

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

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Abstract. The process of $\text{Dy}_2\text{Zr}_2\text{O}_7$ ($r_{\text{Dy}^{3+}}/r_{\text{Zr}^{4+}} = 1.426$) 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$.

1. Introduction

Complex oxides formed in the binary systems $\text{Ln}_2\text{O}_3\text{-MO}_2$ (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_2O_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 $r_{\text{Ln}^{3+}}/r_{\text{M}^{4+}}$ [1]. The “pyrochlore – fluorite” phase transition takes place at $r_{\text{Ln}^{3+}}/r_{\text{M}^{4+}} \sim 1.46$ [1]. According to updated radius-ratio rules for $\text{Ln}_2\text{M}_2\text{O}_7$ the radius-ratio limits are as follows: disordered fluorite $< 1.21 < \delta$ -phase $< 1.42\text{--}1.44 < \text{pyrochlore} < 1.78\text{--}1.83 < \text{monoclinic pyrochlore} < 1.92$ [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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ ($r_{\text{Dy}^{3+}}/r_{\text{Zr}^{4+}} = 1.426$) 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ pellet. On the other hand, in [13,

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14] have been shown that $\text{Dy}_2\text{Hf}_2\text{O}_7$ ($r_{\text{Dy}^{3+}}/r_{\text{Hf}^{4+}} = 1.446$) 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$, 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 $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.5% purity) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (99% purity). Precursor (mixed Dy-Zr hydroxide) was prepared by co-precipitation of metal salts solution with ammonia $\text{NH}_3 \cdot \text{H}_2\text{O}$ (analytical grade) [15]. The $\text{Dy}_2\text{Zr}_2\text{O}_7$ powders were prepared by calcination of precursor at 600-1400 °C for 3 h in air. The $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\text{Dy}_2\text{O}_3 \cdot \text{ZrO}_2 \cdot 12.7 \text{H}_2\text{O}$. 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.

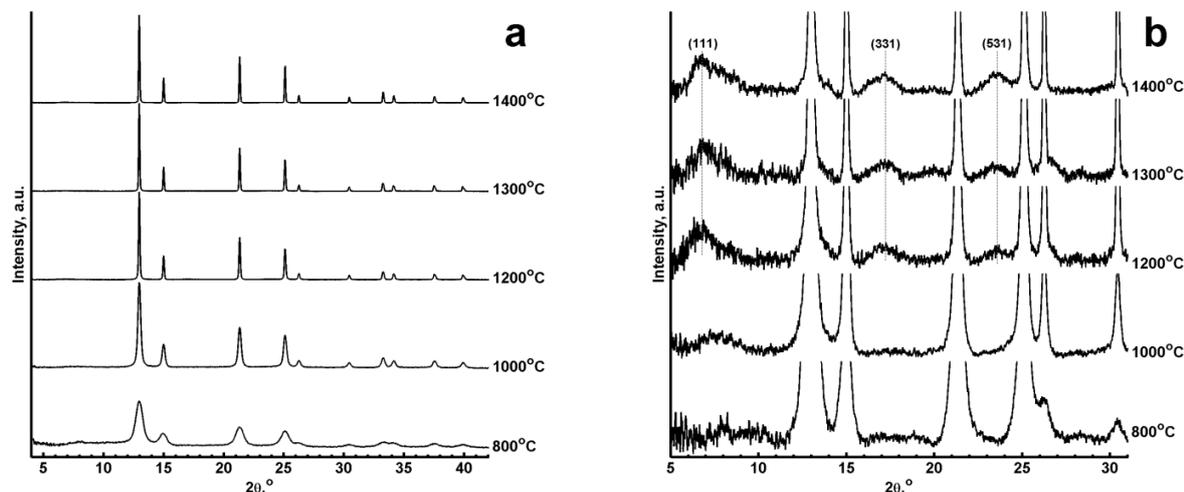


Figure 1. XRD patterns of $\text{Dy}_2\text{Zr}_2\text{O}_7$ powders obtained by calcination of the precursor at different temperatures (shown on the corresponding curves) for 3 h in the air: (a) general pattern, (b) in a narrower range. In brackets are the reflection indices of the pyrochlore phase.

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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$.

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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\text{Ln}_2\text{Hf}_2\text{O}_7$ (Ln = Sm – Dy) [19] and $\text{Gd}_2\text{Zr}_2\text{O}_7$ [20].

Table 1. Temperature dependence of atomic crystal structure parameters of $\text{Dy}_2\text{Zr}_2\text{O}_7$ powders.

		Temperature, °C				
		800	1000	1200	1300	1400
<i>Fm-3m</i>	CSL, nm	8	21	217	-	302
	ϵ , %	0.599	0.165	0.497	-	0.108
<i>Fd-3m</i>	CSL, nm	-	-	4	5	8
	ϵ , %	-	-	7.461	6.543	9.239
<i>a</i> , Å		5.2388	5.2338	5.2318	5.2344	5.2304

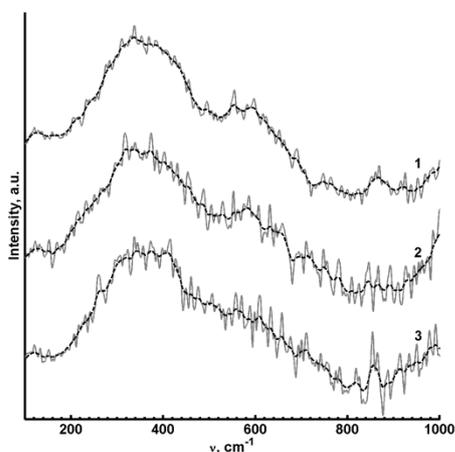


Figure 2. Raman spectra of $\text{Dy}_2\text{Zr}_2\text{O}_7$ powders (1, 2) and ceramic pellet (3) prepared by calcination at different temperatures: 1 – 1200; 2 – 1400; 3 – 1450 °C

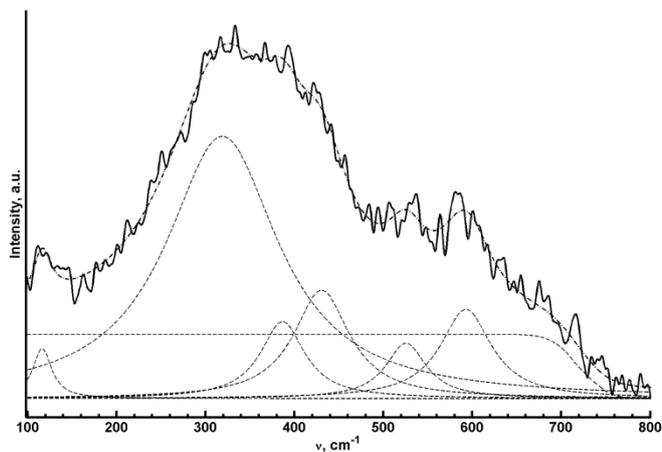


Figure 3. Raman spectrum of $\text{Dy}_2\text{Zr}_2\text{O}_7$ (1450°C/4 h): solid line – experimental spectrum; dashed lines approximation curves.

Raman spectroscopy data are represented in Figure 2. One can see that the Raman spectra of $\text{Dy}_2\text{Zr}_2\text{O}_7$ pellet (1450 °C/4 h) include few broaden modes. The similar spectra were represented at [12]. Quantitative analysis of the received Raman spectrum of $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\text{Dy}_2\text{Zr}_2\text{O}_7$

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 $\text{Dy}_2\text{Zr}_2\text{O}_7$ 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 $\geq 800^\circ\text{C}$ 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 $\geq 1200^\circ\text{C}$ 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.

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