La$_2$Hf$_2$O$_7$ crystal and local structure changes on the fluorite – pyrochlore phase transition

V V Popov$^{1,2,3}$, A P Menushenkov$^1$, A A Yastrebtsev$^1$ and Ya V Zubavichus$^2$

$^1$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: victorvpopov@mail.ru

Abstract. The process of La$_2$Hf$_2$O$_7$ ($r_{\text{La}^{3+}}/r_{\text{Hf}^{4+}} = 1.63$) nanocrystals formation and evolution upon calcinations up to 1400 °C has been investigated by means of synchrotron radiation X-ray diffraction (XRD) and Raman spectroscopy. It has been shown that isothermal calcination at 800 °C/3h of the X-ray amorphous precursor firstly leads to the formation of oxide nanocrystalline powders with a defect fluorite structure. In the temperature range 900 – 1000 °C we observed the nucleation and growth of pyrochlore nanodomains inside a well crystalline fluorite matrix. The pyrochlore-type superstructural ordering of cations and anions appears at calcinations temperature higher than 1000 °C.

1. Introduction

The compounds and solid solutions formed in «$Ln_2$O$_3$ - MO$_2$» systems ($Ln$ – lanthanides, $M$ – titanium subgroup elements) has intensively investigated due to their important scientific interest (order-disorder phase transitions [1, 2]; geometrically frustrated magnets [3], etc.) and technological applications (thermal barrier coatings [4]; solid electrolytes in high temperature solid oxide fuel cells [5]; neutron absorbing materials [6]; nuclear waste storage materials [7], etc.). The application functionality of materials depends on the crystal and local structure of used materials. The structural phase transition from the order $Fd\overline{3}m$ pyrochlore structure to the disorder $Fm\overline{3}m$ defect fluorite structure involves the randomization of the oxygen ions among the 48f, 8b, and 8a sites, and the cations between the 16c and 16d sites [8].

Lanthanides hafnates are the less investigated in the Ln$_2$M$_2$O$_7$ family. During some years we actively investigated the specific features of the structure formation in “boundary” compounds Ln$_2$Hf$_2$O$_7$ ($Ln$ = Sm – Dy) with the cation ratio $r_{\text{Ln}^{3+}}/r_{\text{Hf}^{4+}} \sim 1.46$ [9–11]. The aim of the present work is to study the formation and evolution of crystal and local structures in La$_2$Hf$_2$O$_7$ ($r_{\text{La}^{3+}}/r_{\text{Hf}^{4+}} = 1.63$), which has the most thermodynamically stable pyrochlore phase among Ln$_2$Hf$_2$O$_7$ group, upon isothermal calcination of an amorphous precursor. We simultaneously observed the processes of cation ordering using synchrotron radiation X-ray diffraction and anion ordering using Raman spectroscopy upon the “fluorite - pyrochlore” phase transition.

2. Experimental

$^3$To whom any correspondence should be addressed.

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The starting materials were La(NO$_3$)$_3$∙6H$_2$O (99.96% purity) and HfOCl$_2$∙8H$_2$O (99.7% purity). Precursor (mixed La-Hf hydroxide) was prepared by co-precipitation of metal salts solution with ammonia NH$_3$∙H$_2$O (analytical grade) [12]. The La$_2$Hf$_2$O$_7$ powders were prepared by calcination of precursor at 600-1400 °C for 3 h in air. A more detailed experimental procedure was described in Refs [9–11].

The thermal behaviour of the dried powders was studied from 100 to 1400 °C using thermogravimetric analysis and differential scanning calorimetry (TG/DSC, Netzsch STA 409 PC Luxx) with a heating rate of 10 K min$^{-1}$ in an argon flow of 30 mL/min in corundum crucibles. Crystal structure of La$_2$Hf$_2$O$_7$ synthesized powders was studied by X-ray powder diffraction at “Structural Materials Science” beamline of the Kurchatov synchrotron radiation source. Measurements were carried out in the transmission mode at $\lambda = 0.68886$ Å. The Rietveld full-profile analysis of X-ray diffraction patterns was performed with the Jana2006 software [13].

FT–Raman spectra were recorded at research analytical center JSC “VNIICht” on the Nicolet iS50 FT–IR spectrometer (Thermo Scientific) equipped with iS50 Raman module with a laser excitation wavelength of 1064 nm. The spectra were measured in wave number range from 100 to 3700 cm$^{-1}$ and were averaged out of 256 scans with a time interval of 2 s and a resolution of 4 cm$^{-1}$.

3. Results and discussion
The freshly washed precipitate of mixed La-Hf hydroxide was strongly hydrated (~ 95% water). The XRD study showed that both wet and dry powders were amorphous. However, XRD pattern indicated the presence of the first broad maximum which pointed to origin of the local order in the precursor structure.

According to TG-analysis, the dry precursor had formula La$_2$O$_3$∙HfO$_2$∙10.7 H$_2$O. Significant parts of weight loss up to 300 °C (~ 50% of total) and above 950 °C (6% of total) indicate a high degree of hydration and strong retention of OH$^-$-groups in the crystal lattice of the synthesized samples.

It has been found that primary crystallization of precursor occurs between 700-800 °C/3 h. At 800 °C the powder appears to be nanocrystalline (coherent scattering length – CSL – 35 nm). Its XRD patterns show reflections corresponding to a fluorite structure (Fm-3m) with a unit cell parameter (a) of ~5.33 Å. A further increase in the calcination temperature leads to the narrowing of diffraction peaks (Figure 1a) owing to the increase of CSL values and the decrease in microstrain values ($\varepsilon$) (Table 1).

Figure 1. XRD patterns of La$_2$Hf$_2$O$_7$ powders obtained by calcination of the precursor at different temperatures (shown on the corresponding curves) at 3 h in the air: (a) general pattern, (b) in a narrower range. In brackets are the reflection indices of the pyrochlore phase. * - impurity of HfO$_2$. 
The crystallization pattern for La$_2$Hf$_2$O$_7$ starts qualitatively changing at temperature \(~\sim 1000^\circ C\). The XRD patterns of the powders synthesized at temperatures \(\geq 1000^\circ C/3\) h show the appearance of superstructure peaks (111) (main), (311), (531) and others, which point to the onset of pyrochlore cationic ordering (\(Fd-3m\)). From Figure 1b, it can be noted that the superstructure reflections remain significantly broader than the basic peak characteristic of fluorite. The XRD quantitative analysis (Table 1) enables to suggest that, in the case of La$_2$Hf$_2$O$_7$ sample calcinations in temperature range 900-1000 \(^\circ C\), the cationic ordering in the pyrochlore phase presumably occurs in separate regions (nanodomains) distributed over bulk crystals with the fluorite structure. It should be noted, that the observed “amorphous \(\rightarrow\) fluorite \(\rightarrow\) pyrochlore” phase transformation is consistent with Ostwald’s step rule. Similar results were obtained earlier for Ln$_2$Hf$_2$O$_7$ (Ln = Sm – Dy) [11] and Gd$_2$Zr$_2$O$_7$ [14].

### Table 1. Temperature dependence of atomic crystal structure parameters of La$_2$Hf$_2$O$_7$ powders.

| Crystal structure | Parameter | Temperature, °C | 800 | 1000 | 1200 | 1300 | 1400 |
|------------------|-----------|----------------|-----|------|------|------|------|
| \(Fm-3m\)       | CSL, nm   |                | 35  | 115  | 149  | 445  | 839  |
|                  | \(\varepsilon\), % |             | 1.258 | 1.083 | 0.242 | 0.032 | 0.022 |
| \(Fd-3m\)       | CSL, nm   |                | -   | 17   | 72   | 375  | 462  |
|                  | \(\varepsilon\), % |             | -   | 0.317 | 0.386 | 0.743 | 0.610 |
|                  | \(a\), Å  |                | 5.3328 | 10.7253 | 10.7531 | 10.7644 | 10.7546 |
|                  | % wt. HfO$_2$ (XRD / Raman) |       | - | 2.4 / 1.2 | 4.1 / 4.4 | 4.8 / 5.1 | 6.2 / 6.1 |

The results of Raman spectroscopy investigations are presented in Figure 2. As shown in Figure 2, all the six pyrochlore modes \(E_g\) (321 cm$^{-1}$), \(A_{1g}\) (499 cm$^{-1}$) and \(4F_{2g}\) (304 main, 401, 520 and 755 cm$^{-1}$) are observed in the Raman spectra of La$_2$Hf$_2$O$_7$ powders prepared at temperature \(\geq 1000^\circ C\). These results are in good agreement with [15].

Quantitative analysis of the obtained Raman spectra showed that the process of anion ordering of pyrochlore type in La$_2$Hf$_2$O$_7$ powders begins at a lower temperature than the process of cation ordering (according to XRD data). However at calcinations temperature higher than 1100 \(^\circ C\) both the cation and anion sublattice of La$_2$Hf$_2$O$_7$ became fully ordered. So above this temperature the “fluorite - pyrochlore” phase transformation is fully completed. As shown in Figure 3, the Raman spectra of La$_2$Hf$_2$O$_7$ (1400 °C/3h) clear indicate the presence of monoclinic HfO$_2$ impurity. The HfO$_2$ contents calculated from Raman spectra were in good agreement with XRD data (Table 1).
4. Conclusion
The evolution of La$_2$Hf$_2$O$_7$ crystalline and local structures upon calcination of initial mixed hydroxide has been studied simultaneously by using of synchrotron radiation XRD and Raman spectroscopy methods. It has been shown that isothermal calcination of the X-ray amorphous precursor at temperatures $\geq 800$ °C first leads to the formation of oxide nanocrystalline powders with a defect fluorite structure and reveals an increase in coherent scattering lengths and a decrease in microstrain values upon calcination temperature increase. Heat treatment at temperature $\geq 1000$ °C initiates nucleation and growth of nanodomains with pyrochlore-type superstructural ordering of cations and anions inside a microcrystalline fluorite matrix. At calcinations temperature higher than 1100 °C both the cation and anion sublattice of La$_2$Hf$_2$O$_7$ became fully ordered and the “fluorite - pyrochlore” phase transformation is fully completed.

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References
[1] Jiang C, Stank C R, Sickafus K E et al 2009 First-principles prediction of disordering tendencies in pyrochlore oxides Phys. Rev. B 79 104203-1–104203-5
[2] Blanchard P E R, Liu S, Kennedy B J et al 2013 Investigating the local structure on lanthanoid hafnates Ln$_2$Hf$_2$O$_7$ via diffraction and spectroscopy J. Phys. Chem. C 117 2266-73
[3] Gardner J S, Gingras M J P, Greedan J E, 2010 Magnetic pyrochlore oxides Rev. Modern Phys. 82 53–107
[4] Pan W, Phillpot S R, Wan C et al 2012 Low thermal conductivity oxides MRS Bull. 32 917–22
[5] Yamamura H, Nishino H, Kakinuma K et al 2003 Electrical conductivity anomaly around fluorite–pyrochlore phase boundary Solid State Ionics 158 359–65
[6] Risovany V D, Zakharov A V, Muraleva E M et al 2006 Dysprosium hafnate as absorbing material for control rods J. Nucl. Mater. 355 163–70
[7] Ewing R C, Weber W J, Lian J 2004 Nuclear waste disposal - pyrochlore (A$_2$B$_2$O$_7$): Nuclear waste form for the immobilization of plutonium and “minor” actinides J. Appl. Phys. 95 5949–71.
[8] Nachimuthu P, Thevithasan S, Stutthanandan V et al 2005 Near-edge X-ray absorption fine-structure study of ion-beam-induced phase transformation in Gd$_3$(Ti$_{1-y}$Zr$_y$)$_2$O$_7$ J. Appl. Phys. 97 033518-1–033518-5
[9] Popov V V, Petrunin V F, Korovin S A et al 2011 Formation of nanocrystalline structures in the Ln$_2$O$_3$-MO$_2$ systems (Ln = Gd, Dy; M = Zr, Hf) Russ. J. Inorg. Chem. 56 1538–44
[10] Popov V V, Menushenkov A P, Zubavichus Ya V et al 2013 Characteristic features of the nanocrystalline structure formation in Ln$_2$Hf$_2$O$_7$ (Ln = Gd, Dy) compounds Russ. J. Inorg. Chem. 58 1400–7
[11] Popov V V, Zubavichus Ya V, Menushenkov A P et al 2015 Lanthanide effect on the formation and evolution of nanocrystalline structures in Ln$_2$Hf$_2$O$_7$ Compounds (Ln = Sm–Dy) Russ. J. Inorg. Chem. 60 16–22
[12] Popov V V 2015 Formation Regularities of Dispersed Hydrated Oxide Systems Russ. J. Inorg. Chem. 60 420–7
[13] Petricek V, Dusek M and Palatinus L 2014 Crystallographic computing system JANA2006: General features Z. Kristallogr. 229 345–52
Popov V V, Zubavichus YaV, Menushenkov A P et al 2014 Short- and long-range order balance in
nanocrystalline Gd$_2$Zr$_2$O$_7$ powders with a fluorite–pyrochlore structure

Russ. J. Inorg. Chem. 59 279–85

[14] Kumar S, Gupta H C 2012 First principles study of dielectric and vibration properties of pyrochlore hafnates Solid State Sci. 14 1405–11