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## Crystal Structure and Short-Range Oxygen Defects in La- and Nd-Modified ZrO<sub>2</sub>

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### Abstract

The crystal structure of rare-earth modified zirconia and the associated oxygen defects were studied by neutron diffraction. A Rietveld analysis of the neutron powder patterns of heat treated samples of La- and Nd-10mol%-ZrO<sub>2</sub> revealed the composition of a major tetragonal phase (space group P4<sub>2</sub>/nmc) and a minor cubic phase (space group Fm3m). The short-range oxygen defects structure was examined by a Fourier-filtering technique. A real-space correlation function, obtained from a Fourier transform of the filtered residual diffuse scattering, showed evidence of static, oxygen-vacancy induced atomic displacements along the <111> and other directions of the pseudocubic cell.

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## Introduction

Adding various metal oxides to zirconia not only removes the disruptive structural phase transformations of pure  $ZrO_2$  and partially stabilizes the cubic and tetragonal phases at low temperatures but also improves the physical properties (e.g., thermal shock resistance and ionic conductivity) to meet the demands for technological applications. Partially stabilized zirconia using alloying oxides such as calcia, magnesia and yttria has been the subject of numerous investigations.<sup>1</sup> When the dopant cation has a lower valency than the Zr ion (+4), oxygen vacancies are formed to preserve electroneutrality. It has been found that the phase formation and the defect structure are very sensitive to processes of the synthesis such as agglomeration in the precursor and heat treatments of the samples.

In the case of rare-earth modified zirconia, although the high-temperature, rare-earth rich phases have been previously characterized<sup>2-5</sup>, the metastable phases of low-concentration rare-earth (other than La and Ce) doped zirconia were reported<sup>6</sup> only recently. These rare-earth doped zirconia were prepared by coprecipitation from an aqueous solution of zirconium oxychloride and rare earth chlorides, followed by heat treatments up to 1200° C. They show good thermal stability and large surface area for use as a catalyst support. Using x-ray diffraction and Raman scattering evidence of both metastable cubic and tetragonal phases as well as microstrain and short-range ordering due to defects was found in the 10 mol% Nd, Gd, Dy and Yb doped powders heat treated up to 1000° C. X-ray diffraction patterns of the 10 mol% La and Nd samples heated to 600° C indicated a dominant pseudocubic structure in disagreement with the Raman results. The broad peak profiles and the insensitivity to the oxygen atoms by x-rays have hindered a quantitative analysis of the crystal structure. The neutron scattering cross sections of oxygen, zirconium and rare-earths are comparable, thereby offering a means to better characterize the crystal and defect structure of these materials. Here we present the results of neutron diffraction studies of the La and Nd 10mol% doped  $ZrO_2$ .

which were subjected to heat treatment at 600 and 800° C for 3 hours. Rietveld analyses of the diffraction patterns revealed the presence of a major tetragonal phase and a minor cubic phase in all the samples. The residual diffuse scattering, analyzed by a Fourier-filtering technique, showed evidence of short-range defect structure induced by oxygen vacancies. In particular, the derived real-space pair correlation functions indicated atomic relaxation along the  $<111>$  direction of the pseudocubic cell and additional small displacements of atoms surrounding the oxygen vacancies in other directions.

## Results and Discussion

About 10 g each of La and Nd 10mol% doped  $\text{ZrO}_2$  powders,  $\text{La}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  heat treated to 600° C and  $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  heat treated at 600 and 800° C, were studied by neutron diffraction at room temperature using the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. Details concerning the method of samples preparation have been given previously elsewhere.<sup>6</sup> The data were collected by detectors at a back-scattering geometry (a mean detector angle of 148°) for which a resolution of  $\Delta d/d = 0.25\%$  can be achieved (d is the atomic plane spacing).

Pure  $\text{ZrO}_2$  has three polymorphs: a cubic fluorite structure (space group Fm3m) above 2640 K, a tetragonal structure (P4<sub>2</sub>/nmc) between 1400 and 2640 K, and a monoclinic structure (P2<sub>1</sub>/c) below 14000 K. Rietveld refinements of the neutron powder patterns of the La and Nd doped  $\text{ZrO}_2$  were carried out using a two-phase analysis: the tetragonal and cubic structures of the parent compound. The rare-earth atoms are assumed randomly substituting the Zr atoms. Fig. 1 shows the observed, background-subtracted and the fitted powder pattern over the 0.48-1.66 Å d-spacing range of the  $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  sample heated at 800° C. Similar results were also obtained for the  $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  and  $\text{La}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  samples heated at 600° C. In general, the peaks are broadened considerably by the effects of small grain sizes (crystallite  $\eta$

$\approx 30$  nm) and large compositional fluctuations of the metastable phases as indicated by the previous x-ray studies.<sup>6</sup> However, all the Bragg peaks and their intensities are adequately accounted for by the tetragonal and cubic two-phased structure. It turns out that the tetragonal form is the dominant phase in all cases. Similar Rietveld analysis of the x-ray data, on the other hand, failed to unambiguously distinguish these phases probably due to the lack of sensitivity to the oxygen atoms and the rather poor resolution of the x-ray measurements.

We now discuss the defect structure associated with the oxygen vacancies in these materials. A close examination of the residual intensities of the Rietveld analyses revealed evidence of a very broad, oscillatory component characteristic of diffuse scattering from defects of short-range order (e. g., see Fig. 1). Such diffuse residual intensities were analyzed by a Fourier-filtering technique to extract information regarding the nature of the defect structure. The details of this technique have been previously described elsewhere.<sup>7</sup> Briefly, the oscillatory component was fitted by a smooth function thereby filtering out the sharp features due to the crystalline contribution. The fitted function is then Fourier transformed into the real space, yielding a correlation function,  $D(r)$ , similar to the radial distribution function used to describe amorphous materials.  $D(r)$  displays maxima at interatomic spacings characteristic of the short-range interactions giving rise to the diffuse scattering. The obtained  $D(r)$  for the  $Nd_{0.1}Zr_{0.9}O_{1.95}$  sample heated at  $800^\circ C$ , as shown in Fig. 2, shows maxima at about 2.12, 2.69, 3.57 and 4.27 Å. Analyses of the other two samples show similar features. To facilitate a better fit of the crystalline component, the inverse Fourier transform of  $D(r)$  truncated at an appropriate value of  $r_{max} = 5$  Å is subtracted off from the observed data, followed by a further Rietveld refinement. An example of the results of the Fourier-filtered fit is displayed in Fig. 3 which shows a better agreement with the two-phased crystal structure. A summary of the Fourier-filtered, Rietveld refinements for the three samples is given in Table I.

The neutron-diffraction results indicate that although the crystal structure of La- and Nd-doped  $ZrO_2$  can be adequately explained by the tetragonal and cubic phases, there also exists a small disordered component characteristic of short-range atomic correlation. This disordered structure is caused by atomic relaxation from the crystallographic positions induced by nearby oxygen vacancies. To the best of our knowledge we are not aware of any detailed investigation of oxygen-vacancy induced defects in these series of rare-earth modified zirconia. Similar defects in yttria-stabilized zirconia, on the other hand, have been studied extensively by many authors<sup>8-12</sup>. For example, the results of an EXAFS study was attributed by Catlow *et al.*<sup>8</sup> to the preference of oxygen vacancies sited adjacent to  $Zr^{4+}$  rather than  $Y^{3+}$  ions, for which relaxation of cations leads to a disparity of the mean Zr-O and Y-O distances. A range of atomic displacements along the pseudocubic  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions were reported from x-ray or neutron scattering studies.<sup>9-11</sup> The present neutron-diffraction results of La- and Nd-doped  $ZrO_2$  agree qualitatively with these interpretations. The correlation function of the defect structure obtained from Fourier-filtering suggests a distribution of Zr(La, Nd)-O distances centered at  $2.12 \pm 0.03$  Å corresponding to relaxation along the  $\langle 111 \rangle$  direction and additional atomic correlation at  $2.66 \pm 0.04$ ,  $3.55 \pm 0.04$  and  $4.32 \pm 0.05$  Å. Clearly, a systematic study of rare-earth modified zirconia at various stoichiometry and temperatures would be helpful in understanding the crystal and defects structure.

## Acknowledgment

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Table I. The crystal structure derived from Rietveld refinement.

	La <sub>0.1</sub> Zr <sub>0.9</sub> O <sub>1.95</sub> heated at 600°C	Nd <sub>0.1</sub> Zr <sub>0.9</sub> O <sub>1.95</sub> heated at 600°C	Nd <sub>0.1</sub> Zr <sub>0.9</sub> O <sub>1.95</sub> heated at 800°C
Tetragonal P4 <sub>2</sub> /nmc <sup>a</sup>			
a (Å)	3.6447 (5)	3.6346 (5)	3.6293 (3)
c (Å)	5.2034 (10)	5.2020 (11)	5.1895 (8)
z	0.0324 (6)	0.0392 (8)	0.0412 (6)
Composition (%)	94.8	74.5	74.7
Cubic Fm3m <sup>b</sup>			
a (Å)	5.1149 (20)	5.1403 (11)	5.1540 (7)
Composition (%)	5.2	25.5	25.3
Weighted R (%)	4.7	6.8	6.0

<sup>a</sup> 2 Zr (a) 3/4, 1/4, 3/4; 1/4, 3/4, 1/4;  
4 O (d) 1/4, 1/4, z; 1/4, 1/4, z+1/2; 3/4, 3/4, -z; 3/4, 3/4, -z+1/2.

<sup>b</sup> 4 Zr (a) 0, 0, 0; F.C.

8 O (c) ±(1/4, 1/4, 1/4); F.C.

## Figure Captions:

Figure. 1 Rietveld profile fit in the 0.48-1.66 Å region of d-spacing for the  $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  sample that was subjected to heat treatment at 800°C. The symbols (+) are the observed, background subtracted intensities. The solid line represents the calculated crystalline intensities. Tick marks of the top and bottom rows indicate the positions of the Bragg reflections for the cubic and tetragonal phases, respectively. The residual intensities are shown at the bottom of the figure.

Figure. 2 Correlation function,  $D(r)$ , calculated from the filtered residual intensities from the Rietveld refinement of the  $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  data (see Fig. 1). The features below 2 Å are noise due the truncation of data.

Figure. 3 Final Rietveld profile fit for the  $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  sample after Fourier-filtering. Only the 0.48-1.08 Å region of d-spacing is shown.

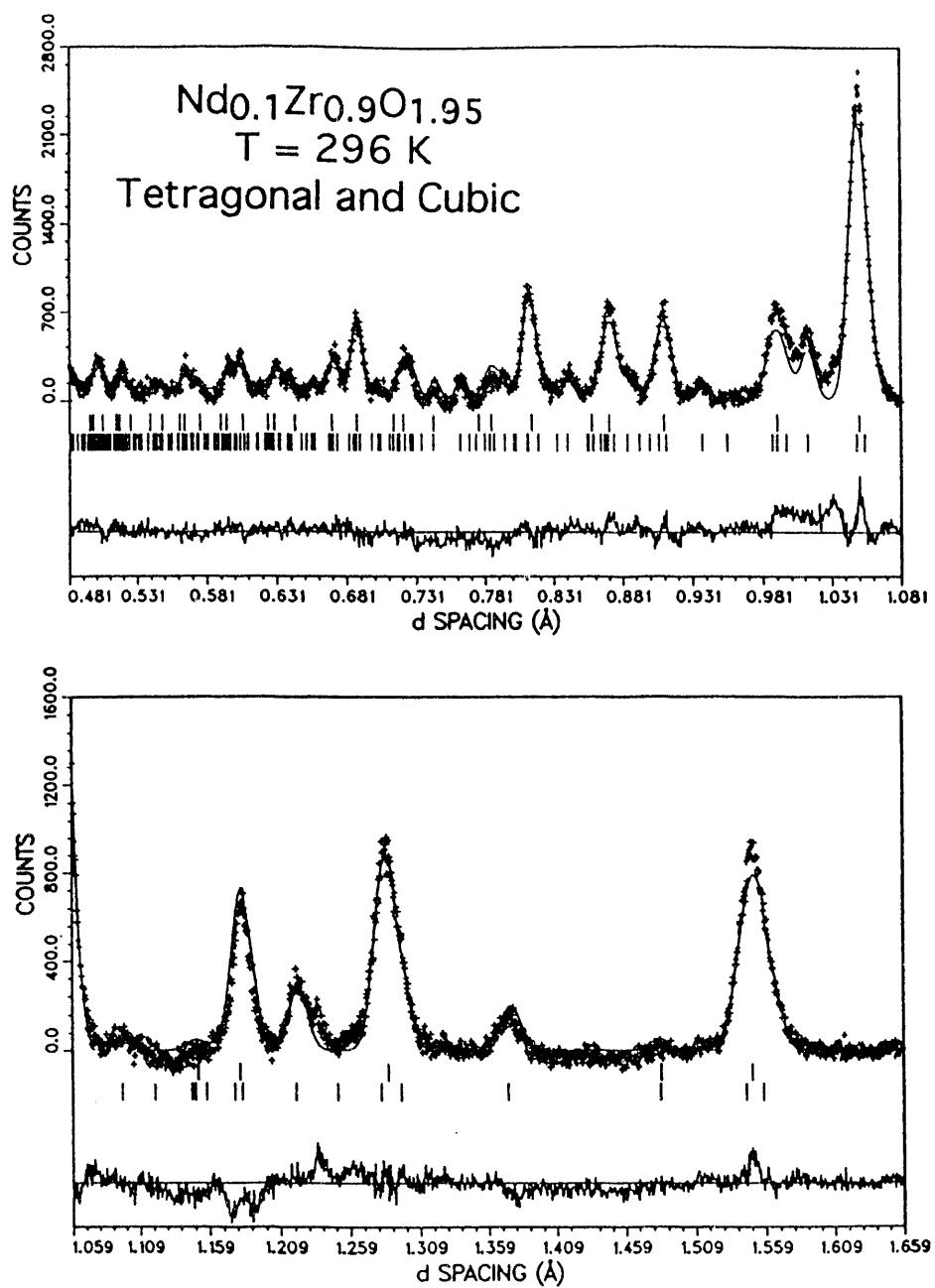


Figure. 1

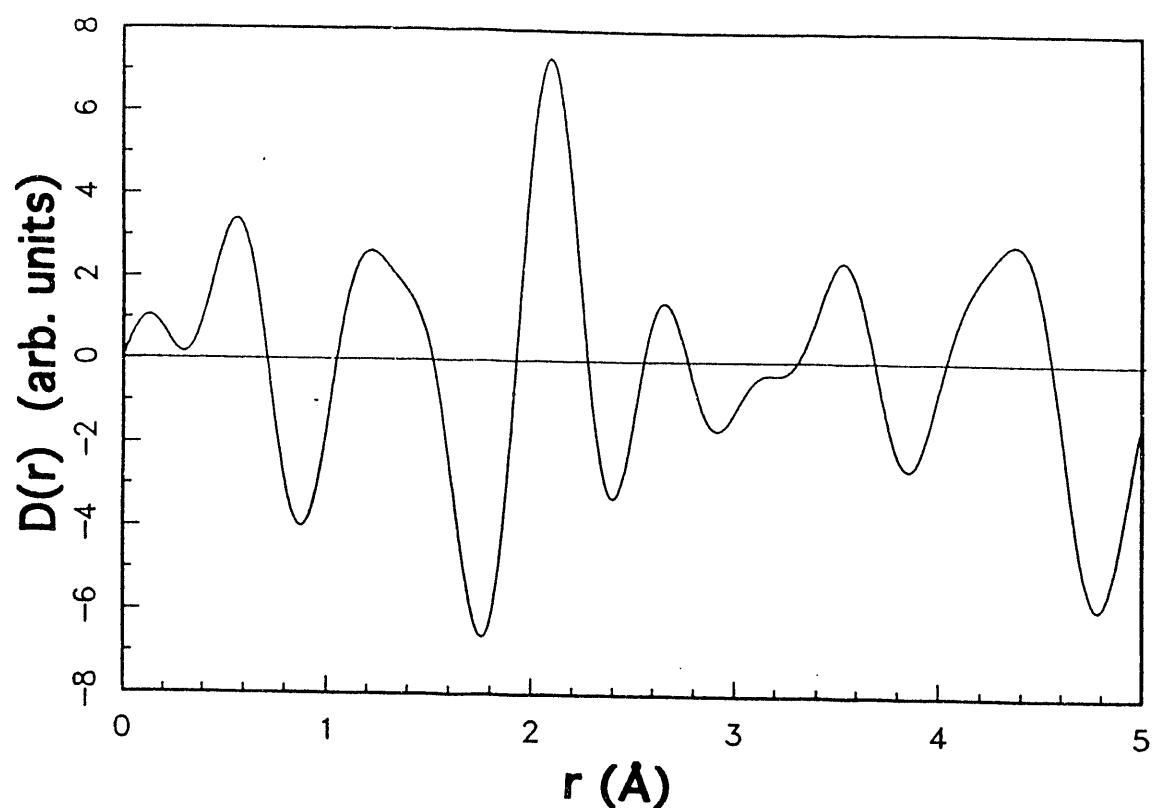


Figure. 2

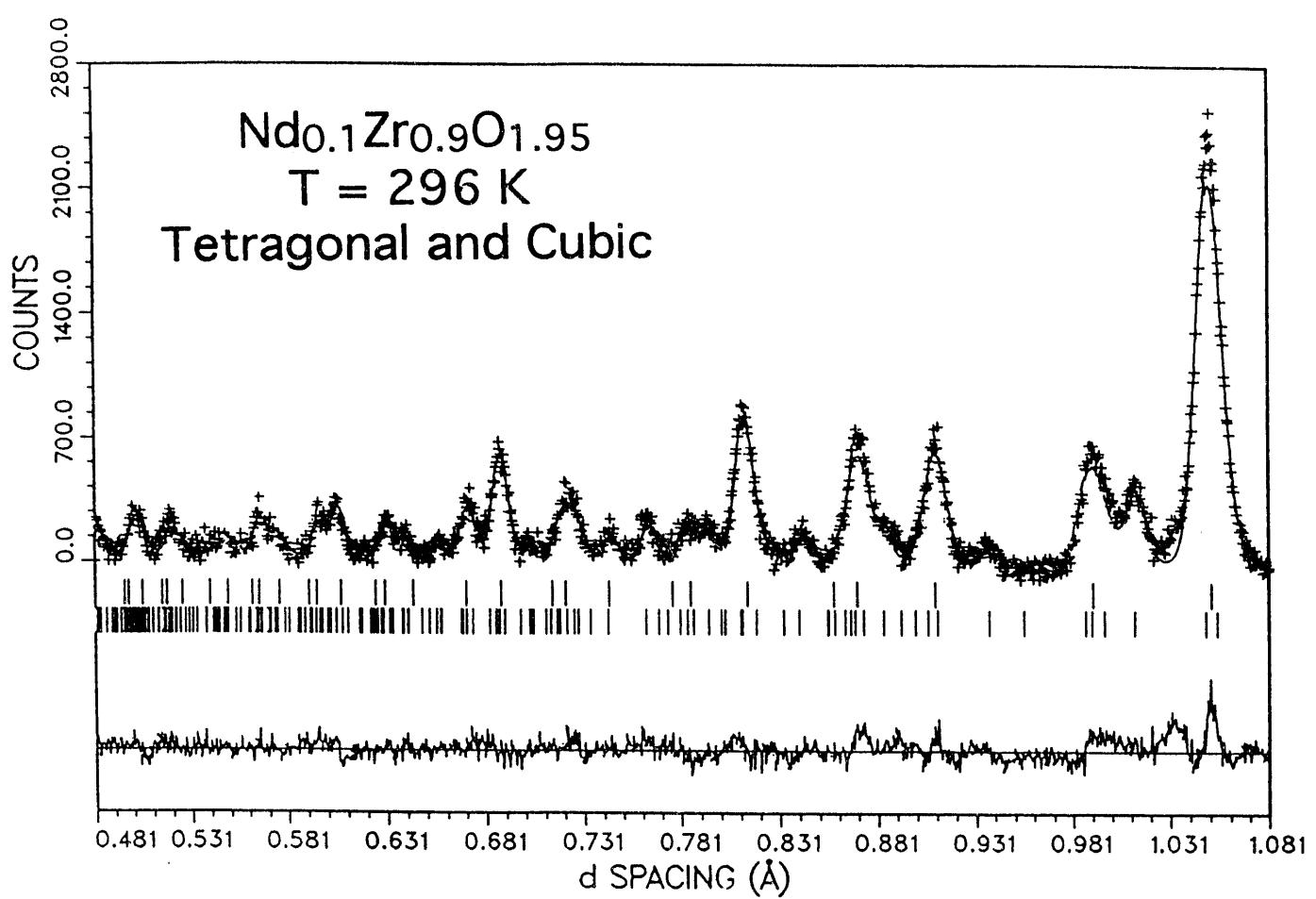


Figure. 3

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