

Some structural aspects of ionic conductivity in zirconia stabilised by yttria and calcia

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Nanopowders with nominal constant oxygen vacancy concentrations of 8, 10, and 12 mol % were prepared in the ternary $\text{ZrO}_2\text{--CaO--Y}_2\text{O}_3$ system. The constant oxygen vacancy concentrations were obtained by incorporating calcia and yttria into zirconia solid solutions at different ratios. The Rietveld refinement method was used to characterise the structural changes in the zirconia solid solution. X-ray diffraction analysis was also used to characterise the phase composition of the samples and lattice parameters of the cubic phase. The four-probe method was applied for determining electrical properties of the samples. The conduction properties of the samples were characterised with respect to their structural features.

Key words: *zirconia; ionic conductivity*

1. Introduction

Fully stabilized cubic zirconia has been actively investigated as an oxide ion conductor in solid oxide fuel cells (SOFC), oxygen sensors, or electrochemical oxygen pumps [1, 2]. Consequently, several approaches have been taken to improve the electrical properties of zirconia materials. Structural modification of cubic zirconia is one of promising ways to ameliorate the ionic conductivity of zirconia-based electrolytes. The ionic conductivity of zirconia solid solutions (s.s.) is strictly related to the ionic radius and valency of cations incorporated into the zirconia structure [3, 4]. It is well known that for fluorite-structure oxides the conductivity is optimised by matching the size of the dopant and structural ions [5]. A special form of ion site instability occurs, however, when a compound is on the verge of a transition between two phases, one of which is a slight distortion of the other. In such a case, an unstable structure should have its maximum ionic conductivity at the minimum stabilizing dopant concentration

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[6]. Structural stress and the formation of complex defects (e.g., a host or dopant cation with an oxygen vacancy) should also be taken into consideration when explaining the connection between structure and ionic conductivity.

It is worth noting that the phase transition, and therefore the ionic conductivity, of zirconia could be controlled by the presence of two stabilizing cations in its structure. A few papers have concerned yttria-stabilised zirconia materials, additionally containing rare earth elements [7, 8]. In these materials, depending on the chemical and phase composition, an improvement (mostly) or in some cases a decrease in ionic conductivity was observed. Strickler et al. [9] found that a relatively big addition of calcia to cubic zirconia stabilised with yttria decreased its ionic conductivity. Several works on the electrical properties of $\text{CaO}-\text{Y}_2\text{O}_3-\text{ZrO}_2$ materials were reported by Gong et al. [10–12]. Generally, single-phase samples were characterised by better electrical properties as compared to “pure” yttria-stabilised material, and the ionic conductivity showed a local maximum for the equimolar doping composition.

The aim of the present work was to prepare solid-state electrolytes with constant vacancy concentrations in the ternary $\text{CaO}-\text{Y}_2\text{O}_3-\text{ZrO}_2$ system and to investigate their structural and electrical properties.

2. Experimental

Three series of zirconia powders, containing nominally 8, 10, or 12 mol % of oxygen vacancies were prepared by introducing yttria and calcia to zirconia in appropriate proportions. The samples throughout the work are marked as 8CnYm (8% series), 10CnYm (10% series), and 12CnYm (12% series), where n and m indicate the fractions of the oxygen vacancies introduced to the zirconia structure by CaO and Y_2O_3 , respectively. The values of n and m ranged from 0 to 100%, with a step of 10%.

Zirconyl, yttrium, and calcium chloride aqueous solutions were used as starting materials to prepare the zirconia solid solution nanopowders. Each solution was dropwise introduced into a vigorously stirred, concentrated NaOH solution, and then the slurry was hydrothermally treated for 4 h at 240 °C. The powders were washed with water solutions of ammonia and then additionally washed with propanol. After drying at room temperature, the granulated powders were isostatically cold-pressed under the pressure of 200 MPa. The green bodies of the 8, 10, and 12 series were pressurelessly sintered for 2 h at 1300, 1400, and 1500 °C, respectively.

The Rietveld refinement method, based on precise X-ray diffraction measurements, was used to characterise the structural changes in the zirconia cubic phase. The phase composition of the sintered bodies and lattice parameters of the respective phases were also determined.

The four-probe method was applied to recognise the electrical properties of the samples. Measurements were performed at temperatures from 300 to 1000 °C with an external current source. Partially reversible platinum electrodes deposited from paste were applied.

3. Results and discussion

The phase compositions of the sintered bodies are shown in Figure 1. In the samples containing 8 mol % of oxygen vacancies, the cubic phase was observed only in samples stabilised mainly by yttria (up to 8C50Y50). Increasing the calcia content in the stabilising mixture caused tetragonal phase formation. The samples of 10 series with a calcia-to-yttria ratio smaller than 70:30 were fully cubic, and the others were composed of both cubic and monoclinic phases. X-ray diffraction analysis showed that the sintered bodies of the 12 series were composed of cubic zirconia alone.

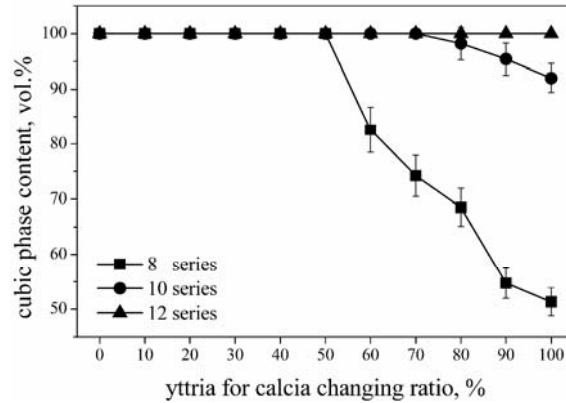


Fig. 1. The compositional dependence of cubic zirconia phase content

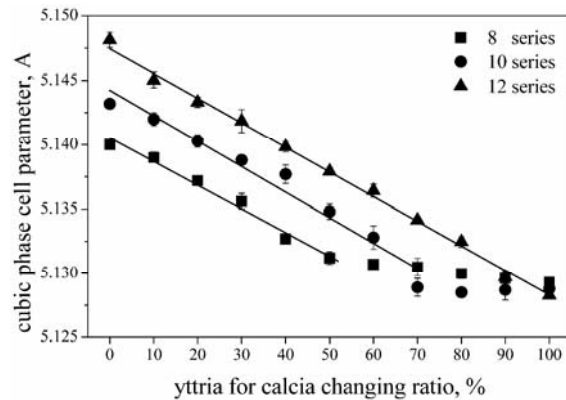


Fig. 2. The compositional dependence of cubic zirconia cell parameters

Figure 2 presents the lattice parameters of the cubic phase as a function of the chemical composition for each experimental series. Variations of the cubic phase lattice parameters in the single-phase regions are linear and can be related to the molar ratios of the stabilizing cations. In the bi-phase regions, the cubic phase lattice parameters change to a smaller degree (series 8) or are almost constant (series 10).

This is probably connected with differences in the chemical compositions of both zirconia phases, the total concentration of the stabilisers as well as the calcia-to-yttria molar ratio in both phases being significant.

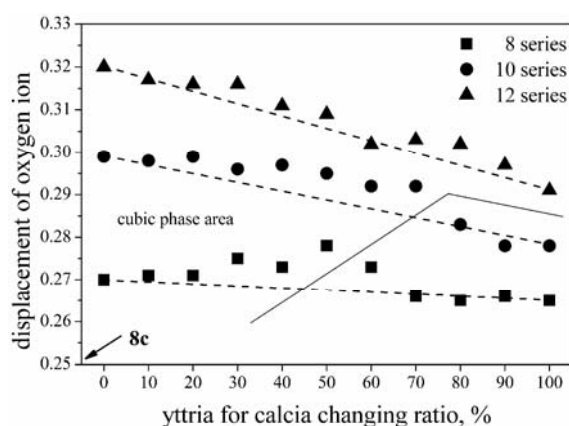


Fig. 3. Displacement of oxygen ions from site 8(c) to the site 48(g)

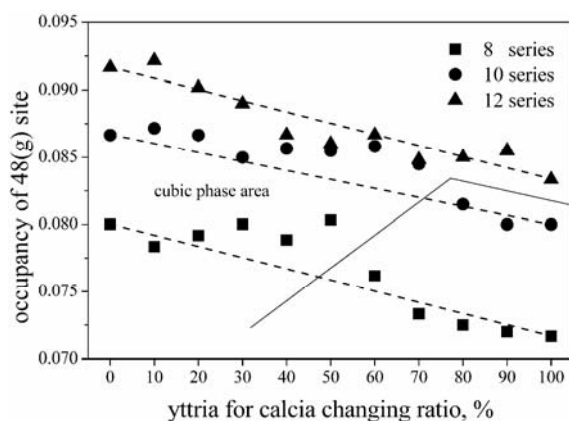


Fig. 4. The occupancy of the 48(g) site by oxygen ions

An initial model for Rietveld refinement was based on the real cubic zirconia structure determined by EXAFS as well as X-ray diffraction methods. Ishizawa et al. [13] stated that in yttria-stabilized zirconia Y ions occupy the 4(a) sites, whereas Zr ions occupy the 32(f) sites. Almost half of the O ions occupy 8(c) sites and the rest are shifted along $\langle 001 \rangle$ and occupy 48(g) sites [13]. A similar distortion of the elementary cell was found in cubic zirconia stabilized with calcia [14]. Figure 3 presents oxygen ion displacements, as a fraction of the cell parameter, from position 8(c) to position 48(g). The extreme points on the chart, corresponding to samples containing only one stabilizer, were connected by the dashed line, representing graphically a “mixture rule”. It is shown that oxygen ion displacement for some samples of the

8 and 10 series differ from the mixture rule and that these differences are larger in the case of the 8 series. Changes in the occupancy factor of oxygen ions at 48(g) sites exhibit a similar character (Fig. 4). In samples of the 8 and 10 series, distinct differences between the mixture rule and determined values are visible. Contrary to the changes in the anion sublattice, the changes in zirconium ion displacement from the 4(a) position to the 32(f) position are almost linearly related to the chemical compositions of the samples. A comparison of the results from Figures 2–4 implies that in the samples brought closer to the stabilization threshold, the oxygen sublattice becomes more distorted and the amount of moveable oxygen ions increases. This effect decreases with the total content of stabilizing oxides. The mentioned facts are in good agreement with the mechanism of the cubic-to-tetragonal phase transition, in which oxygen ion movements are much more extensive than the movements of the cations [15].

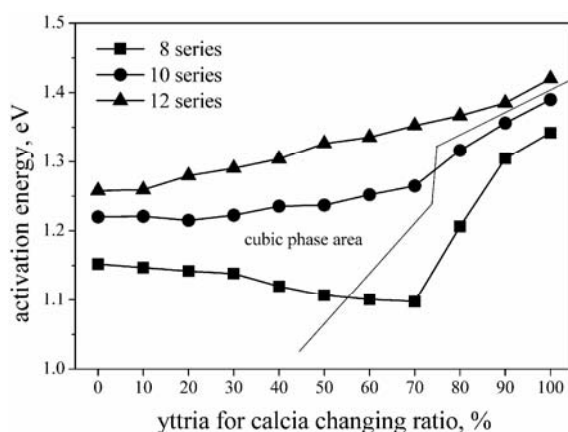


Fig. 5. The compositional dependence of the activation energy of ionic conductivity

Four-probe measurements revealed that the temperature dependences of ionic conductivities drawn in the Arrhenius coordinates have a linear character for all samples investigated. Basing on these relationships, the activation energies of ionic conductivity were calculated. Figure 5 shows the influence of sample chemical composition on the activation energy. In all series, samples containing the same oxygen vacancy concentrations and stabilized only by calcia have higher activation energies than those stabilized with yttria. Changes in activation energy with chemical composition are linear in the case of samples with 12 mol % of oxygen vacancies. For the 10 series, a deviation from linearity towards lower activation energies arises. This effect is much stronger in the 8 series, where a distinct minimum of the activation energy is observed. In this case, the lower activation energies are attributed to samples closer to the transformation verge.

Taking into account the relations between chemical compositions, phase content, and structural changes, it can be stated that an increase in oxygen sublattice distortion at the verge of the phase transition is responsible for the decrease in the activation

energy of ionic conductivity. This effect, in the studied materials, is caused by an exchange of the weaker stabiliser (calcia) by the stronger one (yttria) and generally diminishes with increasing total stabilizer content. The decrease in the lattice parameter of the cubic phase with calcia content could be considered an additional factor; distances between equivalent ion positions during diffusion are shorter.

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