ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 637–640

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Preparation and conductivity measurement of Eu doped $BaTiO_3$ nanoceramic

D. Hreniak[a,*], W. Strek[a], J. Chmielowiec[b], G. Pasciak[b], R. Pazik[a],
S. Gierlotka[c], W. Lojkowski[c]

[a] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, ul. Okolna 2, Wroclaw, Poland*
[b] *Electrotechnical Institute, Division of Electrotechnology and Materials Science, ul. M. Sklodowskiej-Curie 55/61, Wroclaw, Poland*
[c] *Institute of High Pressure Physics UNIPRESS, Polish Academy of Sciences, ul. Sokolowska 29/37, Warsaw, Poland*

Accepted 15 December 2004
Available online 5 July 2005

Abstract

The new method of fabrication of Eu^{3+}:$BaTiO_3$ nanoceramics obtained from the sol–gel derived nanocrystalline powders is reported. It is demonstrated that under special conditions the obtained ceramics were characterized by black color. Their structural and morphology properties are described. The results of conductivity measurements are presented. The activation energy from the alternating current measurements is determined. An application of Eu^{3+}:$BaTiO_3$ nanoceramics for the solid oxide fuel cell systems is discussed.

Keywords: Nanostructures; Sol–gel synthesis; Ionic conduction

1. Introduction

It is well known that perovskite-type oxides can be used both as electrolytes and as electrodes or oxygen separation membranes for solid oxide fuel cell (SOFC) [1–4]. The principal parameters, which determine a possibility of oxide materials for application as electrolytes in the efficient SOFC, are high ionic conductivity at low temperatures. Besides of that the low reactivity with contacts and chemical stability at working conditions are critical for the purposed applications. At the present time, the most promising materials demonstrate the relatively stable high ionic conductivity (close to 0.1 S/m) at the temperature below 900 °C. The ferroelectric properties of $BaTiO_3$ nanocrystallites were recently a subject of massive investigations. The size effects on the ferroelectric domain creation and the formation of tetragonal structure of barium titanate were found and described in detail [5–8]. The pure and donor activated $BaTiO_3$ ceramics composed of microsized crystals were the subject of a few reports on their electrical properties and are widely used in the electronic devices as high permittivity capacitors and PTCR [9,10].

In this work, we present a novel method of fabrication of $BaTiO_3$ nanoceramics. It is shown that such nanoceramics may be applied as electrode materials in the SOFC systems.

2. Experimental

2.1. Samples

Preparation of $BaTiO_3$ (BT) nanocrystals has been presented by us elsewhere [11]. Barium acetate and titanium butoxide were used as starting materials. Acetyl acetone and acetic acid were selected as solvents of titanium butoxide and barium acetate, respectively. Dissolved barium acetate was added dropwise to titanium butoxide solution with stirring. The obtained solutions were vigorously stirred at 50 °C for about 2 h. The 1 mol% of europium nitrate versus barium acetate was then added. The obtained sol was heated at approximately 100 °C for 24 h to form barium titanate

---

[*] Corresponding author. Present address: P. Nr. 1410, 50-950 Wrocław 2, Poland. Tel.: +48 71 343 5021; fax: +48 71 344 1029.
E-mail address: hreniak@int.pan.wroc.pl (D. Hreniak).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.098

gel. The samples of crushed gels were heated at 875 °C to form doped nanocrystalline BT powder. The structural and spectroscopic studies of Eu^{3+} doped BT prepared by the same way were earlier reported by us [8]. The obtained white powder was milled in agate mortar and hot-pressed to pellet under 2.2 GPa at 800 °C. The pellet was dark gray and maintained this color after all performed measurements. For electrical measurements, the sample in a form of tablet $Ø = 3$ mm, $h = 1$ mm was prepared. The screen-printed porous Pt electrodes were applied.

2.2. Apparatus

The microstructure and morphology of the powders and ceramics was investigated using a Siemens D5000 powder diffractometer. For electrical measurements, the RLC meter HP 4284A was used.

3. Results and discussion

The electrode material and the oxygen separation membrane play a crucial role for the completed optimization of efficiency of fuel cell devices. The first should be characterized by mixed ionic-electron conductivity and high specific surface for increasing of the ionic charges recombination probability. The second should be high density ceramic for gases separation and high ionic conductivity.

One of the main problem in the obtaining of completed SOFC with high quality is integration by sintering process of separate parts of fuel cell in one construction. These difficulties result both from difference in the thermomechanical properties of materials which are using for electrolyte and electrode and from occurring of solid state reactions on the contacts between them. These effects can create cracks and intermediate phases, which can conduct to the decreasing of electrical efficiency whole cell. Presumably, the much better parameters should be achieved if both components (electrolyte and electrode) have exactly these same thermomechanical properties and are absolutely non-reactive chemically. The simplest case is if the same material could be used both for electrolyte and electrode fabrication. Then, only problem is forming the stable ionic conductivity in the electrolyte part and mixed in the electrode part. It can be achieved by a controlling size of crystals of both components. Recently, the dependence of crystallite size on the electric properties of oxide materials has been found. It has been reported that the mechanism of electron conductivity is governed by the grain sizes of ceramic [12].

The XRD patterns of obtained samples and the reference standards of the crystal are presented in Fig. 1. The diffraction pattern of the Eu^{3+}:$BaTiO_3$ nanopowder annealed at the temperature 875 °C shows the cubic structure (JCPDS #31-0174) of BT. The average size of crystallites for used powders was estimated by well-known Scherrer equation from broadening of XRD peaks and was found as 30 nm. However, as it can be seen already for the nanoceramic prepared from this same powder after hot-pressing process the sample demonstrates the tetragonal of BT (JCPDS #05-626) and narrower peaks which correspond to bigger crystallites. Such behavior can be explained by well-known influence of the size of grains on the structure of BT and transformation from cubic to tetragonal structure for nanocrystals sizes above ∼50 nm [5,8]. The density of the obtained ceramics was estimated to be 95% of the theoretical density for the $BaTiO_3$.

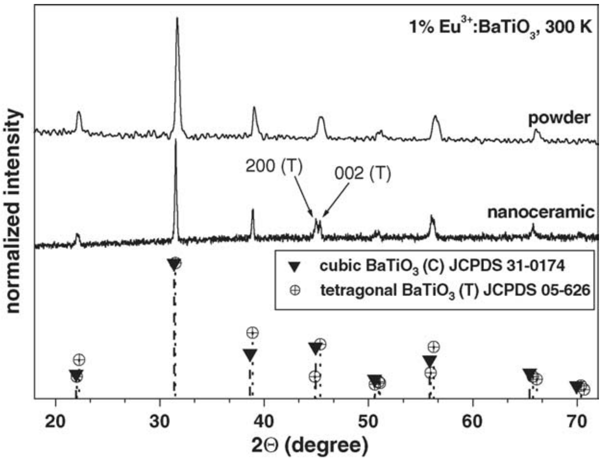

Fig. 1. XRD patterns of powders and nanoceramics of nanocrystalline Eu^{3+}:$BaTiO_3$.

Electrical measurements of the black BT nanoceramic were performed in air and vacuum (10^{-1} Torr) atmospheres using the impedance spectroscopy (IS) method. The real and imaginary part of the impedance (impedance spectra) was measured at the frequency range from 20 Hz to 1 MHz at various temperatures (300–900 °C). The results are presented in the form of Nyquist plots in Fig. 2.

At low temperatures 400–600 °C, the well resolved semicircular arc appears similar to impedance spectra of typical superionic conductors (for example, stabilized ZrO_2 and BICUVOX) [13,14]. This arc is attributed to bulk properties (probably ionic O^{2-} conductivity) of nanoceramic and diminishes with increase of temperature. Generally impedance of BT bulk in vacuum atmosphere is higher than in air because a vacuum causes the reduction of oxygen contains in the samples and a number of the O^{2-} carriers. At lower frequencies and higher temperatures (800–900 °C), the start of other semicircular is traceable and can be ascribed to the electrode polarization effect or grain boundary. Additionally in these ranges of frequencies and temperatures there appears a straight line connected probably with diffusion of oxygen ions from inside to surface of sample. This effect is evident in vacuum atmosphere. On the basis of Nyquist plots, the resistive component of total impedance was established. This resistive component was used to derive the values of ionic conductivity in the function of temperature for BT nanoceramic. An Arrhenius plot for this material is illustrated in Fig. 3. As expected, the conductivity of sample increases with increasing temperature and generally is higher

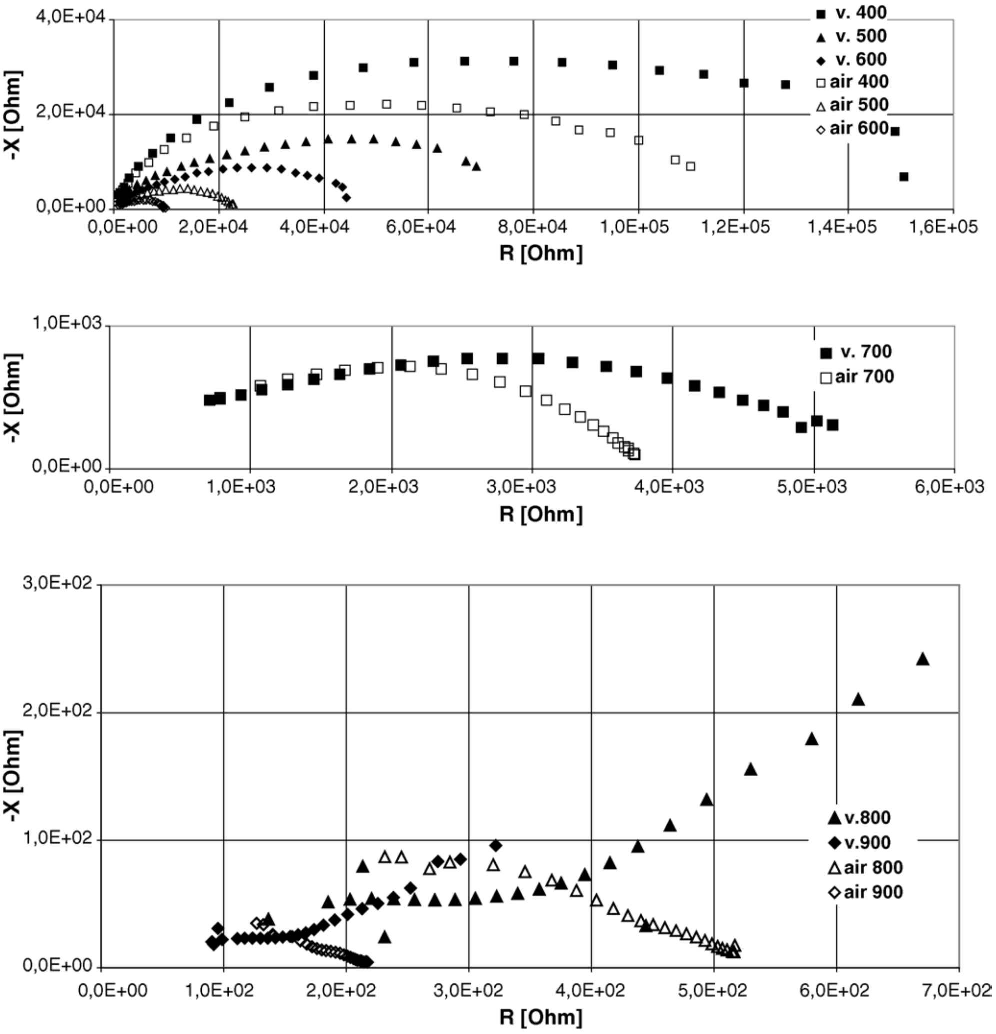

Fig. 2. The Nyquist plots of Eu^{3+}:$BaTiO_3$ nanoceramic at temperatures 400–900 °C (v., vacuum 10^{-1} Torr).

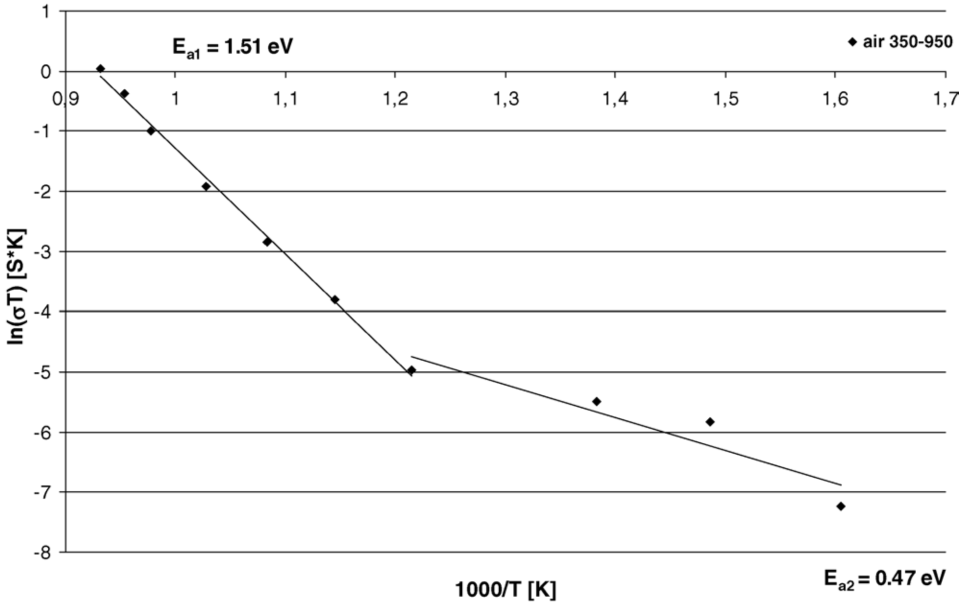

Fig. 3. The Arrhenius plot of Eu^{3+}:$BaTiO_3$ nanoceramic (in air).

in air than vacuum atmosphere. Two activation energies 0.47 and 1.51 eV of conducting process at low and high temperatures were calculated. For explanation of this phenomenon, more structural and electrical investigations should be performed. Since the calculated value of ionic conductivity of BT nanoceramic at 900 °C is 0.01 S/cm, so it is potential candidate for applications in SOFC as electrode material. An ionic character of conductivity was determined by use of DC Wagner method with electron blocking ZrO_2 electrodes. Ionic conductivity of BT determined by use of this method was 1.3×10^{-5} S/cm (600 °C) and it was two times smaller than the same value determined with IS method. It may be due to small dimensions of the sample for DC measurements which are responsible for electrode polarization effect.

4. Conclusions

In this paper, we have presented the novel method of fabrication of Eu^{3+}:$BaTiO_3$ nanoceramics. Their structural and morphology characteristics were determined. Following the ionic conductivity measurements at the temperature range 350–900 °C the conductivity at 900 °C was determined to be close to 1 S/m pointing on possible application of this material as electrode for the SOFC engineering.

Acknowledgments

This work was partly realized in the frame of grant “New electrolytes for Solid Oxide Fuel Cells” and was financially supported by the Polish Ministry of Scientific Research and Information Technology, under contract No. 4 T10A 013 24. One of us (D. Hreniak) is holder of the scholarship of the Foundation for Polish Science (FNP).

References

[1] T. Ishihara, T. Shibayama, H. Nishiguchi, Y. Takita, J. Mater. Sci. 36 (2001) 1125–1131.

[2] R. Polini, A. Pamio, E. Traversa, J. Eur. Ceram. Soc. 24 (2004) 1365–1370.

[3] X.J. Chen, K.A. Khor, S.H. Chan, J. Power Sources 123 (2003) 17–25.

[4] F.M. Figueiredo, F.M.B. Marques, J.R. Frade, J. Electroceram. 7 (2001) 47–56.

[5] M.H. Frey, D.A. Payne, Phys. Rev. B 54 (1996) 3158–3168.

[6] K. Saegusa, E.R. Wendell, H.K. Bowen, J. Am. Ceram. Soc. 76 (1993) 1505–1512.

[7] M.-S. Zhang, J. Yu, W. Chen, Z. Yin, Prog. Cryst. Growth Charact. Mater. 40 (2000) 33–42.

[8] W. Strek, D. Hreniak, G. Boulon, Y. Guyot, R. Pazik, Opt. Mater. 24 (2003) 15–22.

[9] S. Urek, M. Drofenik, J. Eur. Ceram. Soc. 19 (1999) 913–916.

[10] M.-B. Park, N.-H. Cho, C.-D. Kim, S.-K. Lee, J. Am. Ceram. Soc. 87 (2004) 510–512.

[11] D. Hreniak, E. Łukowiak, K. Maruszewski, R. Pązik, W. Stręk, Mater. Sci. 20 (2002) 43–50.

[12] N. Setter, R. Waser, Acta Mater. 48 (2000) 151–178.

[13] M. Kleitz, F. Petitbon, Solid State Ionics 92 (1996) 65–74.

[14] G. Pasciak, K. Prociow, W. Mielcarek, B. Gornicka, B. Mazurek, J. Eur. Ceram. Soc. 21 (2001) 1867–1870.