MONITORING TECHNIQUE FOR NANOCRYSTALLINE STABILIZED ZIRCONIA FROM SOME MEDICAL PROSTHESIS

Adriana SAVIN 1, Mihail-Liviu CRAUS 1,2, Vitalii TURCHENKO 2, Alina BRUMA 3, Sylvie MALO 4, Tatiana E.  
KONSTANTINOVA 5 and Valerii V. BURKHOVETSKY 5

1 Nondestructive Testing Department, National Institute for Research and Development for Technical Physics, Iasi, 
Romania
2 Frank Laboratory for Neutron Physics, Joint Institute for Nuclear Research, Dubna Russia
3 National Institute of Standards and Technology, Gaithersburg, MD USA
4 Laboratory of Crystallography and Materials Science (CRISMAT), CNRS-ENSICAEN- Université de Caen 
Basse Normandie, Caen, France;
5 Department of Physical Materials Science, Donetsk Institute for Physics and Engineering named after O.O. 
Galkin of National Academy of Sciences of Ukraine, Donetsk, Ukraine

asavin@phys-iasi.ro

Abstract
The medical prosthesis components made from (ZrO2)-based ceramics present a very good biocompatibility as 
well as especially mechanical properties. Much more, the problems of nondestructive examination for these 
elements, which assure both comfort and maximum safety to the patient, are imperative for these medical implants. 
Our aim is to obtain zirconia doped with Ce ceramics, to determine their structural and mechanical characteristics 
by various methods (XRD, ND, SEM, RUS).

Keywords: X-ray and neutron diffraction; crystallites; Zr-based ceramics; Ce dopants; resonant ultrasound 
spectroscopy

1. Introduction
Biocompatibility is one of the most important features for the ceramics used in medical 
prosthesi, weather biopassive, bioactive or resorbable ceramics [1]. Medical ceramics 
materials include a wide range of bioactive composites such as glasses, glass-ceramics and 
ceramic-polymers. From this class of materials ceramics may be manufactured either in porous or dense forms, bulk or granules and, most recently, as a form of coating [2]. From all 
the properties of ceramics used in medicine as implants, biocompatibility and resistance to 
mechanical stress are one of the most important features when designing new materials for 
such applications. It has been well established in literature that tetragonal Zr-based ceramics 
are one of the most desirable, strongest and inert form of ceramics available [3]. The implants 
should be modular i.e. adapting the shape of the implant and the geometry of the prosthesis 
to each patient is of primordial importance. Moreover, both the primary surgery or revision 
procedures should be considerably simplified. A crucial feature of ceramic-based medical 
implants is the mechanical resistance under stress. If the stress exceeds a certain limit 
deformation and mechanical failure will push the material to crack into splinters. These limits 
are material specific, however, the mechanical properties and the stress intervals are specified 
in the BS EN ISO 13356/2013 standard and every implant material should be designed in 
order to accomplish these specifications. The present paper proposes complementary methods 
for the study of the phase stability and mechanical properties of Zirconium based ceramics, 
specifically ZrO2 composites doped with Ce ions. By combining characterization techniques
based on X-ray (XRD) and neutron diffraction (ND) with microstructure characterization based on microhardness measurements and non-destructive evaluation methods based on Resonant Ultrasound Spectroscopy (RUS), we aim to investigate the properties of the most suitable ceramics used for potential medical applications.

2. Materials and methods

The samples were sinterized using standard ceramic technology, starting from a mixture of ceria and zirconia which are used in proportions established a priori. The samples have undergone a process of grinding and pressing in the form of cylinders and sintered in air at a temperature of 1500 °C for a total of six 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) and a BRUCKER AXS D8- Advance diffractometer) with Cu-Kα radiation. A powder diffraction software package which includes the standards of the Crystallography Open Database (COD) [http://www.crystallography.net] was used to determine the phase composition. The structural analysis of ceramic samples Zr1-xCexO2 was performed at room temperature using the time-of-flight High Resolution Fourier Diffractometer HRFD) instrument at the IBR-2 pulsed reactor in JINR Dubna, Russia [4]. At this diffractometer the correlation technique of data acquisition is used, which provides a very high resolution (∆d/d ≈ 0.001). It is practically constant in a wide interval of dhkl spacings. The high-resolution diffraction patterns were collected by detector, placed at back scattering angles (2θ = ±152°, dhkl = 0.6 – 3.6 Å). The crystalline structure constants, atomic positions were determined by using FullProof Software. The crystallite shape and size has been characterized using a Scanning Electron Microscope JSM-6490LV. The resonance frequencies of the samples have been analyzed using a Resonant Ultrasound Spectroscopy (RUS) technique. For this purpose, the ceramic sample is supported by two piezoelectric US sensors, emission - reception placed at opposite edges of the ceramic cylinders. A Network/Spectrum/Analyzer 4395A Agilent USA generates a sweep frequency between 80 kHz and 250 kHz in 1 kHz step. The signal is amplified into a Power amplifier AC 1012 AG&TC Power Inc. USA and applied to an US emission sensor P111.O.06P3.1 type, selected for the large bandwidth. The signal delivered by the reception sensor, identical to the emission one, is applied to the B port of the 4395A Agilent, the spectrum being acquired by a PC that is used also to program the functioning of the equipment with a numerical code developed in Matlab 2014b, via PCIB interface. The command of the power amplifier is made with the same PC via RS232 interface.

3. Results and discussions

The crystallite structure for the three analyzed samples is shown in Figure 1 (a)-(c). For the three compositions studied here, it is observable that the size of the crystallites varies from 2-6 µm. The sample containing a Ce concentration of x=0.09 is formed by an agglomeration of crystallites which appears more faceted and pronounced, in contrast to the observed structure of the sample at compositions x=0.13 and x=0.17 where the shape of the crystallites appears to be more planar and the faceting character is less evident.

The electron microscopy indicated important change of the samples with the increase of Ce concentration.
Determination of chemical composition has been carried out by EDX (the electrons bundle reach the sample, products a characteristic radiation for each element by the envisaged zone) (Figure 1 (d)-(f)). The characteristic radiation intensity determines the concentration of each element from the envisaged zone. Few determinations were performed for each sample and the average concentrations for each element has been determined.

4. XRD analysis

Figure 3 and table I are emphasizing the X-ray diffractograms of the Zr1-xCexO2 samples (nominal composition). The diffractogram is relieve the existance of three phases, namely cubic (space group Fm3m), tetragonal (space group P42/nmc) and monoclinic (space group P21/c). As observed from Table 1, the relative concentrations of phases depend on the ratio between the Zr and Ce concentrations. Moreover, as the concentration of Ce is increasing, the unit cell volume of the monoclinic phase is decreasing, while the tetragonal unit cell slowly increases, as shown in Table 1. In Table 1, we are presenting a set of crystallographic features for each of the samples in the compositional range (x=0.09 – 0.17).
Table 1 shows that the Ce concentration influence on the characteristics of the resulting material, as follows. The X-ray and neutron data of the compound Zr1-xCexO2 (x=0.09-0.17) emphasize the fact that the samples are not homogeneous, and the phase composition and each phase of the investigated samples is dependent on the Zr/Ce ratio. Our XRD analysis has shown that for x=0.09. It is visible that the tetragonal phase is stabilized for all the compositions. The monoclinic phase exist in the far ends of the compositional range, and the cubic phase disappears at a composition of x=0.17.

Table 1. Refined structural parameters of Zr1-xCexO2 (x=0.09-0.17) nominal composition at room temperature, obtained by processing the data collected using BRUCKER AXS D8 - Advance diffractometer with Cu-Kα radiation. (x represents the nominal Ce concentration; a,b, c – unit cell constants; β- angle of monoclinic unit cell; D – average size of crystalline blocks; ε- microstrains ).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>x = 0.09</th>
<th>x = 0.13</th>
<th>x = 0.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, (Å)</td>
<td>5.3797</td>
<td>5.220</td>
<td>5.223</td>
</tr>
<tr>
<td>b, (Å)</td>
<td>5.2171</td>
<td>5.222</td>
<td>5.223</td>
</tr>
<tr>
<td>c, (Å)</td>
<td>5.1993</td>
<td>5.220</td>
<td>5.223</td>
</tr>
<tr>
<td>β, (°)</td>
<td>99.059</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>Vcell, (Å³)</td>
<td>144.11</td>
<td>142.20</td>
<td>142.50</td>
</tr>
<tr>
<td>Volume fraction</td>
<td>0.514</td>
<td>0.826</td>
<td>0.552</td>
</tr>
<tr>
<td>D(Å)</td>
<td>198</td>
<td>514</td>
<td>368</td>
</tr>
<tr>
<td>ε*10³</td>
<td>56</td>
<td>140</td>
<td>46</td>
</tr>
<tr>
<td>Rwp, %</td>
<td>14.3</td>
<td>10.4</td>
<td>10.4</td>
</tr>
</tbody>
</table>

5. Neutron diffraction data

Neutron diffraction (ND) performed on Zr1-xCexO2 (x=0.09-0.17) indicated that the sample corresponding to x=0.09 contains only two phases: one tetragonal (P42/nmc) and other monoclinic (P21/c) (Table. 2). The increase of concentration of Ce ions leads to changing of crystal structure from monoclinic to tetragonal (P 42/nmc) with two formula units (Z=2) per unit cell. (Table 2).

Table 2. Refined structural parameters of Zr1-xCexO2 (x=0.09-0.17) at room temperature, obtained by processing the data collected using the High Resolution Fourier Diffractometer (neutron diffractometer) at IBR-2 reactor FLNP-JINR (x represents the nominal Ce concentration; a, b, c – unit cell constants; β- angle of monoclinic unit cell; Vcell – unit cellvolume ).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>x = 0.09</th>
<th>x = 0.13</th>
<th>x = 0.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, (Å)</td>
<td>5.2039</td>
<td>5.220</td>
<td>5.223</td>
</tr>
<tr>
<td>b, (Å)</td>
<td>5.2148</td>
<td>5.222</td>
<td>5.223</td>
</tr>
<tr>
<td>c, (Å)</td>
<td>5.3767</td>
<td>5.220</td>
<td>5.223</td>
</tr>
<tr>
<td>β, (°)</td>
<td>98.938</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>Vcell, (Å³)</td>
<td>144.140</td>
<td>68.476</td>
<td>69.720</td>
</tr>
<tr>
<td>R, %</td>
<td>14.0</td>
<td>10.4</td>
<td>10.4</td>
</tr>
</tbody>
</table>
We consider that the difference between the XRD results and ND results are due to a change of the chemical composition of the samples, which have other chemical composition at surface comparing with the bulk samples.

6. Resonant ultrasound Spectroscopy

Resonant ultrasound spectroscopy (RUS) is a complex method, involved scanning the resonance structure of a compact specimen such as cube, sphere or short cylinder [5], and represent a means of determining material mechanical properties of an elastic object by exciting the resonant frequencies (normal modes) of the object. The measurements are carried out with sensors with contact. The coupling of the sensor with specimen influences which modes are measured. When the sample is pinned on its edge, more modes are excited and the modes are better defined than when the sensors are placed on the ends of the cylinder (Figure 3). The probe is fixed between the emission and reception sensors in order to accomplish the condition of stress free surface. This type of placement (classical RUS) assures weak elastic coupling with the transducer, reducing the loading, in the same time, the corners are elastic active (that is, they are never nodes), thus coupling all normal vibration modes. An important aspect of RUS analysis is correct identification of normal modes excited so that the measured frequencies might be correlated with those determined by inverse problem. As a nondestructive method RUS offers unique advantages, research of materials science used of RUS include measurement of elastic constants with accurately on samples as small as 100µg [6]. During the period, the researchers covered nearly all of the important aspects of RUS [7-9] (resonant sphere technique, rectangular parallelepiped of an anisotropic, crystalline material as well as for spheres of isotropic materials, extending the limits of technique). We employed RUS method (in our case a ceramic cylinder) in order to estimate the presence of low density regions, state of sintering, and the presence and development of small cracks in the structure, by evaluating the complete elasticity matrix. The elasticity of a material is the predisposition of a material to return to a minimum energy configuration. In principle, all of this information can be acquired from a single, accurate measurement of an object’s resonant spectrum. Resonant (or natural) frequencies of a system can be either measured or calculated by solving equations of motion for the known shape [10]. The reverse is also true; if resonant frequencies of an object are known, its elastic properties can be determined [11-13]. 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. We have used an equipment configuration as the one shown in Figure 3.

![Figure 3. RUS Experimental setup schematic block diagram. Thin lines correspond to coaxial cable for sinusoidal wave transmission; thick lines are GPIB cable for digitalized data](image-url)
In order to determine mechanical properties of a compact specimen (in our case a ceramic cylinder), the resonance structure is scanned by RUS [5, 9, 11, 14]. This analysis comes in completion and adds more information related to the structural analysis performed above. 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 it has a suite of advantages; among them is 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 [10]. The reverse is also true: if resonant frequencies of an object are known, its elastic properties can be determined.

The method is based on the estimation of resonant eigenfrequencies, based on an eigenvalue and eigenfunction method [2] described using the relation developed in [5]. In the case of cylindrical samples, having diameter approx. equal with height, the first mode is the fundamental torsional mode allowing the direct determination of shear modulus. RUS involves scanning the resonance structure of a compact specimen (in our case a ceramic cylinder) with the aim of determining its mechanical properties [5], [15]. RUS involve three parts:
- one of this method implies the obtaining of a resonant ultrasound spectrum, meaning obtaining the frequency answer for a certain excitation for the analyzed sample;
- need to develop a computing method which can help in predicting the resonant ultrasound spectrum for the estimated parameters;
- the third component represents the iterative refinement of the estimated parameters, in agreement with the measured spectrum.

Each of the steps mentioned above have multiple solutions. The solutions of the eigenvalue and eigenfunction problem can only be found via numerical methods. The shear modulus was determined by identification of lowest torsion mode and use of relation \[ f = \frac{m}{2L} \sqrt{\frac{G}{\rho}} \] with \( f \) frequency measured; \( L \) length of sample; \( G \) isotropic shear modulus; \( \rho \) density of sample; \( m \) is an integer (for the fundamental \( m=1 \)). The densities of the samples were obtained by means of Archimedes’ method, by using water as fluid.

Due to the fact that the samples in the compositional range \( x=0.09-0.17 \) are axisymmetric, isotropic, and homogeneous [8], we can conclude that every mode observed on samples must fall into the following three categories [5]: torsional axisymmetric pure share motion; extensional axisymmetric mixtures of compression and shear modulus; flexural modes along paths that are tilted with respect to the cylinder axis (these modes occur in pairs named doublets, with the same resonance frequency).

The RUS method allowed the validation of the data obtained via X-ray and neutron diffraction. We are emphasizing the resonance spectra of the samples in the compositional range \( x=0.09-0.17 \) in Figure 4.

The RUS spectrum describes a large amplitude response detected when the frequency corresponds to one of the samples eigenfrequencies.

It is immediately observed that for the three samples, there is a pronounced amplitude response in intervals of frequency corresponding to the samples eigenfrequency. The amplitude responses in the swept frequency range are in tight connection to the sample’s properties, especially the ones related to the density. The eigenfrequency intervals exhibit a slight shift towards smaller values as the density of the samples. It is important to specify that the simulated information is useful to determine which of the resonances are observables for an investigated spectrum.
The optimization problem has been numerically computed in Matlab 2014a. Because the number of peaks and the corresponding frequencies is relatively small, the inversion was only applied to determine the Elastic (E) and shear (G) moduli and not the geometrical dimensions and densities of the cylindrical samples made from zirconia. An increase of the relative density with Ce concentration take places (Table 3).

Table 3. Some crystallographic and mechanical characteristics of Zr$_{1-x}$Ce$_x$O$_2$ samples.

<table>
<thead>
<tr>
<th>Ce concentration (x)</th>
<th>Molecular Mass</th>
<th>Crystallographic Structure (ND)</th>
<th>Relative Density (%)</th>
<th>Elasticity Modulus (GPa)</th>
<th>Shear Modulus (GPa)</th>
<th>Poisson Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>127.62</td>
<td>monoclinic + tetragonal</td>
<td>88.9</td>
<td>145.85</td>
<td>56.49</td>
<td>0.291</td>
</tr>
<tr>
<td>0.13</td>
<td>129.58</td>
<td>tetragonal</td>
<td>94.7</td>
<td>168.53</td>
<td>64.47</td>
<td>0.307</td>
</tr>
<tr>
<td>0.17</td>
<td>131.53</td>
<td>tetragonal</td>
<td>99.9</td>
<td>193.43</td>
<td>73.16</td>
<td>0.322</td>
</tr>
</tbody>
</table>

We considered that a decrease of the pores concentration takes place with the increase of the Ce concentration in the samples.

7. Conclusions

We employed a set of complementary methods for the determination of crystallographic and mechanical characteristics of a class of ceramics usually employed for biomedical applications, namely Zr$_{1-x}$Ce$_x$O$_2$. We are showing that a set of crystallographic phases are obtained in our samples, with a predominant stabilization of the tetragonal phase for the entire compositional range. Moreover, we emphasize strong mechanical properties of this crystallographic phase and more importantly, for the highest Ce concentration, indicating that, for this composition, x=0.17, these samples can be considered successful candidates for medical prosthesis applications.

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