INFLUENCE OF SINTERING TEMPERATURE ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF CERIA-BASED COMPOSITES

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Lucrarea studiază influenţa temperaturii de sinterizare asupra microstructurii şi a proprietăţilor electrice pentru un nou compozit pe bază de cerie, în scopul utilizării acestuia ca electrolit solid pentru celulele de combustie de medie temperatură (IT-SOFC). Compozitul a fost obţinut prin metoda sol-gel şi sinterizat la trei temperaturi diferite:1300 ^{0}C, 1400 ^{0}C si 1500 ^{0}C.

Investigaţiile structurale au fost realizate prin SEM şi EDX, iar proprietăţile electrice au fost determinate prin spectroscopie dielectrică.

Rezultatele acestor analize arată ca probele sinterizate la temperatura de 1500 ^{0}C au cele mai bune proprietăţi structurale şi electrice.

In this paper the influence of sintering temperatures on the microstructure and electrical properties for a new composite based on ceria was studied in order to be used as solid electrolyte for intermediate temperature fuel cells with solid electrolyte IT-SOFC. The composite was obtained by sol-gel method and sintering at different temperatures (1300 ^{0}C, 1400 ^{0}C and 1500 ^{0}C).

The structural investigation was realized by SEM and EDX and the electrical properties were determined by dielectric spectroscopy.

The results of these investigations show that the samples sintered at 1500 ^{0}C has the best structural and electrical properties.

Keywords: Y_2O_3, CeO_2, α- Al_2O_3, sintered bodies, SEM, EDX, dielectric spectroscopy.

1. Introduction

Solid oxide fuel cells (SOFC) are of two types based on their operating temperatures: high temperature (SOFC) and intermediate temperature (IT-SOFC). The problem encountered in commercializing IT-SOFC has motivated researchers

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to develop materials that could allow the SOFC operation at intermediate temperatures. Many research groups around the world are involved in developing cathode, anode and electrolyte materials for IT-SOFC [1]. Most of the problems regarding these cells are due to the choice of electrolyte, because the electrolyte must satisfy a number of conditions: the average particle diameter < 100 nm, average grain diameter < 1 μm, low porosity (P < 10 %), electrical and ionic conductivity as large as possible at the operating cell temperature (is of the order of 10^{-3} S/cm at 600 ^{0}C) [2].

The most commonly used SOFC electrolyte, which operates in the temperature range 900 - 1000^{0}C is yttria - doped zirconia. Among the electrolytes used for IT-SOFC, the most studied are those based on cerium dioxide (CeO_2), known as ceria [3]. They are doped with yttrium trioxide (Y_2O_3), scandium trioxide (Sc_2O_3), $Y_2O_3 + Sc_2O_3$, samarium (Sm), gadolinium (Gd), etc [4].

Doping of ceria with various cations has been previously used to increase the electrical conductivity with one order of magnitude and to stabilize its crystalline structure into cubic-tetragonal phase, however the mechanical properties begin to degrade around 10 mol% yttria [5]. Reinforcement of the doped ceria matrix with alumina, or (150 ppm) yttria - doped alumina, has been proposed to improve the structure and the mechanical and electrical properties [6, 7].

Structural, electrical properties of intermediate temperature fuel cells with solid electrolyte (IT-SOFC) depend on the amount, the type and quantity of doping used and the sintering temperature of the electrolytes [8]. It is known that the structure depends of the sintering temperature (decrease of sintering temperature can lead to decrease of the mean grain value) [1, 9]. Jadhav et al. [1], found for sintered samples of gadolinia-doped ceria (GDC), the average grain size of: 2 μm, 2.5 μm and 3 μm, at the sintering temperatures of: 1300°C, 1400°C, respectively 1500°C. The dielectric constant ε_r of doped ceria - based materials is probably relatively small and some authors [10] reported values as low as $\varepsilon_r = 11$. Ref. [11] estimated $\varepsilon_r = 30$. These estimate values were obtained by taking into account the values of the bulk resistance and area to thickness ratio. Another work reported by Sandeep Kumar [12] found the relative permittivity $\varepsilon_r' = 700$ at a temperature of 700 K and a frequency $f = 1$ MHz. This shows that significant differences might be found from different sources.

In this paper a study of the influence of sintering temperature on structural and electrical properties of a new ceria-based ceramic composite is presented.

2. Experiments

Three samples of ceramic composite were used. Ceramic composite is presented in Table 1.

Table 1

Ceramic composite

Sample	Sintering temperature T_s [^{0}C]	Ceramic composite (formula)	Components	
			Name	Notation
A	1 300	(95 %) 10 Y_2O_3: CeO_2 + (5 %) (150 ppm) Y_2O_3: α - Al_2O_3	(95 %)(10 mol %) yttria doped ceria	10YDC
B	1 400			
C	1 500		(5 %) (150 ppm) yttria doped alpha alumina	150 Y_2O_3 : α - Al_2O_3

The samples were denoted A, B and C and have been prepared from sol-gel from pures nanopowders followed by mechanical homogenization and compaction into disc shapes with a diameter of 10 mm and a thickness of 1 mm, isostatic pressing at 10 MPa, and sintering for two hours at 1300 ^{0}C (sample A), 1400 ^{0}C (sample B), and 1500 ^{0}C (sample ^{0}C).

Structural investigations (grains shape, average grains diameter, porosity) of the samples were performed by scanning electron microscopy (SEM) and the qualitative elemental analysis (to determine the nature and distribution of chemical elements inside the samples) was made by energy dispersive X-ray spectroscopy (EDX). To obtain the SEM and EDX images, a scanning electron microscope type HITACHI 2600N was used.

The electrical properties were determined by the dielectric spectroscopy method, with a NOVOCONTROL dielectric spectrometer. Measurements of the real ε_r' part of the complex relative permittivity and the real σ' part of the complex conductivity were performed at a $1V_{rms}$ voltage, $f = 10^5$ Hz frequency and 100, 200, 300 and 400 ^{0}C temperatures.

3. Results and discussions

3.1. Morphological characterization

A part of the results obtained by SEM for the samples A, B and C are shown in Figures 1 - 6, and EDX are shown in Figures 7 and 8.

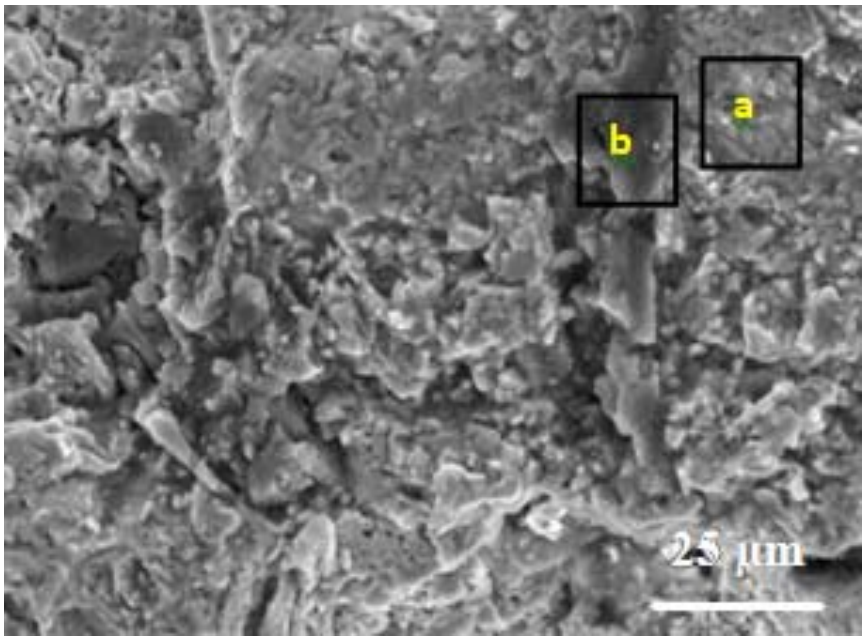

Fig. 1. Scanning electron micrograph of sample A: a –10YDC area, b –150 Y_2O_3 : α - Al_2O_3 area.

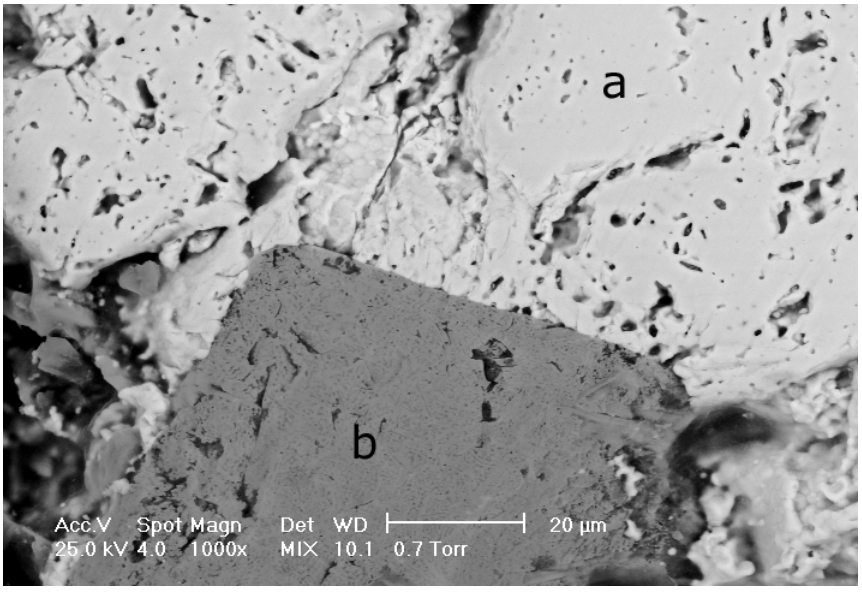

Fig. 2. Scanning electron micrograph of sample A: a –10YDC area, b –150 Y_2O_3 : α - Al_2O_3 area.

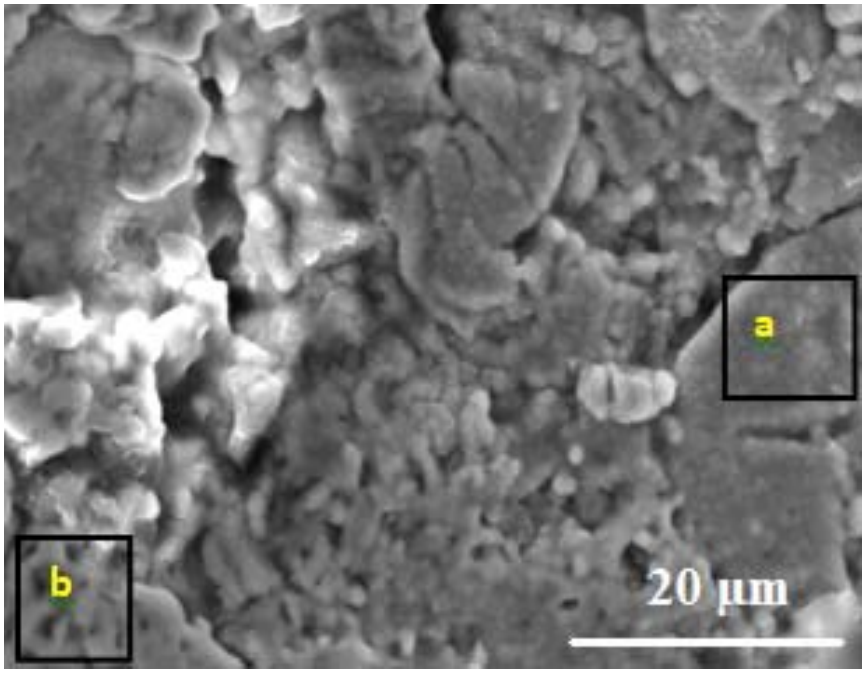

Fig. 3. Scanning electron micrograph of sample B: a –10YDC area, b –150 Y_2O_3 : α - Al_2O_3 area.

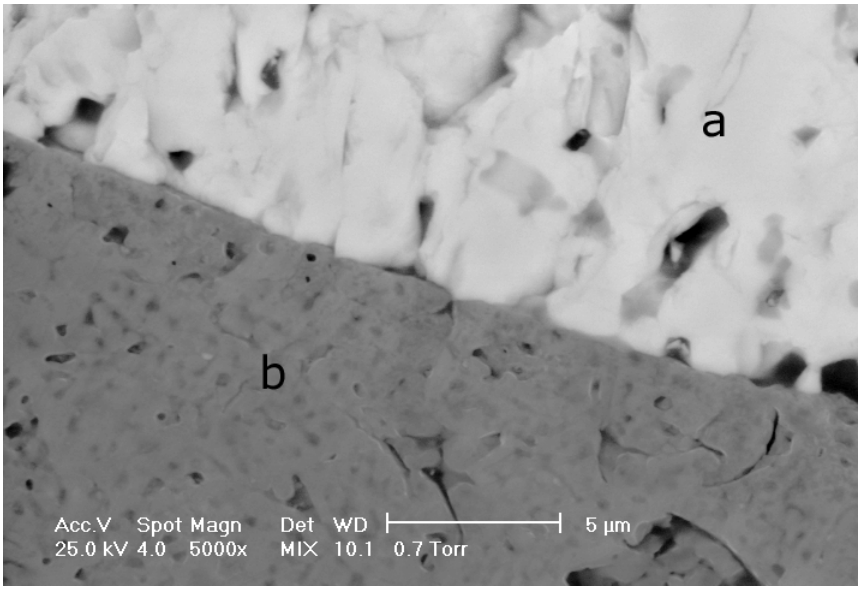

Fig. 4. Scanning electron micrograph of sample B: a –10YDC area, b –150 Y_2O_3 : α - Al_2O_3 area.

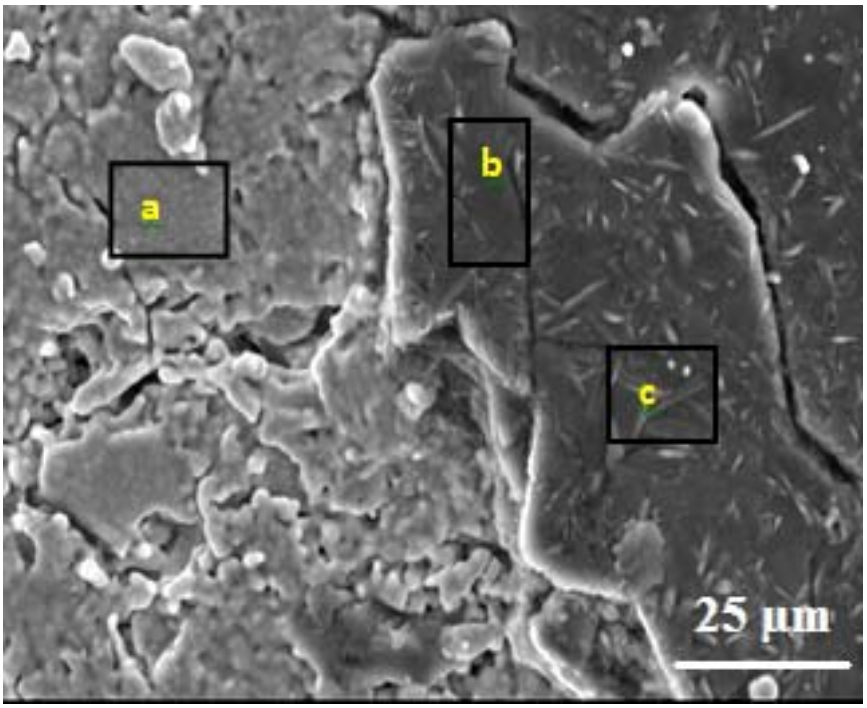

Fig. 5. Scanning electron micrograph of sample C: a – 10YDC area, b – 150 Y_2O_3: α - Al_2O_3 area, c – magnetoplumbite area

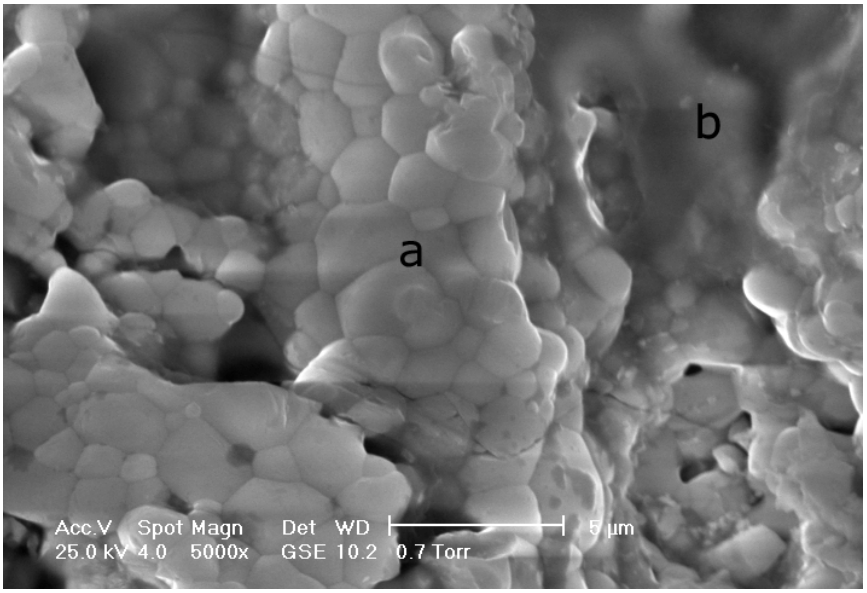

Fig. 6. Scanning electron micrograph of sample C: a – 10YDC area, b – 150 Y_2O_3: α - Al_2O_3 area

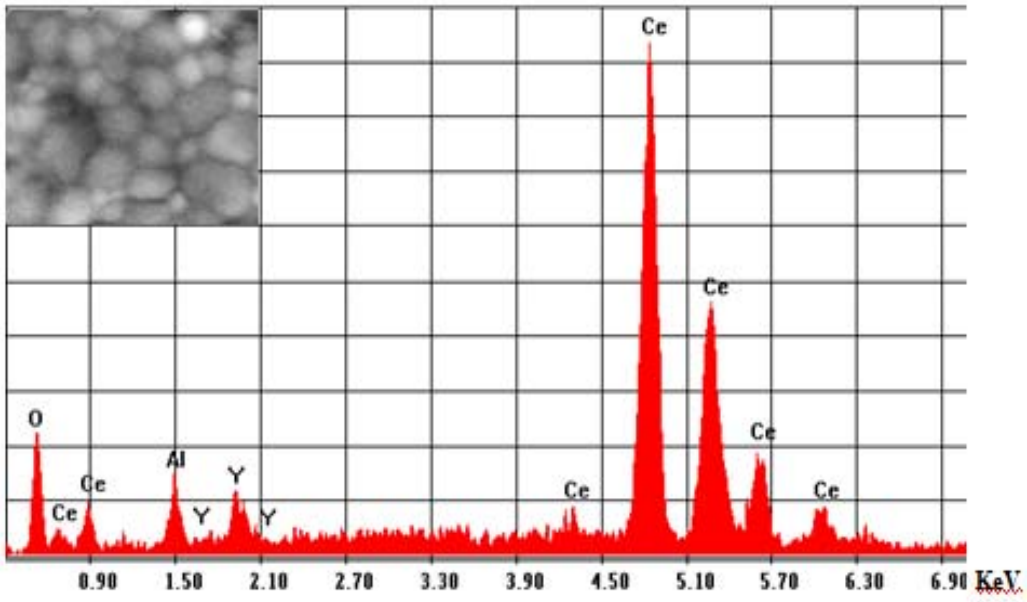

Fig. 7. Energy dispersive X-ray spectrum of sample C for a – 10YDC area.

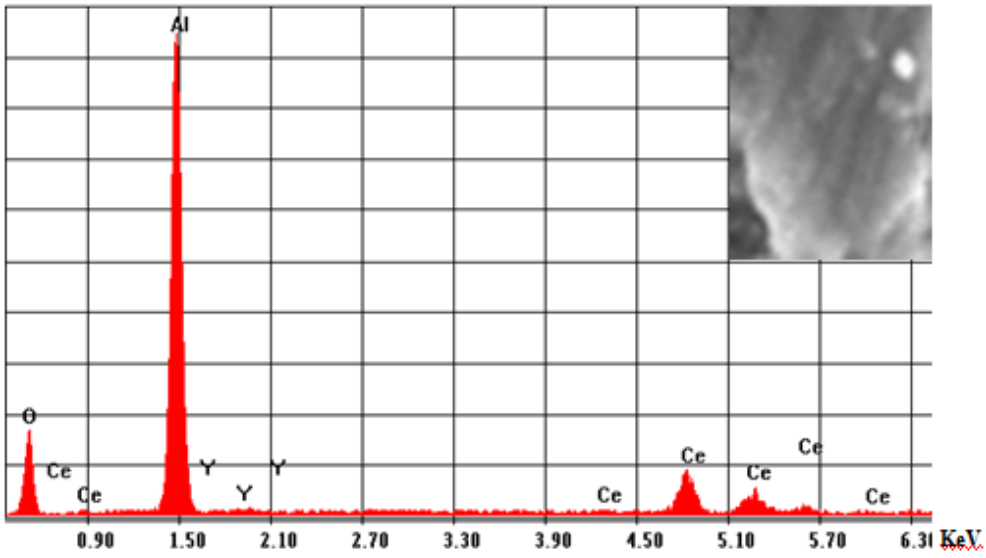

Fig. 8. Energy dispersive X-ray spectrum of sample C for b – 150 Y_2O_3 : α - Al_2O_3 area.

The samples A, B, C show two different structural areas, corresponding to the two components of the composite: matrix of 10YDC (denoted a) and reinforcing of 150 Y_2O_3:α - Al_2O_3 (denoted b).

Grain size was measured from a series of scanning electron micrographs using the linear interception procedure.

In Figures 1 and 2, SEM analyses for sample A, the 10YDC area show spherical grains with the average value of grains diameter (0.45 ± 0.02) μm. As for 150 Y_2O_3:α - Al_2O_3 area, agglomerates with dimensions between 2 and 15 μm, having a very low porosity, were observed. A low intergranular porosity (*P < 0.8*) was observed. In ceria-based matrix, the low doped alumina forms compact areas, with different dimensions which are uniformly distributed in the matrix, especially in the case of lesser than 4 μm agglomerates.

In sample B, spherical grains of 10 YDC (a - area), where the average value of grains diameter is (0.78 ± 0.05) μm, were found (Figs. 3 and 4). The 150 Y_2O_3: α - Al_2O_3 area is formed by agglomerates of an average dimension of 2.8 μm. The alumina agglomerates are uniformly distributed in the ceria matrix and have a very low porosity. A very low intergranular porosity (*P < 0.5%*) was observed.

The Figures 5 and 6 which represent the sample C show the 10YDC areas exhibiting grains of spherical shape and an average diameter of (1.48 ± 0.074) μm. The 150 Y_2O_3: α - Al_2O_3 area is formed by agglomerates of average diameter of (58.5 ± 1.05) μm. The lamellar grains observed on the alumina agglomerates (c area) have an average diameter of (5.8 ± 0.82) μm. In sample C the matrix based on ceria reinforced with low doped alumina uniformly distributed in the matrix, and a few intergranular pores, $P < 0.3$ % is observed.

Lamellar grains composed of a mixture between Ce, Y and Al, which represents the magnetoplumbite (MP) - like $CeAl_{11}O_{17}$ [13], are found on the alumina agglomerates (Fig. 5 c area).

The morphological characterization of all samples (A, B and C) reveals that, the porosity decreases when the sintering temperature increases and, the average grain size increases with sintering temperature.

Figures 7 and 8 present the EDX results for sample C, the best sample of all concerning the morphology, a high compaction therefore a low porosity. These results consist in the spectra which are plots of X-ray intensity signals (y axis) vs. characteristic energies of elements (x axis). EDX spectra for a and b areas show the presence of cerium, yttrium, oxygen, respectively aluminium, yttrium, oxygen elements (Figs. 7 and 8). The presence of these elements was detected for all the three samples. The EDX spectra for samples A, B and C, prove that the chemical composition of the material was respected.

Structural investigations showed that the porosity decreased when the sintering temperature was increased to 1300 up to 1500 °C. Due to the

dependence of the electrical properties on the porosity (a smaller porosity is favourable for electrical properties), the best value of sintering temperatures is 1500 °C. This result is in concordance with that obtained by L. D. Jadhav [1], which evidenced that the GDC relative densities increased when the sintering temperature was increased.

3.2. Electrical properties

The real part of the relative permittivity (ε_r') and the real part of conductivity (σ') was measured for all samples (A, B and C). The results are presented in Figures 9 and 10.

The amount of the physical quantities (ε_r' and σ') increase with increasing sintering temperature. Thus we can see that differences between the variations of these physical quantities are very small between the samples B and C. On the other hand, the differences for the variations of the real component for the relative complex permittivity of these samples are very high for temperature above 1500°C (Fig. 9). The augmentation with temperature of ε_r' values is due to the charge carriers increase in mobility.

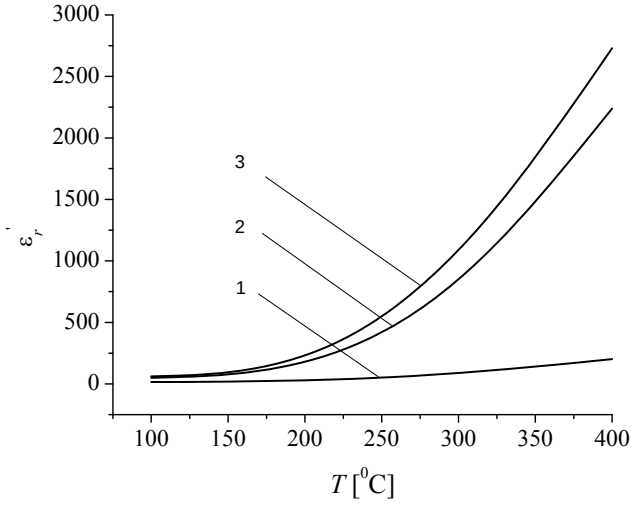

Fig. 9. Variation of the real component of complex permittivity with temperature measured at $f = 10^5$ Hz frequency for samples A (1), B (2) and C (3).

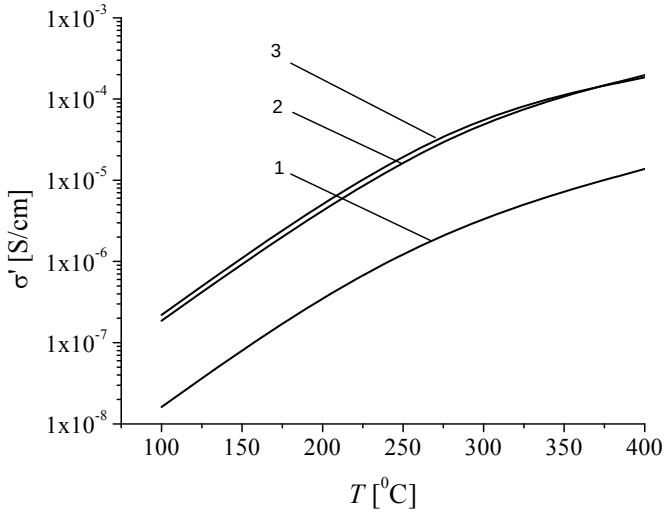

Fig. 10. Variation of the real component of complex conductivity with temperature measured at $f = 10^5$ Hz frequency for samples A (1), B (2) and C (3).

The values of the real component of complex conductivity (Fig. 10) also increase with temperature. Conductivity augmentation with temperature is due to the conducting ions diffusion intensification, diffusion constant having the expression:

$$D = \frac{f}{6} a^2 \exp\left[-\frac{W_b}{kT}\right] \quad (1)$$

where: f is the frequency of ions oscillation, a is a network constant, W_b is the amplitude of the potential barrier, k – the Boltzmann constant, T – the temperature [14].

The conductivity rises with the increase of the sintering temperature of samples. The conductivity for the sample sintered at 1500 °C, measured at 400 °C is of $1.84*10^{-4}$ S/cm, which is not far from the order of magnitude (10^{-3} S/cm) obtained for temperatures of 600 °C.

Since the doped ceria behaves as pure ionic conductors in air, with negligible electronic conductivity, the increase of conductivity is attributed to the augmentation of grain interior conductivity [1, 15].

4. Conclusions

The grained structure of yttria-doped ceria matrix reveals few intergranular pores (P < 0.8% for sample A, P < 0.5% for sample B and P < 0.3% for sample C) and agglomerations of low yttria-doped alumina, with very low porosity.

In the sample C, the lamellar grains containing cerium, yttrium, aluminium (identified by EDX), also reveal the presence of magnetoplumbite (MP)-like $CeAl_{11}O_{17}$, by EDX.

The conductivity for this composite is of the order 10^{-5} S/cm at 400°C for sintered sample at 1 300°C temperature, and 10^{-4} S/cm for the sintered samples at temperature of 1 400°C and 1 500°C.

Because the porosity is a structural parameter, very important for electrical properties and because a smaller porosity is favourable for electrical properties, the best sintering temperature is 1 500°C.

Acknowledgment

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