Features of crystal and local structures of complex oxides formed in the binary system Dy$_2$O$_3$-ZrO$_2$

V V Popov$^{1,2,3}$, A P Menushenkov$^1$, A A Yastrebtsev$^1$, Ya V Zubavichus$^2$, R D Svetogorov$^2$ and N A Kolyshkin$^2$

$^1$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 Dy$_2$Zr$_2$O$_7$ (r$_{Dy^{3+}}$/r$_{Zr^{4+}} = 1.426$) 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. We observed that isothermal calcination of the X-ray amorphous precursor first leads to the formation of oxide nanocrystalline powders with a defect fluorite structure at 800 °C/3 h. The nucleation and growth of pyrochlore phase take place in nanodomains with pyrochlore-type superstructural ordering of cations and anions inside a well crystalline fluorite matrix at ≥ 1200 °C. This is perhaps the first XRD study that reports the presence of a weak pyrochlore-type superstructure in the Dy$_2$Zr$_2$O$_7$.

1. Introduction

Complex oxides formed in the binary systems Ln$_2$O$_3$–MO$_2$ (Ln = lanthanides, M = Zr, Hf) intensively studied in recent years [1–4]. The formation of different types of crystal structure of these compounds depends on the synthesis conditions, types of Ln$_2$O$_3$ and MO$_2$ oxides, temperature, etc. [5]. One of the main factors that determine the type of the resulting crystal structure is the cation radius ratio r$_{Dy^{3+}}$/r$_{Zr^{4+}}$ [1]. The “pyrochlore – fluorite” phase transition takes place at r$_{Dy^{3+}}$/r$_{Zr^{4+}}$ ~ 1.46 [1]. According to updated radius-ratio rules for Ln$_2$M$_2$O$_7$ the radius-ratio limits are as follows: disordered fluorite < 1.21 < δ-phase < 1.42–1.44 < pyrochlore < 1.78–1.83 < monoclinic pyrochlore < 1.92 [6]. The most interesting compounds are located near the lower boundary of “fluorite - pyrochlore” solid state phase transition. These compounds reveal maximum ionic conductivity [2] and the best radiation-tolerance properties [7]. The phase transition from an ordered pyrochlore to a disordered defect fluorite structure is the rare example of simultaneous disorder in both cation and anion sub-lattice [8].

Dysprosium zirconate Dy$_2$Zr$_2$O$_7$ (r$_{Dy^{3+}}$/r$_{Zr^{4+}} = 1.426$) is one of such compound with structure exactly between pyrochlore and fluorite phase (or δ-phase). It has been reported, based on XRD studies, that Dy$_2$Zr$_2$O$_7$ has a defect fluorite structure with complete disorder of the metal ions and oxygen vacancies [9, 10]. Recent theoretical work [11] showed that the “order-disorder” transformation temperature (793 K) in Dy$_2$Zr$_2$O$_7$ is too low for the formation of ordered pyrochlore structure. However few years ago Sayed et al. [12] using Raman spectroscopy experimentally found the formation of a weak pyrochlore-type ordering in the Dy$_2$Zr$_2$O$_7$ pellet. On the other hand, in [13, ...

$^3$ To whom any correspondence should be addressed.
14] have been shown that Dy$_2$Hf$_2$O$_7$ ($r_{\text{Dy}^{3+}}/r_{\text{Hf}^{4+}} = 1.446$) manifested a weakly tendency to form pyrochlore structure in ceramic pellets.

The aim of the present work is to study the formation and evolution of crystal and local structures in “boundary” compound Dy$_2$Zr$_2$O$_7$, upon isothermal calcination of an amorphous precursor by combined X-ray diffraction (XRD) using synchrotron radiation (information about cation ordering) and Raman spectroscopy (anion ordering).

2. Experimental

The starting materials were Dy(NO$_3$)$_3$·5H$_2$O (99.5% purity) and ZrOCl$_2$·8H$_2$O (99% purity). Precursor (mixed Dy-Zr hydroxide) was prepared by co-precipitation of metal salts solution with ammonia NH$_3$·H$_2$O (analytical grade) [15]. The Dy$_2$Zr$_2$O$_7$ powders were prepared by calcination of precursor at 600-1400 °C for 3 h in air. The Dy$_2$Zr$_2$O$_7$ powder (800 °C/3 h) was further compacted as pellet and sintered at 1450 °C in air for 4 h to get the final ceramic material. A more detailed experimental procedure was described in Refs [14–17].

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 Dy$_2$Zr$_2$O$_7$ synthesized powders and pellet 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 [18].

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 Dy-Zr hydroxide was strongly hydrated (~ 95% water). The XRD study showed that both wet and dry powders were amorphous. However, XRD pattern indicates first broad maximum and thus the presence of near order in the precursor structure.

According to TG-analysis, the dry precursor had formula Dy$_2$O$_2$ZrO$_2$.12.7 H$_2$O. Significant parts of weight loss up to 344 °C (~ 63% of total) and above 900 °C (~ 10% of total) indicate a high degree of hydration and strong retention of OH-groups in the crystal lattice of the synthesized samples.

**Figure 1.** XRD patterns of Dy$_2$Zr$_2$O$_7$ powders obtained by calcination of the precursor at different temperatures (shown on the corresponding curves) for 3 h in the air: (a) general pattern, (b) in a narrower range. In brackets are the reflection indices of the pyrochlore phase.
It has been found that primary crystallization of precursor occurs at 800 °C/3 h. At 800 °C the powder appears to be nanocrystalline (coherent scattering length – CSL – 8 nm) with a fluorite structure (Fm-3m) in accordance with XRD data. A further increase in the calcination temperature leads to the narrowing of diffraction peaks (Figure 1a) owing to the increase of CSL and the decrease of microstrain values (ε) (Table 1). The diffraction patterns for Dy2Zr2O7 strongly change at calcination temperature higher than 1200 °C. The XRD patterns of the powders synthesized at temperatures ≥ 1200 °C/3 h show the appearance of superstructure peaks (111), (331), and (531), which point to the onset of pyrochlore cationic ordering (Fd-3m) (Figure 1b). This is perhaps the first synchrotron radiation XRD study that reports the presence of a weak pyrochlore-type superstructure in the Dy2Zr2O7.

Figure 1b shows that the superstructure reflections remain significantly broader than the basic peaks characteristic of fluorite. The XRD quantitative analysis (Table 1) enables to suggest that, upon the calcinations of Dy2Zr2O7 the cationic ordering formation of the pyrochlore phase presumably occurs in separate regions (nanodomains) distributed inside of bulkier crystals with the fluorite structure. Similar results were obtained earlier for Ln2Hf2O7 (Ln = Sm – Dy) [19] and Gd2Zr2O7 [20].

Table 1. Temperature dependence of atomic crystal structure parameters of Dy2Zr2O7 powders.

| Temperature, °C | 800 | 1000 | 1200 | 1300 | 1400 |
|----------------|-----|------|------|------|------|
| Crystal structure | Parameter  | CSL, nm | ε, % | CSL, nm | ε, % | a, Å |
|-----------------|------------|---------|------|---------|------|------|
| Fm-3m           | CSL, nm    | 8       | 0.599| 21      | 0.165| 217  |
|                 | ε, %       | 0.497   | -    | 0.497   | -    | -    |
| Fd-3m           | CSL, nm    | -       | -    | 4       | 5    | 8    |
|                 | ε, %       | -       | -    | 7.461   | 6.543| 9.239|
|                 | a, Å       | 5.2388  | 5.2338| 5.2318 | 5.2344| 5.2304|

Figure 2. Raman spectra of Dy2Zr2O7 powders (1, 2) and ceramic pellet (3) prepared by calcination at different temperatures: 1 – 1200; 2 – 1400; 3 – 1450 °C

Figure 3. Raman spectrum of Dy2Zr2O7 (1450°C/4 h): solid line – experimental spectrum; dashed lines approximation curves.

Raman spectroscopy data are represented in Figure 2. One can see that the Raman spectra of Dy2Zr2O7 pellet (1450 °C/4 h) include few broaden modes. The similar spectra were represented at [12]. Quantitative analysis of the received Raman spectrum of Dy2Zr2O7 pellet showed five of the six pyrochlore structure modes: $E_g$ (386 cm$^{-1}$), $A_{1g}$ (525 cm$^{-1}$) and $3F_{2g}$ (319 main, 430, 593 cm$^{-1}$). The Raman spectroscopy is sensitive to "oxygen-cation" vibrations and gives information about the local structure ordering of the anionic sublattice. Thus our Raman spectroscopic data shown that Dy2Zr2O7...
ceramics reveal a tendency to form the weak pyrochlore-type ordering in anion sublattice. In addition to our XRD data (Figure 1b) this result points to the both the cation and anion pyrochlore-type ordering in the nanodomains inside the well crystalline fluorite matrix.

4. Conclusion
The evolution of Dy$_2$Zr$_2$O$_7$ crystalline and local structures upon calcination of initial mixed hydroxide has been studied by a complex of XRD and Raman spectroscopy methods. It has been shown that isothermal calcination of the X-ray amorphous precursor at temperatures ≥ 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 ≥ 1200 ̊C initiates nucleation and growth of nanodomains with pyrochlore-type superstructural ordering of cations and anions inside a microcrystalline fluorite matrix.

Acknowledgements
The authors thank N.A. Tsarenko (JSC “VNIIChT”) for her help in Raman experiments. This work was partly supported by Ministry of Education and Science of the Russian Federation within agreement No. 14.587.21.002 and in the framework of the state assignment 3.1540.2014/K.

References
[1] Subramanian M A, Aravamudan G and Subba Rao G V 1983 Oxide pyrochlores – a review Prog. Solid State Chem. 15 pp 55–143
[2] Yamamura H, Nishino H, Kakinuma K et al 2003 Electrical conductivity anomaly around fluorite–pyrochlore phase boundary Solid State Ionics 158 359–65
[3] Shimamura K, Arima T, Idemitsu K et al 2007 Thermophysical properties of rare-earth-earth-stabilized zirconia and zirconate pyrochlores as surrogates for actinide-doped zirconia Int. J. Thermophys. 28 1074–84
[4] Blanchard P E R, Liu S, Kennedy B J et al 2012 Does local disorder occur in the pyrochlore zirconates? Inorg. Chem. 51 13237–44
[5] Andrievskaya E R 2008 Phase equilibria in the refractory oxide systems of zirconia, hafnia and yttria with rare-earth oxides J. Eur. Ceram. Soc. 28 2363–88
[6] Stanek C R, Jiang C, Uberuaga B P et al 2009 Predicted structure and stability of A$_3$B$_3$O$_{12}$ δ-phase compositions Phys. Rev. B 80 174101–1–174101-11
[7] Sickafus K E, Grimes R W, Valdez J A et al 2007 Radiation-induced amorphization resistance and radiation tolerance in structurally related oxides Nature Mater. 6 217–23
[8] Blanchard P E R, Liu S, Kennedy B J et al 2013 Investigating the order–disorder phase transition in Nd$_{2-x}$Y$_x$Zr$_2$O$_7$ via diffraction and spectroscopy. Dalton Trans. 42 14875–82
[9] Qiang X, Wei P, Jingdong W et al 2005 Preparation and thermophysical properties of Dy$_2$Zr$_2$O$_7$ ceramic for thermal barrier coatings Mater. Letters. 59 2804–8
[10] Tong Y, Yu Z, Lu L et al 2008 Rapid preparation and characterization of Dy$_2$Zr$_2$O$_7$ nanocrystals Mater. Res. Bull. 43 2736–41
[11] 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
[12] Sayed F N, Grover V, Bhattacharyya K et al 2011 Sm$_{2-x}$Dy$_x$Zr$_2$O$_7$ Pyrochlores: probing order-disorder dynamics and multifunctionality Inorg. Chem. 50 2354–65
[13] Mandal B P, Garg N, Sharma S M et al 2006 Preparation, XRD and Raman spectroscopic studies on new compounds RE$_2$Hf$_2$O$_7$ (RE = Dy, Ho, Er, Tm, Lu, Y): Pyrochlores or defect-fluorite? J. Solid State Chem. 179 1990–4
[14] Popov V V, Menushenkov A P, Zubavichus Ya V et al 2016 Features of crystal and local structures of compounds formed in “Dy$_2$O$_7$-HFO$_2$” system Russ. J. Inorg. Chem. 61 (in press)
[15] Popov V V 2015 Formation Regularities of Dispersed Hydrated Oxide Systems
[16] 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

[17] 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

[18] Petricek V, Dusek M and Palatinus L 2014 Crystallographic computing system JANA2006: General features Z. Kristallogr. 229 345–52

[19] Popov V V, Zubavichus Ya V, Menushenkov A P et al 2015 Lanthanide effect on the formation and evolution of nanocrystalline structures in Ln$_3$Hf$_2$O$_7$ compounds (Ln = Sm–Dy) Russ. J. Inorg. Chem. 60 16–22

[20] Popov V V, Zubavichus Ya V, 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. 59 279–285