Crystal structure and electrical conductivity evaluation of $Ba_{0.50}Sr_{0.50}Co_{0.80}Fe_{0.20}O_{3-d}$ obtained by complexing method

Everton Bonturim[a]; Reinaldo Azevedo Vargas[b]; Marco Andreoli[c]; Emília Satoshi Miyamaru Seo[d]
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP
Centro de Ciência e Tecnologia de Materiais (CCTM)
Av. Prof. Lineu Prestes, 2242 - Cidade Universitária (USP) - São Paulo/SP
[a]ebonturim@ipen.br, [b]ravargas@ipen.br, [c]mandreol@ipen.br, [d]esmiyseo@ipen.br

Abstract. The mixed oxide $Ba_{0.50}Sr_{0.50}Co_{0.80}Fe_{0.20}O_{3-\delta}$ (BSCF), studied as a cathode in Intermediate Temperature Solid Oxide Fuel Cells, can be prepared by liquid phase synthesis, resulting in a stoichiometrically homogeneous material with good particle size distribution. The BSCF was synthesized by a complexing process, known as EDTA-Citrates, where you can control the reaction temperature and the pH of the precursor, the latter being essential for the control of ionic species in solution. The particulates formed were characterized by X-ray diffraction (XRD) to verify the crystalline structure of the material and the ceramic was characterized by resistivity measurements for the determination of electrical conductivity. XRD confirmed the presence of the perovskite-type cubic crystal structure at pH 4.0 and 6.0. According to the results of resistivity measurements, the electrical conductivity of this material is higher in the ceramic when synthesized at pH 6.0.

Keywords: Powder; cathode material; ITSOFC; electrical conductivity

Introduction

The oxide groups that are of Perovskite structure are of great importance to studies of cathode components for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC). Perovskite oxide, described by the stoichiometric formula ABO_3, have been considered important due to their potential application as solid oxide fuel cell electrode materials, gas sensors, oxygen permeable membranes and catalysts for steam and hydrocarbon reforming due to their mixed conductivity, with ionic and electronic transport mechanism[1,2].

Several Perovskite type oxides, such as barium based oxides, have been studied as oxygen permeable membranes due to their high oxygen ion permeability[2,3,4]. The Sr-doped compositions have been given much attention because of their high electrical conductivity. The substitution of a divalent cation (Sr^{2+}) for (Ba^{2+}) can be responsible for the formation of

oxygen vacancies, resulting mostly in a higher ionic conductivity in traditional cathode materials such as $BaCoO_3$. However, the development of alternative cathode materials with high electrochemical performance is critical for the fabrication of intermediate temperature solid oxide fuel cells (IT - SOFCs).[5,6,7,8]

The $Ba_{(x)}Sr_{(1-x)}Co_{(y)}Fe_{(1-y)}O_{3-d}$ (BSCF) presents the physical, chemical and microstructural characteristics appropriate for electrode materials as the cathode of a ITSOFC (500-700ºC)[6,7,8]. The challenge of Solid Oxide Fuel Cells is to investigate how to lower their operating temperature, thus enabling the use of materials more accessible for construction.[9,10] In this case, the BSCF powder, obtained by a complexing method, using EDTA and citrates salts, has been studied and characterized in detail.

The study for synthesis of BSCF powder has shown that some parameters may affect the characteristics such as morphology, crystallite size, conductivity and surface microstructure of the powder. The relationship between the powder synthesis route and the cathode properties is important for optimizing cathode performance.[1,2]

The EDTA-citrate synthesis method was study by Shao and Haile[8]; this method is based on complexing agents with a mixture of salts and the cation(s) of interest. This synthesis method allows for fine control of the majority of the characteristics of the final product, e.g., composition with pure phase, grain size, morphology, stoichiometry, among others. In order to study the effects caused by the variation of pH in the precursor solution, this paper shows the main features of the crystalline structure and the electrical conductivity of BSCF obtained in synthesis at 4.0 and 6.0 pH values.

Experimental

The BSCF powder with stoichiometry $Ba_{0,50}Sr_{0,50}Co_{0,80}Fe_{0,20}O_{3-\delta}$ has been prepared by the EDTA-Citrate synthesis method, consisting of barium, strontium, cobalt and iron nitrate

salts mixed in a buffer solution of EDTA (ethylenediaminetetraacetic acid) and NH_4OH, with subsequent addition of citric acid. The precursor solution contains NH_3-EDTA: citric acid: metal ions with molar ratio 1:1.5:1 and control of pH was varied at 4.0 and 6.0, with NH_3-H_2O. The solution was stirred and heated until the formation of viscous gel and subsequently taken to heat treatment at 200°C for 5h. The product formed has the appearance of a sponge "puff" and then is calcinated at 900°C for 5h.

The identification of the crystal structure and evaluation of crystallinity of BSCF with different pH values was made by X-ray diffraction using the Rigaku Diffractometer (XRD), model Multiflex, with graphite monochromator, using Cu-Kα radiation (wavelength λ = 1.5418 Å). The samples were scanned in the 2θ range 10-90º at a scan rate of 0.02°/min.

The electrical conductivity properties were measured in air by a system built for measuring the temperature dependence of the DC electrical resistivity using the four-probe method. The samples were sintered at 1000°C for 1h and then cutting bar-shaped specimens were prepared in a diamond saw, depositing the contacts with Pt ink and curing the contacts at 600°C for 1h.

Results and discussion

X-ray diffraction patterns of BSCF powders calcined at 900°C for 5 hours in air, obtained with pH variation at 4.0 and 6.0, are shown in Figure 1. The results show the main peaks of the single phase crystalline perovskite cubic structure; in this case it is evident that calcination at 900°C is important for structure.

The perovskite cubic structure was indexed according to data from the file crystallography #01-075-6980 available in the database PDF-2. Although these same XRD results were observed for the powders at different pH conditions, reliability should be further investigated with other compositional analysis techniques.

In other works, studies using infrared spectroscopy indicate the possibility of formation of intermediates during the synthesis of BSCF at different pH conditions, such as $BaCO_3$ that is undetected by the XRD technique.[11]

The results of electrical resistivity measurements were expressed by their inverse, the electrical conductivity, as showed in Figure 2. The mixed ionic and electronic conductor (MIEC), as BSCF, works via diffusion mechanisms and mobility of electron holes and oxygen vacancies; the electrical conductivity is comprised of both electronic and ionic conductivities in these materials.[2]

The conductivity of BSCF increases with temperature, reaching a maximum at 392°C for powder synthetized at pH 6.0 and 409°C for powder synthetized at pH 4.0. The results showed that BSCF synthetized at pH 4.0 had a conductivity of 55.57 $S.cm^{-1}$ whereas when synthetized at pH 6.0 it was 60.45 $S.cm^{-1}$; these values are higher than those reported in the literature.[2,14,15]

The electrical conduction of this material could be attributed to a p-type small polaron hopping mechanism. The decrease in conductivity at high temperatures (>400°C) can be attributed to reduction of electron holes due the conversion of the tetravalent ions, Co and Fe, to their trivalent state, which results in an increase of oxygen vacancies.[2,10,12,13]

The activation energy (Eat) for BSCF at low temperatures, where small polaron conduction is observed[2,14], can be calculated from slope of the linear part of the Arrhenius curve in temperature range 32°C – 400ºC, and the activation energy at high temperature for BSCF synthetized at pH 4.0 and 6.0, in temperature range 678°C – 800°C. The Arrhenius plots of conductivity for low and high temperatures are shown in Figure 3.

The activation energy was measured for these systems and from low temperature it was found to be 36.99 $kJ.mol^{-1}$ for BSCF synthetized at pH 4.0 and 35.09 $kJ.mol^{-1}$ for BSCF synthetized at pH 6.0. The activation energy values for the high temperature case were found

to be 6.80 kJ.mol^{-1} for BSCF synthetized at pH 4.0 and 4.98 kJ.mol^{-1} for BSCF synthetized at pH 6.0. Studies show that low activation energies can contribute to polaron hopping, thus an electrical conductivity increase was observed for powder obtained at pH 6.0.

According to Wei (2006), the activation energy found for BSCF in the same stoichiometry synthetized in this work was 38.6 kJ.mol^{-1}; results published by Jung (2010) show activation energy value of 55.96 kJ.mol^{-1} at same conditions.[14,15]

Conclusion

The sol-gel synthesis using the EDTA-Citrate complexing method was shown to be viable for obtaining $Ba_{0.50}Sr_{0.50}Co_{0.80}Fe_{0.20}O_{3-\delta}$ powders at different pH values. The synthesis parameters for the control of pH value and temperature of calcination are most important for pure phase formation, crystalline structure and crystallinity of the resulting BSCF. The electrical conductivity of BSCF synthetized at pH 6.0 was found to be more suitable for application as a cathode within intermediate temperature solid oxide fuel cell.

Acknowledgements

The authors gratefully acknowledge the funding from CNPq, the support by IPEN-CNEN/SP and University of São Paulo (USP). We also wish to thank the professionals at CCTM-IPEN for the XRD analysis and the professionals of the CCCH-IPEN laboratories for their help with electrical resistivity measurements.

References

[1] MARTÍNEZ, J. P., et al. Fuel cell studies of perovskite-type materials for IT-SOFC. 2006; 159: 914-921.

[2] PATRA, H., et al. Effect of process parameters on combined EDTA-citrate synthesis of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ perovskite. Powder Technology. 2011; 209: 98-104.

[3] DIETHELM, S.; HERLE, J. V.; J. Eur. Ceram. Soc. 2004; 24: 1319-1323.

[4] KIM, J.M. et al.; J. Membr. Sci. 2005; 250: 11-16.

[5] SHAO, Z.P et al.; Sep. Purif. Technol. 2001; 25: 97-116.

[6] ZHOU, W.; RAN, R.; Z. SHAO, J.; Progress in understanding and development of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ based cathodes for intermediate-temperature solid-oxide fuel cells: A review. J. Power Sources. 2009; 192: 231-246.

[7] MAGUIRE, E. et al. Cathode materials for intermediate temperature SOFCs. Solid State Ionics. 2000; 127: 329-335.

[8] SHAO, Z.; HAILE, M. A high-performance cathode for the next generation of solid-oxide fuel cells. Nature. 2004; 431: 170-173.

[9] Leng, Y.; Chan S.H.; Liu, Q.; Development of LSCF–GDC composite cathodes for low-temperature solid oxide fuel cells with thin film GDC electrolyte. International Journal of Hydrogen Energy. 2008; 33: 3808–3817.

[10] WEI, B. et al. Electrochemical characteristics of Ba0.5Sr0.5Co0.8Fe0.2O3-d – Sm0.2Ce0.8O1.9 composite materials for low-temperature solid oxide fuel cell cathodes. Mater. Lett. 2006; 60: 3642.

[11] BONTURIM, E. et al. Effect pH variation of powder materials of the composite oxide $Ba_{(x)}Sr_{(1-x)}Co_{(y)}Fe_{(1-y)}O_{3-d}$ obtained by Citrate-EDTA Method. Materials Science Forum. 2012; 727-728: 764-768.

[12] HUNG, I. M. et al. Effect of pH value on the synthesis and characterization of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ powders prepared by the citrate-EDTA complexing method. J. Material Science. 2010; 45:3824-3832.

[13] CHEN, Z. et al. Assessment of $Ba_{0.5}Sr_{0.5}Co_{1-y}Fe_yO_{3-d}$ (y=0.0-1.0) for prospective application as cathode for IT-SOFCs or oxygen permeating membrane. Electrochimica Acta. 2007; 52: 7343-7351.

[14] WEI, B. et al. Crystal structure, thermal expansion and electrical conductivity of perovskite oxides $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-d}$ ($0.3 \leq x \leq 0.7$). J. European Ceramic Society. 2006; 26: 2827-2832.

[15] JUNG, J. I. et al. Oxygen stoichiometry, electrical conductivity and thermopower measurements of BSCF ($Ba_{0.5}Sr_{0.5}Co_xFe_{1-x}O_{3-d,}$ $0 \leq x \leq 0.8$). Solid State Ionics. 2010; 181: 1287-1293.

Figure Captions

Figure 1. XRD patterns of BSCF powder obtained at pH 4.0 and 6.0 and calcined at 900°C for 5h. The (*) symbol indicates the indexed peaks of BSCF cubic perovskite phase.

Figure 2. Temperature dependence of the electrical conductivity of BSCF synthetized at pH 4.0 and 6.0, calcinated at 900°C for 5h and sintered at 1000°C for 1h.

Figure 3. Arrhenius plots of the conductivity of BSCF synthetized at pH 4.0 and 6.0, calcinated at 900°C for 5h and sintered at 1000°C for 1h in the low temperature range (a) and at the high temperature range (b).

Figure 1

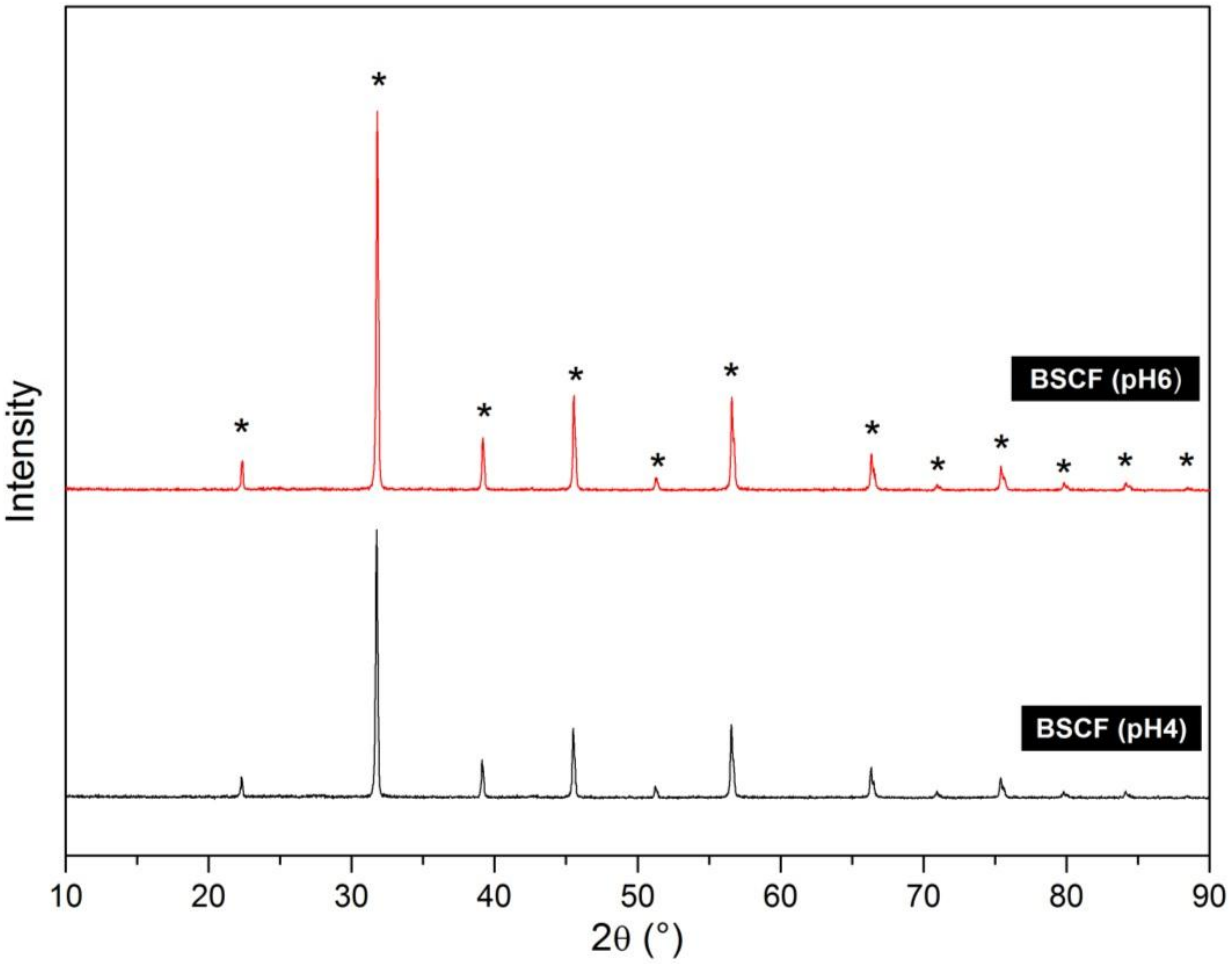

Intensity
BSCF (pH6)
BSCF (pH4)
10
20
30
40
50
60
70
80
90
2θ (°)

Figure 2

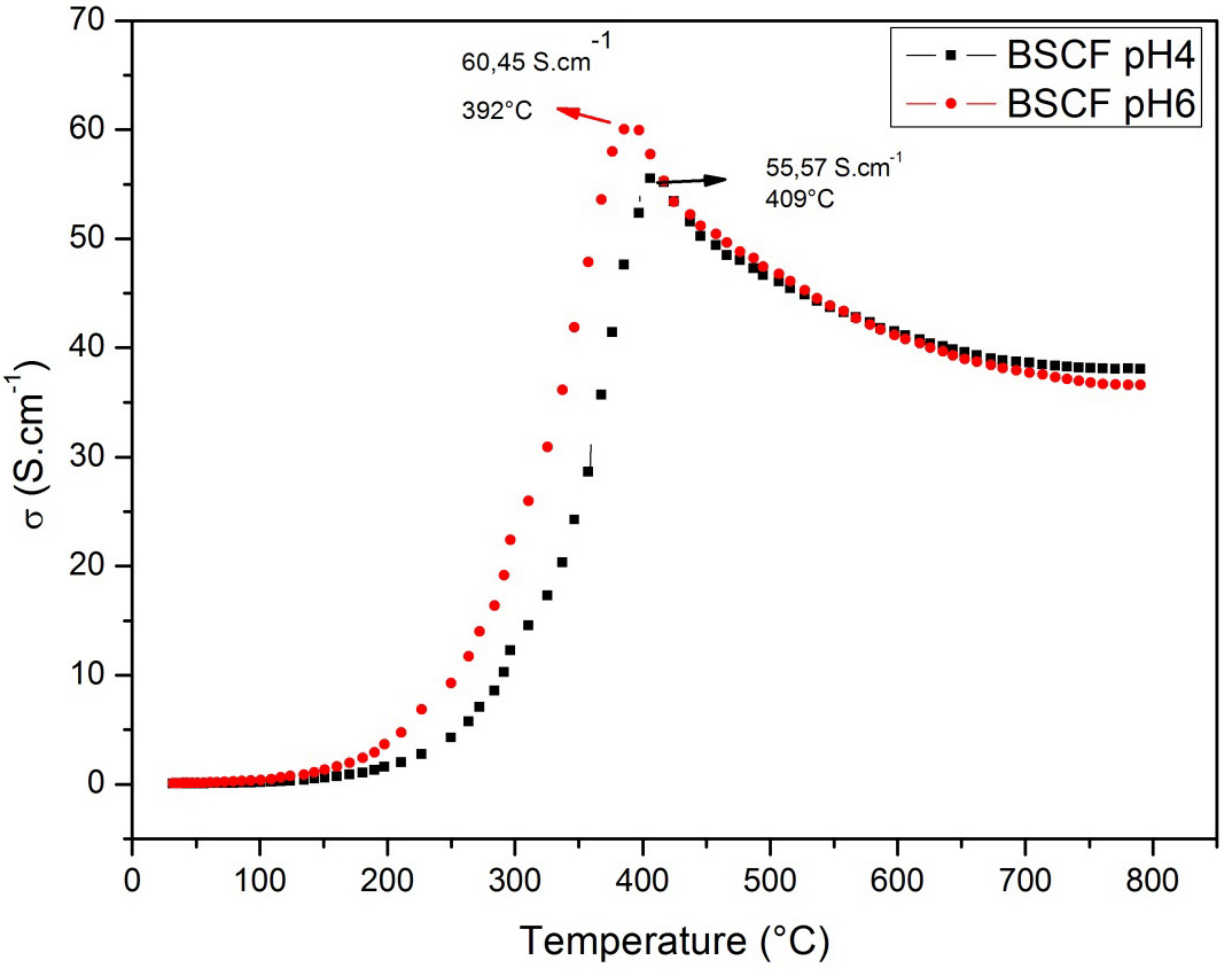
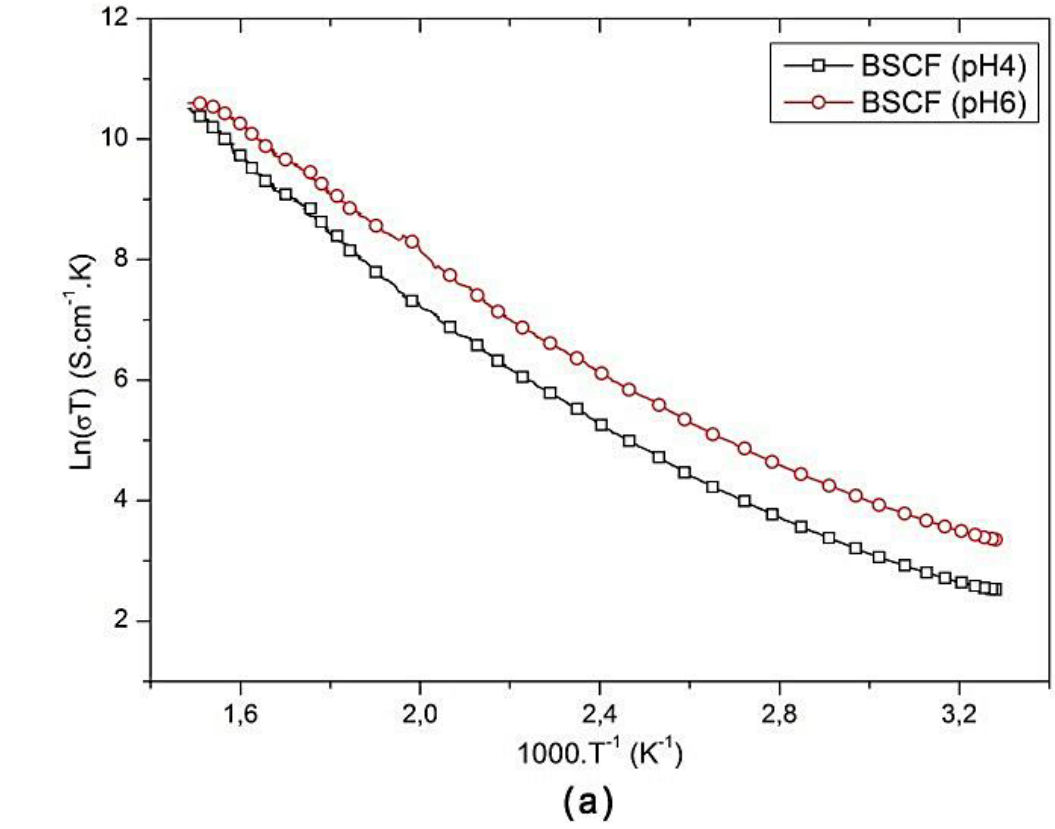
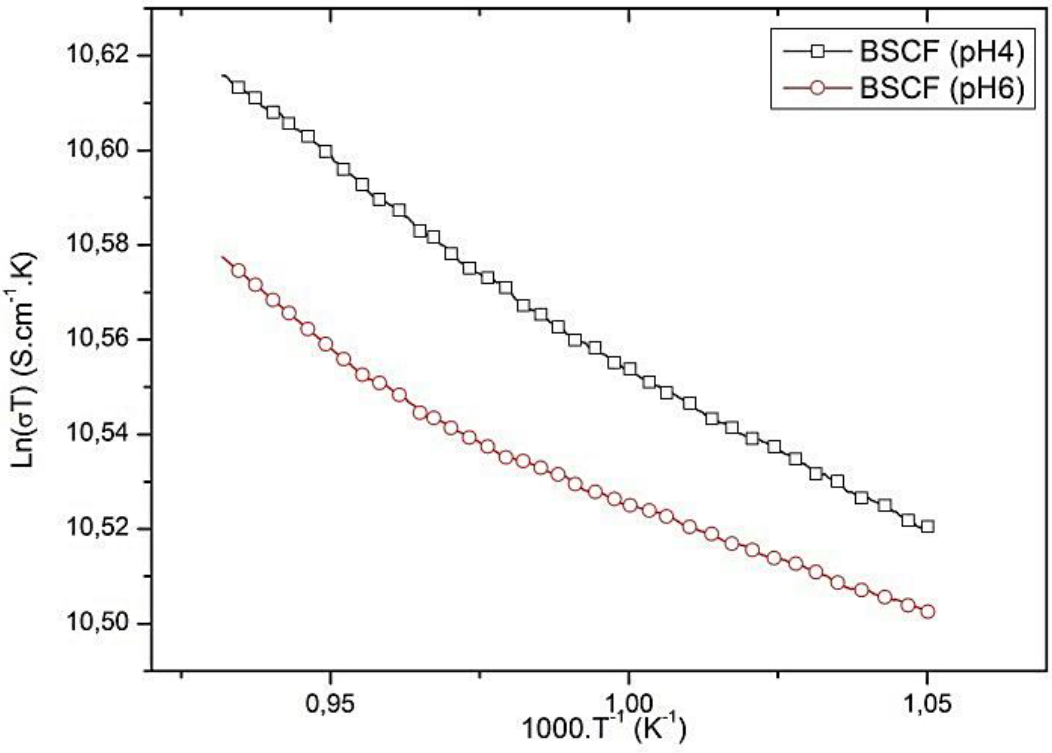

60,45 S.cm-1
392°C
55,57 S.cm-1
409°C
BSCF pH4
BSCF pH6
σ (S.cm-1)
Temperature (°C)
0
10
20
30
40
50
60
70
0
100
200
300
400
500
600
700
800

Figure 3


BSCF (pH4)
BSCF (pH6)
Ln(σT) (S.cm-1.K)
1000.T-1 (K-1)
12
10
8
6
4
2
1,6
2,0
2,4
2,8
3,2

(a)


BSCF (pH4)
BSCF (pH6)
Ln(σT) (S.cm-1.K)
1000.T-1 (K-1)
10,62
10,60
10,58
10,56
10,54
10,52
10,50
0,95
1,00
1,05

(b)