

The role of local structural distortions in the stabilisation of undoped nanocrystalline tetragonal zirconia



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HIGHLIGHTS

- the undoped tetragonal HT structure is stable at room temperature if the grain size is small enough (below 20 nm).
- undoped and very low Y-doped zirconia are studied by means of PDF refinement and traditional crystallography.
- a local orthorhombic distortion is clearly visible in all samples.
- the low symmetry distortion may be responsible for the room temperature stabilisation, due to the local strain increase.

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ABSTRACT

Nanopowders of pure or very lightly doped zirconia were studied by means of total scattering and pair distribution function analysis, with the aim of understanding how the size of the particles (if a size limit of about 20 nm is not exceeded) tends to stabilise the tetragonal polymorph at room temperature. Total scattering and PDF analyses, together with Rietveld refinements, showed that the tetragonal model is indeed applicable to the average structure of these nanocrystalline zirconia samples, and provided comparable results. However, all the samples, with no influence from the dopant content, showed a similar local distortion for $r < 10$ Å. In this region, the data were fitted with two slightly different tetragonal structures, with a tetragonal distortion that decreases with the R_{\max} used, giving rise to a structure closer to the average tetragonal one (given by Rietveld as well as by average PDF refinements). In the first coordination shell, however, an orthorhombic distortion fits very well both in intensity and in position. This distortion may be responsible of the increased RMS strain local level, and therefore of the stabilisation of the high temperature structure at room temperature.

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1. Introduction

The polymorphism of zirconium oxide (zirconia, ZrO_2) is a deeply investigated topic, for its fundamental aspects and because many technological applications [1] in areas such as energy conversion [2], electrochemical sensors [2], thermal coatings [3], and structural ceramic materials are based on the performing properties of the tetragonal and/or cubic polymorphs. These are thermodynamically stable above 1175 and 2370 °C, respectively, while the monoclinic form is stable in the lowest temperature range. It is well known that doping zirconia with lower valence cations (Ca^{2+} and Y^{3+} are the most popular) produces a good solid electrolyte. Doping

both stabilizes the high temperature polymorphs and strongly enhances oxygen ion transport in these phases by supplying oxygen vacancies through compensation of the substitutional defects.

It is now clear that nano-structured materials are an effective route for achieving both issues without doping, or with fairly lower amounts of doping. A size-induced stabilization of the tetragonal polymorph has been first found by Garvie [4,5] to the best of our knowledge. For other reports on the stabilization of tetragonal zirconia in forms of nanopowders or thin films, we refer to the literature quoted by Shukla and Seal [6] (and references therein). These authors have also reviewed the controversial mechanism by considering the effects of surface energy, strain energy, pressure, structure, phase and chemical impurities, and water vapor, and propose that generation of excess oxygen ion vacancies within the nanocrystalline ZrO_2 is primarily responsible for the room temperature stabilization of the tetragonal phase.

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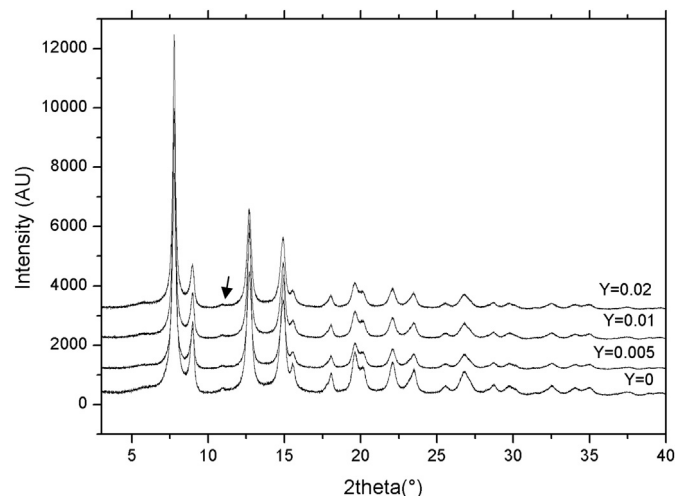


Fig. 1. Data sets of the nanocrystalline zirconia samples. The small peak indicated by an arrow is the (102) of the tetragonal structure.

The present paper is part of a project focussed on fabrication and functional characterization of the fully dense oxides with nanometre-sized grains, which can be produced by sintering of nanopowders without significant grain growth using the high-pressure field-assisted rapid sintering (HP-FARS) technique [7,8]. We here discuss the structural aspects of the starting nanosized powders of this promising fabrication route. Interest into the local structure of size-stabilized zirconia samples is also due to a complex thermal behaviour, where a slow transition of the tetragonal phase into the monoclinic one has been reported to be essentially triggered by the release of the microstrain [9].

Their very limited coherence (just a few nanometres) makes nanocrystals difficult to study. A local probe is necessary in order to highlight the local differences with respect to the average structure obtainable from conventional crystallography. Even in obtaining the latter, difficulties arise when investigating nanocrystals, as the integrated intensities of Bragg's peaks can be determined only with large uncertainty because of the extremely broad profile. Local probes that have been used include EXAFS, Raman spectroscopy, solid state NMR, and also total scattering with PDF analysis. While the scientific literature reports thousands of papers variously dealing with the structure of tetragonal zirconia, we hereafter account only for the few of them concerning the local structure of pure as well as doped nanocrystalline materials.

When investigating the local structure of undoped tetragonal zirconia nanocrystals with different grain sizes in the range of 10 nm, Acuna et al. [10] have shown that the tetragonal model with 4 + 4 equal distances in the first coordination shell of Zr does not fit the EXAFS data, if the Debye–Waller factors of the two subsets are constrained to equal values. When the latter parameters are instead left free to vary independently, the results unquestionably show that one of the two sub-shells is much more disordered than the other one. This can be summarized as a model with 4 + 2 + 2 different Zr–O distances.

Table 1
Rietveld refinements results.

Sample	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i> √2	< <i>D</i> > <i>v</i> (Å)	RMS strain	<i>U</i> (Zr,Y)	<i>U</i> (O)	<i>X</i> (O)	<i>R</i> _{wp} (%)
Y0	3.5963(2)	5.1684(5)	1.015	97.1(1)	0.0015(8)	0.013(1)	0.028(9)	0.282(1)	6.49
Y0.005	3.5964(2)	5.1706(5)	1.017	93.2(1)	0.0024(8)	0.011(1)	0.024(9)	0.281(1)	6.25
Y0.01	3.5972(2)	5.1692(5)	1.016	95.6(1)	0.0023(3)	0.012(1)	0.028(8)	0.280(2)	6.25
Y0.02	3.5988(2)	5.1692(6)	1.016	86.1(2)	0.0021(3)	0.013(1)	0.030(8)	0.278(1)	6.40

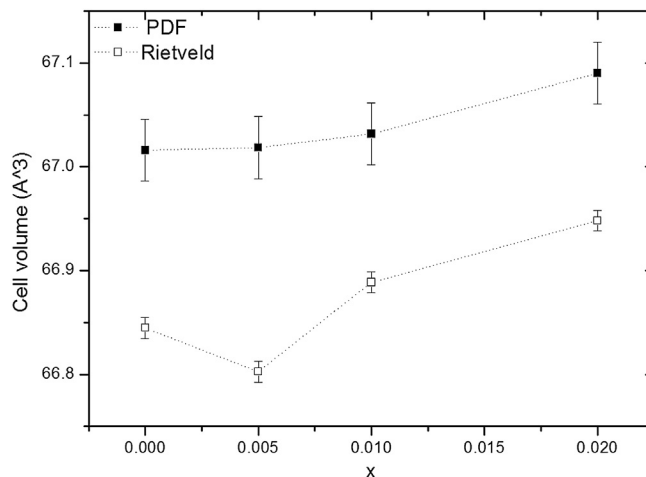


Fig. 2. Comparison of the cell volumes as a function of Y content for Rietveld and average PDF refinements. The dotted line is just a guide for the eye.

Gateshki et al. [11], on the other hand, have shown that the nanocrystalline zirconia obtained from ball-milling of pure monoclinic zirconia, seemingly retains locally its monoclinic structure, while the average structure shifts towards a tetragonal/cubic arrangement. The same local 'monoclinic' environment has been confirmed by two other papers from the same first author [12,13] on nanocrystalline zirconia, synthesised in different ways.

Here we will present the results of a series of total scattering experiment with high energy synchrotron X-rays on undoped (or very lightly doped) nanocrystalline zirconia samples ($Zr_{1-x}Y_xO_2$ with $x = 0.005, 0.01, \text{ and } 0.02$).

The experimental data are processed both in a classical crystallographic way, with the Rietveld method [14] and with the Pair Distribution Function (PDF) approach [15] (and references within). PDF refinements allow to evaluate the local as well as the average structure at the same time, because the whole powder diffraction pattern is taken into account in the assessment of the atomic pair distribution function for the sample under study. As known, heterovalent cation such as Y^{3+} (in place of Zr^{4+}) injects oxygen vacancies: the local environment of zirconium and oxygen atoms in samples with small quantities of Y ($x = 0.005, 0.01, \text{ and } 0.02$) can be directly compared with that of undoped samples obtained through the same synthetic route. The results show that the PDFs of the different samples allows to characterise the variations of local and the average structures, as well as the presence of local distortions and their features.

2. Experimental

ZrO_2 nanopowders with a dopant ($YO_{1.5}$) content ranging between 0 and 2 at.% Y (i.e., from undoped ZrO_2 to $Zr_{0.98}Y_{0.02}O_{2-x/2}$) were obtained using a modified Pechini method, described in details elsewhere [7–9]. The obtained products were calcined at 500 °C for 1 h, in order to avoid the formation of monoclinic zirconia and to promote the smallest possible grain size.

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