

# Oxygen ion dynamics in yttria-stabilized zirconia as evaluated by solid-state $^{17}\text{O}$ NMR spectroscopy

Tillmann Viehhaus, Thunu Bolse, Klaus Müller \*

*Institut für Physikalische Chemie, Universität Stuttgart, Germany*

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## Abstract

Solid-state  $^{17}\text{O}$  NMR measurements between room temperature and 973 K were performed for the first time on  $^{17}\text{O}$ -enriched yttria-stabilized zirconia samples. Spin–lattice relaxation is found to exhibit a strong temperature dependence which can be traced back to motional displacements of the oxygen ions and which is almost unaffected by the actual sample constitution. Analysis of the spin–lattice relaxation data provides the motional correlation times. The derived activation energies are relatively low with values of about 30 kJ/mol. In addition, large temperature effects are observed for the  $^{17}\text{O}$  NMR line widths, and thus for spin–spin relaxation, which are again attributed to the oxygen ion mobility. In this case, the underlying oxygen motions, however, occur on a length-scale which is different from that probed by spin–lattice relaxation.  
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## 1. Introduction

Advanced ceramic materials are of increasing scientific and industrial interest since they possess a wide spectrum of outstanding properties, exploited during many applications. Non-stoichiometric oxides are well-known for their oxygen transport properties and are excellent candidates, for instance, for solid-state electrolytes, electrodes or separation membranes [1]. Oxygen transport in these oxides occurs via diffusion of oxygen ions with an enhanced mobility at higher temperatures, i.e., at temperatures above 600 °C [1,2].

Yttria-stabilized zirconia (YSZ) represents a well-known example for such ceramic materials [3]. They attracted much attention in connection with the usage as solid oxide fuel cell (SOFC) membranes, since they possess an unusual high ionic conductivity due to the inherent high concentration of oxygen vacancies [1–3]. Former investigations have demonstrated that YSZ exhibits a maximum ionic conductivity at yttria contents between 7 and 10 mol%. Numerous studies have been reported so far which addressed the oxygen transport in YSZ, and the

importance of external factors, such as porosity, temperature, etc. Oxygen transport was primarily examined by electric conductivity or diffusion experiments, whereas X-ray, neutron scattering or EXAFS studies provided structural information [4–10].

Electric conductivity and diffusion techniques represent bulk methods. However, other techniques are available which provide more direct information about the oxygen dynamics on a molecular level. Among these, dynamic solid-state  $^{17}\text{O}$  NMR spectroscopy probes the oxygen mobility directly [11,12]. Recently,  $^{17}\text{O}$  NMR techniques have been used to examine the oxygen mobility in various materials with oxygen mobility, such as ceria and yttria-stabilized ceria [13–15],  $\text{Bi}_2\text{O}_3$  [16], MgO [17] and related compounds with enhanced oxygen mobility [18–23].

In this contribution, we present the first variable temperature  $^{17}\text{O}$  NMR study for a series of  $^{17}\text{O}$ -enriched YSZ samples. Solid-state  $^{17}\text{O}$  NMR investigations (analysis of spectra and spin–lattice relaxation data) are performed between room temperature and 973 K, which provide a first direct insight into the oxygen mobility in these materials. In addition, samples with different grain sizes, i.e., micro- and nanocrystalline samples, are investigated.

\* Corresponding author. Tel.: +49 711 685 64470; fax: +49 711 685 64467.  
E-mail address: [k.mueller@ipc.uni-stuttgart.de](mailto:k.mueller@ipc.uni-stuttgart.de) (K. Müller).

Table 1  
YSZ samples used in the present work

Sample name	Sample preparation	Yttria content (mol% Y <sub>2</sub> O <sub>3</sub> )
YSZ 8	Sintered sample	8
YSZ 4	Sintered sample	4
YSZ 70 nm	Dc sputtered sample	6.9
YSZ 150 nm–1	Dc sputtered sample	7.8
YSZ 150 nm–2	Prepared in solution and sintered	7.8

Former diffusion and conductivity measurements on nanocrystalline ceria and zirconia have shown that the diffusion and conductivities in the bulk and grain boundary region might be different [4–7,9,24–33]. For instance, it has been demonstrated that the electric conductivity can be enhanced significantly in highly textured YSZ thin films at thicknesses below 60 nm [33]. In summary, however, contradictory results exist in literature, i.e., there is experimental evidence for faster oxygen ion mobility in the grain boundary as well as in the grain volume. Likewise, it has been reported from EXAFS and solid-state NMR studies [34–36] that the sample preparation route (e.g., sol–gel route, ball milling, etc.) for nanocrystalline oxides is very crucial, and in general has a large impact on the structural features of the zirconia samples which in turn also affects the conductivity and diffusivity in these materials. As a result, the intergrain regions are either highly disordered or ordered as the bulk materials, depending on the actual preparation route. For the sol–gel process, it has been further demonstrated that a finite amount of hydroxyl groups remains, even after heating to 500 °C [35,36].

The present <sup>17</sup>O NMR investigations should thus also provide information about the effect of grain boundaries on the corresponding <sup>17</sup>O NMR parameters. It is demonstrated that both the spin–lattice and spin–spin (from NMR line widths) relaxation data strongly depend on sample temperature and exhibit some alteration with sample constitution. These NMR quantities can be directly related to the inherent oxygen ion mobility of the present oxide ceramics.

## 2. Experimental

The various YSZ samples are summarized in Table 1. Samples with microcrystalline yttria-stabilized zirconia containing 4 and 8 mol% yttria (YSZ 4, YSZ 8) were purchased from Tosoh Inc. (Shiba, Japan), and were kindly provided by Dr. H. Näfe (Max-Planck Institut für Metallforschung, Stuttgart). Nanocrystalline yttria-stabilized zirconia samples (YSZ 70 nm, YSZ 150 nm–1, YSZ 150 nm–2) were kindly supplied by Prof. H.-J. Schaefer (Institut für Theoretische und Angewandte Physik, Universität Stuttgart). The corresponding preparation schemes are described elsewhere [28–30]. All NMR experiments were performed on <sup>17</sup>O-enriched samples. <sup>17</sup>O enrichment of the samples was achieved by solid–gas exchange for 4 h at 700 °C using 85 at.% enriched <sup>17</sup>O<sub>2</sub> (Campro Scientific, Berlin). NMR experiments were carried out on Bruker MSL 300 and CXP 300 spectrometers (Bruker, Rheinstetten) operating at static magnetic fields of 7.05 T (<sup>1</sup>H frequency: 300.13 MHz),

using a 7 mm high-temperature magic angle spinning (MAS) probe (Doty Scientific, Columbia) and a 5 mm double tuned probe for static samples (Bruker, Rheinstetten). The <sup>17</sup>O resonance frequency was 40.7 MHz. <sup>17</sup>O NMR spectra were recorded under static and MAS conditions with either single pulse or Hahn echo excitation schemes, using  $\pi/2$  pulse widths between 3 and 3.5  $\mu$ s. <sup>17</sup>O spin–lattice relaxation measurements were performed employing the saturation recovery pulse sequence, whereas spin–spin relaxation data ( $1/T_2^*$ ) were taken directly from the experimental <sup>17</sup>O NMR line widths (line width in Hz =  $1/(\pi T_2^*)$ ). In the nutation experiments, the signal intensities are detected as a function of the r.f. pulse length. <sup>17</sup>O chemical shifts are given with respect to H<sub>2</sub><sup>17</sup>O ( $\delta=0$  ppm). Temperature calibration of the high-temperature MAS probe was done with lead nitrate as described in literature [37,38]. Theoretical nutation curves were calculated using the simulation program described in Ref. [39].

## 3. Results and discussion

The first high-temperature solid-state <sup>17</sup>O NMR investigations for yttria-stabilized zirconia in a temperature range between 293 and 973 K under static (non-spinning) and MAS conditions will be reported in the following. Representative static single pulse <sup>17</sup>O NMR spectra for two zirconia samples are given in Fig. 1. For pure ZrO<sub>2</sub>, two superimposed NMR lines are visible which arise from different oxygen sites in the monoclinic baddeleyite structure. They are clearly distinguishable in the corresponding variable temperature <sup>17</sup>O MAS NMR spectra, shown in Fig. 2, with <sup>17</sup>O chemical shift values of 325 and 403 ppm [40].

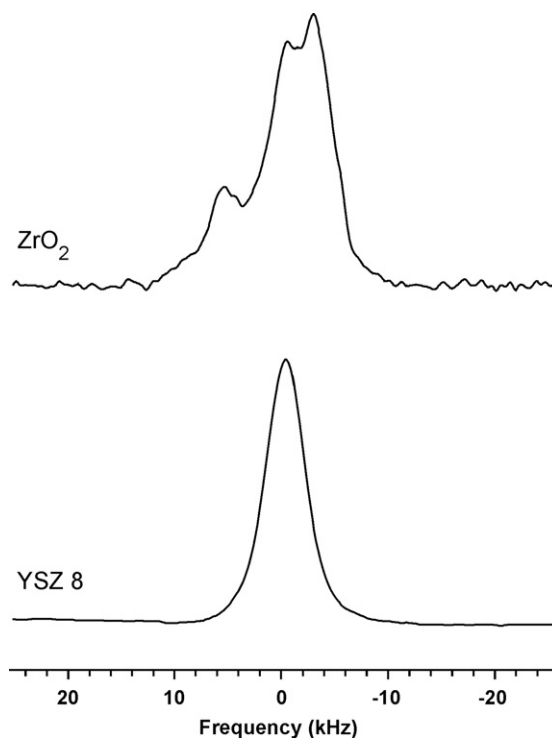


Fig. 1. Static <sup>17</sup>O NMR spectra of pure ZrO<sub>2</sub> and YSZ 8 at 293 K.

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