



Ionic conductivity of apatite-type solid electrolyte ceramics $\text{Ca}_{2-x}\text{Ba}_x\text{La}_4\text{Bi}_4(\text{SiO}_4)_6\text{O}_2$ ($0 \leq x \leq 2$)

M. Abbassi^a, R. Ternane^{a,*}, I. Sobrados^b, A. Madani^c, M. Trabelsi-Ayadi^a,
J. Sanz^b

^aLaboratoire d'Application de la Chimie aux Ressources et Substances Naturelles et à l'Environnement (LACReSNE), Université de Carthage, Faculté des Sciences de Bizerte, 7021 Zarzouna, Bizerte, Tunisia

^bInstituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Cantoblanco, 28049 Madrid, Spain

^cLaboratoire de Physique des Matériaux, Université de Carthage, Faculté des Sciences de Bizerte, 7021 Zarzouna, Bizerte, Tunisia

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Abstract

A complex impedance of oxyapatites $\text{Ca}_{2-x}\text{Ba}_x\text{La}_4\text{Bi}_4(\text{SiO}_4)_6\text{O}_2$ ($0 \leq x \leq 2$) prepared by solid state reaction has been investigated. The formation of apatites has been checked by X-ray diffraction, FTIR, Raman and ^{29}Si MAS-NMR techniques. The electric impedance data indicate that relaxation phenomena are strongly dependent on temperature in the 923–1048 K range. The bulk resistance decreases with increasing temperature, showing a typical negative temperature coefficient of resistance (NTCR). ac-Conductivity measurements have been performed on a wide range of frequencies and temperatures. The complex modulus plots have confirmed the presence of bulk contributions. The complex impedance analysis suggests the presence of non-Debye relaxations that would be associated with correlation on ions motion.

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1. Introduction

At present, the finding of new solid electrolytes for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs) conditions efficient and cheap energy production. Among the most technologically promising ionic conducting electrolytes, ceramic samples with apatite-type structure fulfill most of the IT-SOFCs device requirements, working in the temperature range from 873 to 1073 K [1–11].

Oxyapatites, with general formula $\text{Me}_{10}(\text{XO}_4)_6\text{O}_2$ (space group $\text{P6}_3/\text{m}$), are based on isolated XO_4 tetrahedra that share oxygens with Me polyhedra to form a rigid network. In these compounds, O (5) oxide ions, occupying the center of one-dimensional channels running along the *c*-axis, are responsible of ionic conduction. Me cations are located on 7 and 9 coordinated sites, labeled respectively Me_I and Me_II sites.

The apatite's structure can tolerate an appreciable number of structural defects, vacancies and interstitial atoms, varying the electrical properties appreciably with cation doping.

It should be pointed out that so far, there has hardly been extensive literature on apatites containing Bi^{3+} . Two leading syntheses are to be mentioned; one by Huang et al. [12] and the other by White et al. [13]. Both of them held the belief that due to the presence of $6s^2$ lone pair of electrons, Bi^{3+} substitution leads to a distortion in the Ca site, resulting in three different Ca sites, Ca(1), Ca(2) and Ca(3). This results in the loss of mirror plane and the space group thus changes from ideal $\text{P6}_3/\text{m}$ to P6_3 . Similarly, the phosphate analogs $\text{Ca}_8\text{Bi}_2(\text{PO}_4)_6\text{O}_2$ and $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2$ have been reported more recently [14].

In apatite-type silicates, Eu^{3+} luminescence has been used as a local structure probe in understanding the preferential occupancy of Bi^{3+} in the irregular hexacoordinated Ca_II site [15,16]. More recently, new bismuth calcium silicon oxide, $\text{Ca}_4\text{Bi}_{4.3}(\text{SiO}_4)(\text{HSiO}_4)_5\text{O}_{0.95}$, with an apatite structure has been synthesized and its structure has been refined [17].

*Corresponding author. Tel.: +216 98 90 19 16; fax: +216 72 59 05 66.

E-mail address: rternane@yahoo.fr (R. Ternane).

However, no systematic study has focused on the ionic conductivity in Bi^{3+} containing apatite-type silicates to our knowledge.

Complex impedance spectroscopy is a well-established method to investigate electrical properties of materials. This technique offers enormous possibilities to investigate the electrical and electrochemical properties of materials. Thanks to this technique, the study of relaxation phenomena, and the resolution of bulk, grain boundaries and electrode–electrolyte interface contributions are often produced.

In this work, $\text{Ca}_{2-x}\text{Ba}_x\text{La}_4\text{Bi}_4(\text{SiO}_4)_6\text{O}_2$ ($0 \leq x \leq 2$) oxyapatites have been prepared by solid state reaction as a first step. Then, the structural characterization of prepared materials has been performed with XRD, FTIR, Raman and MAS-NMR techniques. Finally, oxygen conductivity and electrical properties of these oxyapatites have been investigated by complex impedance spectroscopy.

2. Experimental

2.1. Synthesis

The oxyapatites $\text{Ca}_{2-x}\text{Ba}_x\text{La}_4\text{Bi}_4(\text{SiO}_4)_6\text{O}_2$ ($0 \leq x \leq 2$) have been prepared by solid state reaction, using high purity SiO_2 (99.99%), CaCO_3 (99%), La_2O_3 (99%), BaCO_3 (99.9%) and Bi_2O_3 (99%) powders. Stoichiometric amounts of reactants have been ground and heated in covered platinum crucibles at 1173 K for 24 h and at 1523 K for 24 h.

2.2. Experimental techniques

X-ray diffraction (XRD) patterns have been recorded with a Bruker D8-advance diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray diffraction data have been collected over the 10° – 60° 2θ range with a 0.02° step and at regular intervals of 12 s. The crystalline phases have been identified using the International Centre for Diffraction Data (ICDD) powder diffraction files.

Fourier transformed infrared (FTIR) spectra have been obtained with a Bruker spectrometer, in the 4000 – 400 cm^{-1} range, using the KBr pellet technique. Raman spectra have been recorded at room temperature in the spectral range 100 – 1200 cm^{-1} in a Dilor XY spectrometer equipped with a CCD detector and a Spectra Physics Ar laser (excitation at 514.5 nm).

The ^{29}Si MAS-NMR spectra have been recorded at 79.49 MHz , using a Bruker MSL400 spectrometer (9.4 T). The sample has been rotated at 10 kHz around an axis inclined 54.44° with respect to the external magnetic field (MAS technique). NMR signals have been recorded after $\pi/2$ radio-frequency pulse ($5 \mu\text{s}$) irradiation. Accumulations have reached 100, each separated from its successor by 20 s. To improve signal/noise ratios, a 100 kHz filter has been used.

Electrical conductivity measurements of apatite materials have been performed using an automatically controlled HP4192A analyzer working at 120 frequencies, log-scaled between 5 Hz and 13 MHz . In electrical measurements, a sinusoidal signal of 50 mV has been used. High temperature measurements have been performed between 748 and 1073 K under air atmosphere. Powders have been pressed under 5 t cm^{-2} and sintered at 1523 K . Electrodes have been prepared by painting Pt paste on both sides of the sintered pellet surfaces, which have been then heated at 1028 K to ensure good electrical contacts. Conductivity values have been estimated with the relation

$$\sigma = \frac{l}{RS} \quad (1)$$

where R is the resistance deduced from impedance diagrams and S and l are the area and the thickness of pellets, respectively.

3. Results and discussion

3.1. X-ray diffraction

Powder XRD patterns of prepared $\text{Ca}_{2-x}\text{Ba}_x\text{La}_4\text{Bi}_4(\text{SiO}_4)_6\text{O}_2$ compounds correspond to well crystallized phases. XRD patterns have been fitted with the hexagonal unit cell (S.G. P6_3 (173)). XRD patterns have showed that all prepared samples are single phases displaying the apatite structure. No peaks of additional phases have been detected. Crystal data deduced from XRD analysis are given in Table 1.

As shown in Fig. 1 and Table 1, lattice parameters are influenced by the Ba content. The a and c parameters and unit cell volume (V) increase with Ba^{2+} incorporation to the apatite ($r_{\text{Ba}^{2+}} = 1.38 \text{ \AA}$, $r_{\text{Ca}^{2+}} = 1.06 \text{ \AA}$) [18]. The evolution of a and c unit cell parameters follows a linear dependence, indicating the occurrence of a continuous solid solution in oxyapatites network (Vegard's law).

Table 1
Unit cell parameters of $\text{Ca}_{2-x}\text{Ba}_x\text{La}_4\text{Bi}_4(\text{SiO}_4)_6\text{O}_2$ oxyapatites.

Ba content (x)	0	0.5	1	1.5	2
a (\AA)	9.635	9.648	9.673	9.726	9.779
c (\AA)	7.125	7.143	7.172	7.237	7.323
V (\AA^3)	384.056	386.111	389.685	397.494	406.593
Crystal system	Hexagonal				
Space group	P6_3				

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