Electrical conductivity of $BaCeO_3$ synthesized by new sol-gel method

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Polycrystalline $BaCeO_3$ was prepared using new sol-gel processing at low temperature. The sample was characterized by X-ray diffraction and transmission electronic microscopy. The refined lattice parameters were found to be equal to: a = 8.782 Å, b = 6.240 Å, c = 6.217 Å. Electrical conduction was studied in the temperature range 150 to 950°C. The apparent conductivity of compacted samples was found to increase with temperature in a non linear way, from $\sigma = 2.49\ 10^{-7}$ S.m^{-1} at T =150°C to $\sigma = 1.55\ 10^{-3}$ S.m^{-1} at T =950°C. The activation energy is not constant and was found to increase from about 0.21 eV (in the temperature range: 150°C - 450°C) to 0.94 eV (in the temperature range 450°C - 950°C).

Key words: $BaCeO_3$, sol–gel, electrical impedance, characterization, activation energy, protonic conduction.

I- INTRODUCTION

By the past, $BaCeO_3$ and related compounds were intensively investigated because of their potential applications in solid oxide fuel cells (SOFC)[1,2], hydrogen separation membranes and hydrogen sensors [3,4]. Recently, these materials were also found to be of broad interests as catalysts for oxidation reactions because of their ability to conduct oxygen and to support significant variations in oxygen contents [5].

The nature of the conductivity has given rise to many debates about the predominance of protonic conduction, depending on the temperature, the chemical purity of the ceramic [6]. The microstructure and the presence of carbon dioxide in the ambient atmosphere was also considered as potential parameter that could favor one or the other of the possible conductivity mechanisms [7].

In this study, our focus is to carry out a new synthesis route of $BaCeO_3$ using cerium and barium acetates as precursors. The use of these starting products allows to considerably decrease the synthesis temperature of the of the title compound, comparing to the classical solid state synthesis making use of barium carbonate and cerium oxide formerly reported by various authors [7,8]. Its characterization was achieved using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Electrical measurements of impedance were carried out in the range of temperature: 150-950°C.

II- EXPERIMENTAL PROCEDURE

Appropriate amounts of barium acetates and cerium acetates (supplied from ALDRICH, 99,9%) corresponding to the stoichiometric formula of $BaCeO_3$ were dissolved in isopropanol. The obtained solution was stirred during 1 hour at room temperature. The solution was then dried at 80° C under continuous stirring until formation of gel. The resulted gel was dried at 80°C for 12 hours, the as-obtained powder was also reground in an agate mortar and calcined at 950°C during 5hours with a programmed heating and cooling rate of 5°C/min.After a preliminary indexation using the Winploter software [9], the lattice parameters were refined by least squares method. XRD patterns were collected using a Siemens – Brucker D 5000 diffractometer.

Transmission electron microscopy (TEM) analyses were carried out using a Phillips XL30 equipment to well characterize the synthesized powder. The local composition was determined making use of EDAX

analyses. The conductivity was determined under air atmospheric, in the temperature range 150 - 950 °C. The equipment was a Solatron SI 1260 AC impedance analyzer.

The frequency ranged from 1 Hz to 10^6 Hz. For a given temperature, each measurement was carried out after preliminary heating of 15 min.

The conductivity of the title compound was calculated using the formula:

$$\sigma = \frac{1}{R}\frac{e}{S} \quad \text{(Eq.1)}$$

Where S is the electrode area and e is the separation distance of electrodes (usually the sample thickness). For our sample: $S = 1.13\ 10^{-4}$ m^2 and $e = 7.5\ 10^{-4}$ m. R is the resistance of the sample. It was directly given by the intersect of semi-cercle with the real axis for each temperature in the Nyquist representation.

III- RESULTS AND DISCUSSION

III-1- Characterization

Figure1 shows X-ray diffraction patterns of the synthesized $BaCeO_3$; it only exhibits the Bragg peaks characteristic of $BaCeO_3$ phase (JCPDS file 22-0074). The lattice parameters of the compounds

were calculated and refined by least squares method using a refinement program (PARAM)[10], the refined values compared to literature data [12] are summarized in table 1.

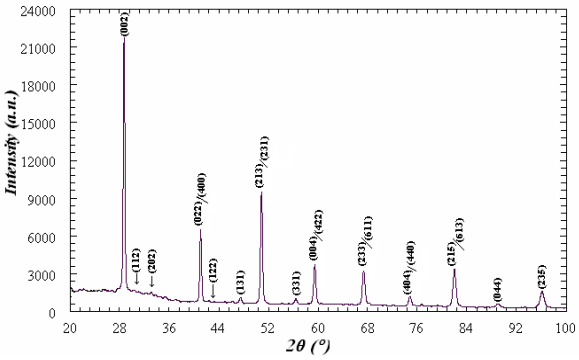

Figure 1: Powder diffraction pattern of $BaCeO_3$

Table 1 : Values of lattice parameters refined using PARAM program compared to the literature data. [12]

	$BaCeO_3$ (our refined cell parameters)	$BaCeO_3$ (literaure data)
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma
Lattice parameters (Å)	a = 8.782 ± 0.003 b = 6.240 ± 0.005 c = 6.217 ± 0.003	a = 8.786 ± 0.001 b = 6.251 ± 0.001 c = 6.220 ± 0.001

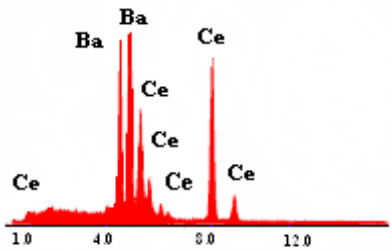

Figure 2: Evidence of Ba and Ce in a sample of $BaCeO_3$ by EDAX.

The X-ray emission (EDAX) analysis shows that only Barium and Cerium elements are present and that they are found in stoichiometric proportion. In addition, no trace of carbon was found (Figure 2). Oxygen is not detected by the analyzer.

	$BaCeO_3$ (refined parameters)	$BaCeO_3$
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma
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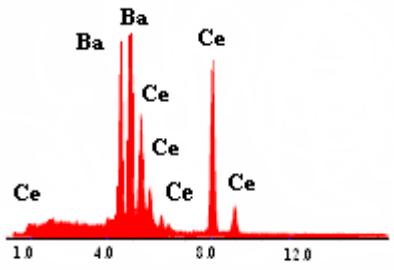

This analysis confirms the presence of $BaCeO_3$ phase (Table 2).

Table 2: Results of compositional analysis

Element	Weight %	Atomic %
Ba (L)	49,88	50,38
Ce (L)	50,12	49,62
Total	100	100

Figure 3 shows characteristic crystals presenting mean linear dimension of 50µm, and having a regular pentagonal geometric form. From Bragg peak profile analyses (XRD data), coherence lengths of 192 nm were estimated: this might be due to the microstructure of these larger geometrical grains, as observed in figure 3 (granular aspect of large crystal).

Nyquist representations (figure 4) were used to interpret the electrical properties of our sample, in the temperature range 150- 950°C in wide frequency range (10^0 - 10^6 Hz). In such

representations, the complex impedances Z = Z' + jZ" are reported in complex plane with x = Z' and y = -Z" [13]. Then it is possible to choose well – adapted equivalent circuit to fit the apparent successive semi-circles observed in the complex plane (Parallel R//C in our case).

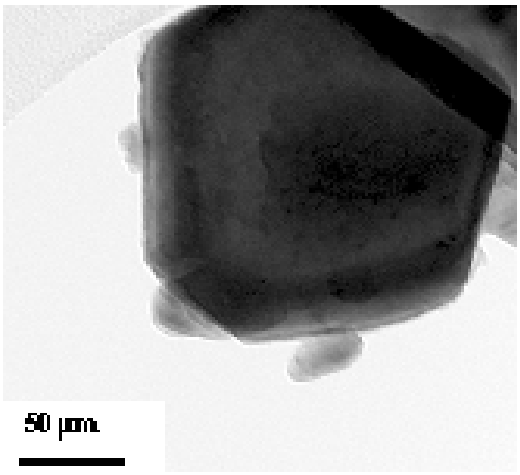

Figure 3: Particle TEM micrograph of $BaCeO_3$.

III-2- Impedance measurements

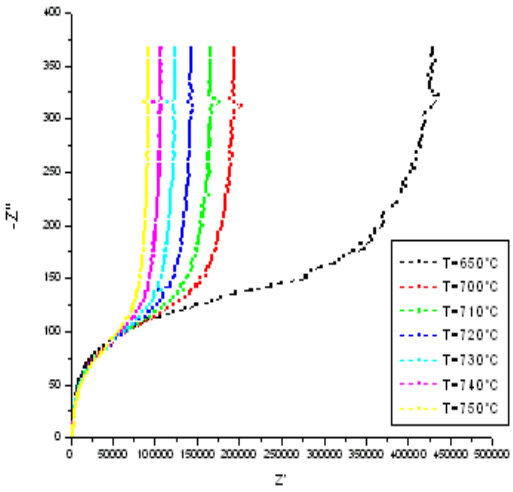

Figure 4: Nyquist representations of impedances obtained for $BaCeO_3$ at different temperature in the range (650°C-750°C).

The absence of electrode reaction semi-circle in the impedance spectra of undoped $BaCeO_3$ was interpreted as the evidence of an electronic contribution; moreover, the water contained in the ambient atmosphere could introduce a protonic contribution even for the undoped material [14].
Indeed, high temperature treatment in presence of moisture allows to protons to be introduced and associated with oxygen anions of the lattice following the reaction:

$H_2O\ (g) + V_o^{\cdot\cdot} + O_o^x \qquad 2OH^{\cdot}$

In which superscripts x, (.) correspond to relative charges of 0, +1 respectively.
Protonic conduction intervenes by jump of the protons from one oxide ion to other and the macroscopic ionic conductivity which results from it is directly connected to the concentration of protons introduced in the material.
The activation energy was calculated from the Arrhenius plot (Figure 5) and using equation: $\sigma=\sigma_0 exp\ (-E_a/K_BT)$ (Eq.2)
Where Ea is the activation energy for conduction, T is absolute temperature and σ_0 is a pre - exponential factor. The calculated value from our measurements (Figure 5) was 0.94eV in the domain temperature of 450°C - 950°C. This value is in good agreement with the value of 1eV found in the literature [13]. The activation energy is not constant and was found to increase from about 0.21 eV in the temperature range: 150°C - 450°C and 0.94 eV in the temperature range T= 450°C -950°C.
The total conductivity calculated using (Eq.1) shows that it increases considerably from $\sigma = 2.49\ 10^{-7}$ S.m^{-1} for T =150°C to $\sigma = 1.55\ 10^{-3}$ S.m^{-1} for T =950°C.

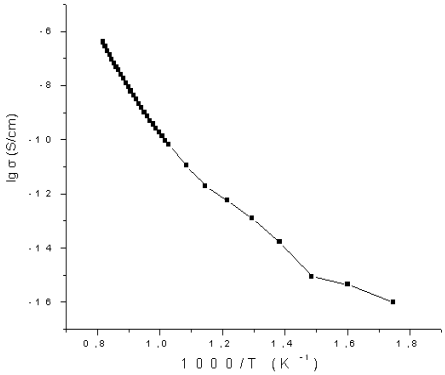

Figure 5: Arrhenius plot of total conductivity of $BaCeO_3$

IV- CONCLUSION

Cerate of barium was synthesized at low temperature via a sol-gel method using acetates of barium and cerium as a precursors, this method avoids the use of carbonates of barium presenting the disadvantage of leaving residues of carbonates disappearing only at very high temperature like cited in work from, in addition, this method allows the advantage to reduce temperature of heat treatment and therefore to minimize crystallite size of the title compound. Both of x-ray diffraction and transmission electronic microscopy confirm the presence of a single phase of $BaCeO_3$, the electrical Conductivity of $BaCeO_3$ was also studied, its value increases considerably at high temperature; contribution of an electronic conduction of this material could explain its electrical behavior in moist environment.

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