PHASE TRANSITIONS IN CERAMIC AND NANOPOWDER DOPED ZIRCONIA

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Abstract
Zirconia (ZrO₂) doped with rare earth are promising materials for structural applications. The substitutions of Zr with rare earth like Y or with Ce allow the obtaining of ZrO₂ based materials resistant to structural changes around room temperature and avoiding the design of stress tetragonal to monoclinic transformation. The metastable phase formation in ZrO₂ can be induced by including in the oxide structure some vacancy defects. The influence of phase stability of ZrO₂ ceramics following the doping with Y has been investigated. Two types of samples were taken into study, obtained by means of ceramic technology and from ZrO₂ nanopowder doped with yttria and submitted to thermal treatment. The structure of these ceramics and nanoceramics and the phase stabilization using X-ray, neutron diffraction, Scanning Electron Microscopy (SEM) were carried out, Resonant Ultrasound Spectroscopy (RUS) has been used to estimate the presence of low-density regions, state of sintering and the presence and development of small cracks in the structure.

Key words: X-ray and neutron diffraction; crystallites; zirconia-based ceramics; Ce dopants; resonant ultrasound spectroscopy

1. Introduction
Modern medical prosthesis include a wide range of bioactive composites glasses, glass-ceramics and ceramic-polymers. Biocompatibility properties and resistance to mechanical stress represent the most important features when designing new materials based on ceramics for medical implants [1]. Biocompatibility has been defined as the ability of a material to perform with an appropriate host response in a specific application [2]. Biocompatibility is one of the most important advantages of zirconia (ZrO₂)-based ceramics. Mechanical properties and bioinert behavior of ceramic materials based on zirconium oxides were extensively investigated in connection with their possible applications hip implants [3]. However, clarification is still required used annual rates of THA [4]. ZrO₂-based ceramics are preferred due to their advanced mechanical properties [5] (high-fracture toughness and bulk modulus, resistance to corrosion, high dielectric constant, chemical inertness, coefficient of thermal expansion similar to iron). It has been shown that, at ambient pressure, pure zirconia exhibits three crystallographic structures...
[6,7]. Ceramics based on the tetragonal modification T-ZrO$_2$ of zirconium dioxide are now one of the strongest and inert ceramics available. When the ZrO$_2$ is mixed with other oxides such as MgO, Y$_2$O$_3$, Ce$_2$O$_3$, tetragonal phase is stabilized.

The object of this paper is to obtain and to investigate the structure, mechanical properties of Zr$_{1-x}$(Ce/Y)$_x$O$_2$ and its modifications due to the various thermal treatments and variation of Ce/Y concentrations in the samples. The volume expansion caused by the cubic to monoclinic transformation induces large stresses, and these stresses cause ZrO$_2$ to crack upon cooling from high temperatures. By combining characterization techniques based on XRD and ND and Resonant Ultrasound Spectroscopy (RUS), a unique approach on evaluating the physical properties of these ceramics is developed, in order to estimate the presence of low-density regions, state of sintering, and the presence and development of small cracks in the structure and to evaluate the elasticity matrix which could help in advancing the understanding of properties and it’s applications.

2. Materials and methods

The mechanical and chemical properties of doped with rare earth or transition elements zirconia are intensively investigated in the last years. The chemical composition and the phase composition of doped zirconia influence the characteristics of the resulting materials. Zirconia doped ceramics are highly chemical and biological inert materials, but the phase composition could suffer change due to the external mechanical factors. The change of relative concentrations of phase volumes leads to an increase of the defaults concentration and at limit to the appearance of splinters. If we used such materials as implants, they must respect the corresponding standard characteristics [8]. The presence of a small concentration of oxygen defaults could lead to a stabilization effect on ratio between phase volumes concentrations. The substitution of Zr with small amounts of Ce or Y allowed obtaining stabilized zirconia. However, the real effect of concentration of oxygen vacancies on the stabilization is not yet explained. The samples with the chemical composition Zr$_{1-x}$Ce$_x$O$_2$ are obtained by a ceramic method and investigated by the methods already presented [9]. Some crystallographic and mechanical features of the samples are presented in Table 1 according to [10]. The obtained at 1500°C samples were tested by the already mentioned methods and subjected to a thermal treatment at 1000°C by steps of 5°C, 15 hours and following the structural changes. Using ultrasound method described in [11] Young modulus, shear modulus and Poisson ratio were determined from longitudinal and transversal velocities, and are presented in Table 1.

Table 1. Some crystallographic and mechanical characteristics of Zr$_{1-x}$Ce$_x$O$_2$ samples.

<table>
<thead>
<tr>
<th>Ce concentration (x) /Sample #</th>
<th>Molecular Mass</th>
<th>Relative Density (%)</th>
<th>Elasticity Modulus (GPa)</th>
<th>Shear Modulus (GPa)</th>
<th>Poisson Ratio</th>
<th>Diameter [mm]</th>
<th>Length [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09 p2</td>
<td>127.62</td>
<td>84.9</td>
<td>132.75</td>
<td>51.6</td>
<td>0.30</td>
<td>10.86</td>
<td>10.0</td>
</tr>
<tr>
<td>0.13 p3</td>
<td>129.58</td>
<td>94.7</td>
<td>154.22</td>
<td>57.98</td>
<td>0.33</td>
<td>10.48</td>
<td>9.53</td>
</tr>
<tr>
<td>0.17 p4</td>
<td>131.53</td>
<td>99.7</td>
<td>172.82</td>
<td>63.54</td>
<td>0.36</td>
<td>10.34</td>
<td>9.17</td>
</tr>
</tbody>
</table>
In agreement with these data the increase of the cerium concentration in the samples and due the thermal treatment, lead to a variation of the mechanical characteristics (i.e. the sample with Ce concentration of 0.17, Table 1). It means that the mechanical characteristics are strongly influenced by the phase composition.

Two types of compact sets from ZrO$_2$ + 3 mol % Y$_2$O$_3$ nanopowders were prepared. Powders for two types of samples were prepared by co-precipitation method [12]. For the first type - from zirconia oxychloride, and for the second type - from zirconia oxynitrate. After drying in a microwave oven and subsequent calcination at 400°C for 2 hours in a furnace of convection heating the powders was sealed by uniaxial (P = 40MPa) and after that by high hydrostatic pressure (HHP = 500MPa). Investigated samples after baric influence were compact sets in the form of tablets with diameter d = 16 mm and height h = 2 mm. Structure of powders and compact sets was investigated by X-ray diffraction (XRD) using a PANalytical device. Investigation of topology breaks of samples were carried out by scanning (SEM) and transmission (TEM) electron microscopy using JSM640LV and JEM-200A (JEOL) devices respectively. Objects for TEM were prepared by two-stage replicas method [13]. Moisture content in powder was determined by thermogravimetric analysis (TGA) using a specialized weights ADS50 (AXIS) at 120°C. Some of the samples were treated in air at 1000°C for 10 hours. The phase composition as well as type of crystal structure of powder samples were analyzed by conventional X-ray diffractometers (Xpert Pro MPD PANalytical diffractometer (Phillips) with CoK$\alpha$ radiation and a BRUCKER AXS D8- Advance diffractometer) with Cu-K$\alpha$ radiation. A powder diffraction software package which includes the standards of the Crystallography Open Database [14] was used to determine the phase composition. The analysis of crystal structure of ceramic samples has been obtained at room temperature with the time-of-flight method at neutron High Resolution Fourier Diffractometer (HRFD) in experimental hall of pulsed reactor IBR-2, Dubna [15].

Resonant ultrasound spectroscopy (RUS) involves scanning of the resonance structure of a compact specimen (in our case a ceramic cylinder) with the aim of determine its mechanical properties [16-19]. In comparison to other ultrasound methods, resonant techniques are particularly interesting because they allow for easy and inexpensive detection of both internal and surface defects with a single test and has a suite of advantages, among which its applicability to small volume specimens. RUS is based on the principle that the mechanical resonant response of solids depend strongly on its elastic moduli, shape and density. Resonant (or natural) frequencies of a system can be either measured or calculated by solving equations of motion for the known shape [20]. The reverse is also true; if resonant frequencies of an object are known, its elastic properties can be determined [17, 20, 21].

Inhomogeneity in an object may be identified from a resonant frequency spectrum by resonant frequency shifts, peak splitting, increases in peak width and changes in amplitude. The method is based on the estimation of resonant eigenfrequencies [22], based on an eigenvalue and eigenfunction method described using the equation

$$\omega^2 K \alpha = E^\circ$$

(1)

where $\alpha$ is a vector comprising the juxtaposed components of $a_{i,\lambda}$ (the coefficient of the decomposition of the displacement field $\tilde{u}$), $K = \frac{1}{2} \int \rho u_i u_i dV$ and $E = E_c + E_p$ is the total energy. Here, $E_c$ represents the kinetic energy of the system, $E_c = \omega^2 K$ , and $E_p$ represents the potential energy of the system, $E_p = \frac{1}{2} \int 2 \sum C_{ijkl} \partial u_i \partial u_j dV$; $C_{ijkl}$ forms the full linear elastic tensor for a homogeneous body (the compliance tensor), $\omega$ is the angular component of
the frequency, \( \rho \) is the mass density, and \( u \) is the elastic displacement field with the direction subscripts \( i, j, k, l \in \{1,2,3\} \). This problem has been solved for the interest cases.

It is evident that the solutions of the eigenvalue and eigenfunction problem can only be found via numerical methods. The resulting small strain elastic vibrations can be described by the wave equation solution using the tensor linear elastic constants. For a homogeneous and isotropic body [11], the matrix \( C \) is

\[
C = \begin{bmatrix}
K + \frac{4G}{3} & K - \frac{2G}{3} & K - \frac{2G}{3} & 0 & 0 & 0 \\
K - \frac{2G}{3} & K + \frac{4G}{3} & K - \frac{2G}{3} & 0 & 0 & 0 \\
K - \frac{2G}{3} & K - \frac{2G}{3} & K + \frac{4G}{3} & 0 & 0 & 0 \\
0 & 0 & 0 & G & 0 & 0 \\
0 & 0 & 0 & 0 & G & 0 \\
0 & 0 & 0 & 0 & 0 & G
\end{bmatrix}
\]

(2)

where \( K \) is the bulk modulus, \( K = \frac{E}{3(1-2\nu)} \) and \( G \) is the shear modulus, \( G = \frac{E}{2(1+\nu)} \), \( E \) represents the Young’s modulus and \( \nu \) is Poisson’s ratio.

3. Results and discussions

3.1. Structural parameters of sintered and treated samples doped with ceria

The substitution of \( \text{Zr}^{4+} \) (0.98 Å, CN=8) with \( \text{Ce}^{4+} \) (1.11 Å, CN=8) should lead to an increase of lattice constants or/and to structural change, implicitly to a change of phase composition. On other hand, the appearance of \( \text{Ce}^{3+} \) cations (1.283 Å), increases the vacancies concentration of oxygen and stabilizes the tetragonal phase, usual observed in compounds like \( \text{ZrO}_{1.99} \) [23]. For the investigated by X ray diffraction untreated samples, when the Ce concentration increases we observed:

1) a monotonously increase of unit cell volume, of the concentration of the tetragonal phase, of the average size of the crystalline blocks and a decrease of microstrains (Table 2);

2) a monotonously decrease for the monoclinic phase concentration until zero \((x=0.17)\) and of the average size of crystalline blocks, while the unit cell volume increases (Table 2). In the same time the microstrains corresponding to tetragonal phase decrease with the Ce concentration;

The treated samples present always a large concentration of monoclinic phase.

1) The XRD data for all treated samples, including that corresponding to \( x = 0.17 \), indicate the presence of large amounts of monoclinic phase (Table 2);

2) The unit cell volumes of tetragonal and monoclinic phases decreases with the increases of Ce concentration of the samples, this decrease being due probably to the increase of the \( \text{Ce}^{4+} \) concentration with the increase of the total concentration of Ce in the samples.
A complete transition from the monoclinic to tetragonal phase was not observed [9], for the treated samples (Table 2), a maximum for the tetragonal phase concentration correspond to x=0.13.

The unit cells volumes of both tetragonal and monoclinic phase decrease with the increase of the Ce concentration in the samples. This effect is due to a larger concentration of Ce$^{3+}$ in some untreated samples. The microstrains decreases at treated samples with the increase of the Ce concentration.

The experimental points, calculated profile and difference curve of neutronograms are presented in Figure 1.

**Table 2** The crystalline parameters (a, b, c, $\beta$), unit cell volume (V), average size of the crystalline blocks (D) and microstrains ($\delta$) for concentrations of Ce (x) in Zr$_{1-x}$Ce$_x$O$_2$

<table>
<thead>
<tr>
<th>x/ treatment</th>
<th>SG</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>$\beta$ (°)</th>
<th>V(Å$^3$)</th>
<th>D(Å)</th>
<th>$\delta$</th>
<th>Tetragonal phase concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09/ untreated</td>
<td>P2/c</td>
<td>5.1911</td>
<td>5.2204</td>
<td>5.3691</td>
<td>99.08</td>
<td>143.68</td>
<td>1400</td>
<td>0.0011</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>P4$_2$/mc</td>
<td>3.6254</td>
<td>3.6254</td>
<td>5.2145</td>
<td>90.00</td>
<td>68.68</td>
<td>302</td>
<td>0.0493</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P4$_2$/nmcm</td>
<td>3.6254</td>
<td>3.6254</td>
<td>5.2145</td>
<td>90.00</td>
<td>68.84</td>
<td>484</td>
<td>0.0031</td>
<td></td>
</tr>
<tr>
<td>0.13/ untreated</td>
<td>P2/c</td>
<td>5.1948</td>
<td>5.2220</td>
<td>5.3808</td>
<td>99.08</td>
<td>144.14</td>
<td>365</td>
<td>0.0037</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>P4$_2$/nmcm</td>
<td>3.6254</td>
<td>3.6254</td>
<td>5.2145</td>
<td>90.00</td>
<td>68.84</td>
<td>484</td>
<td>0.0031</td>
<td></td>
</tr>
<tr>
<td>0.17/ untreated</td>
<td>P2/c</td>
<td>3.6442</td>
<td>3.6442</td>
<td>5.2443</td>
<td>90.00</td>
<td>69.65</td>
<td>1606</td>
<td>0.0006</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>P4$_2$/nmcm</td>
<td>3.6257</td>
<td>3.6257</td>
<td>5.2198</td>
<td>90.00</td>
<td>68.62</td>
<td>412</td>
<td>0.0018</td>
<td></td>
</tr>
<tr>
<td>0.09/ treated</td>
<td>P2/c</td>
<td>5.1990</td>
<td>5.2188</td>
<td>5.3697</td>
<td>98.92</td>
<td>143.92</td>
<td>1199</td>
<td>0.0015</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>P4$_2$/nmcm</td>
<td>3.6257</td>
<td>3.6257</td>
<td>5.2198</td>
<td>90.00</td>
<td>68.62</td>
<td>412</td>
<td>0.0018</td>
<td></td>
</tr>
<tr>
<td>0.13/ treated</td>
<td>P2/c</td>
<td>5.1923</td>
<td>5.2191</td>
<td>5.3715</td>
<td>99.07</td>
<td>143.74</td>
<td>1294</td>
<td>0.0016</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>P4$_2$/nmcm</td>
<td>3.6243</td>
<td>3.6243</td>
<td>5.2242</td>
<td>90</td>
<td>68.62</td>
<td>859</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td>0.17/ treated</td>
<td>P2/c</td>
<td>5.1843</td>
<td>5.2109</td>
<td>5.3561</td>
<td>99.15</td>
<td>142.85</td>
<td>598</td>
<td>0.0007</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>P4$_2$/nmcm</td>
<td>3.6259</td>
<td>3.6259</td>
<td>5.2127</td>
<td>90.00</td>
<td>68.53</td>
<td>458</td>
<td>0.0006</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3. Structural and refinement parameters of Zr$_{1-x}$Ce$_x$O$_2$ (x= 0 – 0.17) at room temperature obtained by processing the data measured with HRFD, Dubna.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Composition</th>
<th>$x=0$ monoclinic</th>
<th>$x=0.09$ monoclinic/tetragonal</th>
<th>$x=0.13$ tetragonal</th>
<th>$x=0.17$ tetragonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, (Å)</td>
<td>5.1453</td>
<td>5.2039</td>
<td>3.6233</td>
<td>3.6358</td>
<td>3.6452</td>
</tr>
<tr>
<td>b, (Å)</td>
<td>5.2091</td>
<td>5.2148</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>c, (Å)</td>
<td>5.3116</td>
<td>5.3767</td>
<td>5.2159</td>
<td>5.2378</td>
<td>5.2471</td>
</tr>
<tr>
<td>$\beta$, °</td>
<td>99.2252</td>
<td>98.9383</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>V, (Å$^3$)</td>
<td>140.522</td>
<td>144.14</td>
<td>68.476</td>
<td>69.237</td>
<td>69.720</td>
</tr>
<tr>
<td>R$_{wp}$, %</td>
<td>9.53</td>
<td>14</td>
<td>10.4</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>R$_{exp}$, %</td>
<td>7.35</td>
<td>6.62</td>
<td>4.2</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.68</td>
<td>4.44</td>
<td>6.16</td>
<td>5.4</td>
<td></td>
</tr>
</tbody>
</table>

The phase composition obtained by XRD is due to a thin layer on the samples surface, while the data obtained by neutron diffraction correspond to the entire volumes of the samples. The untreated samples corresponding to x=0.17 are formed by a thin layer and an inner core with the same tetragonal structure. A small difference was observed between the unit cell volumes corresponding to these regions.

An important difference there is between the sample corresponding to x=0.09 and x=0.13: The first and second sample have surface layers formed by a mixture of monoclinic and tetragonal phases;
The inner volume of the first sample \((x=0.09)\) contains a monoclinic and a tetragonal phases, while the second sample \((x=0.13)\) contain only a tetragonal phase. The average values of microstrains for the entire samples [9] corresponding to \(x=0.13\) and \(x=0.17\) is about 0.0023.

Fig. 1 Diffraction patterns: a) \(\text{ZrO}_2 - 3\) mol \% \(\text{Y}_2\text{O}_3\) powder, (1), the compact \(P = 40\) MPa (2) and the compact \(P = 500\) MPa (3) for Cl (samples); b) the powder (1), the compact \(P = 40\) MPa (2) and the compact \(P = 500\) MPa (3) for N (b) samples.

A smaller dependence of microstrains on the Ce concentrations as in the thin layers on the surface of the same samples appeared [9] (Table 2).

### 3.2. Structural parameters of sintered and treated samples

TEM images of powders obtained from chloride and nitrate precursors and corresponding microdiffraction patterns are shown on Figure 2a and Figure 1 a1, and Figure 2 b and Figure 2 b1 respectively.

Fig. 2. TEM images of powder system \(\text{ZrO}_2 - 3\) mol \% \(\text{Y}_2\text{O}_3\), 400 °C obtained from chloride (a) and nitrate (b) precursors, and corresponding microdiffraction patterns for this powders (a1, b1 respectively).
The first one is slightly aggregated, but aggregates in both cases are loose, particles are relatively weak interconnected and can be easily separated by low-energy mechanical fields [24]. Microdiffraction structure (Figure 2, a1, Figure 2, b1) is identical for both types of powders. The presented microdiffactograms do not allowed to obtain a difference between cubic or tetragonal phases. Structure corresponds to reflections of Fluorite-like face-centered lattice of cubic crystal system with tetragonal distortions Fm3m or tetragonal (P42 / nmc) modification. The samples CL1 and N1 (Figures 1, a1; 1, b1) contains only one phase. This phase can be identified as cubic (Fm3m) or tetragonal (P42 / nmc), but a mixture between these phases cannot be excluded [25]. This type of structure is also characteristic for compacts obtained using low pressures (curves №2: CL2, N2: Figures 1, a2 and 1, b2). After influence of HHP in both samples small amount (16 and 14% for Cl and N samples, respectively) of monoclinic (secondary) phase can be identified, which is typical for these materials at high pressures [26]. The cubic phases differ from the tetragonal ones by the dimensions of the mosaic blocks (about 11-12 nm for the cubic phases and 6 – 7 nm for the monoclinic ones) and microstrains (0.0028-0.006 for the cubic phases, respectively 0.0034-0.0043 for the monoclinic ones (Table 4-5)). Unit cell volumes vary slightly with applied pressure. In agreement with the TEM data, initial powders derived from both chloride and nitrate precursors were relatively uniformly distributed in volume of samples and have a single phase (t-ZrO2) with average particles size d = 9 nm. The data obtained by TEM measurements are characteristic for a very thin layer (around 100 nm or 1000 Å), while the XRD gave information concerning a thicker layer (10 – 100 µm).

### Table 4 Variation of lattice constants (a, b, c), β angle, unit cell volume (V), average size of crystalline blocks (D), microstrains (ε) and space group (SG P42/nmc) for CL samples

<table>
<thead>
<tr>
<th>Code</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>β(°)</th>
<th>V(Å³)</th>
<th>D (Å)</th>
<th>ε</th>
<th>SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL1</td>
<td>5.117₆</td>
<td>5.117₆</td>
<td>5.117₆</td>
<td>90.0</td>
<td>134.0₃</td>
<td>130.3</td>
<td>0.0060</td>
<td>Fm3m</td>
</tr>
<tr>
<td>CL2</td>
<td>5.103₆</td>
<td>5.103₆</td>
<td>5.103₆</td>
<td>90.0</td>
<td>132.9₃</td>
<td>124.6</td>
<td>0.0056</td>
<td>Fm3m</td>
</tr>
<tr>
<td>CL3_cubic</td>
<td>5.128₁</td>
<td>5.128₁</td>
<td>5.128₁</td>
<td>90.0</td>
<td>134.8₆</td>
<td>114.8</td>
<td>0.0060</td>
<td>Fm3m</td>
</tr>
<tr>
<td>CL3_monoclinic</td>
<td>5.176₉</td>
<td>5.165₄</td>
<td>5.322₀</td>
<td>99.₁₈</td>
<td>140.4₉</td>
<td>66.₉</td>
<td>0.0034</td>
<td>P2₁/c</td>
</tr>
</tbody>
</table>

Investigation of electrical properties of powders by the electrochemical impedance spectroscopy (EIS) was conducted in [15]. The EIS-data shows that the surface component of nanoparticles conductivity for samples obtained from nitrate precursor is on a three orders of magnitude lower than that for samples obtained from chloride precursor ($\sigma_{\text{Cl}} = 1.87 \times 10^{-3} \text{Ohm}^{-1} \text{m}^{-1}$ respectively).

### Table 5 Variation of lattice constants (a, b, c), β angle, unit cell volume (V), average size of crystalline blocks (D), microstrains (ε) and space group (SG P42/nmc) for N samples

<table>
<thead>
<tr>
<th>Code</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>β(°)</th>
<th>V(Å³)</th>
<th>D (Å)</th>
<th>ε</th>
<th>SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>5.10₉₆</td>
<td>5.10₉₆</td>
<td>5.10₉₆</td>
<td>90.₀</td>
<td>133.₄₂</td>
<td>1₁₁</td>
<td>0.₀₀₂₈</td>
<td>Fm3m</td>
</tr>
<tr>
<td>N2</td>
<td>5.₁₂₆₅</td>
<td>5.₁₂₆₅</td>
<td>5.₁₂₆₅</td>
<td>9₀.₀</td>
<td>1₃₄.₇₂</td>
<td>₁₂₅</td>
<td>0.₀₀₅₂</td>
<td>Fm3m</td>
</tr>
<tr>
<td>N3_cubic</td>
<td>5.₁₀₅₅</td>
<td>5.₁₀₅₅</td>
<td>5.₁₀₅₅</td>
<td>9₀.₀</td>
<td>1₃₃.₀₇</td>
<td>₁₀²</td>
<td>0.₀₀₆₀</td>
<td>Fm₃m</td>
</tr>
<tr>
<td>N3_monoclinic</td>
<td>5.₁₈₃₅</td>
<td>5.₂₂₅₅</td>
<td>5.₂₆₈₅</td>
<td>₉₉.₁₈</td>
<td>₁₄₀.₈₈</td>
<td>₇₀</td>
<td>0.₀₀₄₃</td>
<td>P₂₁/c</td>
</tr>
</tbody>
</table>

It can be seen that mass fraction of water in samples obtained from chloride precursor is almost on two times higher than in samples obtained from nitrate precursor: 11.5 and 6.4 wt% respectively. Water in case of oxide nanoparticles is most likely adsorbate [27, 28],
however, surface in case of particles obtained from chloride precursor coated with a more dense layer of ionized water than in case of powders obtained from nitrate precursor. Consequently, chemical prehistory determines physical properties of nanoparticles surface, in particular its degree of hydration.

3.3 Resonant ultrasound spectroscopy

The calculation of vibration modes of elastic objects with free boundaries is a classic problem in mechanics. Unfortunately, exact analytical solutions exist only for few cases such as isotropic spheres, cylinders and certain models of a parallelepiped [29]. In most cases, approximation methods as finite element method (FEM) or Rayleigh-Ritz method must be used for estimating the eigen-frequencies of normal modes [30].

Using finite element method, vibration modes are obtained, the amplitude of signal in in spectra has dependence by properties (especially to the crystallographic structure and density) of the sample. The simulated information [10] is very important to determine which of the resonances are observables for investigated spectra and correspond to those experimentally obtained. The inhomogeneities inside the material can be identified from the resonance spectrum, by changes of the resonance frequency, splitting of peaks/increasing of their width, and modifications in amplitude [19]. The main elastic properties of the sample are obtained by used the inversion of data, that implying conjugate gradient method minimizing the objective function [10]. The optimization problem was numerically solved using Matlab 2014. The inversion was applied only for determination of $E$ and $G$, and not for geometrical dimensions and respectively for densities of the cylindrical samples made from zirconia. The variation of crystallographic structure from sample modifies the position of the peaks from spectrum as well as their amplitude. Figure 3 presents the resonance spectrum between the 260 kHz and 340 kHz.

![Resonance ultrasound spectra for samples p2–p4.](image)

4. Conclusions

The $Zr_{1-x}Ce_xO_2$ samples treatments parameters can strongly changes the phase composition, lattice constants, microstrains and average size of the crystalline blocks. A treatment at low temperature could induce an increase of monoclinic phase concentration. Always there are two region in the samples, with will differ one to another by the concentrations of monoclinic and tetragonal phases.
Nanopowders doped with yttrium have a much smaller average size of crystalline blocks as compared with the doped cerium zirconia powders. On other hands, we have another phase composition in the case of nanopowders. It seems that such nanopowders are formed by a thin layer with a possible tetragonal structure and a core volume with a cubic structure. For some nanopowders, the presence of a small amount of foreign phase, attributed to a monoclinic structure was observed. The Resonant Ultrasound Spectroscopy had emphasized the material inhomogeneities by identification in resonance spectra of splitting of peaks/increasing of their width, and modifications in amplitude.

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References


