Electrochimica Acta 134 (2014) 176–181

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Charge carrier relaxation and phase transition in scandium stabilized zirconia ceramics

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ARTICLE INFO

Article history:
Received 4 March 2014
Received in revised form 15 April 2014
Accepted 20 April 2014
Available online 30 April 2014

Keywords:
Scandium stabilized zirconia
Impedance spectroscopy
Charge carrier relaxation
Distribution of relaxation times.

ABSTRACT

Structural, electrical properties and charge carriers relaxation phenomena of 10 mol% Sc_2O_3–90 mol% ZrO_2 ceramics have been investigated in frequency range 1 Hz to 10 GHz and temperature interval from room temperature to 900 K. Temperature dependencies of electrical conductivity and dielectric permittivity of the compound showed an abrupt jumps in temperature range from 790 to 820 K. Differential thermal analysis and X-ray diffraction studies confirmed that the ceramics undergoes a structural phase transition from rhombohedral to cubic in this temperature region. Grain boundary contribution to total electrical conductivity was not noticeable in impedance spectra of low temperature phase, while it shows up at high temperature phase. The impedance spectra were also analyzed in terms of distribution of relaxation times by using Tikhonov regularization method. The distribution of charge carrier relaxation times in grains tend to narrow with increasing temperature in the temperature ranges far from phase transition, while a significant broadening of the distribution was observed in the temperature range of phase transition. The separation of grain and grain boundary contributions to total conductivity was enabled due to observation of corresponding peaks in obtained distribution of relaxation times function. The behavior of grain boundary conductivity around the phase transition temperature region revealed that crystalline structure of the crystallites affects electrical properties of grain boundary medium.

1. Introduction

Scandium stabilized zirconia (ScSZ) shows highest conductivity among all zirconia based electrolytes [1,2]. This property is attributed to a smaller ionic radius of Sc^{3+} which lowers steric blocking effect to the movement of oxygen ions [3]. It is shown that ScSZ has poor stability with lower than 10 mol% Sc_2O_3 concentrations, but systems with higher amount of Sc additions are far more stable [4,5]. However, the transitional combination of 10 mol% Sc_2O_3 stabilized zirconia (10ScSZ) has the highest conductivity among ScSZ compounds and considered to be a suitable electrolyte for solid oxide fuel cells (SOFC) [4].

Different authors provide slightly different phase diagrams of system Sc_2O_3-ZrO_2 [6–9], although all of these charts contain a phase transition point at about 600 °C for the 10ScSZ. Chiba et al. indicate rhombohedral phase (so called β-phase) of ScSZ with about 10-13 mol% Sc_2O_3 at room temperature, which transforms to cubic (c-phase) at around 600 °C [7]. More recent studies have shown that 10-11ScSZ systems contain both cubic and rhombohedral phases at low temperatures [4,10]. It should be noted that the latter studies indicate different phase transition temperatures, what are explained by effect of grain size of sintered ceramic specimens to character of ScSZ phase transitions [11,12].

Many authors state that the temperature dependence of conductivity of ScSZ with close to 10ScSZ exhibits an abrupt conductivity change in the region of this phase transition [10,11,13,14]. This phenomenon was found to be dependent on composition and annealing time of the sample [15]. Detailed analysis of frequency dispersion of electrical properties (e.g. admittance, impedance, electric modulus and dielectric permittivity), which is caused by mobile charge carrier relaxation in electrical field, would give more information about the conduction mechanism in this material. Most solid oxide ion conductors exhibit non-Debye type relaxation behaviour, which rather would be represented by a continuous distribution of relaxation times (DRT). Numerous studies have been carried out to estimate the DRT behaviour of dielectric systems (e.g. [16–20]), whereas a much more limited number of works have examined DRT of ionically conductive systems [21–24]. Most of existing studies are dedicated to the DRT function related to the interface electrode - solid electrolyte, while our previous works

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http://dx.doi.org/10.1016/j.electacta.2014.04.112
0013-4686/

[25,26] analyse temperature behaviour of DRT of the mobile charge carriers in the bulk of solid oxide conductors. We could not find in literature any study, which would analyse the DRT function behaviour in the vicinity of phase transition in ScSZ or any other ionic conductor.

In this paper we present a detailed study of electrical properties of 10ScSZ ceramic samples in wide temperature range, which covers a phase transition region. Temperature behaviour of specific conductivity and dielectric permittivity in grain, and specific and total conductivities in grain boundary medium was discussed. Peculiarities of DRT function for mobile ions were also investigated in detail using Tikhonov regularization technique [27] and the methodology described in our previous work [25].

2. Experiment

2.1. Preparation and characterization of ceramic samples

Polycrystalline 10ScSZ ceramic samples were prepared by uniaxially cold pressing the powder (Fuel Cell Materials) in a steel die of 8 mm at 100 MPa and sintering of the compacts at 1773 K temperature in an air atmosphere for 1 h. Microstructure of sintered samples was characterized using a scanning electron microscope JEOL JSM-6510LV. As it is shown in Fig. 1, grain size of obtained specimens is in the range of 10 μm. Density of the obtained products was determined by geometric and Archimedes methods. The reached density value was not lower than 97% of theoretical value, which was taken as 5.54 g/cm^3 [15].

The crystal structure at different temperatures of synthesized ceramic pellets was determined by X-Ray diffraction (XRD) analysis on a PANalytical X‘pert MPD PRO diffractometer (CuKα radiation). XRD measurements were taken at temperatures up to 840 K in the 2θ range of 5–60° with step size of 0.03°. Initial XRD analysis of the samples at room temperature showed that the principal phase of the pattern is rhombohedral (β-phase) (Fig. 2); low intensity peaks of cubic phase were also observed, which is typical for this kind of material [11,12]. Differential thermal analysis (DTA) of obtained ceramic sample was performed with a "SDT Q600" (TA Instruments) equipment using Al_2O_3 as a reference material. The DTA data were collected at 292-1173 K (20 K/min) under air flow 100 mL/min. The DTA curve shows an endothermic peak at 834 K and exothermic one - at 786 K temperature upon heating and cooling cycles, respectively (Fig. 3), i.e. considerable thermal hysteresis was observed. However, the transition temperatures itself slightly depend on heating/cooling rate and at 20 K/min thermal hysteresis loop was found to be of value around 48 K. XRD study at 840 K temperature (Fig. 2) detected single *c*-phase of present sample.

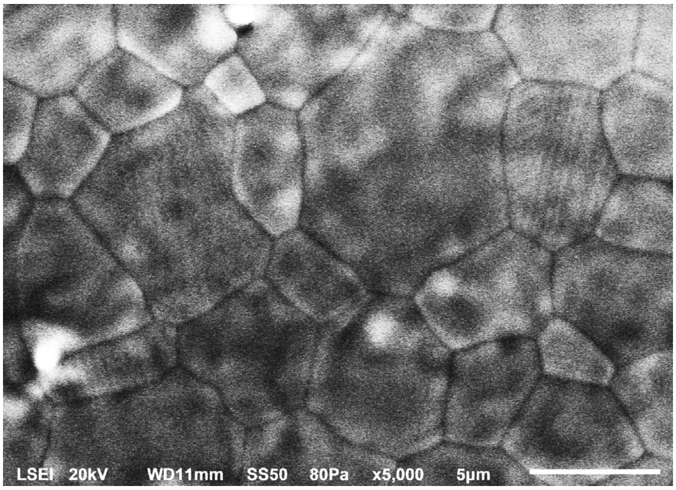

Fig. 1. SEM image of prepared 10ScSZ ceramics.

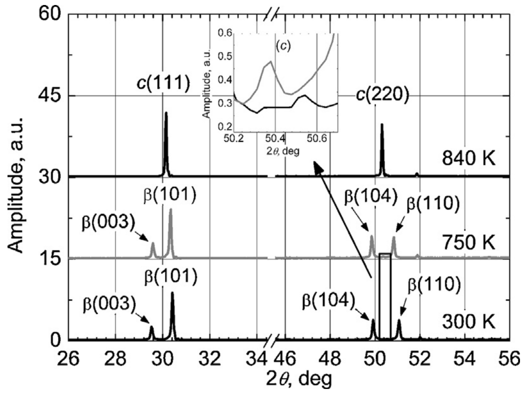

Fig. 2. X-ray diffraction patterns of 10ScSZ ceramics sintered at 1500 °C. Inset: low intensity cubic phase peaks.

2.2. Methods for electrical measurements and data processing

Sintered ceramics were processed to cylindrical samples of height 1.5–5 mm and diameter up to 3 mm with platinum paste electrodes. For the measurements of electrical properties two different impedance spectroscopy techniques were used. Most of measurements were performed using recently developed impedance spectrometer (frequency range from 0.1 Hz to 10 GHz [28]) which provided 8 frequency points per octave. In order to distinguish volume and interface processes in the low frequency range (from 10 Hz to 2 MHz) a 4-electrode method also was used [29]. All measurements were carried out in an atmospheric air; temperature stability during measurements was around ±0.2 °C.

The obtained impedance data were checked by integral Kramers–Kronig relations as described in [26]:

$$z'_{KK}(\omega) = \left(\frac{2}{\pi}\right) \int_0^\infty \frac{x \cdot z''_m(x) - \omega \cdot z''_m(\omega)}{x^2 - \omega^2} dx, \tag{1}$$

$$z''_{KK}(\omega) = -\left(\frac{2\omega}{\pi}\right) \int_0^\infty \frac{z'_m(x) - z'_m(\omega)}{x^2 - \omega^2} dx, \tag{2}$$

where ω and *x* are angular frequencies, *Z*' and *Z*" –real and imaginary parts of complex impedance, respectively. Straightforward integration, without any extrapolation or other procedures, was

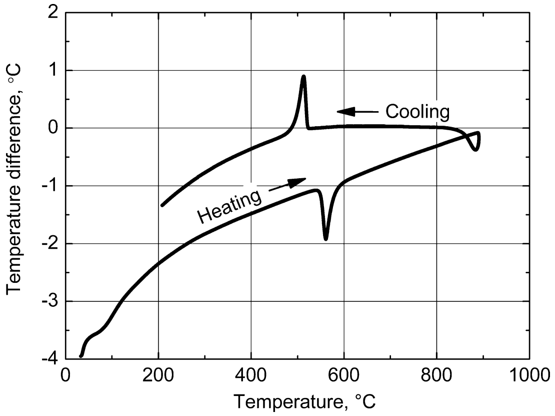

Fig. 3. DTA curve for 10ScSZ ceramics.