The Gd$_2$O$_3$-HfO$_2$ and Gd$_2$O$_3$-ZrO$_2$ systems can exist in either pyrochlore (Fd$_3$m) or fluorite (Fm$_3$m) crystalline structure depending on the conditions of preparation [1,2]. Their possible application is quite important - Gd$_2$O$_3$-HfO$_2$ is a prospective neutron absorbing material [1] with high absorption cross section. Gd$_2$O$_3$-ZrO$_2$ system has the highest intrinsic ionic conductivity ($\sim 10^{-2}$ S/cm at 1000 K) of any pyrochlore compounds [3,4] comparable to that of yttrium-stabilized zirconium — the electrolyte most commonly investigated as solid-oxide fuel cells. Comparison of electrical properties for these related materials is also important [4]. These compounds non-stoichiometry can play a great role and influence the ionic conductivity [4]. Diminishing the crystalline size below 100 nm could cause dramatic changes in physical-chemical properties for such compounds [5].

We present the study of local structure peculiarities in nanocrystalline powders of Gd$_2$Hf$_2$O$_7$ and Gd$_2$ZrO$_5$ prepared at different temperatures.

Gd$_2$Hf$_2$O$_7$ nanopowders were prepared by co-precipitation method. Starting materials Gd(NO$_3$)$_3$ and HfOCl$_2$ with molar ratio Gd$_2$O$_3$:HfO$_2$=1:2 were mixed with an ammonia solution (pH 10). The precipitates of mixed Gd and Hf hydroxides were washed, dried and then annealed at different temperatures (700, 800, 900, 1000 and 1200 °C) during 3 hours. The size of crystallites obtained was found 6, 7, 10, 15 and 50 nm according to the annealing temperatures. The same method was used to obtain the powders of Gd$_2$ZrO$_5$ with molar ratio Gd$_2$O$_3$:ZrO$_2$=1:1. The size of crystallites was 5, 10 and 50 nm for 800, 1000 and 1200 °C correspondingly.

XRD spectra of obtained powders were recorded on DRON-UM 1 diffractometer using CuK$_\alpha$ radiation. Information about phase composition and atomic microstructure from XRD data was obtained by Rietveld method [6] using FullProf (WinPlotr) [7] calculation program. $\chi_{\text{LIII}}$-Gd and $\chi_{\text{LIII}}$-Hf EXAFS spectra were measured at E4 station of HASYLAB synchrotron center (DESY,

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**Fig. 1:** Gd$_3$Hf$_2$O$_7$ $\chi_{\text{LIII}}$-Gd EXAFS Fourier transform module

**Fig. 2:** Gd$_3$Hf$_2$O$_7$ $\chi_{\text{LIII}}$-Hf EXAFS Fourier transform module
Hamburg) at 10 and 300 K. VIPER software [8] was used for EXAFS spectra processing and modeling. Backscattering amplitudes and phases were calculated using FEFF 8 [9].

Figures 1-2 show Fourier transform module of EXAFS-function $\chi(k)$ weighted by $k^2$ for $L_{III}$-Gd and $L_{III}$-Hf absorption edges in Gd$_2$Hf$_2$O$_7$ at 10 K. Evolution of the samples local structure is clearly seen as an increase in the gadolinium local environment ordering in 2.5-4.0 Å region. At the same time, the Fourier peak corresponding to the first coordination sphere containing 8 oxygen atoms weakens (it is clearly seen for the sample with 50 nm particles), that may on the one hand evidence the weakening of interatomic interaction or on the other hand the decrease in number of neighbouring atoms. Hafnium local environment undergoes similar changes to a lesser extent, keeping the disordered structure. Only for the 50 nm particles sample we can suppose some second coordination sphere ordering. Comparative modeling give preference to the fluorite structure, however considerable difference between Gd and Hf environment indicate the presence of some higher complicated structure. We could not reveal pyrochlore structure for annealing temperatures of 1200 ºC and lower.

Figure 3 shows Fourier transform module of EXAFS-function $\chi(k)$ weighted by $k^2$ for $L_{III}$-Gd absorption edge of Gd$_2$ZrO$_5$ at 10 K. Evolution of the samples local structure with crystallites size is characterized by a noticeable ordering in the second coordination sphere of Gd local environment (2.5-4.5 Å). The magnitude of the first coordination sphere decreases with the crystallites growth evidencing the redistribution of oxygen atoms through the sample. Modeling determines the pyrochlore structure for the sample annealed at 1200 ºC and fluorite structure for the lower temperatures thus confirming that non-stoichiometry of the compound could promote the forming of pyrochlore structure [4].

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References