	<b>Experiment title:</b>  XAFS studies of fluorite-pyrochlore phase transition in nano-structured $\text{Ln}_2\text{M}_2\text{O}_7$ (Ln = Gd, Tb, Dy; M = Ti, Zr)	<b>Experiment number:</b>  HC-3039
<b>Beamline:</b>  BM08	<b>Date of experiment:</b>  From: 21-06-2017 to 25-06-2017	<b>Date of Report:</b>  20.07.2017
<b>Shifts:</b>  12	<b>Local contact:</b>  Francesco D'Acapito, Alessandro Puri	
<b>Names and affiliations of applicants (*indicates experimentalists)</b> Alexey Menushenkov* – NRNU MEPhI (apmenushenkov@mephi.ru) Andrei Ivanov – NRNU MEPhI* Victor Popov – NRNU MEPhI* Bulat Gaynanov - NRNU MEPhI*		

## Report:

### 1. Introduction

Complex oxides of  $\text{Ln}_2\text{O}_3\text{-MO}_2$  system (Ln is a lanthanide and M is a titanium subgroup element) have been intensely investigated over recent years because they demonstrate a variety of fascinating physical effects, such as order-disorder phase transitions, geometrically frustrated magnetism, etc. In addition, these materials have wide technological applications, which include thermal barrier coatings, solid oxide fuel cells, photocatalysis, neutron absorbing and nuclear waste storage materials. The phase diagrams of the  $\text{Ln}_2\text{O}_3\text{-MO}_2$  systems are quite complicated. One of the main factors that determine the resulting crystal structure is the ratio of the cation radii  $\text{Ln}^{3+}/\text{M}^{4+}$  ( $\gamma$ ). Recently we have shown that for  $\text{Ln}_2\text{M}_2\text{O}_7$  (Ln = Gd, Tb, Dy; M = Zr, Hf) compounds the pyrochlore-fluorite phase transition takes place at the ratio  $\gamma \sim 1.46$  [1]. Since the  $\text{Ti}^{4+}$  radius is noticeably smaller than  $\text{Zr}^{4+}$  (or  $\text{Hf}^{4+}$ ), the  $\text{Ln}_2\text{Ti}_2\text{O}_7$  (Ln = Gd, Tb, Dy) compounds with  $\gamma = 1.74$ ; 1.72 and 1.70, respectively, are expected to have the most perfect pyrochlore structure.

The structure of the  $\text{Ln}_2\text{M}_2\text{O}_7$  complex oxides is strongly affected by the crystallite size, which can also be changed by varying the synthesis conditions. When this size is relatively small (less than 3-5 nm), the local crystal structure differs from the average one, although the latter often determines important properties of compounds such as thermal stability, electrophysical and optical properties, catalytic activity, etc [2]. We use specially developed procedure of two-step chemical synthesis including preparation of the amorphous precursors (mixed hydroxides Ln-M) by coprecipitation and subsequent calcination of the precursors at different temperatures from 600 to 1400°C which allows us to prepare almost single-phase complex oxides of different crystal sizes (from few nm to few hundred nm) and structure types (amorphous, fluorite, pyrochlore) [3].

The aim of this project was to investigate the formation and evolution of crystal and local structure of Ln titanates and compare the results with those obtained for Ln zirconates.

## 2. Experiment

EXAFS- and XANES- spectra were measured for the series of  $\text{Ln}_2\text{M}_2\text{O}_7$  ( $\text{Ln} = \text{Gd, Tb, Dy}$ ;  $\text{M} = \text{Ti, Zr}$ ) powders with different crystal sizes and structures which were previously characterized by XRD and Raman spectroscopy. The measurements were carried out above the  $K\text{-Ti}$  (4966 eV),  $K\text{-Zr}$  (17998 eV) and  $L_3\text{-Gd}$  (7243 eV),  $L_3\text{-Tb}$  (7514 eV),  $L_3\text{-Dy}$  (7790 eV) edges in transmission mode at room temperature at beamline BM08 (LISA). Samples  $\text{Gd}_2\text{Ti}_2\text{O}_7$ ,  $\text{Tb}_2\text{Ti}_2\text{O}_7$ ,  $\text{Dy}_2\text{Ti}_2\text{O}_7$ ,  $\text{Gd}_2\text{Zr}_2\text{O}_7$  and  $\text{Dy}_2\text{Zr}_2\text{O}_7$ , annealed at 1200°C, were also measured at temperature range from 10K to 250K. EXAFS-spectra were collected up to 16-18  $\text{\AA}^{-1}$  in momentum space for  $K\text{-Ti}$  and  $K\text{-Zr}$  edges, while for  $L_3\text{-Ln}$  ( $\text{Ln} = \text{Gd, Tb, Dy}$ ) the length of spectra was limited by  $L_2\text{-Ln}$  edges. The high signal/noise ratio allows us to conduct the analysis of the absorbing atoms local environment up to 6  $\text{\AA}$  in real space. From the Debye-Waller factor temperature dependence we have determined the Einstein temperatures which characterize the stiffness of interatomic bonds in the nearest environment of absorbing atoms.

One of the important parts of our investigations was to compare the stiffness of  $\text{Ti-O}$ ,  $\text{Ln-O}$ ,  $\text{Ti-Ti(Ln)}$  and  $\text{Ln-Ln(Ti)}$  interatomic bonds in  $\text{Ln}$  titanates. It is important because  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{Gd, Tb, Dy}$ ) have the same crystal structure but quite different magnetic structures: long-range ordered ( $\text{Gd}_2\text{Ti}_2\text{O}_7$ ), spin-liquid ( $\text{Tb}_2\text{Ti}_2\text{O}_7$ ) and spin-ice ( $\text{Dy}_2\text{Ti}_2\text{O}_7$ ).

## 3. Results

Using XRD and Raman spectroscopy, we have found that in the case of titanates  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{Gd, Tb, Dy}$ ) due to the small radius of the  $\text{Ti}^{4+}$  cation the crystallization of amorphous precursors leads directly to the formation of a pyrochlore structure, in contrast to the zirconates  $\text{Ln}_2\text{Zr}_2\text{O}_7$  ( $\text{Ln} = \text{Gd, Tb, Dy}$ ), in which a fluorite structure is observed in the initial stage of crystallization.

Our analysis of the local structure of titanates by EXAFS spectroscopy allowed us to draw the following conclusions:

1) EXAFS-FT spectra at the  $\text{Ti } K\text{-edge}$  in titanates  $\text{Ln}_2\text{Ti}_2\text{O}_7$  ( $\text{Ln} = \text{Gd, Tb, Dy}$ ) point to the formation of the second (metallic) coordination shell upon transition from amorphous state to pyrochlore phase (see Fig. 1 (a) for different annealing temperatures).

2) EXAFS-FT spectra at the  $L_3\text{-Ln}$  show the splitting of the first  $\text{Ln-O}$  coordination shell onto two oxygen shells upon transition from amorphous state to pyrochlore phase. It is worth noticing that the splitting value increases along with the pyrochlore phase formation as the annealing temperature increases from 750 to 1200 °C.

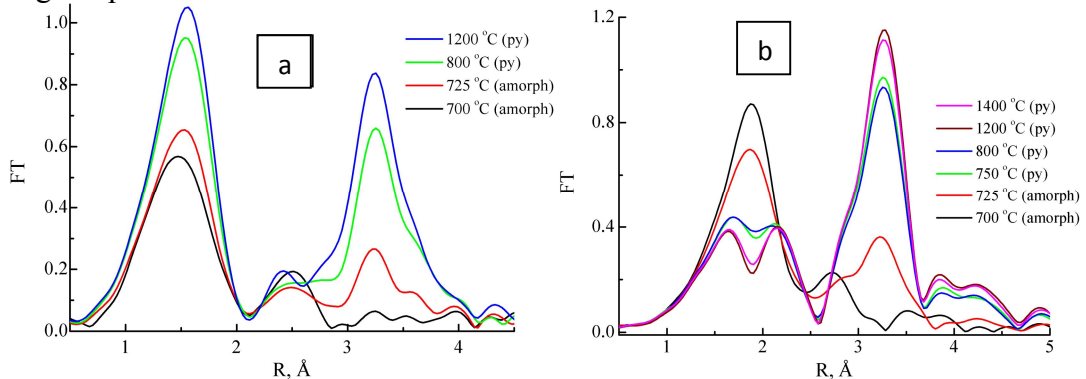


Fig. 1. EXAFS-FT spectra above  $K\text{-Ti}$  (a) и  $L_3\text{-Dy}$  (b) for  $\text{Dy}_2\text{Ti}_2\text{O}_7$ , synthesized at different annealing temperatures. The spectra were measured at room temperature.

3) We firstly observed that the formation of the titanium environment (titanium sublattice) takes place already at the initial stage (annealing temperature 725 °C) of the transition from the amorphous state to pyrochlore phase, while the  $\text{Ln}$  sublattice forms afterwards.

Thus the splitting observed in EXAFS-FT spectra at  $\text{Ln } L_3\text{-edge}$  splitting may be used as an effective indicator of the pyrochlore phase formation in  $\text{Ln}$  titanates.

4) Comparison of titanates with different types of  $\text{Ln}$  cations has shown that  $\text{Tb}_2\text{Ti}_2\text{O}_7$  and  $\text{Dy}_2\text{Ti}_2\text{O}_7$  are characterized by a larger amplitude of peaks on EXAFS-FT spectra compared to

Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (see Fig. 2), which is accompanied by the more pronounced splitting of the first oxygen shell. It is probably connected with the more ordered structure in Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Dy<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> characterized by the lower Debye-Waller factor values.

5) It was found that temperature decrease leads to different changes in the  $L_3$ -Ln FT peak amplitude of the first Ln-O(1) and the second Ln-O(2) coordination shells for all investigated compounds Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (Ln = Gd, Tb, Dy). The Ln-O(1) peak amplitude essentially increases, while Ln-O(2) peak amplitude stays practically the same the temperature range from 300 to 10 K (see Fig. 3). It indicates different stiffness of the Ln-O(1) and Ln-O(2) interatomic bonds.

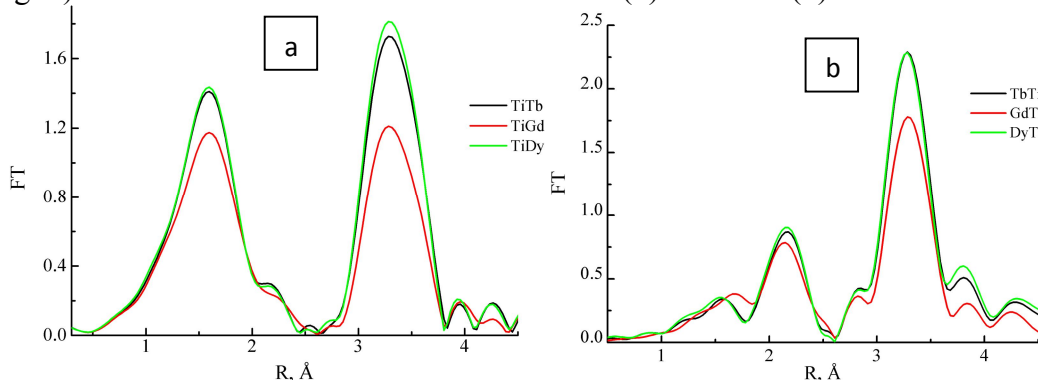


Fig. 2. EXAFS-FT spectra above  $K$ -Ti (a) and  $L_3$ -Ln (b) edges for Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (Ln = Gd, Tb, Dy), synthesized at 1200°C. The spectra were measured at 10 K.

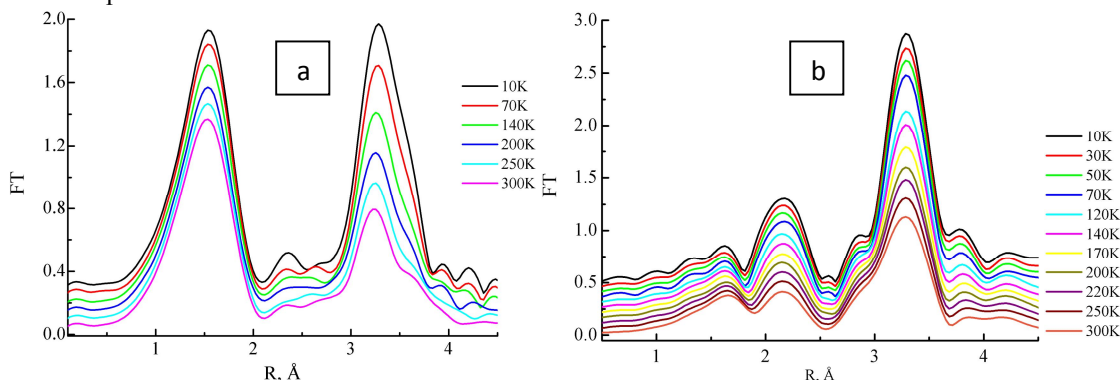


Fig. 3. Temperature dependent EXAFS-FT spectra above  $K$ -Ti (a) и  $L_3$ -Tb (b) edges for Tb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> annealed at 1200°C.

As concerned the Ln zirconates Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (Ln = Gd, Tb, Dy), the EXAFS-FT spectra above  $K$ -Zr and  $L_3$ -Ln demonstrated weaker temperature dependence of the FT peak amplitude for both the first (Ln, Zr)-O and the second (Ln, Zr)-(Ln, Zr) coordination shells in comparison to analogous spectra for titanates. It is pointed to the stronger stiffness of interatomic bonds in zirconates than in titanates. Besides we observed that temperature dependence of the FT peak amplitude for Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> with pyrochlore structure is more pronounced in comparison with Dy<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, which is characterized by disordered fluorite structure.

### Conclusion:

Thus we firstly investigated the local structure peculiarities of complex nano-structured oxides Ln<sub>2</sub>M<sub>2</sub>O<sub>7</sub> (Ln = Gd, Tb, Dy; M = Ti, Zr) as a function of the type of Ln and metal ions, crystallite sizes (annealing temperature) and temperature by using XAFS spectroscopy. Several new patterns were found. The new effective indicator of the pyrochlore phase formation was found. The paper for J. of Alloys and Compounds is being under preparation. The obtained results showed that taking advantage of small ion size of Ti<sup>4+</sup> one can achieve in practice the completely reversible phase transition "order-disorder-order" in the series of complex oxides with general formula Ln<sub>2</sub>M<sub>2</sub>O<sub>7</sub>, which we will propose as a continuation of this project.

### References

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