

Short communication

# Influence of Cu on the properties of gadolinium-doped barium cerate

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## Abstract

In the present work the effect of copper oxide addition on the densification behavior and electrical conductivity of  $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$  (BCG) type ceramics is investigated. Small addition (1 mol%) of this sintering additive reduces both the calcination temperature (by  $\sim 250^\circ\text{C}$ ) and the sintering temperature (by  $\sim 150^\circ\text{C}$ ) and promotes at the same time the densification process. According to the X-ray diffraction analysis the  $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$  samples with  $0 \leq x \leq 0.2$  and the  $\text{BaCe}_{0.9-y}\text{Gd}_{0.1}\text{Cu}_y\text{O}_{3-\delta}$  samples with  $0.0075 \leq y \leq 0.07$  are single-phase. It was found that the samples with Cu, when sintered at  $1450^\circ\text{C}$  for 3 h, have  $\sim 95\%$  of relative density compared with pure  $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$  samples that have  $\sim 86\%$ . It was also found that the electrical conductivity of Cu-containing samples sintered at  $1450^\circ\text{C}$  is comparable to those without Cu sintered at  $1600^\circ\text{C}$  in oxidizing and reducing atmospheres. Cu-containing samples exhibit significantly higher conductivity in both air and hydrogen atmosphere.

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**Keywords:** Gadolinium-doped barium cerates; Copper additives; Electrical conductivity

## 1. Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising and highly efficient systems for electrical power generation. However, their high operation temperature ( $\sim 1000^\circ\text{C}$  for a SOFC based on yttria-stabilized zirconia) introduces a series of problems such as (i) high cost of the used materials, (ii) interaction between the components, (iii) ceramic degradation and (iv) thermal expansion mismatches [1]. In order to reduce SOFCs' operation temperature, the development of new types of electrolytes that will exhibit sufficient conductivity and stability at lower temperatures and consequently, new methods for their preparation are required.

Protonic conductors such as  $\text{BaCeO}_3$ ,  $\text{SrZrO}_3$  and  $\text{BaZrO}_3$  are considered as good candidates for intermediate temperature SOFC electrolyte materials, due to the fact that they exhibit high protonic conductivity at lower temperatures than  $\text{O}^{2-}$  conducting electrolytes, such as YSZ [2]. For example, in the work of Taniguchi et al. a hydrogen-air fuel cell using BCG electrolyte with a thickness of 0.5 mm exhibited good performance

at  $800^\circ\text{C}$ . Its short-circuit current was  $0.9 \text{ A cm}^{-2}$ , and there was hardly any degradation of BCG electrolyte in 1600 h of operation [3]. It has also been reported [4] that  $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$  ceramics have almost negligible electronic (hole) conductivity and are characterized of high ionic conductivity under fuel cell conditions. Furthermore, solid oxide fuel cells based on protonic ( $\text{H}^+$ ) conductors, fed by different fuels such as hydrogen, ethanol and methane have exhibited higher efficiencies than SOFCs based on oxygen ion ( $\text{O}^{2-}$ ) conductor electrolytes [5–7].

The perovskite-type oxides based on  $\text{BaCeO}_3$  belong to the group of protonic conductors in moist atmosphere when doped with trivalent cations such as  $\text{Gd}^{3+}$  [8–10]. Gd-doped barium cerates are usually prepared by a conventional ceramic process consisting of calcining mixtures of the respective oxides and carbonates at elevated temperatures ( $\geq 1000^\circ\text{C}$ ), followed by sintering the pressed powders at  $1600^\circ\text{C}$  [1]. The sintering temperature can be reduced by using very high pressure value; Su et al. reported that after pressing at 70 MPa the sintering temperature was  $1400^\circ\text{C}$  [11]. However, for the time being, there are some problems related with the preparation of these materials; in particular, the high synthesis temperature and the insufficient density of the sintered samples. In order to solve these problems, several analytical chemistry routes such as the oxalate co-precipitation technique [12] and the Pechini method [8,11,13] have been employed.

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It is widely known that one of the simplest ways to increase the ceramic density and/or to decrease the sintering temperature is the introduction of sintering additives. For instance, this method has been widely used for the preparation of ceria electrolyte [14–16]. In general, ceria-based ceramics cannot be easily densified at temperatures below 1500 °C [17]. Some transition metal oxides, such as MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and CuO, have been proven to be effective sintering additives for the densification of ceria-based powders [14,18,19]. It was demonstrated that Co<sub>3</sub>O<sub>4</sub> and CuO are the most effective in promoting the densification of nano-sized ceria powders [19]. In our previous work [20], the effect of MO<sub>x</sub> (where M = Cu, Ni, Zn, Fe, Co and Ti) addition on the densification behavior and electrical conductivity of BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> ceramics was studied. It was found that the BCG doping by small amounts of transition metals allows the decrease of sintering temperature and increases ceramic samples' density. Among the examined samples, Co-, Ti- and Fe-doped solutions showed lower conductivity values and higher activation energy of conduction, than BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> and Cu-, Zn- and Ni-doped samples. The conduction behavior of Mn-, Fe- and Co-doped BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> was investigated and it was showed, that the conductivity in air decreases with transition-metal substitution of the Ce-position [21]. The present work aims at the investigation of the influence of copper oxide addition on the sintering behavior and electrical properties of BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> prepared by the conventional solid-state reaction method.

## 2. Experimental

In the present study, ceramic samples with the following compositions were prepared and their properties were examined: (i) BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> ( $x=0, 0.1, 0.15, 0.2, 0.25$ ), (ii) BaCe<sub>0.99-x</sub>Gd<sub>x</sub>Cu<sub>0.01</sub>O<sub>3-δ</sub> ( $x=0, 0.1, 0.15, 0.2$ ), (iii) BaCe<sub>0.9-y</sub>Gd<sub>0.1</sub>Cu<sub>y</sub>O<sub>3-δ</sub> ( $y=0.0075, 0.01, 0.0125, 0.015, 0.03, 0.05, 0.07, 0.1$ ).

The samples were prepared according to the conventional solid-state reaction method using BaCO<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and CuO as starting materials. The powders of the starting materials were mixed in an agate mortar with ethanol for 1 h and then calcined at 1400 °C (BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub>) and at 1150 °C (Cu-containing samples) for 2 h, respectively, with a heating and cooling rate 300 °C h<sup>-1</sup>. After the calcination, the powders were ground and prepared in the form of sheets by rolling with the addition of 5% solution of natural rubber in a mixture of acetone and gasoline (60/40). The samples (20 mm × 5 mm × 2 mm) were cut from the sheets and calcined for the elimination of organic binders at 900 °C, with a heating rate of 1.5 °C min<sup>-1</sup> and a cooling rate of 5 °C min<sup>-1</sup>. Afterwards, the samples were sintered at 1600 °C (BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub>) and at 1450 °C (Cu-containing samples), both for 3 h with a heating and cooling rate of 5 °C min<sup>-1</sup>.

The phase relation was investigated by X-ray diffraction analyses at room temperature using a computer-controlled measuring complex composed of a DRON-3 apparatus and a personal computer, in nickel filtered Cu K $\alpha$  radiation. The XRD data were used to calculate the lattice constants and the the-

oretical density of the ceramics. The apparent density of the sintered materials was determined by the Archimedes method with water and/or calculated from the weight and the dimensions of the samples. It was found that both methods of obtaining the density provided almost the same value. This value was compared with the theoretical density based on the lattice parameter. The microstructure of the samples, i.e. well-polished surface after thermal etching, was observed using scanning electron microscopy (SEM) (Model: JSM-5900 LV).

The electrical conductivity measurements were carried out employing the four-point dc technique in different atmospheres (wet air and wet hydrogen) at the temperature range of 600–900 °C. Platinum paste stripes which were deposited on the inner and outer surface of an YSZ tube, connected with platinum wires, were used as the electrochemical oxygen pump and the oxygen sensor. On the samples' surface four Pt electrodes were deposited on and connected with Pt wires. The one pair was used in order to apply voltage with an electrochemical station (AMEL INSTRUMENTS MODEL 2053). The second pair of electrodes was connected to a multimeter in order to register the voltage of the samples.

## 3. Results and discussion

According to the XRD analysis, the samples of BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> with  $0 \leq x \leq 0.2$  present single-phase of the orthorhombic perovskite-type structure, while the samples with  $x \geq 0.25$  have an extra phase in addition to the perovskite one. It was found that this phase is BaGd<sub>2</sub>O<sub>4</sub>-type oxide. In a previous work it has been reported that BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> compositions of high Gd content ( $x > 0.2$ ) disproportionate into BaGd<sub>2</sub>O<sub>4</sub> + BaO [22]. The XRD patterns of BaCe<sub>0.9-y</sub>Gd<sub>0.1</sub>Cu<sub>y</sub>O<sub>3-δ</sub> are shown in Fig. 1. While Cu-containing samples were single-phased with perovskite structure up to  $y=0.07$ , samples with  $y > 0.07$  presented mixed phases of the perovskite and other undetected phases. Therefore, in this study, the single-phase samples were only further investigated. The relative densities and the lattice parameters determined by the XRD analysis of the sinters are shown in Table 1. It is obvious that the unit cell volume is

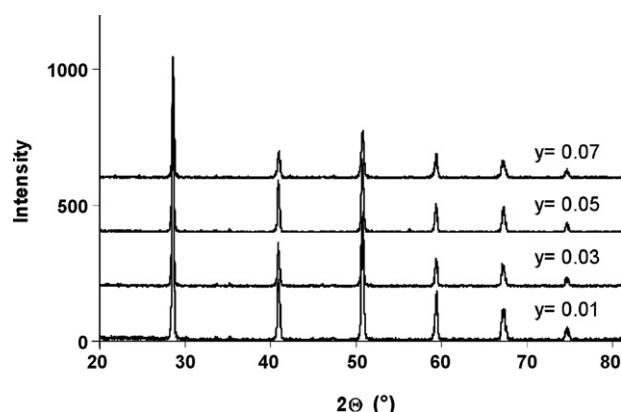


Fig. 1. XRD patterns of the BaCe<sub>0.9-y</sub>Gd<sub>0.1</sub>Cu<sub>y</sub>O<sub>3-δ</sub> samples sintered at 1450 °C for 3 h.

Table 1  
Lattice constants, unit cell volume and relative density of the samples

Compositions	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)	<i>V</i> (nm <sup>3</sup> )	Relative density (%)
BaCe <sub>0.9</sub> Gd <sub>0.1</sub> O <sub>3-δ</sub>	0.8770 (5)	0.6221 (9)	0.6244 (3)	0.3406 (6)	86
BaCe <sub>0.89</sub> Gd <sub>0.1</sub> Cu <sub>0.01</sub> O <sub>3-δ</sub>	0.8801 (7)	0.6212 (6)	0.6236 (3)	0.3409 (3)	94
BaCe <sub>0.87</sub> Gd <sub>0.1</sub> Cu <sub>0.03</sub> O <sub>3-δ</sub>	0.8792 (5)	0.6198 (0)	0.6250 (0)	0.3405 (6)	95
BaCe <sub>0.85</sub> Gd <sub>0.1</sub> Cu <sub>0.05</sub> O <sub>3-δ</sub>	0.8802 (5)	0.6219 (8)	0.6227 (2)	0.3409 (3)	95
BaCe <sub>0.83</sub> Gd <sub>0.1</sub> Cu <sub>0.07</sub> O <sub>3-δ</sub>	0.8780 (7)	0.6240 (6)	0.6302 (1)	0.3412 (5)	96

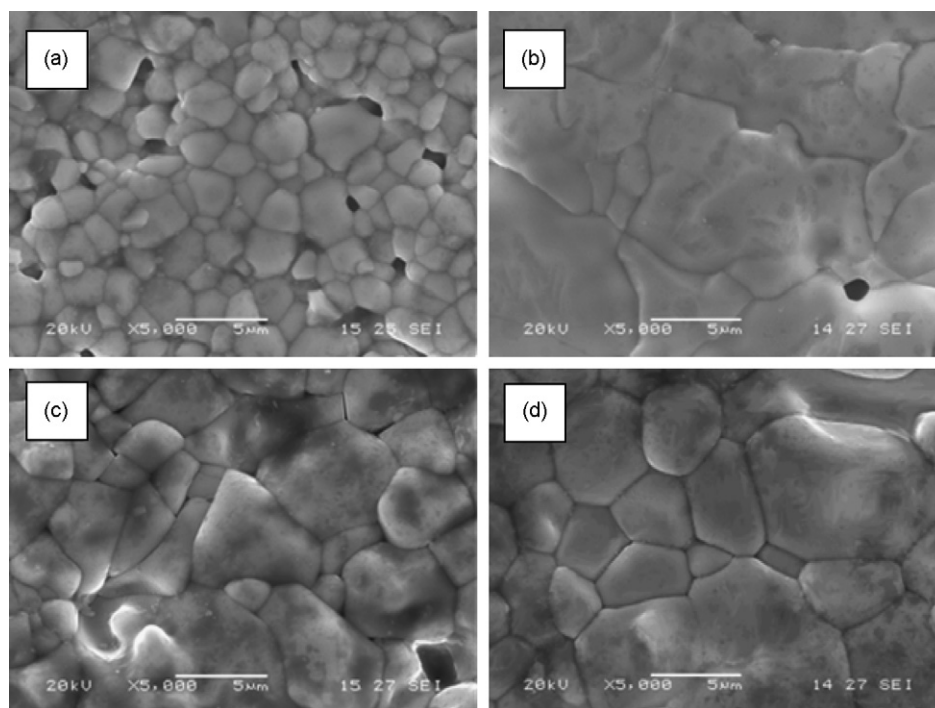


Fig. 2. SEM micrographs of the BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> sample, sintered at 1600 °C for 3 h (a) and BaCe<sub>0.89</sub>Gd<sub>0.1</sub>Cu<sub>0.01</sub>O<sub>3-δ</sub> (b), BaCe<sub>0.87</sub>Gd<sub>0.1</sub>Cu<sub>0.03</sub>O<sub>3-δ</sub> (c), BaCe<sub>0.85</sub>Gd<sub>0.1</sub>Cu<sub>0.05</sub>O<sub>3-δ</sub> (d) samples sintered at 1450 °C for 3 h.

practically independent of Cu content. The relative density of the BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> sample was 86%, while the relative density of the Cu-containing samples was above 95% of the theoretical.

In order to examine the effect of the different Cu doping content on the microstructure of the samples, the technique of scanning electron microscopy was employed. Selected SEM micrographs are shown in Fig. 2. It can be seen that there are many pores along the grain boundaries in pure BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> (Fig. 2(a)), while almost no or little trapped pores can be observed in Cu-containing samples (Fig. 2(b–d)). Moreover, BaCe<sub>0.89</sub>Gd<sub>0.1</sub>Cu<sub>0.01</sub>O<sub>3-δ</sub> exhibits larger grain size (~10 μm) than that of BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-δ</sub> (~2 μm).

The relationship between the total conductivity of BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> and temperature in wet air atmosphere is shown in Fig. 3. As expected the conductivity of BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> in air decreases with the decrease of temperature, following the Arrhenius equation. Moreover, the total conductivity of the BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> system increases with the increase of the gadolinium substitution and at 900 °C reaches the maximum value of 68 mS cm<sup>-1</sup> for *x* = 0.2. At 800 °C the value of conductivity for the same content of Gd is equal to

43 mS cm<sup>-1</sup>. In the work of Bonanos et al. [23] concerning the BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> system the maximum conductivity in wet air was reached for *x* = 0.15 at 800 °C and was equal to 43 mS cm<sup>-1</sup>. Stevenson et al. [24], working with an atmosphere of wet air, confirmed that the conductivity of BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> reaches

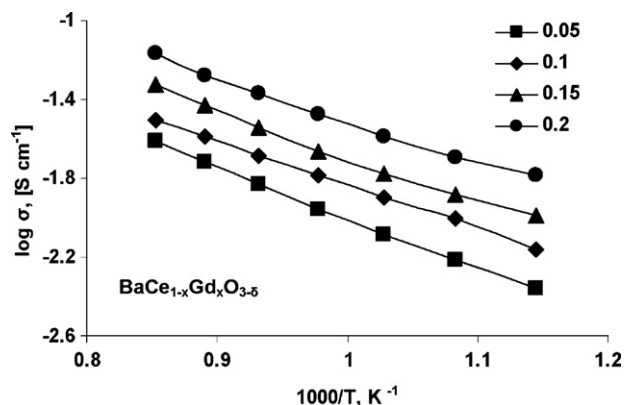
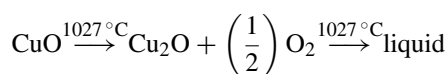


Fig. 3. Dependence of the conductivity of BaCe<sub>1-x</sub>Gd<sub>x</sub>O<sub>3-δ</sub> samples on temperature, in wet air.

a maximum at  $x=0.15$ . Taniguchi et al. observed the highest conductivity in the same system for  $0.20 < x < 0.25$  [4]. The above discrepancies may be caused by the different preparation methods used. For example, Bonanos et al. performed the conductivity measurements on samples sintered at  $1475\text{ }^\circ\text{C}$  [23]. Stevenson et al. used samples sintered at  $1600\text{ }^\circ\text{C}$  [24], while Taniguchi et al. at  $1650\text{ }^\circ\text{C}$  [4]. It was assumed that at higher preparation temperatures the solubility of Gd in  $\text{BaCeO}_3$  may increase and, therefore, the onset of second phase formation may shift to higher doping levels [22]. In turn, the highly doped solid solutions are metastable and might decompose upon ageing at lower temperatures [22].

It was found that during the use of CuO as a sintering additive, a powder densification can be promoted by the phase transition [25]:



One of the possible mechanisms of the sintering promotion due to CuO addition is described in the work of Ran et al. [26].

Fig. 4(a) shows the effect of the amount of Gd on the conductivity of  $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$  in air atmosphere at the temperature range of  $600\text{--}900\text{ }^\circ\text{C}$ , while Fig. 4(b) shows the isothermal variation of the conductivity of  $\text{BaCe}_{0.99-x}\text{Gd}_x\text{Cu}_{0.01}\text{O}_{3-\delta}$  in wet air vs. Gd content ( $x$ ) at the temperature range of  $600\text{--}900\text{ }^\circ\text{C}$ . In Fig. 4(b) it is shown that conductivity reaches a maximum at  $x=0.15$ , with a value of  $92\text{ mS cm}^{-1}$  at  $900\text{ }^\circ\text{C}$  and  $58\text{ mS cm}^{-1}$  at  $800\text{ }^\circ\text{C}$ . As it can be observed, the conductivities of the  $\text{BaCe}_{0.84}\text{Gd}_{0.15}\text{Cu}_{0.01}\text{O}_{3-\delta}$  are higher than those of the  $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ . The samples of  $\text{BaCe}_{0.99-x}\text{Gd}_x\text{Cu}_{0.01}\text{O}_{3-\delta}$

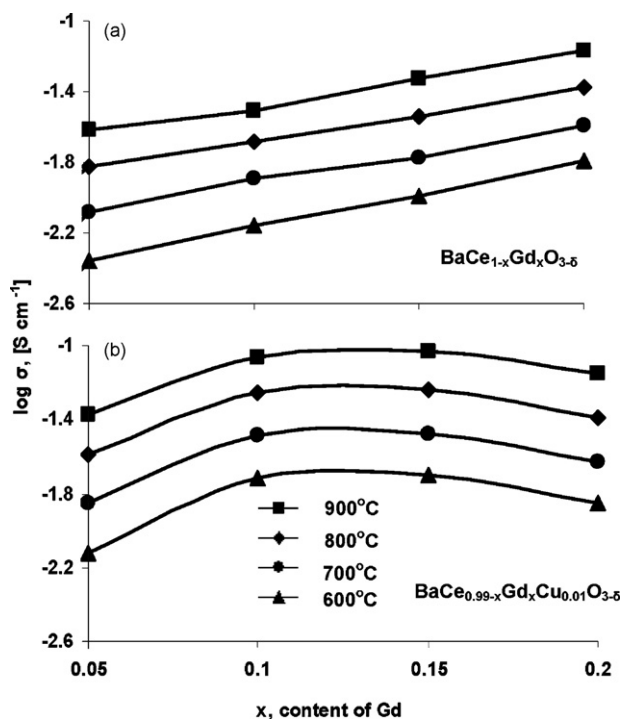


Fig. 4. Effect of Gd doping ( $x$ ) on the conductivity of (a) the  $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$  samples and (b) the  $\text{BaCe}_{0.99-x}\text{Gd}_x\text{Cu}_{0.01}\text{O}_{3-\delta}$  samples, in air at various temperatures.

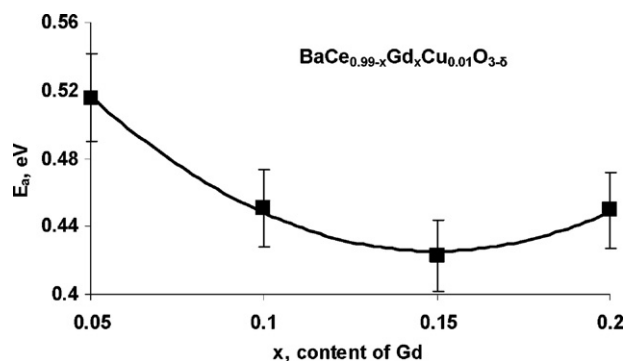


Fig. 5. Dependence of the activation energy of conductivity on  $x$  in  $\text{BaCe}_{0.99-x}\text{Gd}_x\text{Cu}_{0.01}\text{O}_{3-\delta}$  samples, in air atmosphere.

system with  $x=0.1$  and  $x=0.15$  showed almost the same conductivities (Fig. 4(b)). The activation energy of conductivity as a function of Gd content is shown in Fig. 5. The increase of Gd content results in the decrease of activation energy. The lowest value of the latter was registered for 0.15% Gd.

In Fig. 6 the dependence of  $\text{BaCe}_{0.9-y}\text{Gd}_{0.1}\text{Cu}_y\text{O}_{3-\delta}$  conductivity on  $y$ , at different temperatures, is cited. The content of gadolinium is the same in all samples shown in the figure (10 mol%). One can see that the conductivity has a maximum value corresponding to  $y=0.01$ . In the interval  $0.0125 < y < 0.07$ , the conductivity is practically stable; the slightly higher conductivity value at  $y=0.1$ , is probably related with the appearance of additional phases. These additional phases could be probably complexes, including copper oxide, which exhibit high electronic conductivity. The activation energy of conductivity for the  $\text{BaCe}_{0.9-y}\text{Gd}_{0.1}\text{Cu}_y\text{O}_{3-\delta}$  system as a function of Cu content is shown in Fig. 7. It is obvious that the activation energy has a slight tendency to increase with the increase of the copper content.

Finally, Fig. 8 allows the comparison of the conductivity of  $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$  with that of  $\text{BaCe}_{0.89}\text{Gd}_{0.1}\text{Cu}_{0.01}\text{O}_{3-\delta}$  in wet air and wet hydrogen. It is obvious that the conductivity of 1% Cu-containing sample is higher than the one of BCG without copper, in both atmospheres. The higher conductivity can be attributed to the increase of the sample's density. It is not quite clear the reason why the conductivities of Cu-containing samples are practically the same in wet air and wet hydrogen at low temperature values (Fig. 8). However, at higher temperatures

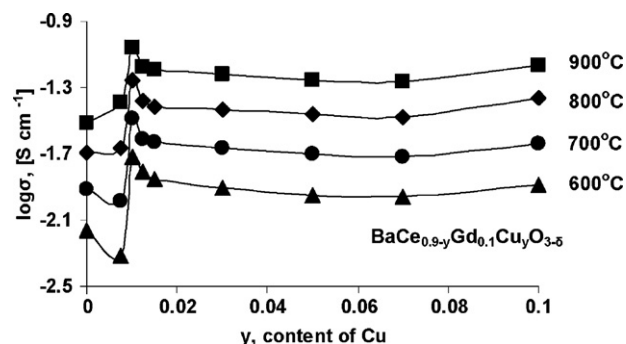


Fig. 6. Dependence of the conductivity on  $y$  in  $\text{BaCe}_{0.9-y}\text{Gd}_{0.1}\text{Cu}_y\text{O}_{3-\delta}$ , at different temperatures in air.



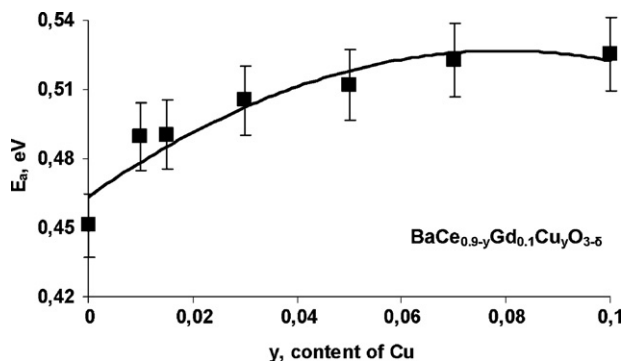


Fig. 7. Dependence of the activation energy of conductivity on  $y$  in  $\text{BaCe}_{0.9-y}\text{Gd}_{0.1}\text{Cu}_y\text{O}_{3-\delta}$  in air.

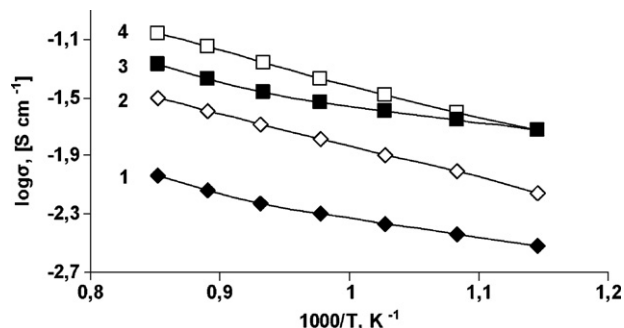


Fig. 8. Temperature dependences of the conductivity of  $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$  in wet hydrogen (1), in wet air (2) and  $\text{BaCe}_{0.89}\text{Gd}_{0.1}\text{Cu}_{0.01}\text{O}_{3-\delta}$  in wet hydrogen (3) and in wet air (4).

the samples' conductivity in hydrogen is lower, than the samples' conductivity in air due to presence of hole conductivity in the oxidizing atmosphere. According to Shimura et al. the hole conductivity depends on the oxide ion vacancy concentration introduced through doping with gadolinium ion ( $\text{Gd}^{3+}$ ) and on oxygen partial pressure [21].

#### 4. Conclusions

The effect of the use of copper as the sintering additive on the sintering behavior, ceramic samples' density and conductivity of gadolinium-doped barium cerates was investigated. It was found that the BCG doping by small amounts of Cu oxide allows the decrease of calcination temperature by  $250^\circ\text{C}$  and sintering temperature by  $150^\circ\text{C}$ . Both density and grain size of the Cu-containing samples were higher than those of the samples without Cu. The density of the samples with Cu was increased by 10–11% comparing with BCG. The comparison of conductivity of undoped and Cu-doped BCG showed that Cu-doped samples have considerable higher conductiv-

ity than undoped samples. More precisely, in wet air the total conductivity of the  $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$  system reached the maximum value of  $68\text{ mS cm}^{-1}$  for  $x=0.2$ , at  $900^\circ\text{C}$ . However, at the same atmosphere and temperature, the conductivity of the  $\text{BaCe}_{0.99-x}\text{Gd}_x\text{Cu}_{0.01}\text{O}_{3-\delta}$  sample reached the value of  $92\text{ mS cm}^{-1}$ , when  $x$  was equal to 0.15. Finally, the maximum conductivity value in the  $\text{BaCe}_{0.9-y}\text{Gd}_{0.1}\text{Cu}_y\text{O}_{3-\delta}$  system corresponded to  $y=0.01$  at  $900^\circ\text{C}$  and was equal to  $87\text{ mS cm}^{-1}$ .

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