# Structural study and electrical properties of $Bi_{1.5-x} Ca_x Sb_{1.5}CuO_7$ Pyrochlore-type solid solution series

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*Abstract*- **Pyrochlore solid solution $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ has been prepared by conventional ceramic solid state reaction with $0 \leq x \leq 0.4$. The samples were characterized by X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and electrical conductivity measurements. The pyrochlore single phase formation was confirmed for all of the x-fractions. The variation of the electrical resistivity versus x of all samples measured by means of a four probe device at room temperature indicates that these still remain insulators. High temperature electrical conductivity measurements at various frequencies using two electrodes device allow us to note the maximum electrical conductivity of $4.7 \ 10^{-3}$ S.cm$^{-1}$ which has been reached at x = 0.2 generating an activation energy of 0.14 eV. For this fraction, Rietveld refinement of the corresponding X-ray powder diffraction pattern confirmed the typical cubic Fd-3m space group with a cell parameter of a = 10.4089(1) Å.**

*Keywords*—— **Pyrochlore, Solid solution, Bismuth, XRPD, Rietveld refinement, SEM, EDX, Electrical conductivity.**

## I. INTRODUCTION

Materials with pyrochlore like-structure are of interest to chemists as well as to physicists because of properties such as high ionic and electronic conductivity [1], magnetic ordering [2], [3] and luminescence [4], [5]. These properties make them applicable in a variety of areas such as Solid Oxide Fuel Cells (SOFCs) [6], [7], catalysis, nuclear waste immobilization etc. They form over a huge compositional range due to the flexibility of the structure [8]. Within the crystal structure of stoichiometric oxide pyrochlores with general formula $A_2B_2O_7$ a larger 8-coordinated A-site (scalenohedra or distorted cube) and a smaller 6-coordinated B-site (octahedra) exist. The structural formula is often written as $A_2B_2O_6O'$ in which O and O' occupy the 48f and 8b Wyckoff sites (origin at -3m on the B-site), respectively. The crystal structure could be described as a substructure of the fluorite ($CaF_2$) structure type (Fm-3m, 225) in which the anionic vacancy and the two A and B cations are ordered. The structure stability of pyrochlores is generally related to the ratio of the two A and B ionic radii and has been observed for $R_A/R_B$ in the range of [1.46 – 1.78].

Smaller ratios lead to the formation of a disordered fluorite structure [8]. The most common charge distributions within the A and B-sites are $A_2^{+3}B_2^{+4}O_7^{-2}$ and $A_2^{+2}B_2^{+5}O_7^{-2}$, the first being however more common than the second one. Bismuth-based pyrochlore compounds are subject of interest because of their particular electric and magnetic properties, which make them promising candidates as electroceramics [9]. Most of them adopt a cubic crystal structure with space group Fd-3m (227) [8]. Non-stoichiometric bismuth zinc niobate, $Bi_3Zn_{1.84}Nb_3O_{13.84}$ exhibits a high relative permittivity, low dielectric loss and a negative temperature coefficient of capacitance [10]. It has been reported that ruthenate pyrochlore compounds are good oxygen reduction catalysts [11] and potential cathode materials [12]. Pure ceramic pyrochlore compound with chemical formula $(Bi_{1.524}Cu_{0.476})(Sb_{1.524}Cu_{0.476})O_{7+\delta}$ exhibits an electrical resistivity of $10^5$ Ω.cm and an effective moment of $\mu_{eff} = 2.27 \ \mu_B$ obtained by magnetic susceptibility measurements performed between 300 and 800 K [13]. Magnetic measurements in a temperature range of [4 – 800K] realized on a new pyrochlore compound $(Bi_{1.56}Co_{0.44})(Sb_{1.48}Co_{0.52})O_7$ revealed, on one hand, a paramagnetic character of the compound and, on the other hand, the oxidation state «+2» of the cobalt cation. The electrical conductivity of the compound reached $1.88 \ 10^{-3}$ S.cm$^{-1}$ at 775 K [14]. Magnetic susceptibility of the pyrochlore solid solution $Bi_{1.5}Sb_{1.5}Cu_{1-x}Mn_xO_7$ measured between 4 and 300 K revealed a paramagnetic behavior of the solution as well as a «+2» oxidation state of the manganese cation. The lowest electrical resistivity reached was $5 \ 10^2$ Ω.cm at 675 K [15].

This study deals with a new pyrochlore solid solution series in which the trivalent cation Bi$^{3+}$ has been partially substituted with the bivalent cation Ca$^{2+}$. The general formula of the solid solution series can be written as $Bi_{1.5-x}^{+3}Ca_x^{+2}Sb_{1.5}^{+5}Cu^{+2}O_{7-\delta}^{-2}$ where δ represents the fraction of oxygen vacancy per formula unit that should be considered to preserve the electro-neutrality of the material. The x-fraction of bismuth exchanged for calcium varies from

0 to 0.4. Polycrystalline samples were prepared by the solid-state reaction route and their properties including crystal structure, microscopic morphology, and electrical conductivity are presented.

## II. EXPERIMENTAL PROCEDURES

The solid solution series $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ was prepared using the conventional solid-state reaction method. The starting materials, with a purity of at least 99.9%, were mixed and well ground for 15 min. Firstly, the mixture underwent a homogenization grinding before being poured into an alumina crucible and calcined at a temperature of 700 °C for 48 hours in a muffle furnace. The calcined powder was reground and recalcined at a temperature of 850 °C for 72 hours. The final product was finely ground in order to prepare disk-shaped samples with a diameter of 10 mm and thickness of 2-3 mm by conventional solid-state powder processing techniques [16]. The disks were sintered in air at 950 °C for 12 hours. The pure phase, the crystal structure and the lattice parameters of the samples were determined using a laboratory X-ray powder diffractometer « Bruker D8 Advance » operating with Cu-K$_{\alpha 1}$ radiation (λ = 1.540598 Å) at room temperature. Grain morphology and average stoichiometric composition were characterized by a scanning electron microscope (SEM) « Hitachi 2500 C » equipped with an energy dispersive analysis X-ray system (EDX). The electrical conductivity of the samples was measured by means of four probe device at room temperature in air, as well as two-electrode cell at various frequencies of the external field «GWINSTEK LCR-821», from room temperature up to 300 °C in air.

## III. RESULTS AND DISCUSSION

### A. Structural Characterization

Fig.1 shows the X-ray powder diffraction (XRPD) patterns of the solid solution series $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ corresponding to the five x-fractions of calcium. All compounds with x = 0 – 0.4, exhibit a single pyrochlore phase characterized by its strongest peak (222) located around 2θ = 29.6 °. This allows us to confirm the partial substitution of bismuth for calcium. Besides, we can notice the progressive decrease of the intensity of the peak (311) with increasing x-fraction of calcium until it disappears at x = 0.4, which is related to the substitution of the heavy bismuth cation in the (311) plans by calcium cation.
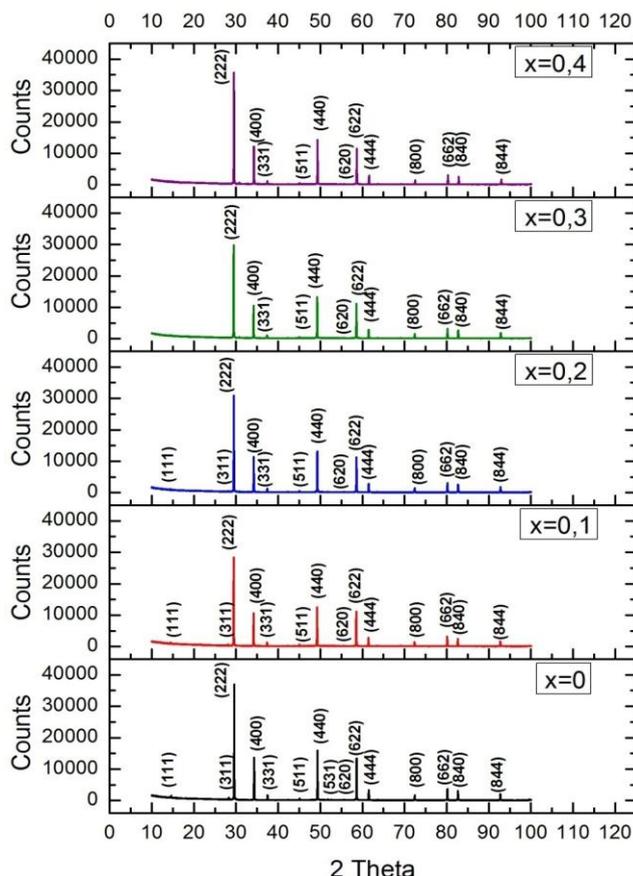


Fig. 1 X-ray diffraction patterns of $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7\delta}$ solid solution.

The refined lattice parameter variation versus x of the solid solution $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ series is shown in Fig. 2.
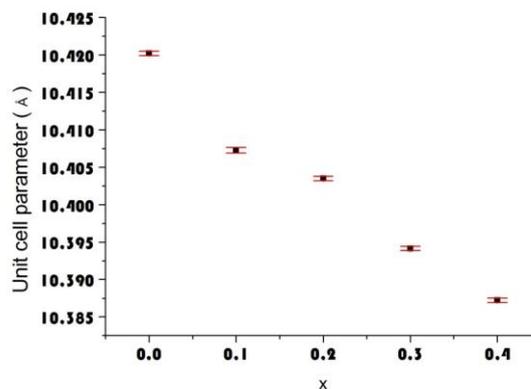


Fig. 2 Lattice parameter of $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ solid solution as a function of the x-fraction of calcium.

The observed weak decrease (0.12%) of the unit cell parameter with increasing x is possibly not only due to the small difference between the sizes of the two cations involved in the exchange ($R_{VIII}(Ca^{2+})$ = 1.12 Å, $R_{VIII}(Bi^{3+})$ = 1.17 Å [17]), but also due to the formation of oxygen vacancies within the pyrochlore crystal structure.
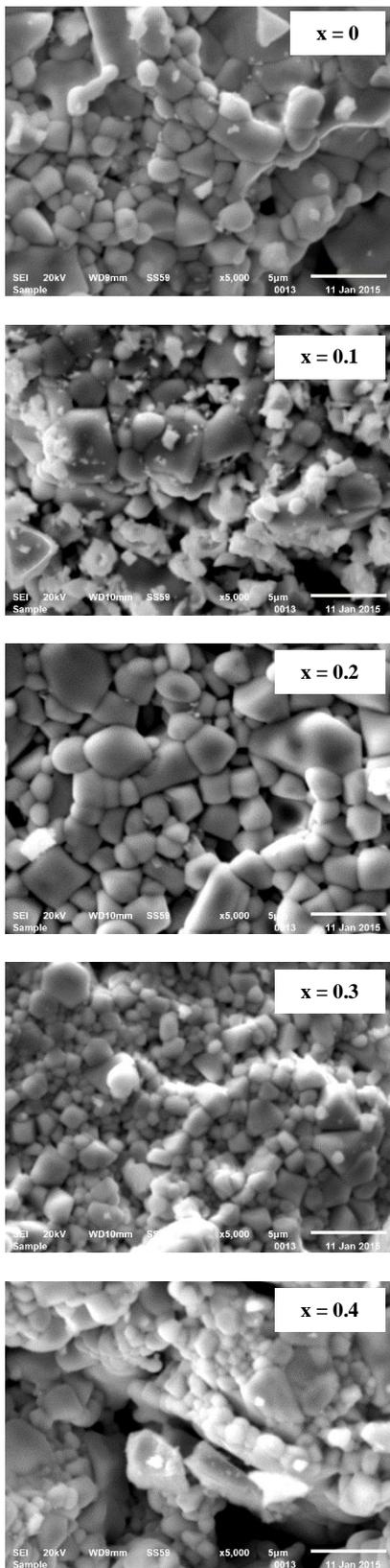
### B. Scanning Electron Microscopy characterisation

Fig. 3 SEM-pictures of $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ solid solution.

The scanning electron microscopy (SEM) pictures of the four disk-shaped compounds corresponding to x = 0 – 0.4, are shown in Fig. 3.

For the three first x-fractions, the samples exhibit relatively big size particles with relatively well-defined grain boundaries. On the other hand, for x = 0.3 and x = 0.4, the samples exhibit mixed small (x = 0.3) and big (x = 0.4) size particles without any apparent grain boundaries. Some areas seem to give evidence of a probable starting fusion of the samples such as that corresponding to x = 0.4. It should be noted the sample corresponding to x = 0.2 has the most regular grain shapes, relatively large grain sizes, and larger grain boundaries.

### C. Scanning Electron Microscopy characterisation

Table 1 gives the results of EDX analysis as atomic percentage of $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-(x/2)}$ solid solution series.

TABLE I
CHEMICAL COMPOSITION of $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-(x/2)}$ SOLID SOLUTION SERIES DETERMINED by SEM/EDX ANALYSIS

| Atom | At% | | | | |
|---|---|---|---|---|---|
| | x=0 | x=0.1 | x=0.2 | x=0.3 | x=0.4 |
| O | 59.64 | 61.78 | 66.69 | 65.46 | 66.95 |
| Sb | 13.55 | 12.93 | 12.60 | 13.58 | 12.01 |
| Ca | - | 2.30 | 3.03 | 3.32 | 3.45 |
| Cu | 13.09 | 12.20 | 9.72 | 10.14 | 11.19 |
| Bi | 13.72 | 10.79 | 7.96 | 7.49 | 6.40 |

A significant increase of calcium percentage associated with a significant decrease of bismuth percentage when increasing the x-fraction of calcium is in agreement with the substitution of bismuth for calcium process. For x = 0.2, the measured stoichiometry is $Bi_{0.95}Ca_{0.36}Sb_{1.5}Cu_{1.16}O_{6.53}$. Energy peaks overlap of Ca and Sb could explain the discrepancy between the experimental and theoretical stoichiometry. Fig. 4 shows EDX-diagrams of the solid solution compounds.
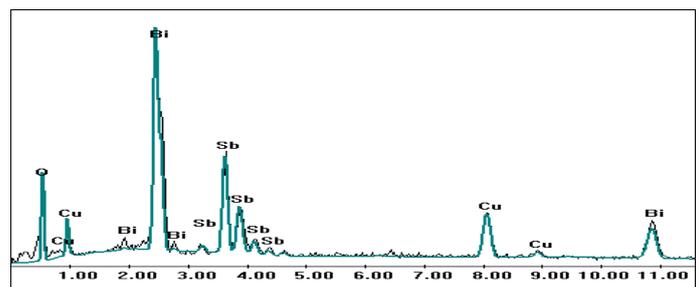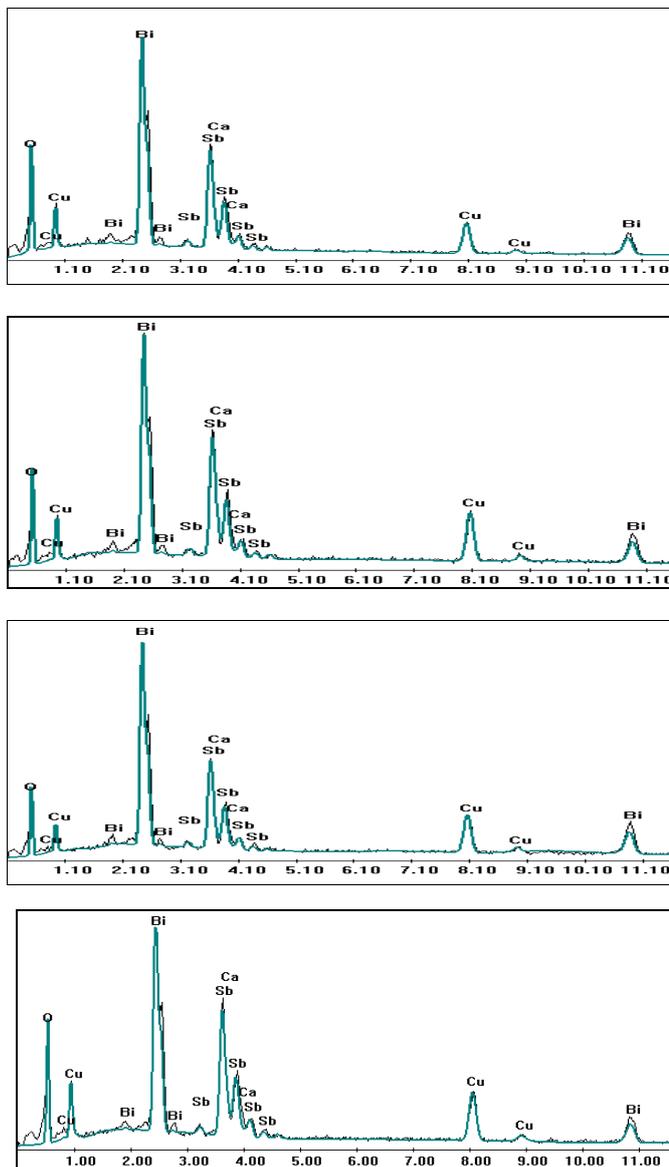
Fig. 4 EDX diagrams of solid solution series $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ compounds.

## D. Electrical Conductivity Characterization

Fig. 5 shows the variation of the electrical resistivity of the pellets versus the x-fraction of calcium of the solid solution series performed with the four probe device at room temperature in air. The increase of the electrical resistivity versus x shows that the calcium doping process does not improve the electrical character of the solid solution. Furthermore, the insulating character of the material tends to increase exponentially starting from x = 0.2. Indeed, an average resistivity of $7.3 \times 10^7$ Ω.cm is measured before it suddenly increases up to $44.4 \times 10^7$ Ω.cm. Therefore, the loss of the electrical neutrality of the solid solution, due to "$Bi^{3+}/Ca^{2+}$" substitution, is most probably compensated by the loss of oxygen from the structure rather than oxidation of copper. If it is, then the chemical formula of the solid solution would be written as $Bi^{+3}_{1.5-x}Ca^{+2}_xSb^{+5}_{1.5}Cu^{+2}O^{-2}_{7-\frac{x}{2}}$ so that

when x bismuth-cations are substituted for x calcium-cations, $\delta = x/2$ oxygen-ions vacancies per formula unit would be generated. Consequently, such solid solution could be an oxygen-ion conductor like most of pyrochlore-like compounds. In order to improve the electrical characterization, we performed high temperature electrical conductivity measurements in air, using two electrodes device, within the temperature range of [25 – 300°C] at various frequencies from 100 Hz to 100 KHz and at 1 Volt.
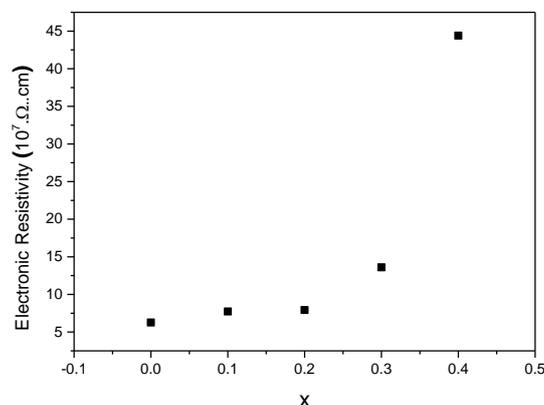


Fig. 5 Electrical resistivity as a function of the x-fraction of calcium of $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ solid solution

Fig. 6 shows the variation of Logσ versus reciprocal temperature at 100 Hz, 500 Hz, 1 KHz, 10 KHz and 100 KHz for all x-fractions of calcium of the solid solution respectively. It confirms that the electrical conductivity of the samples is thermally activated and follows an Arrhenius law. We note that the maximum calculated conductivity of $4.7. 10^{-3}$ S.cm$^{-1}$ is that corresponding to x = 0.2 at 100 KHz and 300 °C. The corresponding activation energy of 0.14 eV was calculated from the slope of the linear fit. This value is to low regarding to the most common values of around 0.3 eV observed with most pyrochlore phases. Consequently, the weak electrical conductivity could be due to only electron displacement, as oxygen displacement cannot be confirmed with maximum measurement temperature not exceeding 300 °C. The absence of any breaking slope of the lines show that none of the samples presents any electrical transition.
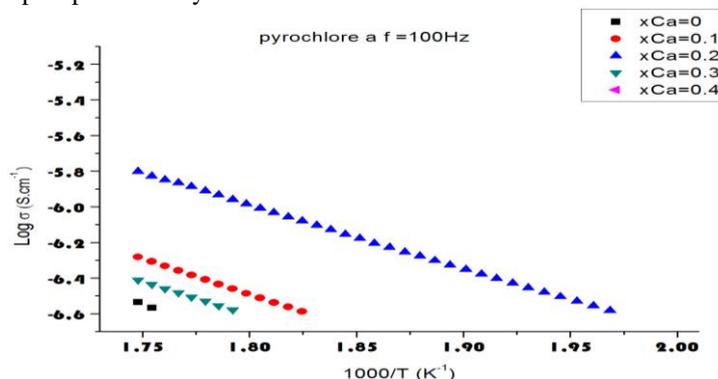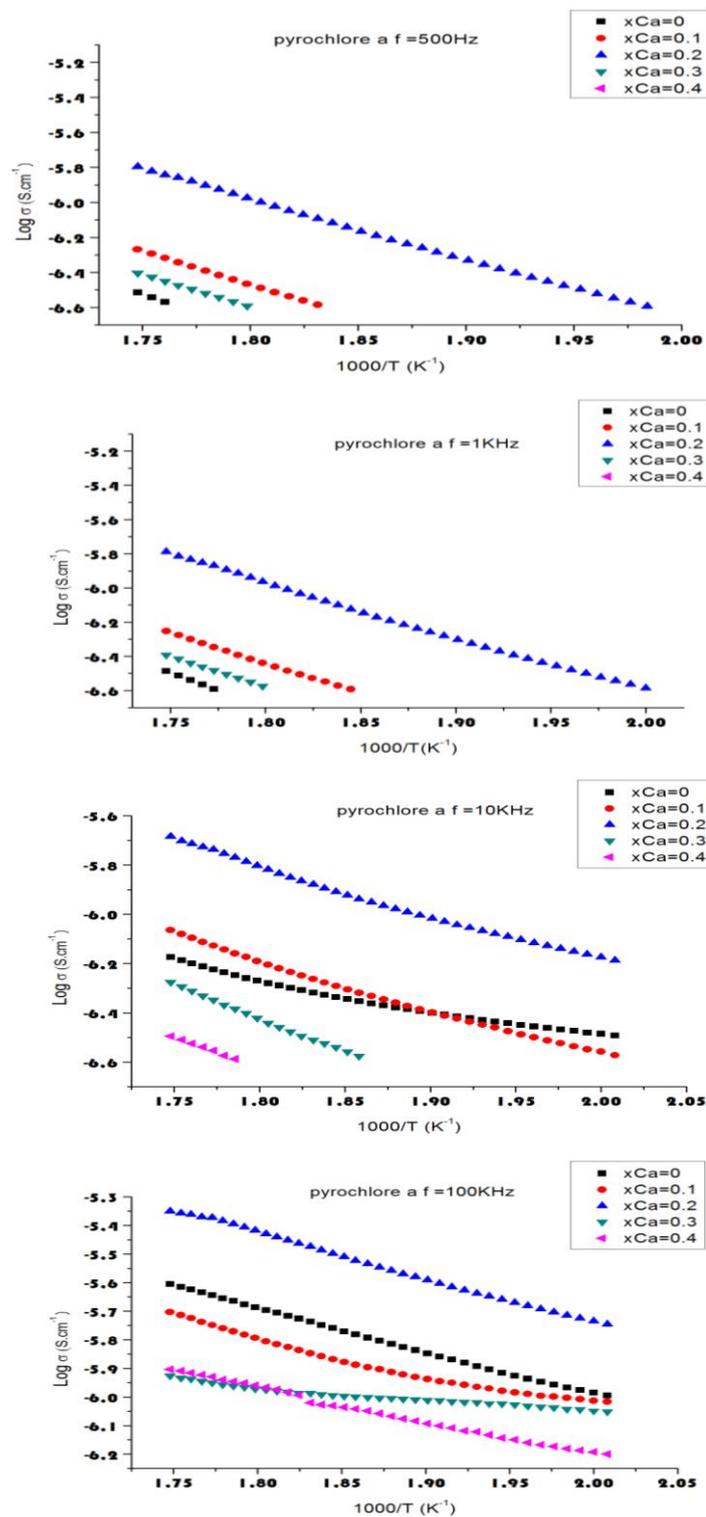
Fig. 6 Variation of Logσ versus 1000/T at various frequencies of Bi$_{1.5-x}$Ca$_x$Sb$_{1.5}$CuO$_{7-\delta}$ solid solution.

### E. Rietveld Refinement

In order to confirm the stoichiometry of the compound corresponding to the fraction x = 0.2 of calcium, we performed a Rietveld refinement based on a former refined pyrochlore compound [13] using the Fullprof program [18]. Table 2 gives the refinement parameters.

TABLE II
RIETVELD REFINEMENT PARAMETERS OF THE Bi/Ca (x = 0.2)
Bi$_{1.5-x}$Ca$_x$Sb$_{1.5}$CuO$_{7-\delta}$ PYROCHLORE

| Instrumental parameters | |
| --- | --- |
| Diffractometer | Bruker D8-Advance |
| Wavelength (Å) | 1.54056 |
| Monochromator | Germanium (111) |
| 2θ range (°) | 10-140 |
| 2θ step (°) | 0.009 |
| Time per step (s) | 60 |
| **Crystallographic parameters** | |
| Global formula | Bi$_{1.3}$Ca$_{0.2}$Sb$_{1.5}$CuO$_{6.9}$ |
| Formula units per cell | Z = 8 |
| Formula mass (g) | 5725.81 |
| Crystal system | Cubic |
| Space group | F d -3 m (227) |
| Cell parameter (Å) | 10.4089(1) |
| Cell volume (Å$^3$) | 1127.7543(5) |
| Density (g/cm$^3$) | 10.019 |
| **Refinement parameters** | |
| Refinement program | Fullprof |
| Number of parameters refined | 39 |
| Number of reflections | 70 |
| Peak shape function | Pseudo-Voigt |

Fig. 7 shows the agreement between observed and calculated XRPD profiles for Bi/Ca (x = 0.2) pyrochlore compound.
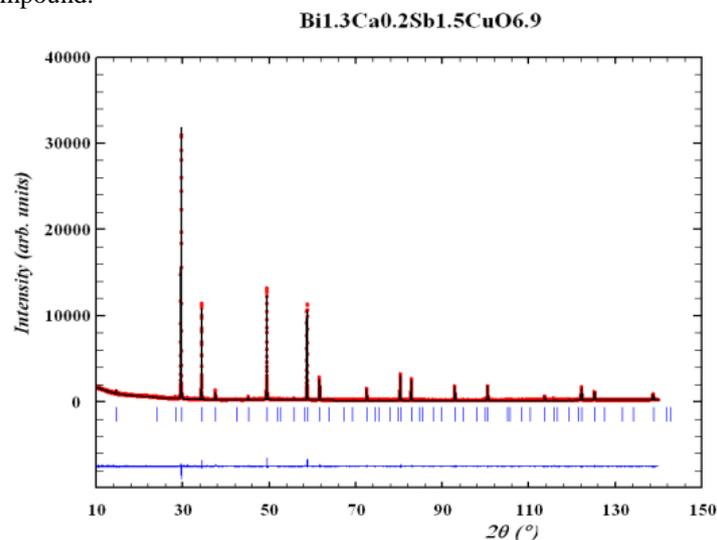


Fig. 7 Rietveld plot of the Bi/Ca (x = 0.2) Bi$_{1.5-x}$Ca$_x$Sb$_{1.5}$CuO$_{7-\delta}$ pyrochlore compound.

Table 3 gives the refined profile parameters of the crystal structure.

TABLE III
REFINED PROFILE PARAMETERS OF THE Bi/Ca (x = 0.2)
$Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ PYROCHLORE STRUCTURE

| | |
|---|---|
| Scale factor | $0.17771(35)10^{-4}$ |
| Zero point | 0.0002 |
| $x(O_{48f})$ parameter | 0.3212(3) |
| Gaussian peak half width parameters ($\text{Å}^2$) | U = 0.00857 <br> V = -0.01040 <br> W = 0.00690(1) |
| $R_{wp}$ (%) | 14.6 |
| $R_p$(%) | 19.9 |
| $R_{Bragg}$ (%) | 5.37 |
| $R_f$ (%) | 6.81 |
| $X^2 (R_{wp}/R_{exp})^2$ | 1.52 |

Significant interatomic distances and bonding angles are given in Table 4.

TABLE IV
INTER ATOMIC DISTANCES (Å) AND BONDING ANGLES (°) OF THE
Bi/Ca (x = 0.2) $Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ PYROCHLORE STRUCTURE

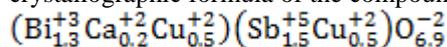| $AO_8$ scalenohedra | | |
|---|---|---|
| A – O1 | 6× | 2.619(5) |
| A – O2 | 2× | 2.2536(1) |
| O1 – A – O2 (a) | | 80.6(1) |
| O1 – A – O2 (b) | | 99.4(3) |
| A – O1 – A | | 89.3(2) |
| $BO_6$ octahedra | | |
| B – O1 | 6× | 1.982(1) |
| B – B | 6× | 3.6801(2) |
| O1 – B – O1 | | 93.3(5) |
| B – O1 – B | | 105.4(3) |

The R-factors values confirm the good agreement between observed and calculated profiles. Refined occupancy, x coordinate of the 48f oxygen atom and isotropic thermal factors of all atoms of the Bi/Ca (x = 0.2) pyrochlore compound are summarized in Table 5.

TABLE V
REFINED ATOMIC PARAMETERS OF THE Bi/Ca (x = 0.2)
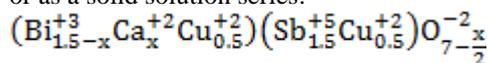$Bi_{1.5-x}Ca_xSb_{1.5}CuO_{7-\delta}$ PYROCHLORE STRUCTURE

| Atom | Site | Occ. | x | y | z | B ($\text{Å}^2$) |
|---|---|---|---|---|---|---|
| Bi | 16d | 0.65 | 1/2 | 1/2 | 1/2 | 3.1(4) |
| Ca | 16d | 0.1 | 1/2 | 1/2 | 1/2 | 3.1(4) |
| Cu(1) | 16d | 0.25 | 1/2 | 1/2 | 1/2 | 3.1(4) |
| Sb | 16c | 0.75 | 0 | 0 | 0 | 0.29(5) |
| Cu(2) | 16c | 0.25 | 0 | 0 | 0 | 0.29(5) |
| O(1) | 48f | 1.0 | 0.3209(12) | 1/8 | 1/8 | 0.5(8) |
| O(2) | 8b | 1.0 | 3/8 | 3/8 | 3/8 | 0.5(8) |

Cations on 16d site exhibit a considerably higher atomic displacement parameter (ADP) than those on 16c site. Relatively high atomic displacement parameters on 16d site are very common in pyrochlore structures. This is due to the fact that the A-site consists of a heavily cube-distorted 8-fold coordination with two sets of "A – O" distances (6 × A – O1 and 2 × A – O2) [9]. This structure relaxation is also caused by the bismuth lone pair which the A-site must accommodate. However, such high values have been obtained only when the A-site is occupied by more than one atom [13]. Taking into account the electrical neutrality of the compound, the crystallographic formula of the compound should be written as:

$$(Bi^{+3}_{1.3}Ca^{+2}_{0.2}Cu^{+2}_{0.5})(Sb^{+5}_{1.5}Cu^{+2}_{0.5})O^{-2}_{6.9}$$

or as a solid solution series:

$$(Bi^{+3}_{1.5-x}Ca^{+2}_xCu^{+2}_{0.5})(Sb^{+5}_{1.5}Cu^{+2}_{0.5})O^{-2}_{7-\frac{x}{2}}$$

in which « x/2 » oxygen vacancies for x calcium per formula unit are generated. Hence, the more the quantity of calcium substituting the bismuth increases, the more oxygen vacancies will be generated.

## IV. CONCLUSION

The solid solution with chemical formula $Bi^{+3}_{1.5-x}Ca^{+2}_xSb^{+5}_{1.5}Cu^{+2}O^{-2}_{7-\delta}$ has been successfully synthesized. XRPD characterization shows that pure and well-crystallized pyrochlore phases were obtained. The unit cell volume of the crystal structure slightly decreases with increasing x. This is not only caused by the smaller size of substituting $Ca^{2+}$ than that of substituted $Bi^{3+}$ but also by the formation of oxygen vacancies, since no electronic conductivity enhancement was found. High temperature conductivity measurements allowed us to find a maximum electrical conductivity of 4.7 $10^{-3}$ S.cm$^{-1}$ at 100 KHz and 300 °C, and an activation energy of 0.14 eV. This latter, much lower than those of most of pyrochlore compounds ($\approx 0.3$ eV), and the low maximum measurements temperature of 300°C, let us suggest that the measured conductivity is most probably due to much more electron displacements than oxygen displacements.

These values have been reached when substituting bismuth for optimal fraction x = 0.2 of calcium leading to the following chemical formula:

$$(Bi^{+3}_{1.3}Ca^{+2}_{0.2}Cu^{+2}_{0.5})(Sb^{+5}_{1.5}Cu^{+2}_{0.5})O^{-2}_{6.9}$$
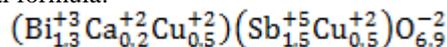
in which «0.10» oxygen vacancies per formula unit would be required to reach the electrical neutrality of the ionic structure, leading to a non-stoichiometric oxygen pyrochlore compound.

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