygen-ionic conductors [3], nuclear waste forms [8]). Regarding the the cation ordering the most interesting are compounds with the ionic radii ratio $R_{\text{Ln}^{3+}}/R_{\text{Me}^{4+}} \sim 1.45$ in which the fluorite ($Fm\bar{3}m$ space group) and pyrochlore ($Fd\bar{3}m$ space group) crystal structures might coexist at room temperature according to the thermodynamic estimation [2, 9].

Previously we reported on the pyrochlore-type superstructure with the doubled lattice parameter compared to fluorite observed in the nanocrystalline powders Gd$_2$Hf$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$ synthesized at 1200$^\circ$C/6 h [10, 11]. The pyrochlore structure was assumed theoretically in Dy$_2$O$_3$-HfO$_2$ [2], and the probable formation of defect pyrochlore structure was experimentally shown in Dy$_2$Hf$_2$O$_7$ [12]. Besides, the modulated pyrochlore-like structure is possible in Dy$_3$HfO$_5$ powders prepared at 1600$^\circ$C/3 h [10]. Therefore, the aim of present work was the detailed investigation of binary nanocrystalline compounds formation in the Dy$_2$O$_3$-HfO$_2$ system with molar component ratio 1 : 1 by the combination of modern experimental techniques using the X-ray and synchrotron radiation.

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2. Experimental

The Dy₂O₃-HfO₂ samples were prepared by coprecipitation from a solution of Dy(NO₃)₃ and HfOCl₂ salts and annealing of the resulting mixed hydroxides (precursors) in the 400 – 1600°C/3 h temperature range as reported in [10, 11]. The powder XRD patterns were measured at "DRON-UN1" diffractometer using the CuKα radiation, 0.05° step and 10 s exposure, and processed by Rietveld method.

The powder XRD patterns for the pair distribution function (PDF) study were collected at BW5 beamline of DORIS-III positron storage ring (DESY, Hamburg, Germany) in transmission geometry using the photon energy of 100 keV (λ = 0.1239 Å). The full structure factors and pair distribution functions were calculated from experimental XRD patterns with PDFgetX2 [13]. PDFgui [14] was used to fit the experimental data. The X-ray absorption spectra were measured at C beamline of DORIS-III in transmission geometry above the L₃-Dy (7790 eV) and L₃-Hf (9561 eV) absorption edges at temperature ~ 110 K. The extraction and fitting of EXAFS-functions χ(κ) was performed using VIPER software pack [15]. Amplitudes and phases of photoelectron back scattering were calculated with FEFF code [16] using the parameters of fluorite structure and diffraction data.

The anomalous XRD measurements were performed at STM beamline of Kurchatov synchrotron radiation source (Moscow, Russia) in transmission geometry using the imaging plate detector. The two wavelengths were used: λ₁ = 1.3183 Å (E₁ = 9405 eV) and λ₂ = 1.2976 Å (E₂ = 9555 eV), the latter is close to the L₃-Hf (9561 eV) absorption edge. The SAXS curves were measured also at STM beamline using the X-ray photons of wavelength λ = 1.033 Å.

Figure 1. The powder XRD patterns of Dy₂HfO₅ samples prepared by isothermal annealing of precursor at different temperatures

Figure 2. The effect of annealing temperature on the size of nanocrystalline particles

Figure 3. The SAXS curves of Dy₂HfO₅ samples annealed at different temperatures
3. Results and discussion

The powder X-ray diffraction study shows that the composition of amorphous precursor is Dy$_2$O$_3$-HfO$_2$: (200 – 250)H$_2$O. However, the presence of two broad maxima in XRD patterns at 20 $\sim$ 30 – 31$^\circ$ and 20 $\sim$ 50 – 52$^\circ$ as well as two ”metal-oxygen” and ”metal-metal” coordination shell contributions in EXAFS spectra indicate the crystal structure of precursor particles not to be completely disordered and tend to form the fluorite structure. Upon isothermal annealing at the temperatures up to 600$^\circ$ the samples preserve the amorphous structure (fig.1), but the degree of order increases and partially crystallized clusters of $\sim$ 2 nm size with the fluorite-like structure are observed in samples annealed at 400 – 600$^\circ$ [10]. The most significant increase of the coherent-scattering region is observed in the 800 – 1400$^\circ$ annealing temperature range (fig.2). All XRD patterns are described quite well with the fluorite structure model as shown by Rietveld refinement.

The more precise values of nanocrystallite size vs. different heat treatment were estimated from the small angle scattering curves (fig.3). Depending on the annealing temperature the three types of scattering curves are observed (fig.3). In the low-temperature region 400 – 600$^\circ$C the dominating size of scattering centers is clearly visible as the bending of the curves, which is related to the switching from one asymptotic scattering mode (the Porod mode, the slope about -4 in double logarithmic scale) to another (the Guinier mode, the almost horizontal plateau). The position of bending correlates with the dominating size of particles. The SAXS curves shape in the region of small scattering vectors $s < 0.03$ Å$^{-1}$ indicates the formation of aggregates confirmed by additional LTNA study of surface areas. In the transition region 600 – 1200$^\circ$C the curves shape undergoes the maximum change, which corresponds to the transfer from the nanocrystalline to well crystalline state. In the high-temperature region $\geq$ 1200$^\circ$C the SAXS curves are almost identical for all the samples. The linear shape of curves (the Porod mode) corresponds to scattering on the large centers with the size much bigger than 50 nm. The sizes of SAXS scattering centers are in quite good agreement with the XRD coherent-scattering regions for the samples annealed at relatively low temperature $\leq$ 1000$^\circ$C (fig.2).

Atomic pair distribution functions (PDF) $G(r)$ study demonstrates the formation of cubic fluorite structure upon annealing of amorphous precursor. Fig.4 shows the gradual formation of clear $G(r)$ maxima corresponding to separate coordination shells in the local environment of atoms. Besides, the annealing temperature increase causes the rise of structure order resulting in increase of the interatomic distances range, in which the pair correlation function $G(r)$ maxima are still distinguishable (fig.4). For the low annealing temperature samples ($\leq$ 800$^\circ$C) the

**Figure 4.** The full pair distribution functions $G(R)$ of Dy$_2$HfO$_5$ samples annealed at different temperatures

**Figure 5.** The comparison of experimental and model PDF for the sample annealed at 1600°C
obtained particle sizes are in qualitative correlation with the XRD coherent-scattered regions and the grain sizes estimated by SAXS. In case of higher annealing temperature \( > 1000^\circ \text{C} \) the error of crystalline size estimation by PDF increases, which might also be due to a lack of angular resolution of imaging plate detector [17]. While, at low annealing temperature the accuracy of PDF in estimating the particle size is quite high (fig.2).

The pair distribution function \( G(r) \) of sample annealed at \( 1600^\circ \text{C} \) was fitted with theoretical PDF based on the model of \( \text{HfO}_2 \) oxide fluorite structure (fig.5). As result, the lattice parameter \( (a = 5.248 \text{Å}) \) and the anisotropic displacement parameters \( (U_\text{ii}(\text{Hf})=0.0291 \text{Å}^2 \) and \( U_\text{ii}(\text{O})=0.1227^2) \) were refined. The fig.5 shows that the fluorite model describes well the long-range order of crystal structure but doesn’t adequately describe the local structure up to 8 Å because doesn’t take into account the presence of two different scattering centers Dy and Hf.

The study of EXAFS spectra revealed the significant difference of Dy and Hf local environments for the whole temperature series of \( \text{Dy}_2\text{HfO}_5 \) samples, e.g. the discrepancy between the first coordination shell radii or interatomic Dy-O and Hf-O distances exceeds 0.2 Å. The significant variation is obtained for the second bunch of interatomic ”metal-metal” distances also. It means that Dy\(^{3+} \) and Hf\(^{4+} \) cations with the different ionic radii distort the local environment in different way while formally remaining in the similar crystallographic position of the fluorite structure. Upon the annealing temperature increase the first maximum of EXAFS spectra corresponding to the coordination shell with 8 oxygen atoms shifts slightly to smaller interatomic distances, while its intensity decreases (fig.6). At the same time the second maximum appears, which corresponds to the coordination shells with 12 atoms of Dy and Hf.

The combined EXAFS and PDF study demonstrates that upon the annealing temperature increase to \( 1600^\circ \text{C} \) the processes of ordering and Dy/Hf local environment differentiation come to saturation. The detailed investigation of PDF variation vs. annealing temperature confirms the discrepancy between Dy-O / Hf-O and Dy-Dy / Dy-Hf / Hf-Hf local interatomic distances revealed by EXAFS. The first two peaks of \( G(r) \) function which correspond to first two coordination shells around metal ion have a very asymmetrical shape, and the positions of different contributions to these peaks coincide with the interatomic distances determined from EXAFS spectra (fig.7). Thus, the data independently obtained from EXAFS and PDF are in good agreement with each other and point out the difference of the samples local crystal structure from the fluorite.

There is some inconsistency between the results of local sensitive EXAFS and PDF methods and XRD results, which point out the fluorite-type structure without any ordering of Dy and
Hf cation positions. Note that Dy and Hf atoms are hardly distinguishable by the conventional XRD due to a small difference in their atomic scattering factors. For more detailed study of long-range order role in the local distortions of fluorite structure reflected in the discrepancy between Dy and Hf local environments, the measurements of anomalous synchrotron radiation diffraction were performed, which allow to enhance the contrast between the scattering power of atoms. The results indicate that even for well crystallized Dy$_2$HfO$_5$ sample ($1600^\circ$C/3h) the resonant diffraction pattern is absent from the superstructure reflexes corresponding to pyrochlore-type unit cell with of the doubled spacing comparing to the fluorite unit cell. Such a sharp rise of superstructure reflexes (in particular with 331 index of pyrochlore unit cell) was shown in our recent study of related Gd$_2$Hf$_2$O$_7$ samples annealed at $1200^\circ$C/6 h [10, 11].

4. Conclusion
The evolution of Dy$_2$O$_3$-HfO$_2$ (1 : 1) crystal structure parameters upon the isothermal annealing of initial mixed amorphous hydroxide was studied by the complex of synchrotron methods. In the low annealing temperature region (400–600°C) the gradual ordering of precursor amorphous structure occurs and the nanoclusters of <2 nm size form. The transition region (600 – 1200°C) corresponds to the maximum change of atomic and crystal structure parameters, such as XRD coherent scattering region, interatomic distances etc. In the high annealing temperature region ($\geq 1200^\circ$C) the crystallization of samples saturates and only the insignificant changes of atomic and crystal structure parameters are observed. The resulting nanocrystalline oxide compounds have the fluorite-type crystal structure with the pronounced discrepancy between Dy and Hf local environments, but without the superstructural ordering of cation positions.

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