	Experiment title: Fully reversible phase transition "order-disorder-order" in complex oxides of rare-earth elements	Experiment number: HC-3613
Beamline: BM25A	Date of experiment: From: 13-06-2018 to 19-06-2018	Date of Report: 02.07.2018
Shifts: 16	Local contact: German Rafael Castro	
Names and affiliations of applicants (*indicates experimentalists) Alexey Menushenkov* – NRNU MEPhI (apmenushenkov@mephi.ru) Andrei Ivanov – NRNU MEPhI* Victor Popov – NRNU MEPhI* Bulat Gaynanov - NRNU MEPhI* Alexey Yastrebsev – NRNU MEPhI*		

Report:

1. Introduction

Complex oxides with general formula $A_2^{(3+)}B_2^{(4+)}O_7$ (A = lanthanide (Ln); B = Ti, Zr, Hf) are unique systems for investigation of the order-disorder phase transitions. Earlier we have shown that the hafnates $Ln_2Hf_2O_7$ (Ln = La-Dy) [1] and zirconates $Ln_2Zr_2O_7$ (Ln = La-Dy) [2] undergo “fluorite (disorder) → pyrochlore (order)” phase transition depending on the calcination temperature of initially amorphous precursor and cation radii ratio $\gamma = r_{A(3+)}/r_{B(4+)}$. It was shown that the ratio (γ) is one of the main factors that determine the resulting crystal structure type. During the ESRF project HC-3039 in 2017 we had shown that in the titanates $Ln_2Ti_2O_7$ (Ln = Gd, Tb, Dy) the crystallization of amorphous precursors leads to direct formation of the pyrochlore (Py) (sp.g. $Fd-3m$) structure and the fluorite (Fl) phase (sp.g. $Fm-3m$) does not appear in contrast to the Ln hafnates and zirconates. The splitting of the first oxygen sphere $Ln-O$ in titanates is a clear indicator of a pyrochlore ordered structure [3].

Nowadays there are two fundamentally different approaches to the synthesis of Ln complex oxides with different chemical and phase composition. The first, which is more often used, is the solid-state synthesis by calcinations of the mixture of individual oxides at elevated temperatures. It is impossible to analyse the formation of the crystalline structure. The second method is synthesis from the liquid phase. This bottom-up synthesis strategy of is appropriate for studying formation of crystalline phases and possible polymorphic transformations during the process of synthesis [1-3].

The aim of this work (ESRF project HC 3613) was to study completely reversible phase transition “order-disorder-order” by investigation of the formation and evolution of crystal and local structure in a series of complex oxides $(Yb_xPr_{1-x})_2(TiyZr_{1-y})_2O_7$ ($0 < x < 1$, $0 < y < 1$) by using EXAFS and XANES measurements according to the scheme in Fig. 1.

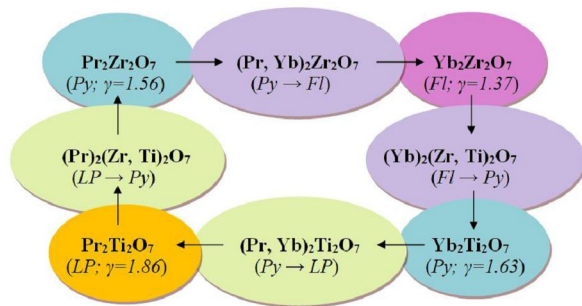


Fig. 1. The scheme of fully reversible phase transition "order-disorder-order" in complex oxides $(Yb_xPr_{1-x})_2(TiyZr_{1-y})_2O_7$.

2. Experiment

EXAFS- and XANES- spectra were measured at series of $(Yb_xPr_{1-x})_2(TiyZr_{1-y})_2O_7$ powders with different crystal sizes and structures which were prepared by calcination of initially amorphous precursors at various temperatures. All samples were previously characterized by XRD and Raman spectroscopy. The measurements were carry out above the Zr K - (17997.6 eV), Yb L_3 - (8943.6 eV) in transmission mode and Pr L_3 -edge (5964.3 eV) in fluorescence mode at room temperature at beamline BM25A (SpLine). EXAFS-spectra were collected up to 15 \AA^{-1} in momentum space for Zr K -edge and for Yb L_3 - edge and up to 10.5 \AA^{-1} for Pr L_3 -edge. The high signal/noise ratio allows us to conduct the analysis of the absorbing atoms local environment up to 6 \AA in real space.

3. Results

From our previous measurements [1-3] we observed that splitting of the first Ln -O shell in the FT modulus of $Ln L_3$ -edge EXAFS spectra appears to be the reliable indicator of the ordered pyrochlore structure formation, while the changes in the pre-edge region of the K -Ti XANES spectra reflect the process of the $Ln_2Ti_2O_7$ electronic structure formation.

Our local structure XANES and EXAFS analysis of $(Yb_xPr_{1-x})_2(TiyZr_{1-y})_2O_7$ powders allowed us to make the following conclusions:

1. An increase the calcination temperature leading to the initiation of crystallization processes at 600 - 700°C and a further "fluorite-pyrochlore" phase transition in mixed zirconates at 1100 - 1300°C (Fig. 2a) leads to a decrease in the peak B_1 amplitude and an increase in the amplitude of the B_2 peak, which can be due to a change in the coordination type of Zr atoms. In the case of the formation of the pyrochlore structure, the rate of change in the ratio B_2/B_1 as a function of temperature is higher than the similar changes in the formation of the fluorite phase (Fig. 2).

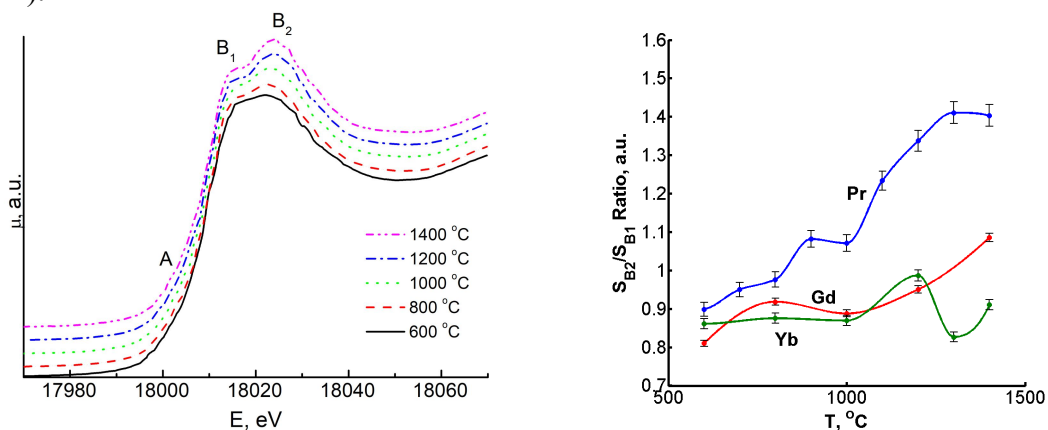


Fig. 2. Zr K -edge XANES spectra of $Gd_2Zr_2O_7$ (a) and B_2/B_1 ratio (b) of Ln zirconates powders calcined to different temperatures

2) XANES analysis has revealed that the shape of $Ln L_3$ -edge is good indicator of crystallization and ordering of pyrochlore phase (Fig. 3a) for compounds with high γ value which brings to perfect pyrochlore structure (such as $Yb_2Ti_2O_7$ $\gamma = 1.63$). XANES spectra for fluorite and layered perovskite (LP) (sp.g. $P2_1$) compounds demonstrate only minor difference (Fig. 3b).

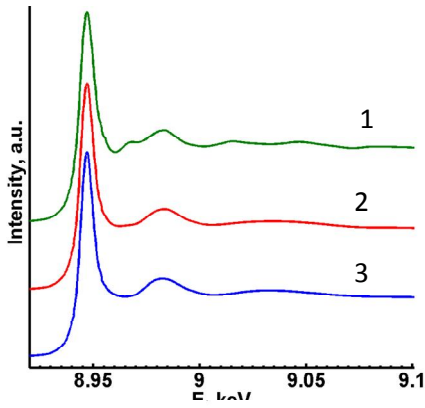


Fig. 3a. Yb L_3 -edge XANES spectra of $\text{Yb}_2\text{Ti}_2\text{O}_7$ powders calcined to different temperatures: 1 – 1400°C (Py); 2 – 750°C (Py+amor); 3 – 600°C (amor).

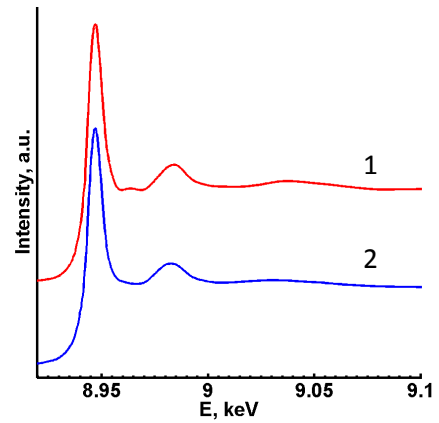


Fig. 3b. Yb L_3 -edge XANES spectra of $\text{Yb}_2\text{Zr}_2\text{O}_7$ (Fl) (a) and $(\text{Yb}_{0.2}\text{Pr}_{0.8})_2\text{Ti}_2\text{O}_7$ (LP) (b) powders calcined at 1400°C.

At the same time, for Ln mixed titanates $(\text{Yb}_x\text{Pr}_{1-x})_2\text{Ti}_2\text{O}_7$ ($\gamma > 1.63$; $x = 0.2$; 0.4; 0.6) XANES analysis also very sensitive to the phase transition “pyrochlore \rightarrow layered perovskite” (Fig. 4a). However for Ln mixed zirconates $(\text{Yb}_x\text{Pr}_{1-x})_2\text{Zr}_2\text{O}_7$ ($\gamma < 1.56$; $x = 0.25$; 0.5; 0.75) XANES analysis give weak information about the phase transition “pyrochlore \rightarrow fluorite” (Fig. 4b).

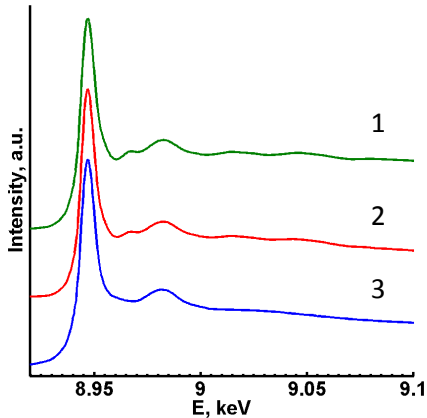


Fig. 4a. Yb L_3 -edge XANES spectra of $(\text{Yb}_x\text{Pr}_{1-x})_2\text{Ti}_2\text{O}_7$ powders calcined at 1400°C with different x : 1 – 0.6 (Py); 2 – 0.4 (Py+LP) 3 – 0.2 (LP).

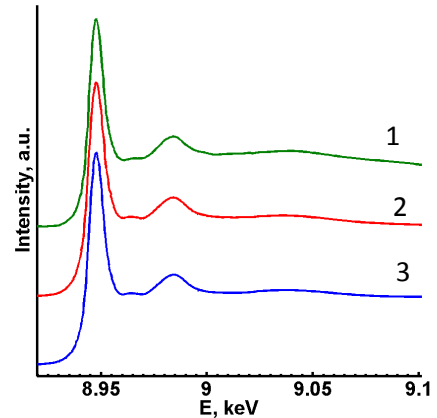


Fig. 4b. Yb L_3 -edge XANES spectra of $(\text{Yb}_x\text{Pr}_{1-x})_2\text{Zr}_2\text{O}_7$ powders calcined at 1400°C with different x : 1 – 0.75 (Py); 2 – 0.5 (Py+Fl) 3 – 0.25 (Fl).

3) It was observed that the shape of the FT-EXAFS- spectra at the Ln L_3 -edge undergoes significant changes both upon the “amorphous \rightarrow crystalline” phase transition and upon the further evolution of the pyrochlore structure.

We have found several typical cases of FT-EXAFS spectra evolution for $(\text{Yb}_x\text{Pr}_{1-x})_2(\text{Ti}_y\text{Zr}_{1-y})_2\text{O}_7$ with different γ values, providing pyrochlore ordering, namely:

a) 1.46 $(\text{Yb}_2(\text{Ti}_{0.4}\text{Zr}_{0.6})_2\text{O}_7 \leq \gamma \leq 1.51$ $(\text{Yb}_2(\text{Ti}_{0.6}\text{Zr}_{0.4})_2\text{O}_7$ there is no observable splitting of the first (metal-oxygen) coordination Ln -O (Fig. 5a).

b) 1.51 $(\text{Yb}_2(\text{Ti}_{0.6}\text{Zr}_{0.4})_2\text{O}_7 \leq \gamma \leq 1.56$ $(\text{Pr}_2\text{Zr}_2\text{O}_7)$ – the first (metal-oxygen) coordination shell (CS) splits into 2 components corresponding to 2 shorter Ln -O(2) and 6 longer Ln -O(1) bonds. The pikes are not clearly separated though (Fig. 5b).

c) 1.56 $(\text{Pr}_2\text{Zr}_2\text{O}_7) \leq \gamma \leq 1.63$ $(\text{Yb}_2\text{Ti}_2\text{O}_7)$ there is evident splitting of the first (metal-oxygen) coordination shell (CS) into 2 components (Fig. 5c).

d) In the composition range $1.65 (\text{Pr}_2(\text{Ti}_{0.3}\text{Zr}_{0.7})_2\text{O}_7) \leq \gamma \leq 1.77 (\text{Yb}_{0.4}\text{Pr}_{0.6})_2\text{Ti}_2\text{O}_7$ the first (metal-oxygen) coordination shell splits into more than 2 components, which corresponds to monoclinic layered perovskite structure (Fig. 5d).

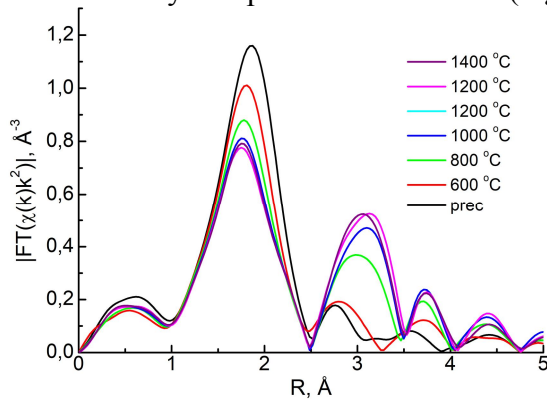


Fig. 5a. Yb L_3 -edge FT-EXAFS of $\text{Yb}_2(\text{Zr}_{0.4}\text{Ti}_{0.6})_2\text{O}_7$ ($\gamma=1.51$) powders calcined to different temperatures.

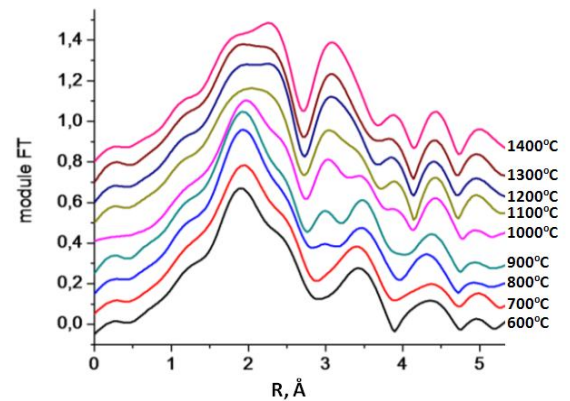


Fig. 5b. Pr L_3 -edge FT-EXAFS of $\text{Pr}_2\text{Zr}_2\text{O}_7$ ($\gamma=1.56$) powders calcined to different temperatures.

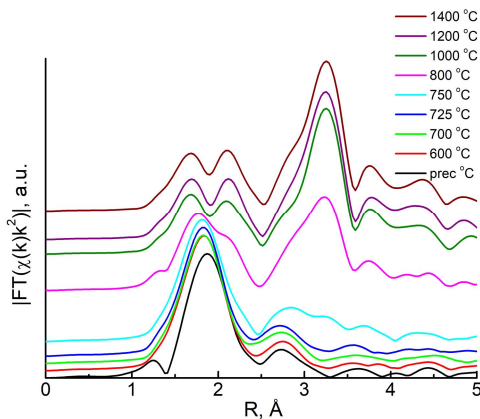


Fig. 5c. Yb L_3 -edge FT-EXAFS of $\text{Yb}_2\text{Ti}_2\text{O}_7$ ($\gamma=1.63$) powders calcined to different temperatures.

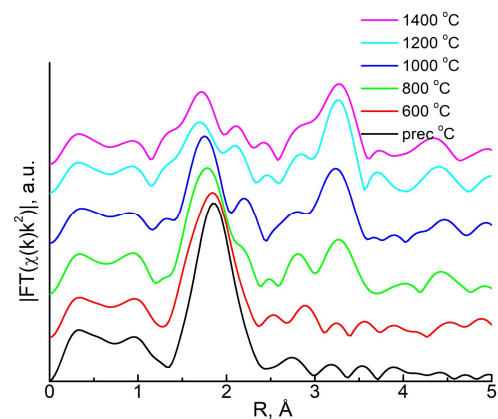


Fig. 5d. Yb L_3 -edge FT-EXAFS of $(\text{Yb}_{0.4}\text{Pr}_{0.6})_2\text{Ti}_2\text{O}_7$ ($\gamma=1.77$) powders calcined to different temperatures.

Conclusion:

Thus we firstly investigated the local structure peculiarities during the fully reversible phase transition “order-disorder-order” in complex oxides $(\text{Yb}_x\text{Pr}_{1-x})_2(\text{Ti}_y\text{Zr}_{1-y})_2\text{O}_7$ ($0 < x < 1$, $0 < y < 1$) by using XANES and EXAFS analysis. The new effective indicators of the formation and evolution the pyrochlore phase were established. Namely the XANES analysis of Zr K -edge, L_n L_3 -edge and EXAFS analysis of L_n L_3 -edge. The boundary between perfect pyrochlore and begging some disorder in pyrochlore structure (to defect fluorite) is near to $\gamma \sim 1.46$ -1.51. The boundary between perfect pyrochlore and beginning formation of layered perovskite structure is near to $\gamma \sim 1.70$. The paper for J. of Alloys and Compounds is in preparing.

References

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- [2] V.V. Popov, A.P. Menushenkov, B.R. Gaynanov et al. J. Phys.: Conf. Ser. 941, (2017) 012079.
- [3] V.V. Popov, A.P. Menushenkov, B.R. Gaynanov et al. J Alloys Compd. 746 (2018) 377-390.