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Ionic conductivity of $CaO–Y_2O_3–ZrO_2$ materials with constant oxygen vacancy concentration

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Abstract

Structural modification of the fully stabilised zirconia is a possible way to improve its electrical properties. Electrical properties, especially ionic conductivity, of cubic zirconia solid solutions are strictly related to the ionic radius and valency of cations incorporated into the zirconia structure. Nanopowders with a constant oxygen vacancy concentration of 8 and 10 mol% were prepared by a hydrothermal treatment of co-precipitated zirconia hydrogels in a NaOH environment. The desired oxygen vacancy concentrations were obtained by introducing calcia and yttria, at different ratios, to the zirconia solid solutions. Phase compositions and lattice parameters of the respective phases were determined using X-ray diffraction analysis. Electrical properties of the samples were described on the basis of complex impedance spectroscopy analysis. It has been stated that substitution of calcia for yttria or yttria for calcia in zirconia solid solutions leads to ionic conductivity enhancement. Samples with a cubic structure, close to the stabilisation threshold, had the highest conductivity.

Keywords: Ionic conductivity; ZrO_2

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1. Introduction

Zirconium dioxide is a well-known material in modern ceramics. Because of its high oxygen conductivity, the stabilised zirconia is of technological interest for the manufacturers of electrochemical devices such as fuel cells, oxygen probes or solid state galvanic cells. Electrical properties, especially the ionic conductivity of zirconia solid solutions, are strongly related to the ionic radius and valency of cations incorporated into the zirconia structure.[1–4] It has been shown namely that conductivity of the cubic zirconia phase increases with the decreasing size of the substituted cation and that the relation between conductivity and radius of the stabilising ion is almost linear. Comparison of conductivities at equivalent vacancy concentrations indicates that enhancement of oxygen ion mobility is a major effect. This can be attributed to smaller lattice distortions or stresses brought about by the stabilising cations, with the radii close to that of zirconium.

It has also been stated that electrical conductivity of zirconia solid solutions is dependent on the amount of the stabilising cation. Regardless of the cation charge, conductivity of zirconia solid solutions increases with its concentration until full stabilisation of the cubic structure is achieved. Then conductivity of the cubic zirconia decreases although oxygen vacancy concentration continues to grow with the doping level. There are several possible reasons for such behaviour: vacancy interactions or formation of vacancy clusters, ordering of vacancies or second phase formation. Order-disorder transition can be also taken into consideration.[5]

Several ternary systems involving yttria-stabilised zirconia have been studied from the viewpoint of structure and electrical properties, the third component being calcia,[1,6–10] magnesia,[11] scandia[12] or a rare-earth oxide.[13] Materials co-stabilised with yttria and other trivalent cations, depending on chemical and phase composition, have generally improved ionic conductivities, although in some cases deterioration of the ionic conductivity has been observed. The results described in the quoted papers are far from complete and their interpretation is rather difficult.

D.W.Strickler et al. have found that a relatively big addition of calcia to the cubic yttria-stabilised zirconia decreases its ionic conductivity [1]. More details on electrical properties of the $CaO–Y_2O_3–ZrO_2$ materials are reported in Refs. 6–10. The investigated materials were

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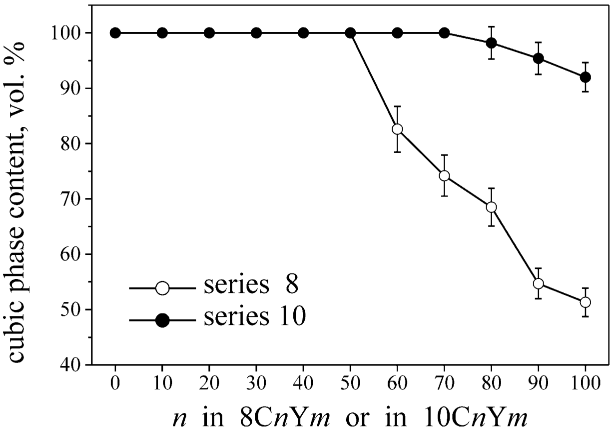

Fig. 1. Phase composition of the sintered bodies.

prepared as mixtures of 8 mol% Y_2O_3–ZrO_2 and 12 mol% CaO–ZrO_2. It has been found that partial substitution of calcia for yttria may enhance the electrical conductivity at elevated temperatures. At lower temperatures, however, the CaO doping lowers the conductivity. This phenomenon has been attributed to the increased concentration of oxygen vacancies and the lower association energy.

The aim of the present work was to investigate the structural properties and ionic conductivity of yttria-and-calcia-stabilised zirconia solid solutions with a constant oxygen vacancy concentration.

2. Experimental

Two series of zirconia solid solution powders were prepared, with oxygen vacancy concentrations of 8 or 10%, by introducing controlled amounts of yttria and/or calcia to the zirconia solid solution. The samples throughout the work are marked as 8C*n*Y*m* or 10C*n*Y*m* where: 8 or 10 are molar concentrations of oxygen vacancies while *n* and *m*—fractions of oxygen vacancies introduced to the zirconia structure by the CaO and Y_2O_3 additives, respectively. The values of *n* and *m* ranged from 0 to 100% at an interval of 10.

As indicated in Ref. 14 the most suitable technique for the preparation of fine and sinterable zirconia powders stabilised with calcia is the hydrothermal treatment of co-precipitated zirconia hydrogels.[14] Following the procedure described in that paper, water solutions of zirconyl, yttrium and calcium chlorides were used as starting materials and concentrated (4 M) NaOH solution, free of carbonates, was the precipitating agent. A solution containing zirconium, yttrium and calcium cations was slowly added to the continuously stirred NaOH solution and final pH was adjusted to 9.6. The obtained slurry was hydrothermally treated for 4 h at 240 °C in the mother NaOH environment under the autogeneous pressure of water vapour. Next, the precipitates were washed with a water solution of ammonium nitrate and ammonia at a controlled pH value in order to eliminate the sodium and chloride ions. After subsequent threefold washing with propanol they were dried at room temperature. The granulated powders were cold isostatically pressed under 200 MPa; a 5% oil-water emulsion was added as a lubricant. Green bodies were pressurelessly sintered for 2 h at 1300 °C (series 8) and at 1400 °C (series 10). The details on the preparation procedure and properties of the powders have been described elsewhere.[15]

The Rietveld refinement method, based on X-ray diffraction measurements, was used to characterise phase composition of the sintered bodies as well as lattice parameters of the respective phases. Complex impedance spectroscopy analysis allowed description of electrical properties of the samples. Partially reversible platinum electrodes deposited from paste were applied. Measurements were performed at 350 °C with Solartron (FRA 1260 + dielectric interface 1294) equipment over the frequency range 1 Hz–1 MHz.

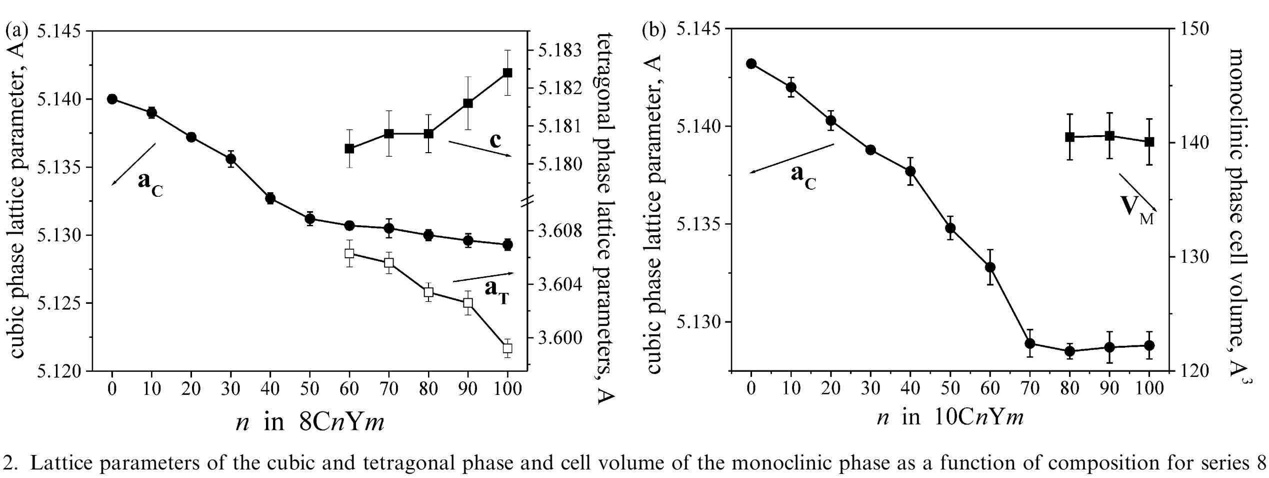

Fig. 2. Lattice parameters of the cubic and tetragonal phase and cell volume of the monoclinic phase as a function of composition for series 8 (a) and series 10 (b).

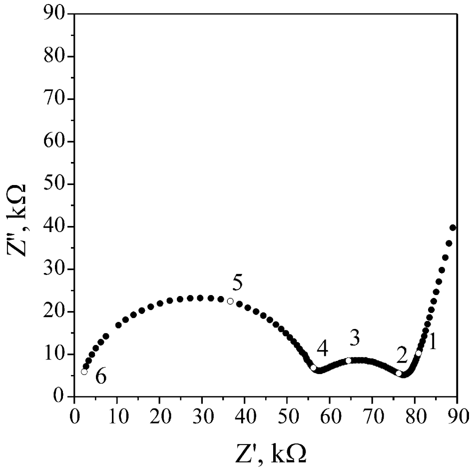

Fig. 3. A typical impedance spectroscopy pattern taken at 350 °C for the 10C50Y50 sample.

3. Results

According to the microscopic observations the obtained powders were mostly composed of nanometric particles, isometric in shape. Relative densities of all samples prepared from those powders were + 98%. Phase compositions of the sintered bodies are shown in Fig. 1. Samples containing 8 mol% oxygen vacancies, with the amount of calcia not exceeding 8C50Y50, were composed of the cubic phase only. Further exchange of yttria for calcia led to the formation of the tetragonal phase. Phase composition of samples with 10 mol% oxygen vacancies varied differently with an increasing relative calcia content. Samples with calcia contents not higher than in 10C70Y30 were fully cubic and others were composed of both: cubic and monoclinic phase. These facts indicate segregation of the stabilising cations in samples with higher calcia contents. Increased total content of the stabilisers and elevated sintering temperature, both intensify the segregation phenomenon.

Fig. 2a and b presents lattice parameters of the cubic and tetragonal phase and cell volume of the monoclinic phase as a function of composition for both experimental series. Two regions can be distinguished on both plots. In the single-phase regions, at smaller calcia contents, variations of the cubic phase lattice parameters can be related to the molar ratios of the stabilising cations. In the biphase regions, the cubic phase lattice parameters change to a smaller degree (series 8) or are almost constant (series 10). This is probably connected with the differences in chemical composition of both zirconia phases; total concentration of the stabilisers as well as calcia to yttria molar ratio in both phases being significant.

A typical impedance spectroscopy pattern, taken at 350 °C, has been approximated with two partially overlapping semicircles and a straight line (Fig. 3). The overall impedance of a polycrystalline sample could be modelled by an equivalent circuit composed of bulk resistance and constant phase angle element (CPE) connection of individual crystallites in-series with impedance due to parallel resistance-CPE effects associated with the crystallite grain boundaries.[16] In this model, the high frequency intersection with the real axis of the impedance could be attributed to the bulk resistance, σ_b, and the semicircle diameter at lower frequencies to the grain-boundary resistance, σ_{gb}.[17] The straight line at the lowest frequencies was related to constant phase angle element responsible for the electrode double layer. The measured resistance values and shape factors of the samples were used for calculating the respective conductivities.

Compositional dependences of bulk conductivity and apparent grain-boundary conductivity of the investigated samples are shown in Fig. 4a and b, respectively. In series 8 the minimum exchange of yttria for calcia

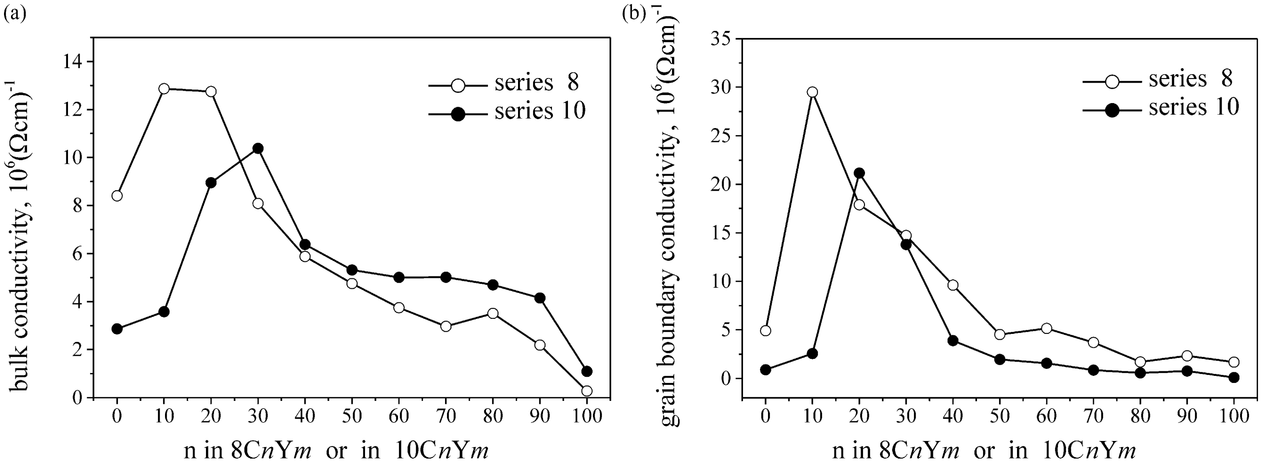

Fig. 4. Compositional dependence of bulk (a) and apparent grain-boundary (b) ionic conductivity of the investigated samples.

(8C10Y90) caused an enhancement of bulk conductivity. Also the next sample in series (8C20Y80) had better electrical properties than one containing exclusively yttria. Further exchange of yttria for calcia led to almost linear decrease of bulk conductivity toward the calcia-stabilised zirconia sample. A similar behaviour was observed in series 10, nevertheless the sample with the higher content of calcium (10C30Y70) showed maximum bulk conductivity. Moreover, for the samples with still higher relative contents of calcia, up to 10C90Y10, the bulk conductivity remained approximately constant.

The variations of apparent grain-boundary conductivity with chemical composition were similar in both experimental series. The 8C10Y90 sample showed maximum conductivity. Then σ_{gb} decreased as the composition approached 8C50Y50. The grain-boundary conductivities for the samples richer in calcium were almost constant. In the case of samples with oxygen vacancy concentration of 10 mol%, the maximum grain-boundary conductivity was observed at 10C20Y80.

4. Conclusions

The results presented in this paper indicate that substitution of calcia for yttria as well as yttria for calcia in the zirconia solid solutions leads to an enhancement of ionic conductivity. In each experimental series, maxima were observed on the bulk and grain-boundary conductivity curves. On comparing the structural and electrical conductivity data, no simple correlation with the stabilising cations ratio could be found. However, it is worth noticing that the conductivity maximum occurred at a composition close to the stabilisation threshold of the cubic phase. The higher the total stabiliser level, the higher the calcia content in the most conductive sample. This suggests that conductivity enhancement was probably not due to the global structural relationships but to some local effects, such as formation of complex defects.

Acknowledgements

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