Pr2M2O7 (M=Zr, Hf) local and crystal structure changes in a fluorite-pyrochlore phase transition.

A P Menushenkov1, V V Popov1,2, B R Gaynanov1,3 and Ya V Zubavichus2

1 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, 115409 Moscow, Russia
2 NRC “Kurchatov Institute”, pl. Akademika Kurchatova 1, 123182, Moscow, Russia
E-mail: BRGaynanov@gmail.com

Abstract. The formation of nanocrystal powders of Pr2M2O7 (M=Zr, Hf) compounds upon calcinations up to 1400°C has been investigated by using X-ray absorption fine structure (XAFS) spectroscopy combined with X-ray powder diffraction (XRD). The structure ordering upon calcination was estimated independently from XRD and EXAFS data. It was found that the phase transition fluorite-pyrochlore occurs at calcination temperature in the range of 900-1000 °C. The appearance of the ordered pyrochlore structure at calcination temperatures above 1000 °C was manifested as splitting of the first oxygen coordination shell of the local praseodymium environment and supported by a sharp reduction of the Debye-Waller factor values of interatomic bonds. Besides we observed the L3-Hf X-ray absorption near edge line shape splitting with increasing of annealing temperature of amorphous precursor due to crystal field influence in high ordered pyrochlore-type structure.

1. Introduction

In the “Ln2O3-MO2” (Ln = lanthanide, M = Zr, Hf) systems, the formation of several intermediate phases was found: phases of stoichiometry formula Ln2M2O7 with pyrochlore (Fd-3m) and fluoride (Fm-3m) types of crystalline structure and a phase with hexagonal structure (R-3), formulated as Ln3M3O12 [1]. The thermodynamic stability of the pyrochlore type compounds can be determined using empirical rule, which identifies the ratio between ionic radii as 1.46 < (rLn3+/rM4+) < 1.78 [2]. Earlier we investigated the fluorite-pyrochlore phase transition in a “boundary” zirconate Gd2Zr2O7 and hafnates Ln2Hf2O7 (Ln = Sm – Dy) with the cation ratio rLn3+/rHf4+~1.46 [3-6]. Among the complex oxides based on Zr, Hf and rare earth ions, Pr2Me2O7 (M=Zr, Hf) has the pronounced inclination to the formation of pyrochlore structure. In the “HfO2 - Pr2O3” phase diagram there exists a considerable pyrochlore phase area and Pr2Hf2O7 (rPr3+/rHf4+ = 1.586) melts congruently at 2420°C (i.e. the liquid has the same composition as the solid compound) [7]. The “ZrO2 - Pr2O3” phase diagram similarly exhibits significant pyrochlore phase area, but Pr2Zr2O7 (rPr3+/rZr4+ = 1.564) melts incongruently at 2220°C [1]. Pr2Zr2O7 and Pr2Hf2O7 reveal the magnetic frustration structure properties [8-9] and may be used as the thermal barrier coatings [10].

The aim of the present work is to study the crystallization processes of an amorphous precursor upon isothermal calcination and to make clear the peculiarities of fluorite - pyrochlore phase transition in Pr2M2O7 (M = Zr, Hf), using combined X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAFS) at synchrotron radiation.

3 To whom any correspondence should be addressed.
2. Experimental section

The starting materials were Pr(NO$_3$)$_3$·6H$_2$O (99.8% purity), ZrOCl$_2$·8H$_2$O (99% purity) and HfOCl$_2$·8H$_2$O (99.7% purity). Precursor (mixed Pr-Zr or Pr-Hf hydroxide) was prepared by co-precipitation of metal salts solution with ammonia NH$_3$·H$_2$O (analytical grade) [11]. The Pr$_2$Zr$_2$O$_7$ or Pr$_2$Hf$_2$O$_7$ powders were prepared by calcination of an amorphous precursor at 600-1400°C for 3 h in air. A more detailed experimental procedure was described in Refs [3-4, 6].

X-ray diffraction investigations of the structure were carried out at the “Structural Materials” beamline of the Kurchatov synchrotron radiation source. Standard mode in the Debye-Scherrer geometry (transmissive mode), was implemented in an environment optimized for high-quality experimental data: the distance the sample - detector is 200 mm; beam size 200x200 mm; the exposure time of 15-30 minutes, the wavelength $\lambda = 0.68886$ Å. Two series of Pr$_2$M$_2$O$_7$ compounds with (M = Zr, Hf) were examined. Each series included 7-9 samples obtained by calcination of initial precursor at different temperatures in a temperature range 600 -1400°C. The Rietveld full-profile analysis of X-ray diffraction patterns was performed with the Jana2006 software [12].

X-ray absorption spectra (EXAFS) of Pr$_2$Me$_2$O$_7$ (Me=Zr, Hf) above the L$_{\gamma}$-Pr (5964 eV), L$_{\gamma}$-Hf (9561 eV) and K-Zr (17998 eV) absorption edges, were measured at i811 beamline of MAXLab (Lund, Sweden) in a transmission mode at room temperature. Processing and modeling of XAFS-spectra were carried out using the VIPER [13]. The amplitudes and phases of photoelectron back scattering in the local environment of zirconium, praseodymium and hafnium atoms were calculated by program FEFF-8.20 [14] using the crystal structure parameters of pyrochlore and fluorite, taken from the work of Blanchard et al. (2013)[15] and from the diffraction data for Pr$_2$Me$_2$O$_7$ (where Me = Zr, Hf).

3. Results and discussion

The XRD study showed that precursors calcinated at 600 °C have the X-ray amorphous structure. However, their structure can’t be considered as completely disordered, since one to several broad peaks were observed in the region of double Bragg angle. Calcination of Pr$_2$Zr$_2$O$_7$ at 700 °C leads to the appearance of crystalline domains in the amorphous structure, which is manifested as the presence of broad diffraction peaks. Upon calcination at 800 °C the beginning of nanocrystallization observed in both Pr$_2$Zr$_2$O$_7$ and Pr$_2$Hf$_2$O$_7$ systems. The increasing of the calcination temperature above 900 °C leads to appearance of about 10 x-ray reflections corresponding to a fluorite structure for all the samples. Besides above 900 °C we observed the gradual narrowing of the diffraction reflexes and the appearance of superlattice peaks (Figure 1), which point to increase of the structure ordering. This is also manifested in increase of crystallite size and decrease of values of microstrain obtained from the analysis of the diffraction patterns (Figure 2). These superstructure reflections are substantially wider than the main peaks of the fluorite-type structure. It suggests that cationic ordering with formation of the pyrochlore phase upon calcination occurs inside the separate regions (nanodomains) distributed over crystals matrix with the fluorite structure.

Analysis of EXAFS-data showed that spectra for calcination temperature up to 800-900 °C are well reproduced by the model of fluorite structure, and bond lengths Pr-O and Me-O slightly increase (Figure 3). However, at higher calcination temperatures the fluorite structure can no longer provide an adequate simulation of EXAFS-function and the analysis was conducted using the pyrochlore structure model. Thus above 1000 °C there is clearly observed splitting of the Pr-O bond length with a weak reducing of M-O distances (Figure 3). This directly points to the restructuring of the local oxygen environment of rare-earth ions as a result of the observed fluorite-pyrochlore phase transition. The values of the Debye-Waller factor (Figure 4) of interatomic bonds decrease with calcination temperature, further pointing to the growth of the degree of local structure ordering in the transition from a disordered fluorite structure to an ordered structure of pyrochlore.
Additionally, the analysis of L$_3$-Hf of the absorption edge (XANES) in Pr$_2$Hf$_2$O$_7$ showed that increase of calcination temperature of the initial precursor up to 800 °C leads to the essential widening of the so-called "white line", corresponding to the main peak in the absorption spectrum (Figure 5). Further increase of temperature above 900 °C leads to splitting of the "white line", which is clearly manifested in the spectral dependence of the second derivative (Figure 6). As the XANES for L$_3$-Hf of the absorption edge arises from the dipole transition $2p_{3/2} \rightarrow 5d_{5/2}$, we believe that the observed effect is connected to the removal of degeneracy 5d level of hafnium and its splitting into $e_g$ and $t_{2g}$ parths as a result of the crystal field influence in the ordered pyrochlore structure. This observation is an additional confirmation of the phase transition fluorite-pyrochlore in Pr$_2$Hf$_2$O$_7$ with increase of calcination temperature above 1000 °C.
Local and crystal structure evolution of Pr$_2$Zr$_2$O$_7$ and Pr$_2$Hf$_2$O$_7$ upon calcinations of the initial X-ray amorphous precursors in the temperature range 600 - 1400 °C has been studied by a combination of X-ray powder diffraction (XRD) and XAFS-spectroscopy using synchrotron radiation. Splitting of the first oxygen coordination shell of the local praseodymium environment and “white line” $L_3$-Hf of the absorption edge into two components was observed in pyrochlore structure at calcination temperature higher than 900-1000 °C. The splitting of $L_3$-Hf edge caused by crystal field influence in high ordered pyrochlore-type structure.

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