

Novel Zirconia-Based Superionic Conductors: The Electrical Conductivity of Y–Zr–O–N Materials

J. Wendel,* M. Lerch,† and W. Laqua*

*Institut für Anorganische und Analytische Chemie I, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, 35392 Giessen, Germany;

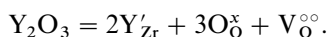
†Lehrstuhl für Silicatchemie, Julius-Maximilians-Universität Würzburg, Röntgenring 10, 97070 Würzburg, Germany

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The effect of nitrogen incorporation into yttria-stabilized zirconia on the electrical conductivity is investigated by impedance spectroscopy. Under isothermal conditions, the conductivity depends on the total concentration of anion vacancies, independent of doping with aliovalent cations (Y^{3+}) or anions (N^{3-}). The analysis of the Arrhenius plots results in higher activation energies for the oxynitrides than for nitrogen-free Y–Zr–O samples. © 1999 Academic Press

INTRODUCTION

Y_2O_3 -stabilized zirconia ceramics are widely used (fuel cells, oxygen sensors, refractories, etc.) and intensively studied materials because of their outstanding electrical properties. Doping zirconia with aliovalent oxides like yttria leads to the formation of oxygen vacancies as described by the following equation:



The approximately random distribution of the vacancies is one of the main reasons for the good ionic conductivity of these materials. A lot of data are published concerning the complex phase relationships in this system, depending strongly on sample history or microstructural features. Overviews are given by Garvie (1) or Stevens (2).

An alternative route for forming anion vacancies in zirconia is the incorporation of nitrogen by nitridation of ZrO_2 at temperatures between 1400 and 2000°C (3–6):



Unfortunately in regard to the electrical properties, the anion vacancies show an ordered arrangement at temperatures below $\sim 1000^\circ\text{C}$ (7, 8). The so-called β -type phases (β' , $Zr_7O_{11}N_2$; β'' , $\sim Zr_7O_{9.5}N_3$) can be described as trigonally distorted fluorite-type structures, built up by stacking Bevan clusters ($Zr_7O_8N_4$) and Zr_7O_{14} units along

the unique axis (4, 5, 9). Above 1000°C , the well-known cubic and tetragonal polymorphs of zirconia are observed in the ZrO_2 -rich part of the ZrO_2 – Zr_3N_4 system (7).

As reported first by Cheng and Thompson (10), it is also possible to nitride yttria-doped zirconia ceramics. The stabilizing effects of both kinds of dopants are additive. Depending on the ratio of incorporated yttria/nitrogen, the materials show different types of structures with ordered or randomly distributed anion vacancies (11). In Y–Zr–O–N samples, anion vacancies due to yttria and nitrogen incorporation exist. Nothing is known about the individual effects of these different dopants on the electrical properties of Y–Zr–O–N materials. Hence, the aim of the present work is to investigate the influence of nitrogen incorporation on the ionic conductivity of these ceramics.

EXPERIMENTAL

All samples in the system Y–Zr–O–N were prepared by direct nitridation of the corresponding oxides in a nitrogen atmosphere. The Y–Zr–O-starting material was prepared by precipitation of the hydrated oxides/hydroxides out of a solution, which contained the cations in the desired mole ratios ($YO_{1.5}$ content: 8, 12, 16, and 20 mol%). Y_2O_3 (Johnson Matthey, 99.999%) was solved in HNO_3 (Merck, p.a., $c = 4.8$ mol/l) under cooling in an ice bath. The Y concentration of this solution was 1.14 mol/l. A second solution was made by adding ice-cooled concentrated HNO_3 to zirconium propoxide (Alfa, 70% solution in propanol). Cooling was necessary to avoid oxidation of propanol to propionic acid. The Zr-concentration of this solution was 1.0 mol/l.

Both solutions were combined under stirring; afterward NH_3 (Merck, p.a., $c = 13.4$ mol/l) was added until no further formation of a precipitate occurred. This suspension was evaporated on a sandbath to dryness. It is not recommended to filter the precipitate off and wash it with water because the Y/ZR ratio could change if parts of the precipitation dissolve in the washing water. The residue resulting

from the evaporation was ground in an agate ball mill for 12 h. From the finely powdered product cylindrical pellets were formed isostatically under a pressure of 3×10^7 Pa. Side products, like ammonium nitrate, which had formed during the precipitation process decomposed quantitatively during the sintering of the pellets. The pellets were first heated in air at 1750°C for 3 days and then nitrided in a resistance furnace. With respect to the nitridation kinetics known from our earlier investigations (9), the following conditions were used to prepare samples within a wide range of incorporated nitrogen: temperature, 1600, 1700, 1900°C ; nitridation time, 2–4 h; nitrogen pressure, 1 bar; graphite heated resistance furnace (KCE, Roedental, Germany). In order to optimize the homogeneity of the samples, the oxynitride pellets were powdered once again. After homogenization, the powders were pressed into pellets (height and diameter: ~ 8 mm) and nitrided a second time. All samples were characterized by X-ray powder diffraction (STOE STADIP, Darmstadt, Germany; $\text{CuK}\alpha_1$ radiation) and hot gas extraction (Leco, Munich, Germany; accuracy of the method: $\sim 1\%$ of the present N/O). The density of the pellets was determined to 77–85% of the theoretical values, increasing with increasing nitridation temperature.

To prevent reaction of the oxynitride materials with oxygen from the surrounding atmosphere, the electrical conductivity of the samples was measured in vacuum (10^{-9} bar) by impedance spectroscopy (Lissajous figure method) between 400 and 1050°C . The equipment was constructed from corundum tubes and rods. The nitrogen content of the sample is the same before and after the measurement procedure.

In order to minimize electromagnetic disturbances, the heating element of the furnace was wound bifilar (Kanthal wire). For the measurement of very high impedances, an impedance transformer (self-constructed) was used. Because of its high common mode rejection ratio, an instrumental amplifier (self-constructed) was used to guarantee very sharp response signals. The four-point method was used to make sure that the influence of the platinum wiring at very low resistances of the ionic conductors could be neglected. The “quotient method” gives precise results for impedances measured at frequencies in the range between 20 Hz and 1 MHz. All of the equipment was evacuated with a rotary valve pump and a turbo molecular pump in serial order. Data analysis was carried out using the program package LISA (12), based on the procedures of Debye (13), Cole-Cole (14), Cole-Davidson (15, 16), and Havriliak-Negami (17, 18).

RESULTS AND DISCUSSION

As shown by Sakka *et al.* (19), randomly distributed anion vacancies are essential for a considerable mobility of the charge carriers in fluorite-type anion conducting materials, e.g., in the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ system. Our recent work on the

quaternary systems Mg-Zr-O-N , Ca-Zr-O-N , and Y-Zr-O-N show that the yttria containing system seems to be most promising one to use to investigate the influence of nitrogen incorporation on the electrical properties of these materials. In contrast to the magnesia and calcia systems, it is possible to obtain samples with randomly distributed anion vacancies, even if low dopant concentrations of yttria are used (11). With increasing content of the dopant oxide the maximal amount of incorporated nitrogen decreases (20, 21). Regarding our *in situ* high temperature X-ray powder diffraction studies of the phase relationships in the ZrO_2 -rich part of the Y-Zr-O-N system (21), samples with 8, 12, 16, and 20 mol% $\text{YO}_{1.5}$ were chosen for the experiments. All pellets were nitrided as described under Experimental; only the sample with the highest yttria content was used just for the investigation of a pure oxide sample with a large concentration of anion vacancies. Increases in the nitridation temperatures led to increased nitrogen content in zirconia materials (6, 22). The chemical compositions of all samples are given in Table 1 and in the respective figures which depict their specific electrical conductivity. Measurements were carried out in the temperature range between 400 and 1050°C . Under these conditions, all oxynitride samples are located in the cubic or tetragonal + cubic phase field of the Y-Zr-O-N system (21). If heating nitrogen containing zirconia materials to temperatures above 500°C , thermal stability of the samples must be ensured. A total pressure of 10^{-9} bar also prevents reaction to nitrogen free materials as reduction to compounds such as ZrN or Zr(O, N) .

The specific electrical bulk conductivity of the nitrogen-free reference samples is depicted in Fig. 1 as a function of temperature. For the material with the lowest yttria content we have disregarded data in the low temperature region, where tetragonal and monoclinic phases coexist. Hysteresis effects which appear in this case are of no relevance in the

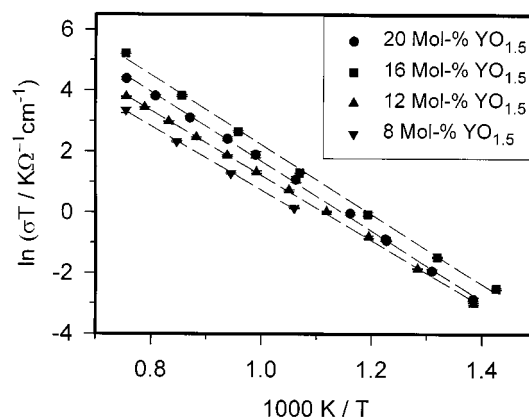


FIG. 1. $\ln(\sigma T)$ of the nitrogen-free samples as a function of the reciprocal temperature (σ : specific electrical bulk conductivity).

frame of this work. The results are in good agreement with known literature data, e.g. (23, 24). Under isothermal conditions, the conductivity first increases with increasing yttria content. At ~ 16 mol% $\text{YO}_{1.5}$, a maximum is reached. Finally, the conductivity decreases with increasing dopant content. In addition, a change in the slope of the Arrhenius plot is observed, which becomes less marked with decreasing yttria content. These effects have been widely discussed in the literature [e.g., 25–29]. The common explanation is that two regions of ionic conductivity exist. At low temperatures ($T < \sim 700^\circ\text{C}$) in the dilute region below 16 mol% $\text{YO}_{1.5}$, simple associates are formed between the cations and the oxygen vacancies. With increasing temperature free vacancies are created by dissociation of the associates. For higher dopant concentrations, more complex defect associates are formed, which results in a decrease of the ionic conductivity. It should be mentioned that very similar defect complexes exist in nitrogen containing zirconia (30). Hence,

nitrogen incorporation should lead to similar defect reactions as compared to doping with yttria.

Figures 2a–2c present the Arrhenius plots for the oxynitride samples, in comparison with the nitrogen-free reference samples. The 16 mol% $\text{YO}_{1.5}$ sample nitrated at 1700°C and also all samples nitrated at 1900°C contain small amounts of rock salt-type (Y, Zr)(N, O, C) phases (31), leading to dominant electronic conduction. These data are not presented in the figures. No indication of significant electronic conductivity was found for the other samples, neither from the analysis of the impedance spectra nor from additional DC measurements.

The main results of our investigations can be described as follows:

(1) For low yttria contents, the incorporation of nitrogen, which is accompanied by an increase of the anion vacancy concentration, leads to an increase of the electrical conductivity (see Fig. 2a). In the case of 12 mol% $\text{YO}_{1.5}$ (Fig. 2b),

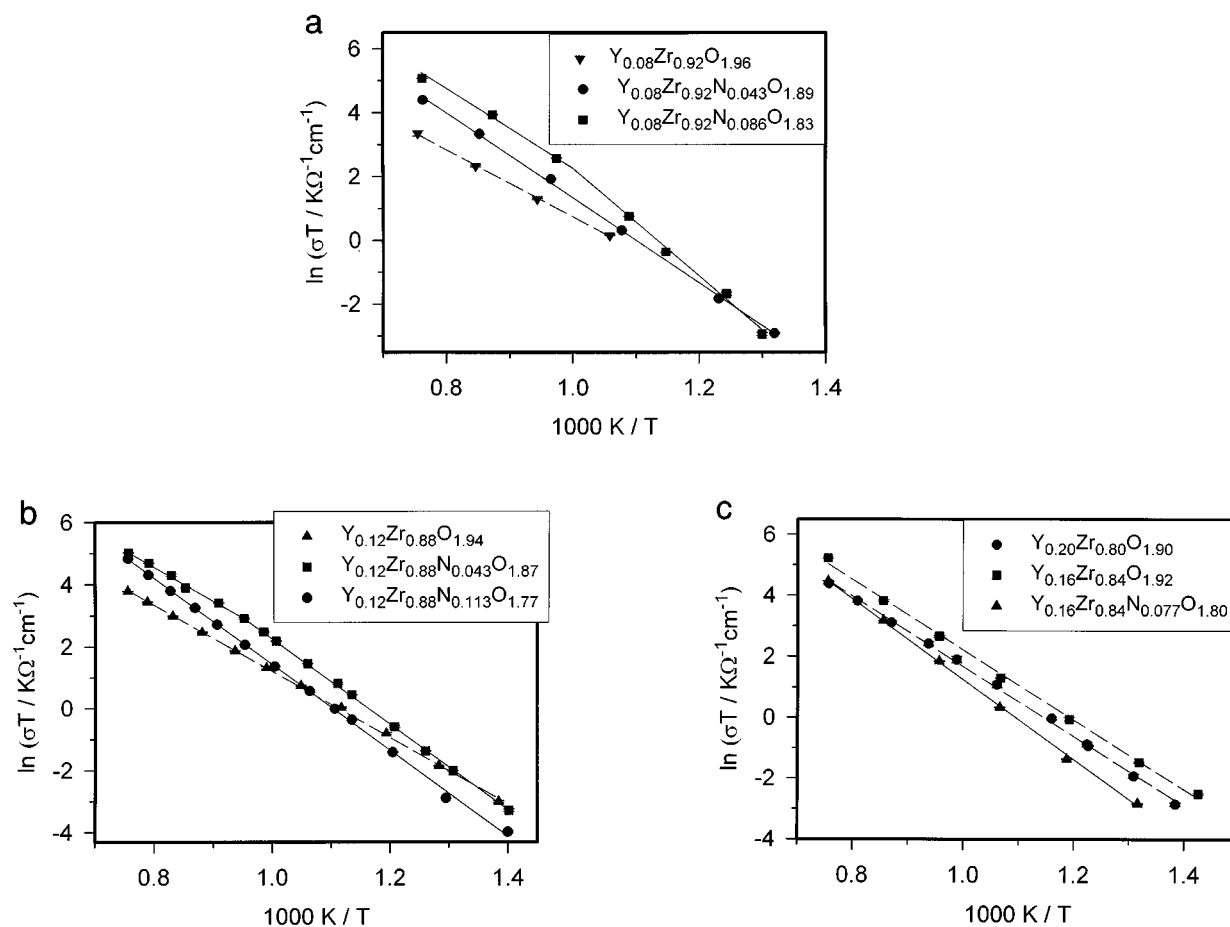


FIG. 2. (a) $\ln(\sigma T)$ of the samples containing 8 mol% $\text{YO}_{1.5}$ as a function of the reciprocal temperature (σ : specific electrical bulk conductivity). (b) $\ln(\sigma T)$ of the samples containing 12 mol% $\text{YO}_{1.5}$ as a function of the reciprocal temperature. (c) $\ln(\sigma T)$ of the samples containing 16 mol% $\text{YO}_{1.5}$ as a function of the reciprocal temperature. For comparison, also the results of the nitrogen-free sample with 20 mol% $\text{YO}_{1.5}$ are depicted.

the conductivity first increases with an increasing amount of nitrogen and then decreases. Finally, for 16 mol% $YO_{1.5}$, the nitrated sample shows a poorer conductivity than the reference sample (Fig. 2c). This behavior is very similar to that of the nitrogen-free samples presented in Fig. 1. The ionic conductivity of the quaternary samples is affected by anion vacancies due to the incorporation of yttria or nitrogen in a nearly identical way. Under isothermal conditions (e.g., 800°C), a conductivity maximum is observed for a total vacancy concentration ($V_{\text{total}} = V_{\text{N}} + V_{\text{Y}}$) of $\sim 4\%$ in the anion lattice, independent of the individual concentrations of V_{N} and V_{Y} (see Fig. 3). Consequently, the formation of complex defect associations seems to be similar for both kinds of dopants. It should be emphasized that V_{N} and V_{Y} cannot be distinguished experimentally, but it is possible to calculate their concentrations from the known chemical composition (10,11,20). As it is established in the Y_2O_3 - ZrO_2 system, the maximum is less pronounced at lower temperatures.

(2) The activation energy, calculated from the Arrhenius plots, is generally increased by the incorporation of nitrogen (see Table 1). Such an effect is known in ZrO_2 - M_2O_3 systems with an increasing ionic radius of the M^{3+} cation (32,33). The increasing activation energy was explained by steric blocking of the dopant cations and by different binding energies between dopant cations and vacancies. In case of the Y-Zr-O-N materials, the activation energy is increased by incorporation of nitrogen, even if the cation sublattice remains unaffected. According to our present knowledge, it is not possible to give a more detailed explanation. Nothing is known about the mobility of nitrogen ions in the anion sublattice. Are the Y-Zr-O-N materials mixed anion conductors? From a formal point of view, the ionic radius of N^{3-} (IV) is 8 pm larger than that of

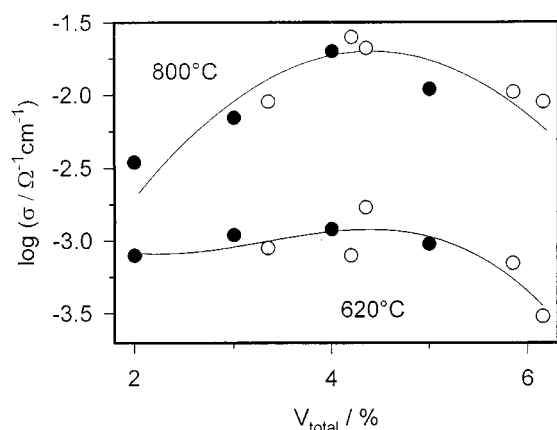


FIG. 3. Specific electrical conductivity of Y-Zr-O-N samples as a function of the total vacancy concentration (V_{total}) at two selected temperatures. Nitrogen-free samples are represented by filled circles.

TABLE 1
Activation Energies for the Conductivity in the Temperature Region above 750°C, Calculated from the Arrhenius Plots of Figs. 2a-2c

Chemical composition	Activation energy (eV)
$Y_{0.08}Zr_{0.92}O_{1.96}$	0.84(3)
$Y_{0.08}Zr_{0.92}N_{0.043}O_{1.89}$	1.05(2)
$Y_{0.08}Zr_{0.92}N_{0.086}O_{1.83}$	1.02(6)
$Y_{0.12}Zr_{0.88}O_{1.94}$	0.90(1)
$Y_{0.12}Zr_{0.88}N_{0.043}O_{1.87}$	0.94(3)
$Y_{0.12}Zr_{0.88}N_{0.113}O_{1.77}$	1.18(2)
$Y_{0.16}Zr_{0.84}O_{1.92}$	0.93(1)
$Y_{0.16}Zr_{0.84}N_{0.077}O_{1.80}$	1.12(2)
$Y_{0.20}Zr_{0.80}O_{1.90}$	0.94(2)

O^{2-} (IV) (34). On the other hand, zirconium-nitrogen bonds have a more covalent character. Another significant difference between commonly used oxide materials and the oxynitrides described here is the distance of interaction between vacancies and dopant ions. For Y-Zr-O materials, the shortest distance cation-vacancy is $\frac{1}{4}\langle 111 \rangle$ of the fluorite-type lattice, whereas a $\sim 15\%$ longer distance ($\frac{1}{2}\langle 100 \rangle$) can be calculated for the distance vacancy-anion in the oxynitride samples. Thus, coulombic interaction between the defects should be affected in this way. Due to the higher activation energy of oxynitride samples, the electrical conductivity of these materials must be superior at temperatures above 1100°C to those known Y-Zr-O materials.

CONCLUSION

The electrical conductivity of zirconia materials is affected by incorporation of yttria and nitrogen in a similar way. Under isothermal conditions, the conductivity is determined by the total anion vacancy concentration, independent of doping the cation or the anion sublattice. This again gives evidence of the important role of anion vacancies concerning the electrical properties of zirconia ceramics. The activation energy is increased by nitrogen incorporation. Our measurements do not allow a complete interpretation of the results so far, especially to the unknown role of nitrogen ions in the conduction process. Nevertheless, nitrogen containing zirconia is an interesting material for the investigation of defect interaction in fluorite-type phases. In the more complex ternary Zr-O-N system (7), it seems to be possible to investigate the properties of anion deficient zirconia materials without dopant ions in the cation sublattice.

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