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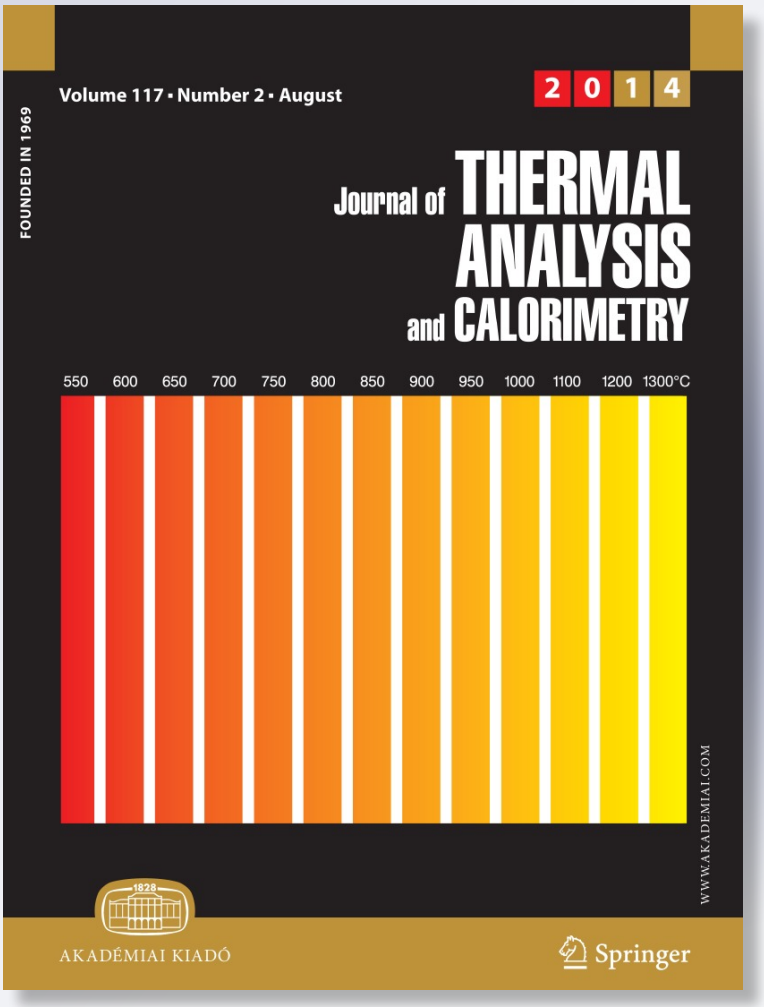

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Thermal and spectroscopic characterization of nanostructured zirconia–scandia–dysprosia

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Abstract Zirconia containing 10 mol% scandia and x mol% dysprosia ($0 \leq x \leq 1.5$) gels was synthesized by simultaneous precipitation at room temperature. The aim of this work is to verify the effect of dysprosium on the cubic phase stabilization of the zirconia–scandia solid electrolyte. The gel was characterized by thermogravimetry, differential scanning calorimetry, and differential thermal analyses. The thermally treated powders were analyzed by Fourier transform infrared spectroscopy, thermal analyses, and X-ray diffraction techniques. For comparison purpose, a commercial zirconia–10 mol% scandia powder was subjected to some characterization techniques. The infrared spectrum shows characteristic absorption bands due to residual material from the synthesis on the surface of the powder particles. Nanostructured powders were obtained after thermal treatments at 500 °C for 2 h. Infrared spectroscopy and X-ray diffraction results evidence the stabilization of the cubic phase in zirconia–scandia containing dysprosium. The thermal stability of the cubic phase during thermal cycling was ascertained by thermal analysis.

Keywords Zirconia · Scandium · Dysprosium · TG–DTA · FTIR · DRX

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Introduction

Solid electrolytes with high ionic conductivity and phase stability have a number of technological applications such as membranes for oxygen separation, oxygen sensors, and in solid oxide fuel cell devices for efficient energy production [1]. Among the solid electrolytes based on zirconia solid solutions, those containing scandia are known to exhibit the highest ionic conductivity values [1–3].

To date, the main concern on zirconia–scandia based solid solutions is to increase the thermal stability of the cubic phase responsible for the high ionic conductivity. Thermal degradation is known to occur for scandia contents below 9–10 mol% [4], whereas for higher contents, the cubic phase decomposes giving rise to a rhombohedric (β) phase with relatively low ionic conductivity [5].

The introduction of small amounts of the second additive has been claimed as a useful approach to stabilize the cubic phase in zirconia–scandia solid electrolyte and to avoid its thermal degradation. Addition of rare earth oxides such as cerium [6], gadolinium [7], holmium [8], samarium [9], ytterbium [10], and yttrium [11], either by solid state or solution methods, has proved to result in cubic phase stabilization of zirconia–scandia. In these studies, the phase transition/stabilization has been investigated mostly by X-ray diffraction (XRD), Raman spectroscopy, and electrical conductivity techniques. Recent works on thermal analysis of zirconia–scandia show that the cubic-to-rhombohedric is the first order phase transition occurring in the 595–630 °C [7, 12].

In this work, the effect of dysprosium addition to zirconia–10 mol% scandia is investigated by thermal analyses and XRD, which are especially useful for studying phase characterization and phase stabilization [13]. To the best of our knowledge, the introduction of dysprosium to acts as

phase stabilizer of the cubic phase in zirconia–scandia has not been reported so far. The ternary solid solution was synthesized by a solution method to ensure chemical homogeneity. The characterization of the product materials was also carried out by elemental analysis and Fourier transform infrared spectroscopy.

Experimental

Solid solutions of nominal contents zirconia–10 mol% scandia–x mol% dysprosia ($x = 0$, 0.5, 1.0, and 1.5) were synthesized by simultaneous precipitation with ammonia, keeping the pH during precipitation between 9 and 10. This method of synthesis is known to produce homogeneous crystalline materials with reduced particle size. It has been already used to prepare dysprosia doped-zirconia nanoparticles [14]. The starting materials were zirconyl nitrate hydrate (99.9 %, Aldrich), scandium (III) nitrate hydrate (99.9 %, Alfa Aesar), and dysprosium (III) nitrate pentahydrate (99.9 %, Alfa Aesar). The concentration of the cation solution was verified by gravimetry and adjusted to 0.1 mol L^{-1}. After precipitation completion, the obtained gels were washed several times with water, followed by isopropanol and absolute ethanol washes. Partial dehydration was obtained with azeotropic distillation using n-butanol and storing in an oven at 50 °C for 50 h before characterization. These extensive procedures of water removal and dehydration were performed to avoid, as much as possible, the formation of OH bridges on the particles surface, which give rise to agglomerates with relatively high strength, known as hard agglomerates [15]. These hard agglomerates constitute a major heterogeneity in ceramic powders and influence their processing, sintering, and final properties [16]. For some characterizations, the dried gels were thermally treated in air at specific temperatures with heating rate of 2 °C min^{-1}. To investigate the effect of dysprosium on phase stabilization in the zirconia matrix, a commercial zirconia-10 mol% scandia (Daiichi Kigenso Kagaku Kogyo, Japan), hereafter named ZSC, was used for comparison purpose.

Thermal characterization was carried out by thermogravimetry, TG, differential thermal analysis, DTA, and differential scanning calorimetry, DSC. These analyses were performed with a simultaneous TG/DTA (Netzsch, STA409) from room temperature up to 1,100 °C in synthetic air (5 mL min^{-1}) with α-alumina as reference material. In these experiments, about 60 mg of the powder was inserted in an open alumina crucible. High precision DSC analysis (Shimadzu, DSC-50) was carried out in nitrogen atmosphere (50 mL min^{-1}) and open platinum crucible from room temperature up to 550 °C. Indium metal (99.9 %) was used for calibration. The heating rate for all these experiments

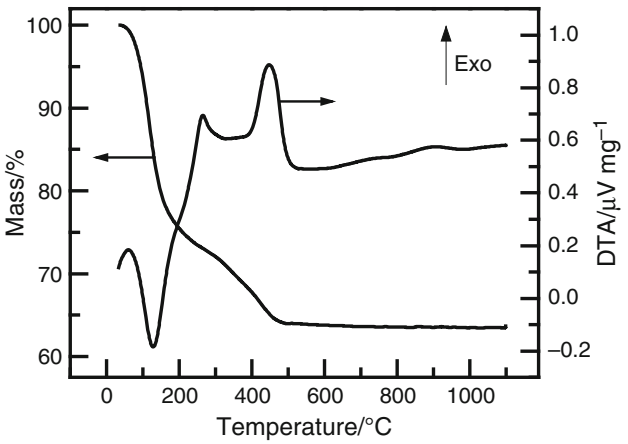

Fig. 1 TG–DTA curves in air of the as-prepared zirconia–10 mol% scandia–1 mol% dysprosia gel

was fixed at 10 °C min^{-1}. Elemental analysis for carbon, hydrogen, and nitrogen in the as-prepared material was performed in a Perkin Elmer, CHN 2400 equipment. Fourier transform infrared spectroscopy, FTIR, analysis was carried out in thermally treated specimens in a Bomem MB100 in the 300–900 cm^{-1} range using KBr pellets. Some as-prepared specimens were analyzed in the diffuse reflectance, DRIFT, mode (Thermo Nicolet Magna 560) spanning from 4,000 to 900 cm^{-1}. XRD, patterns were collected in a diffractometer (Bruker-AXS, D8 Advance) with Ni-filtered Cu K_α ($\lambda = 1.5405$ Å) radiation in the 20–80° 2θ range with 0.05° step size and 2 s time per step. These XRD measurements were performed on as-prepared and thermally treated materials. Identification of the crystalline phases was performed by comparison of the experimental patterns with JCPDS files 37-1484 (monoclinic), 51-1604 (rhombohedric), 51-1603 (tetragonal), and 89-5483 (cubic). The crystallite size was estimated in thermally treated powders by using the Scherrer equation [17] considering the (111) and (101) reflections of the cubic and β-rhombohedric phases, respectively. DTA (SDTQ-600, TA Instruments) measurements were also carried out on commercial ZSC powder and after thermal treatments (1,200 °C for 5 h) of the synthesized material. In this case, data were collected during a heating (700 °C) and cooling (200 °C) cycle with heating and cooling rate of 10 °C min^{-1} in synthetic air (50 mL min^{-1}) with about 30 mg of the materials. Aluminum (99.9 %) was used for calibration.

Results and discussion

The yield of the synthesis method was approximately 95 %. Figure 1 shows results obtained in a simultaneous measurement of TG and DTA in air for the composition with 1 mol% dysprosia. The mass loss up to 500 °C

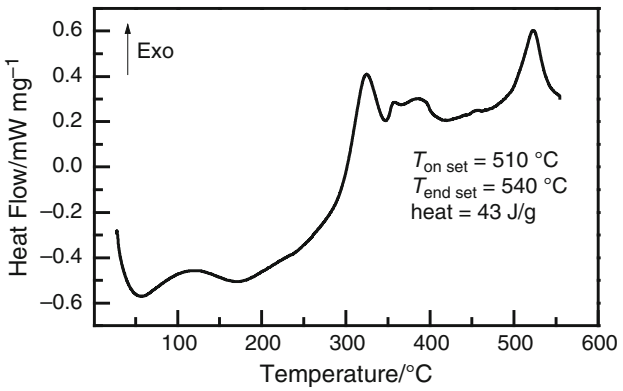

Fig. 2 DSC profile in nitrogen atmosphere of the as-prepared zirconia–10 mol% scandia–1 mol% dysprosia gel

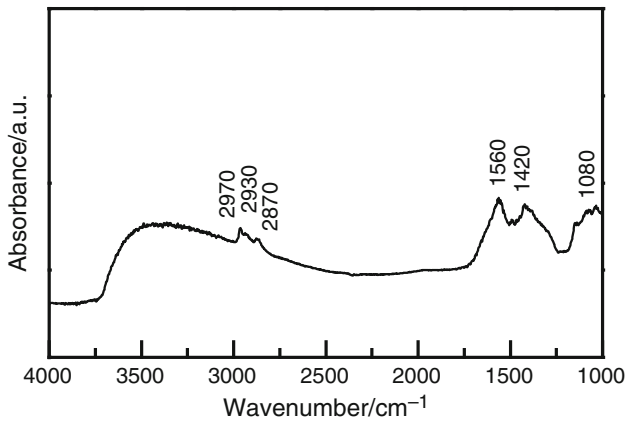

Fig. 3 DRIFT spectrum of the as-prepared zirconia–10 mol% scandia–1 mol% dysprosia gel

amounts 36 %. The theoretical mass loss is 23 % for simple mixed hydroxides formed during the precipitation reaction. High values of experimental mass loss compared to the theoretical value are usually observed in the synthesis of zirconia by solution methods. In a recent work on the preparation of undoped zirconia by the controlled hydrolysis of zirconium oxychloride in the presence of sodium acetate, the reported total mass loss was 44.1 % [18]. The difference between the experimental and theoretical values was attributed to elimination of residual water and organic residues.

It is generally known that water uptake from the surrounding atmosphere may readily occur in nanostructured powders. Then, the difference between the expected and the experimental values of mass loss may be attributed to both residual organic matter from the washing media along with physisorbed water.

Partial evaporation of water and alcohol residues at temperatures below 200 °C is evidenced in DTA curve by the endothermic peak at 127 °C, with onset temperature of 65 °C. The decomposition of the mixed hydroxide is observed in the 200–400 °C range accompanied by alcohol combustion [19]. This decomposition process is related to the exothermic peak at 265 °C. It was shown that in undoped ZrO_2, synthesized by ammonia precipitation, the crystallization temperature is 447 °C [20]. Then, the exothermic peak at 450 °C may be identified with the crystallization of the solid solution.

Figure 2 depicts the DSC profile of the as-prepared gel with 1 mol% dysprosia. No significant difference is observed, when compared to DTA curve of Fig. 1, except by the temperature displacement of thermal events to higher values, due to the inert atmosphere used in DSC experiments.

The chemical composition of the gel surface was analyzed by DRIFT. The spectrum of Fig. 3 shows absorption bands at 2970, 2930, 2870, 1560, and 1420 cm^{-1} evidencing the presence of alcohol residues onto particles surface. In the 3,500 cm^{-1} region of the spectrum, a broad absorption band is observed, which is characteristic of tightly bound OH groups. The absorption band at 1080 cm^{-1} is attributed to C–O stretching and indicates a surface reaction with the formation of an ethoxide [15].

Table 1 summarizes results of elemental analysis for the as-prepared material.

Table 1 Elemental analysis of the as-prepared zirconia–10 mol% scandia–1 mol% dysprosia gel

As-prepared gel	C/%	H/%	N/%
ZrO_2–10 mol% Sc_2O_3–1 mol% Dy_2O_3	8.58	3.02	0.39

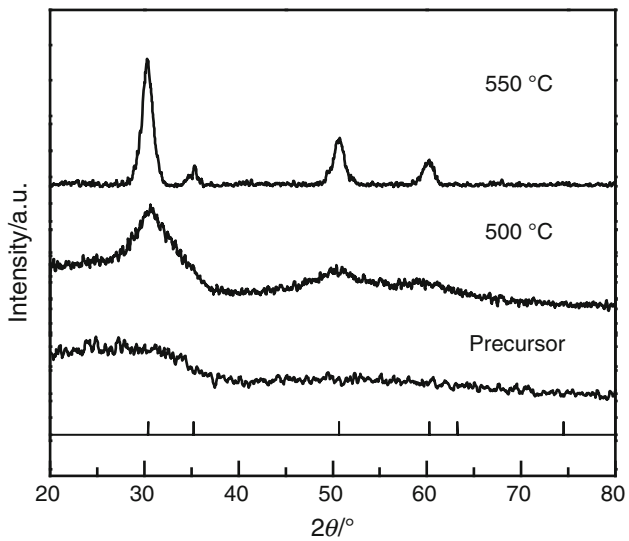

Fig. 4 Room temperature XRD patterns of the as-prepared gel with 1 mol% dysprosia and after heating up to 500 and 550 °C

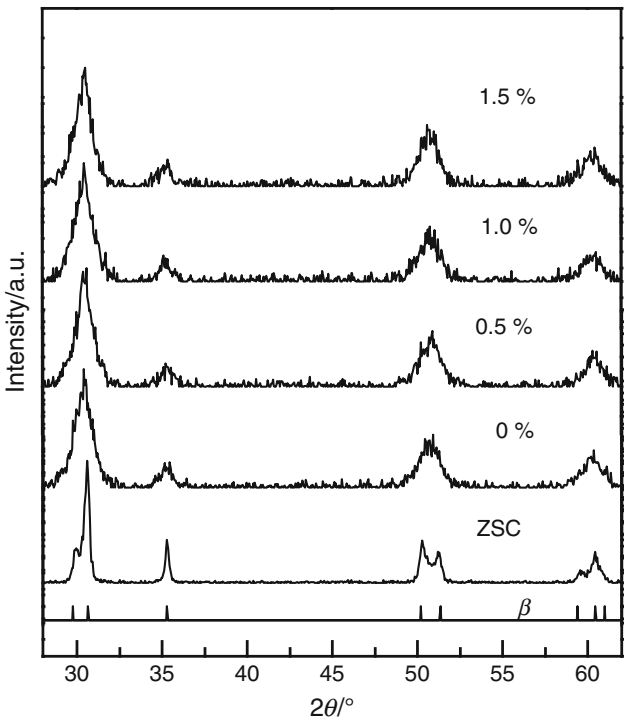

Fig. 5 Room temperature XRD patterns of the synthesized compositions after an isothermal treatment at 500 °C for 2 h and of the ZSC powder

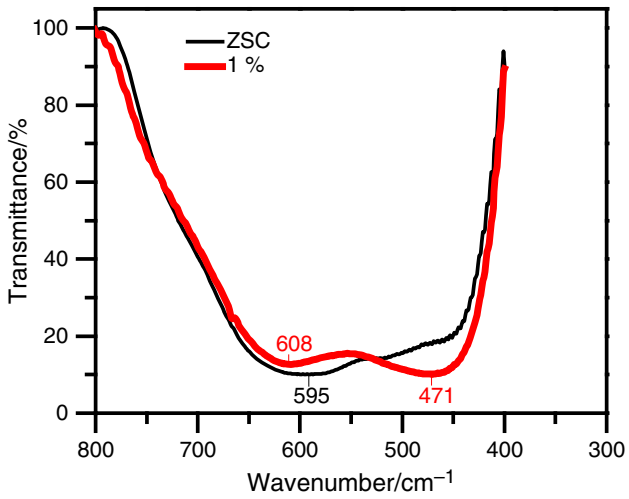

Fig. 6 FTIR spectra of the synthesized nanopowder containing 1 mol% dysprosia thermally treated at 750 °C for 2 h and of the ZSC powder

These results corroborate the hypothesis on the presence of organic residues along with physisorbed water on the particles surface of the as-prepared gel. However, the formation of more complex forms of metal hydroxides may not be discarded.

Figure 4 depicts XRD patterns of the as-prepared material containing 1 mol% dysprosia and after heating (non-isothermal treatment) the gel up to 500 and 550 °C.

It may be seen that the as-prepared material is amorphous to X-rays. After heating up to 500 °C, few broad diffraction peaks appear in the XRD profile, in general agreement with the temperature of crystallization obtained by thermal analysis (Fig. 2). The diffraction peaks become well defined after heating to 550 °C. These XRD peaks are characteristic of the cubic (JCPDS 89-5483), fluorite-type lattice (*Fm3m* space group) of zirconia with angular positions indicated in the bottom of the fig.

It is noteworthy that no diffraction peaks of other crystallographic phases of zirconia (tetragonal, monoclinic, and rhombohedric) were detected in the synthesized zirconia–10 mol% scandia–1 mol% dysprosia solid solution.

Figure 5 shows XRD patterns of the several synthesized compositions after isothermal treatment at 500 °C for 2 h, and of ZSC powder, for comparison purpose.

The XRD patterns of the synthesized compositions are similar with broad diffraction peaks. The zirconia–10 mol% scandia specimen synthesized without dysprosium is indicated by 0 %. An unambiguous identification of the cubic and the rhombohedric phases is difficult, due to the broadening of the diffraction peaks. The angular position of the reflections of the β-rhombohedric phase is indicated in the bottom of the fig. The XRD pattern of ZSC powder is characteristic of the rhombohedric β-phase (JCPDS 51-1604) of zirconia–scandia (*R3* space group). The mean crystallite sizes of the most intense diffraction peak are ~6.5 and ~24.0 nm for the synthesized compositions and the ZSC specimen, respectively.

The FTIR spectra below ~800 cm^{-1} are useful to obtain information on the several crystalline phases of zirconia [21, 22]. Figure 6 shows FTIR spectra in transmission mode of the synthesized zirconia–10 mol% scandia–1 mol% dysprosia thermally treated at 750 °C for 2 h and of the commercial ZSC.

As discussed in [22], the metastable cubic phase in zirconia exhibits only one band at ~480 cm^{-1}, whereas in cubic yttria-stabilized zirconia an additional shoulder at ~610 cm^{-1} is usually observed. Then, the spectrum of the synthesized thermally treated powder with transmittance minima at ~471 and ~608 cm^{-1} is attributed to the cubic phase. The FTIR spectrum of the commercial ZSC powder shows a single band at ~595 cm^{-1}, which do not correlate with monoclinic zirconia (main transmission band at 740 cm^{-1}) nor to the tetragonal (characteristic transmission bands at 435 and 510 cm^{-1}) and may be assigned to the rhombohedric β-phase according to the XRD pattern (Fig. 5).

Figure 7 shows room temperature XRD patterns of the synthesized compositions thermally treated at 500 °C for 2 h and subsequently heated up to 1,450 °C. The Miller

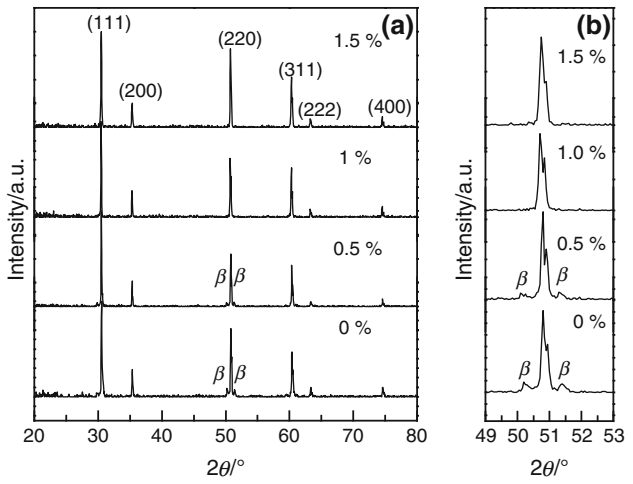

Fig. 7 Room temperature XRD patterns of the synthesized compositions after the heating treatment at 500 °C for 2 h and a subsequent heating up to 1,450 °C: **a** whole angular range, and **b** the 49°–53° range

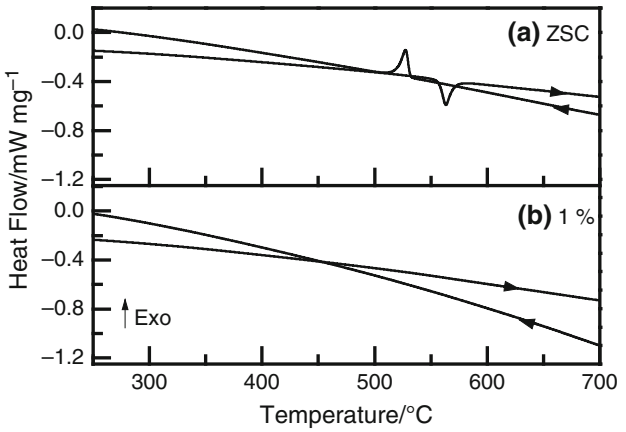

Fig. 8 DTA curves of **a** the synthesized nanopowder containing 1 mol% dysprosia thermally treated at 1,200 °C for 5 h and **b** of ZSC powder during thermal cycling

indexes in Fig. 7a correspond to those of the cubic phase. In Fig. 7b, the 49°–53° angular range is highlighted. As can be seen, the compositions containing 1.0 and 1.5 mol% of dysprosia are cubic, whereas the compositions with 0.5 mol% dysprosia and without additive (0 %) display the characteristic peaks of the rhombohedric phase along with those of the cubic phase.

This result shows that full stabilization of the cubic phase was obtained for compositions with at least 1 mol% dysprosium. For lower contents, the cubic phase is only partially stabilized. In addition, this result evidences that the cubic phase is partially stabilized without the additive suggesting a particle size effect on phase stabilization of zirconia–scandia.

The thermal stability of the cubic phase was verified by DTA. In this case, the thermally treated powders were heated up to 700 and 1,100 °C in distinct thermal cycling experiments. The obtained results in these experiments are similar to each other. As an example, Fig. 8 shows the heating–cooling cycle up to 700 °C of the commercial zirconia–scandia (a) and of the synthesized zirconia–10 mol% scandia–1 mol% dysprosia (b).

During heating, the ZSC material (Fig. 8a) an endothermic peak with onset temperature of 557 °C is readily seen, due to the rhombohedric–cubic phase transition. The reversible phase transition is detected during cooling down by the exothermic peak with onset temperature of 531.5 °C.

The synthesized powder after thermal treatment at 1,200 °C for 5 h (Fig. 8b) does not show any thermal event revealing good stabilization of the cubic phase in the solid solution.

Conclusions

Nanopowders of zirconia–10 mol% scandia–x mol% dysprosia ($x = 0$, 0.5, 1.0, and 1.5) were successfully synthesized by simultaneous precipitation technique. The crystallization of the ternary solid solution occurred at 450 °C. After thermal treatments at 500 °C for 2 h, the powder materials are in the nanosize range with average crystallite size of $\sim$6.5 nm. Stabilization of the cubic phase was revealed by X-ray diffraction and Fourier transform infrared spectroscopy. Specimens with dysprosia contents of 1 mol% or higher do not exhibited the characteristic XRD peaks of the rhombohedric phase. The thermal stability of the cubic phase was demonstrated by differential thermal analysis. The overall results indicate that the ziconia–scandia–dysprosia solid solution may be useful as a single phase solid electrolyte.

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