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Fluorite-pyrochlore phase transition in nanostructured $Ln_2Hf_2O_7$ (Ln = La-Lu)

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ABSTRACT

Complex oxides of the $Ln_2Hf_2O_7$ (Ln = lanthanide) series undergo a fluorite to pyrochlore phase transformation. We have studied the whole process of the crystal and local atomic structure realignment during the crystallization and the phase transition in the series of $Ln_2Hf_2O_7$ (Ln = La-Lu) samples synthesized by the coprecipitation method with the subsequent annealing of mixed hydroxides (precursors). The study employed a combination of x-ray diffraction (normal and anomalous), x-ray absorption spectroscopy, analysis of atomic pair distribution function and Raman spectroscopy. The starting and ending temperatures of the fluorite-pyrochlore phase transition for $Ln_2Hf_2O_7$ compounds have been determined along the lanthanide series La-Dy. The scheme summarizing structure types (amorphous, fluorite and pyrochlore) for the whole $Ln_2Hf_2O_7$ (Ln = La-Lu) series as a function of the Ln cation radius (or the $r_{Ln^{3+}}/r_{Hf^{4+}}$ ratio) and the annealing temperature has been refined.

1. Introduction

Complex oxides forming in the Ln_2O_3-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 [1–9], geometrically frustrated magnetism [10], ionic conductivity [11], etc. In addition, these materials have wide technological applications, which include solid electrolytes in high temperature solid oxide fuel cells [11], thermal barrier coatings (TBCs) [12], neutron absorbing [13] and nuclear waste storage materials [14].

The phase diagrams of the Ln_2O_3-MO_2 systems are complicated. They exhibit the formation of several crystal structure types under specific conditions [15]. These include $Ln_2M_2O_7$ complex oxides with pyrochlore-type superstructural ordering of Ln^{3+} and M^{4+} cationic sites and oxygen vacancies (space group $Fd\overline{3}m$) [1–6,15], solid solutions $[LnM]_2O_7$ with disordered fluorite-type cubic (space group $Fm\overline{3}m$) [1–5,15] or monoclinic (space group $P2_1$) structure [6], and rhombohedral δ-phases $Ln_4M_3O_{12}$ (space group $R\overline{3}$) [16]. The formation of a particular structure depends on the synthesis method, the amount of initial oxides Ln_2O_3 and MO_2, and the annealing temperature [1,3–6,17,18]. The formation of a specific phase, sometimes metastable, is essentially controlled by kinetic factors. The concept of kinetic growth-related transition was proposed in Refs. [19–21] to designate such a type of structural rearrangement. The ratio of the cation radii $\gamma = r_{Ln^{3+}}/r_{Hf^{4+}}$ is one of the main factors that determine the resulting crystal structure type [1]. The fluorite-pyrochlore phase transition takes place at a ratio γ~1.46 [1,3–5,18]. According to the recently refined data the limiting ratios for the different $Ln_2M_2O_7$ structure types are as follows: disordered fluorite $\gamma < 1.21 <$ δ-phase $\gamma < 1.42–1.44 <$ pyrochlore $\gamma < 1.78–1.83 <$ monoclinic pyrochlore $\gamma < 1.92$ [22]. The most interesting compounds are located near the lower boundary of the fluorite-pyrochlore solid state phase transition. These compounds show the maximum ionic conductivity [11] and the highest radiation tolerance [23]. The phase transition from an ordered pyrochlore structure to a disordered defect fluorite structure is a rare example of simultaneous disordering in both the cation and anion sublattices. It involves the randomization of the

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cations between the 16*c* and 16*d* sites, and the oxygen ions over the 48*f*, 8*b* and 8*a* sites [24,25] (see Fig. 1).

Lanthanide hafnates of the $Ln_2Hf_2O_7$ family remain insufficiently investigated despite the fact that some of these compounds and solid solutions are promising as ceramic layers for TBCs [26] and neutron absorbers [27]. The functionality of these materials depends on the peculiarities of their crystal and local structures. For the lanthanide hafnates the experimentally determined upper boundary of the fluorite-pyrochlore phase transition was put between $Sm_2Hf_2O_7$ and $Eu_2Hf_2O_7$ [28], while the lower boundary lies in the region of $Gd_2Hf_2O_7$ and $Tb_2Hf_2O_7$, which show a cation radii ratio γ close to 1.46 [1,4,5,29]. However, the exact lower boundary position for the phase transition is still under debate. Recent theoretical calculations have demonstrated the trend for pyrochlore ordering in $Dy_2Hf_2O_7$ and $Ho_2Hf_2O_7$ [30,31] and even in $Er_2Hf_2O_7$ [30]. Furthermore, there is experimental evidence of pyrochlore ordering in $Dy_2Hf_2O_7$ obtained from Raman spectroscopy [32].

It should be noted that apart from the chemical composition and geometric factor, the structure of the $Ln_2M_2O_7$ oxides is significantly affected by the crystallite size, which can also be changed by varying the conditions of synthesis [18,33]. When this size is relatively small (1–5 nm), the average crystal structure differs from the local one, although the latter often determines important properties of compounds such as thermal stability, electrophysical and optical properties, catalytic activity, etc. [34].

Apparently, the vast majority of publications are dedicated to the properties of well-crystallized compounds $Ln_2M_2O_7$ [3–6,24,29,35,36] prepared by the solid-state synthesis method at elevated temperature, which does not allow information about changes occurring to the crystal structure during the formation process to be obtained. In this paper we use another synthesis method, based on the annealing of precursors, prepared from the solutions of mixtures of the respective salts [18,37–39].

The synthesis from solutions has the advantage of yielding a highly homogeneous cation distribution within the precursor prepared by the coprecipitation, and allows production of almost single-phase nanocrystalline powders with predetermined composition at lower temperatures [40]. Thus this method is appropriate for studying the evolution of crystalline phases and possible polymorphic transformations during the process of $Ln_2M_2O_7$ synthesis. It can be achieved by annealing the initially amorphous precursors at different temperatures [18].

In recent years we actively investigated the structure formation in boundary compounds: $Gd_2Zr_2O_7$ with $\gamma = 1.46$ [41] and $Ln_2Hf_2O_7$ (Ln = Sm-Dy) with γ = 1.45–1.51 [42–45]. The present work addresses the specific features of lanthanide hafnates $Ln_2Hf_2O_7$ crystal and local structures during their emergence and evolution. The samples have been prepared by annealing initially amorphous precursors at different temperatures in a wider row of lanthanides from La to Lu. In this research we have used the combination of normal and anomalous x-ray diffraction, the local structure sensitive methods of extended x-ray absorption fine structure (EXAFS) and near edge structure (XANES) spectroscopy, the analysis of atomic pair distribution functions (PDF) obtained from the high-energy synchrotron x-ray total scattering, and optical Raman spectroscopy. This combination allowed us to observe the successive realignment of both the cation and anion sublattices during the fluorite-pyrochlore phase transition and to build the scheme summarizing the structure types in the full series of lanthanide hafnates $Ln_2Hf_2O_7$ as a function of the lanthanide type (or Ln^{3+} ion radius) and the annealing temperature.

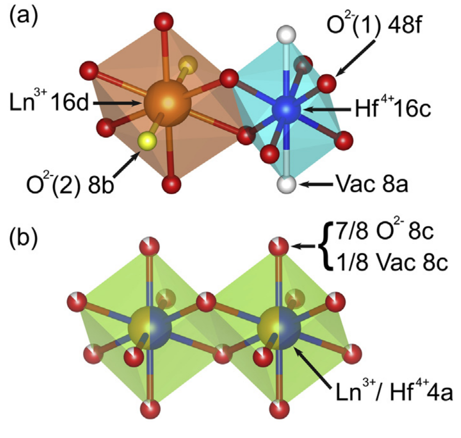

Fig. 1. Representations of the pyrochlore (a) and disordered fluorite structures (b).

2. Experimental

2.1. Synthesis procedure

The lanthanide hafnate series with composition $Ln_2Hf_2O_7$ (Ln = La-Lu) have been synthesized from lanthanide nitrates $Ln(NO_3)_3 \cdot mH_2O$ (the purity 99.96 – 99.99% and m = 4–6 depending on the Ln^{3+} cation) and hafnium oxychloride octahydrate $HfOCl_2 \cdot 8H_2O$ (99.7%) by reverse coprecipitation with subsequent annealing of the resulting mixed hydroxides (precursors). The initial lanthanide and hafnium salts were dissolved while stirring in distilled water. The concentrations of the resulting solutions were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Vista-PRO (Varian) apparatus. After the determination of concentration of different salt solutions they were mixed in an oxide molar ratio $Ln_2O_3:HfO_2 = 1:2$. The resulting solution of the salt mixture with a total concentration of 0.5 mol/l was introduced into 3 mol/l aqueous ammonia with vigorous stirring. The resulting suspension of mixed hydroxides (pH 9.5 – 10.0) was filtered and washed with distilled water until the absence of Cl^- anions confirmed by reaction with $AgNO_3$. The resulting wet precipitate was dried to constant weight in a drying cabinet at 90 °C. The dry powders (precursors) were ground in a mortar, heated in a muffle furnace HT 08/18 (Nabertherm) at a rate of 10 K/min to the required temperatures in the range 600–1600 °C, and then annealed isothermally in air for 3 h. The $Dy_2Hf_2O_7$ powder prepared at 800 °C/ 3 h was finely ground in a planetary ball mill (Pulverisette 7 premium line, 1000 rpm, 30 min), pressed uniaxially into cylindrical pellets by applying a pressure of 180 MPa and then sintered in the air in a muffle furnace at a temperature of 1550 °C in Al_2O_3-crucibles for 4 h.

2.2. Sample characterization

Simultaneous thermal analysis (STA) of precursors, involving the measurement of thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on a Netzsch STA-409 PC analyzer in the temperature range 30–1400 °C at a heating rate of 10 K/min in an argon flow.

The x-ray powder diffraction of the $Ln_2Hf_2O_7$ series at different temperatures was carried out at the Structural Materials Science beamline of the Kurchatov synchrotron radiation source (Moscow, Russia) [46]. Measurements were performed in the transmission mode at $\lambda = 0.68886$ Å and a sample-detector distance of 200 mm, the beam size 200 × 200 μm, using a 2D detector "Imaging plate Fujifilm BAS-5000". The 2D patterns were integrated and converted to conventional $I(2\theta)$ data using the Fit2D program package [47].