

Synthesis and physical properties of pyrochlore cobalt oxides $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$

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Abstract

A new solid solution $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ ($0 \leq x \leq 0.3$) with a pyrochlore-like structure ($\text{A}_2\text{B}_2\text{O}_7$) was synthesized in air by chemical solid-state reaction. The solution crystallized in the cubic system with the Fd-3m space group. A regular decrease of the lattice parameter was observed when calcium replaced bismuth in the A site. The electric measurements showed that the electrical conductivity increased with the temperature and that high values of relative permittivity and dielectric loss were put in evidence. Measurements of magnetic susceptibility indicated a paramagnetic behavior of the samples with an effective moment included between 4.81 and 5.12 μ_B and at a low temperature para-ferromagnetic transition was observed for fractions $x = 0.2$ and 0.3.

Keywords: pyrochlore, bismuth, cobalt, calcium, solid solution, X-ray, electrical conductivity, magnetic susceptibility.

INTRODUCTION

The pyrochlore structure has the general formula $\text{A}_2\text{B}_2\text{O}_7$ where A is the larger cation and B is the smaller one. Mostly A is a trivalent rare-earth ion and bismuth, but can also be a mono or divalent cation, and B may be a 3d, 4d, or 5d transition element having an appropriate oxidation state required for charge balance to give rise to the composition $\text{A}_2\text{B}_2\text{O}_7$. The space group of ideal pyrochlore is Fd-3m with a lattice parameter 'a' of about 10 Å and eight formula units per unit cell [1]. The pyrochlore structure is reported [2, 3] as a network consisting of corner-linked BO_6 octahedra with A atoms filling the interstices forming distorted cubes (Fig. 1). Some pyrochlores exist as insulators whereas some others are semiconductors [4]. There are few pyrochlores exhibiting dielectric, piezoelectric, or ferroelectric properties if A and B remain in the highest oxidation state [1]. In recent years, new pyrochlore compounds with a more complicated composition $(\text{AA}'')_2(\text{B}'\text{B}'')_2\text{O}_7$ have been synthesized [5-15]. There are two criteria for a pyrochlore compound to exist, that is, the ratio of ionic radius of cation at the A site to that at the B site must be between 1.6 and 1.8 and the chemical valence of various ions must assure the electrical neutrality [1]. However, up to the present, few Co-Sb-containing pyrochlore compounds have been reported [16]. This behavior is mainly due to the ceramic methods used during the synthesis of the cobalt pyrochlore compounds where there is an appearance of intermediate phases. These phases are eliminated by an appropriate heating cycle. Such difficulty was encountered during the synthesis of the pyrochlore $\text{Bi}_{1.56}\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_7$ compound [17]. It can

be noted that all the attempts to synthesize the pyrochlore compound by sol-gel method did not give a pure phase, always the pyrochlore structure is accompanied by additional phases. We report here the influence of the partial substitution of bismuth by calcium on the electric and magnetic properties of the $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ solid solution. We used the ceramic method at 1000 °C in air. The difference in charge of the substitution cations causes an oxygen deficit to appear in the $(\text{Bi}_{1.56-x}^{3+}\text{Ca}_x^{2+}\text{Co}_{0.44}^{2+})(\text{Sb}_{1.48}^{5+}\text{Co}_{0.52}^{2+})\text{O}_{7-\delta}^{2-}$ pyrochlore formula. The starting compound $\text{Bi}_{1.56}\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_7$ [17] has been used in photocatalysis for the degradation of rhodamine B [18]. The obtained results prompted us to synthesize this solid solution and see the influence of oxygen deficit on the degradation of rhodamine B. The photocatalysis applications are in progress and will be the subject of a future publication.

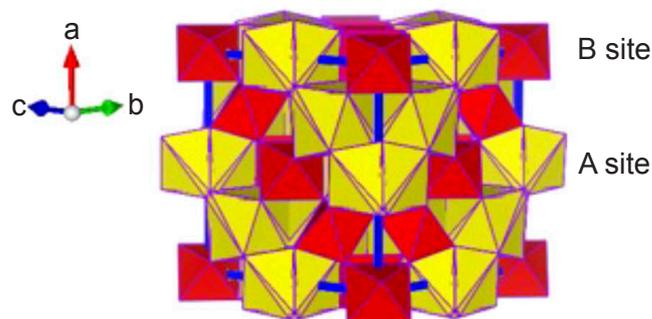


Figure 1: Schematic of $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore structure.

EXPERIMENTAL

The samples were prepared in air by solid-state reactions

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using Bi_2O_3 (99.9%), Sb_2O_3 (99.9%), CaO (99.9%), and Co_3O_4 (99.99%) powders (Aldrich Chem.). Prior to each heating cycle, each sample was mixed by grinding using an agate mortar. After initial heating at 700°C for one day, three successive heat treatments for two days with intermediate grinding were carried out at $800\text{--}1000^\circ\text{C}$. The resulting powder was re-milled and uniaxially pressed into a pellet about 13 mm in diameter and 3 mm in thickness. It was then sintered at 1050°C for 3 days. The specimen was initially characterized by X-ray powder diffraction (X'Pert PRO, PANalytical). Data were collected using $\text{CuK}\alpha$ radiation with 0.02° step size. Polished samples were examined using a conventional scanning electron microscope (SEM, XL30, Philips). The electrical conductivity measurements were carried out using an impedance analyzer (G7220, LocK-in Eg) with 10 mV AC signal amplitude at frequencies between 30 Hz and 120 kHz. The samples used for the electrical measurement were pellets 13 mm in diameter and heated to 1000°C . Both sides of the pellet were coated with platinum as an electrode for impedance complexes' measurement. The dielectric properties were measured with an RLC bridge (PM 6306, Fluke). The electronic conductivity was tested by the two points method on pellets 13 mm in diameter and 2 mm in thickness. The magnetic susceptibility of a powder sample was measured from 4 to 300 K with a superconducting quantum interference device (SQUID) magnetometer.

RESULTS AND DISCUSSION

X-ray diffraction: the compound $\text{Bi}_{1.56}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_7$ belonging to the cubic pyrochlore family with lattice parameter $a=10.44896(2)\text{ \AA}$, refined by Dicvol 6, a program in Fullprof software. The cobalt was distributed between the two sites A and B according to the following formula $(\text{Bi}_{1.56}\text{Co}_{0.44})(\text{Sb}_{1.48}\text{Co}_{0.52})\text{O}_7$ which is a semiconductor compound that has a paramagnetic behavior [18]. The

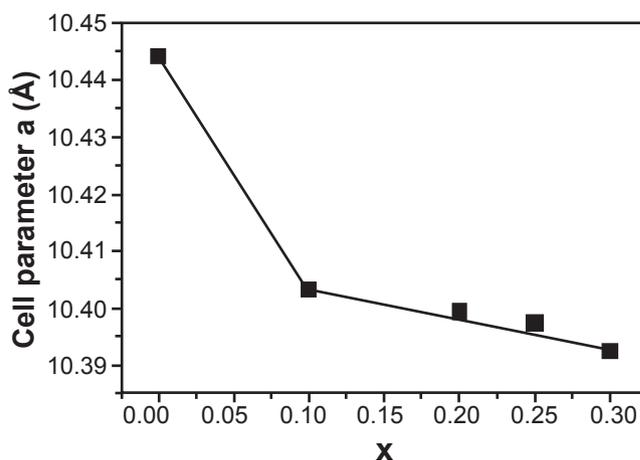


Figure 3: Lattice parameter versus x (in $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$).

substitution of bismuth by the calcium gave a solid solution in the domain $0 \leq x \leq 0.3$ (Fig. 2). All X-ray diffraction pattern peaks of $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ could be indexed in a cubic system with Fd-3m space group. The lattice parameter decreased continually with x (Fig. 3). The ionic radius difference between bismuth ($R_{\text{VIII}}=1.17\text{ \AA}$) and calcium ($R_{\text{VIII}}=1.12\text{ \AA}$) [19] can be a possible reason for this lattice parameter evolution. For $x>0.3$, other peaks were detected beside the pyrochlore peaks, hence $x=0.3$ corresponded to the substitution limit of the bismuth by calcium. The same evolution of the lattice parameter has already been observed in the pyrochlore system $\text{Bi}_{1.524-x}\text{Ca}_x\text{Sb}_{1.524}\text{Cu}_{0.952}\text{O}_{7+\delta}$ [20], but when replacing calcium by lead an irregular evolution of the lattice parameter appears due to the existence in bismuth and lead an electronic lone pairs [21].

The difference in the oxidation state between $\text{Bi}(3+)$ and $\text{Ca}(2+)$ reveals a deficit in the oxygen sites. The structural formula is given by: $(\text{Bi}_{1.56-x}^{3+}\text{Ca}_x^{2+}\text{Co}_{0.44}^{2+})(\text{Sb}_{1.48}^{5+}\text{Co}_{0.52}^{2+})\text{O}_{7-\delta}^{2-}$. The synthesis was carried out under air in a muffle furnace, which shows that the cobalt kept its charge $2+$, for bismuth

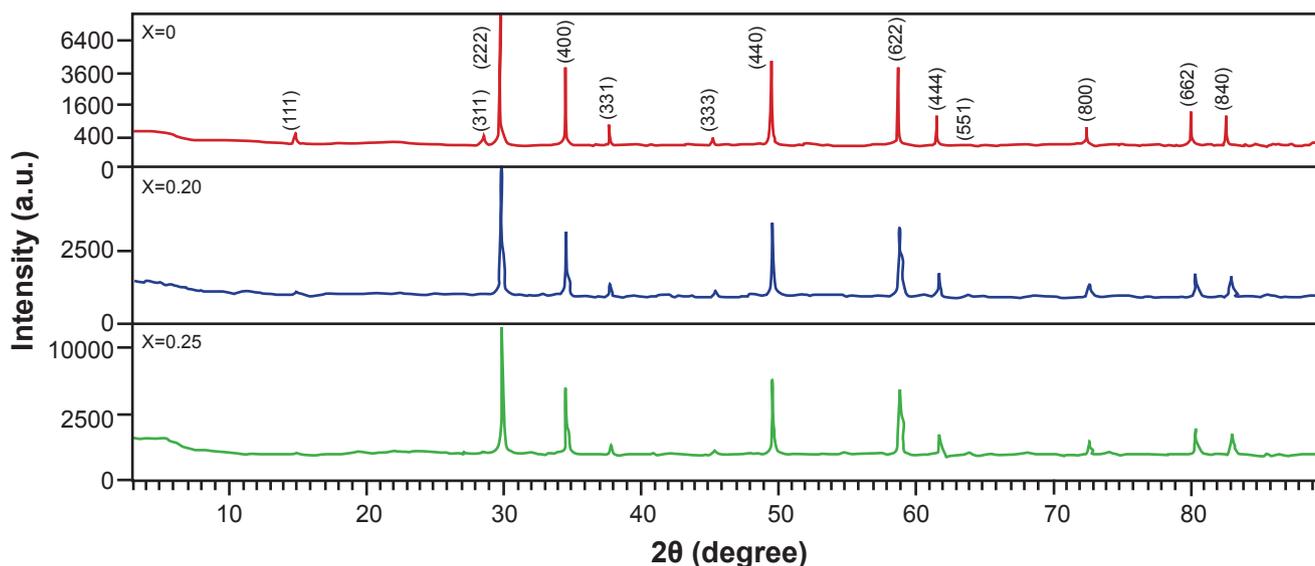


Figure 2: XRD patterns of $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ compounds.

it is always the charge 3+ and the antimony is in charge 5+ [21]. The electrical neutrality of the solid solution gives the following charge balance:

$$(1.56-x)(+3)+x(+2)+0.44(+2)+1.48(+5)+0.52(+2)=(7-\delta)(-2) \quad (A)$$

then, $\delta = \frac{x}{2}$, where δ is the oxygen deficiency and represents 50% of the x value. Table I gives the developed formulas of our synthesized samples. This result showed that there was non-stoichiometric pyrochlore present. There are so many similar compounds that are used in several fields. We cite the example of the oxygen-deficient pyrochlore compound $\text{Bi}_{1.5}\text{ZnNb}_{1.5-x}\text{O}_{7-2.5x}$ [22], which has recently been found to be of great interest for low-temperature sintering ceramics for high-frequency applications. Also, the compound $\text{Bi}_{1.5-2x}\text{Zn}_{1+2x}\text{Nb}_{1.5}\text{O}_{7-x}$ (with $x=0-0.3$) [23], a bismuth pyrochlore structured dielectrics has received much attention for device applications due to their high dielectric constant, low dielectric dissipation, and relatively low firing temperature [24]. Fig. 4 shows SEM micrographs of the external surface of the samples in the form of pellets heated at 1000 °C. In general, the average grain size varied according to the heating cycle and according to the chemical composition of the material. At high temperatures, the diffusion of ions is linked to the physicochemical properties of each cation present in the structure. For the fraction $x=0$, the sample showed grains of different sizes that were welded together. In the fraction $x=0.15$, we can see the disappearance of the granular form towards a flattened surface with the existence of holes scattered throughout the surface. The sample with fraction $x=0.25$ had a more compact surface than the other two fractions. The surface became more homogeneous with a hole decrease observed in the fraction $x=0.15$. It seems that the external aspect of the surface changed with the presence of calcium in the solid solution.

Electrical measurement. Impedance complex: the electrical conductivity in the lacunar pyrochlore $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ increased with the temperature and with the rate of calcium. The electrical conductivity σ increased from 10^{-6} S.cm⁻¹ at 75 °C to 10^{-2} S.cm⁻¹ at 500 °C. The impedance diagrams did not show two semicircles (bulk and grain boundary contributions) and one straight line (electrode effect) but only a flattened semicircle due to the overlapping of both bulk and grain boundary impedance. The conductivity values

Table I - $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ solid solution formulas.

Fraction x	Formula	δ
0	$(\text{Bi}_{1.56}^{3+} \text{Co}_{0.44}^{2+}) (\text{Sb}_{1.48}^{5+} \text{Co}_{0.52}^{2+}) \text{O}_7^{2-}$	0
0.10	$(\text{Bi}_{1.46}^{3+} \text{Ca}_{0.1}^{2+} \text{Co}_{0.44}^{2+}) (\text{Sb}_{1.48}^{5+} \text{Co}_{0.52}^{2+}) \text{O}_{6.95}^{2-}$	0.050
0.20	$(\text{Bi}_{1.36}^{3+} \text{Ca}_{0.2}^{2+} \text{Co}_{0.44}^{2+}) (\text{Sb}_{1.48}^{5+} \text{Co}_{0.52}^{2+}) \text{O}_{6.9}^{2-}$	0.100
0.25	$(\text{Bi}_{1.31}^{3+} \text{Ca}_{0.25}^{2+} \text{Co}_{0.44}^{2+}) (\text{Sb}_{1.48}^{5+} \text{Co}_{0.52}^{2+}) \text{O}_{6.875}^{2-}$	0.125
0.30	$(\text{Bi}_{1.2}^{3+} \text{Ca}_{0.3}^{2+} \text{Co}_{0.44}^{2+}) (\text{Sb}_{1.48}^{5+} \text{Co}_{0.52}^{2+}) \text{O}_{6.85}^{2-}$	0.150

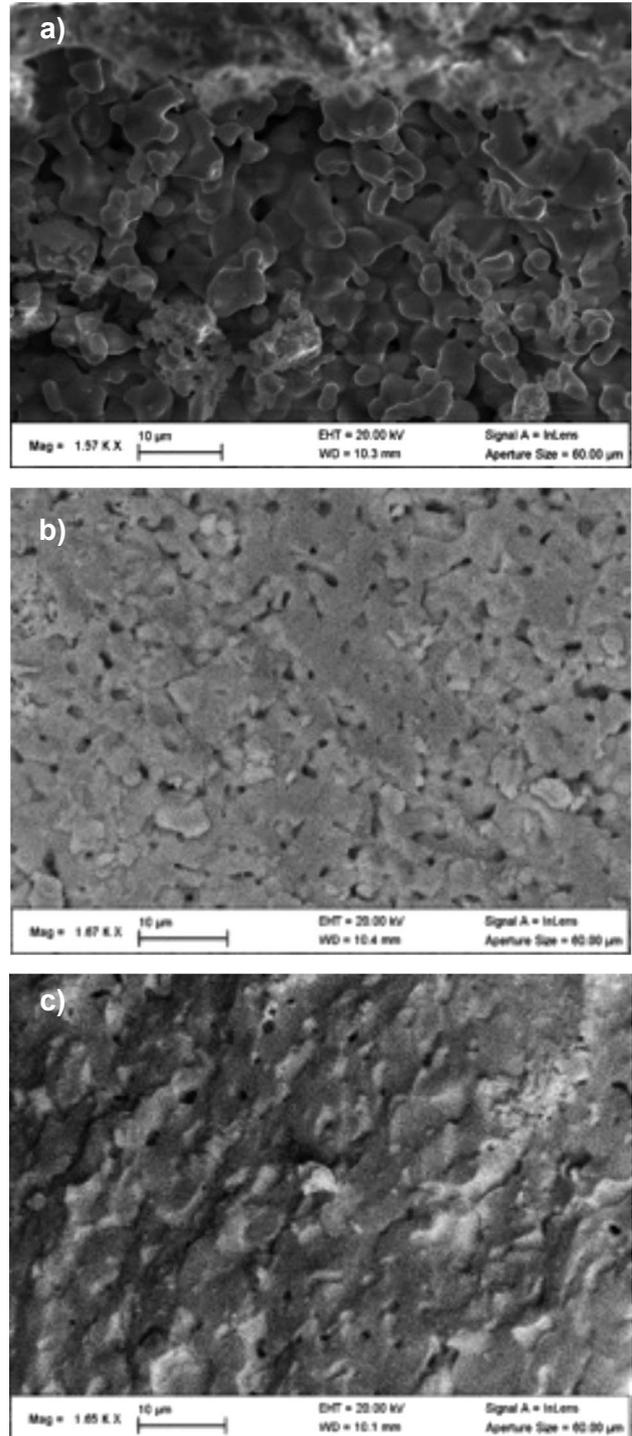


Figure 4: SEM micrographs of the $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ solid solution: a) $x=0$; b) $x=0.15$; and c) $x=0.25$.

were derived from the intersection of the semicircle with the x-axis (inset in Fig. 5); $\log(\sigma)$ plotted versus $1/T$ is also shown in Fig. 5. The overall values of electrical conductivity of these compounds were analyzed by Arrhenius equation. The activation energies measured for $x=0, 0.2$, and 0.3 samples were 0.41, 0.52, and 0.54 eV, respectively. These activation energy (E_a) values were obtained from the experimental points, fitted by least squares to the equation $\log(\sigma.T) = \log(\sigma_0) - E_a/(k.T)$.

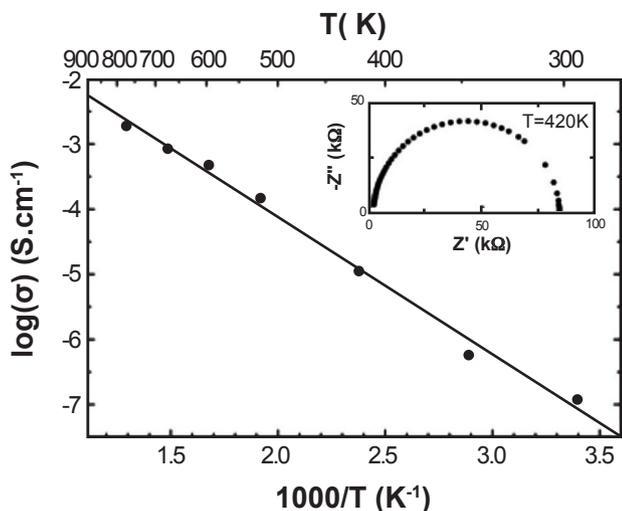


Figure 5: Conductivity (σ) versus inverse temperature ($1/T$) with impedance complex diagram at 420 K (inset) for $x=0$.

Dielectric measurement: the measuring facility allowed electrical resistance measurements by the two-point method between 0 and 175 °C. Fig. 6 shows the resistivity versus temperature. The obtained results at this temperature range showed an electrical resistivity (ρ) varying between 10^7 and $10^3 \Omega \cdot \text{cm}$. The shape of the variation $\rho=f(T)$ showed a semiconductivity behavior of all the samples. The resistivity decreased slightly in compounds containing calcium but not ordered according to the substitution fraction (inset in Fig. 6). At 100 °C, the lowest resistivity reached $3.7 \times 10^3 \Omega \cdot \text{cm}$ for the fraction $x=0.2$. The electrical conductivity of the synthesized compounds is thermally

activated and followed an Arrhenius law:

$$\sigma = \sigma_0 \cdot \exp[-E_a/(k.T)] \tag{B}$$

where σ_0 is a pre-exponential factor and a characteristic of the material, E_a , k , and T are, respectively, the activation energy for conduction, Boltzmann’s constant, and the absolute temperature. Thus, the activation energy for conduction (E_a) can be calculated from the slope of the straight line given by $\log(\sigma)$ versus $1/T$. The calculated activation energies presented results ($0.46 \leq E_a \leq 0.49 \text{ eV}$) very similar to those calculated by the complex impedance method. This showed the possibility of the existence of electronic conductivity in this solid solution. The values of the activation energies were in agreement with other cobalt pyrochlores $\text{Bi}_{1.6}\text{Co}_{0.8}\text{Ta}_{1.6}\text{O}_{7.2-8}$ and $\text{Bi}_{1.49}\text{Co}_{0.8}\text{Ta}_{1.6}\text{O}_{7.0}$ [15].

The relative permittivity and dielectric loss as a function of temperature for samples are shown in Fig. 7. It seems that also relative permittivity (Fig. 7a) and dielectric loss (Fig. 7b) showed a rather strong temperature dependence. In fact, the upturns in the data above ambient temperature indicated that the samples became predominantly conductive. Such behavior was reported in bismuth-based pyrochlores for which dielectric relaxation is observed [25]. One can also observe that the relative permittivity decreased for $x=0.3$ but not for dielectric loss. Both impedance complex spectroscopy and dielectric measurements proved that the conductivity in these compounds is electronic probably caused by the mixed valence of cobalt ($\text{Co}^{3+}/\text{Co}^{2+}$). With the increasing temperature, electrical conductivity increased due to the increase in thermally activated drift mobility of

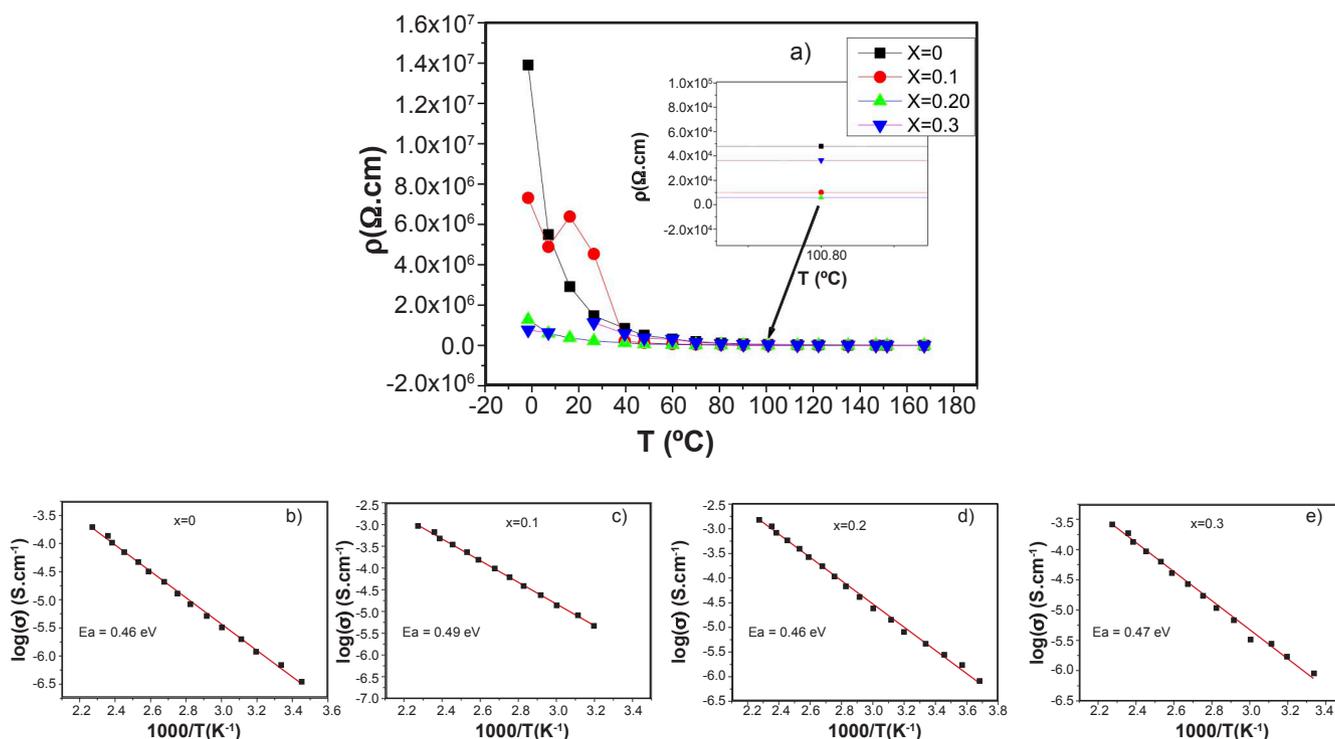


Figure 6: Results of electrical conductivity for $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7.8}$ compounds: a) resistivity (ρ) versus temperature; b-e) conductivity (σ) versus inverse temperature.

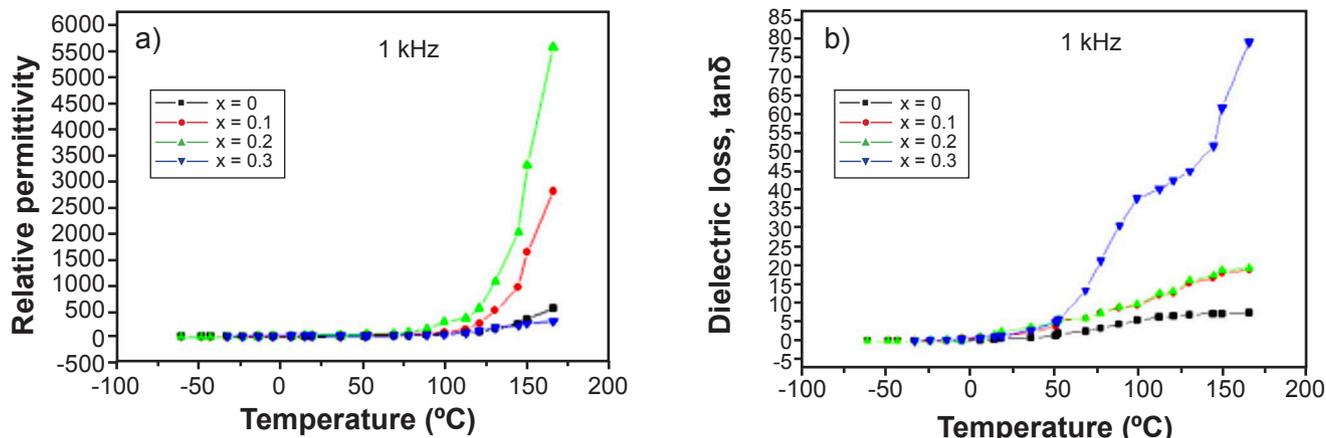


Figure 7: Relative permittivity and dielectric loss for $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ compounds at a frequency of 1 kHz.

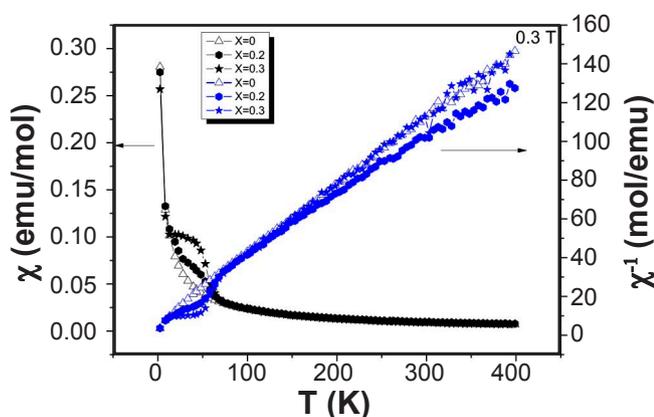


Figure 8: Magnetic susceptibility (χ) and inverse magnetic susceptibility versus temperature of $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ solid solution.

Table II - Magnetic properties of $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$ solid solution.

Fraction x	$\mu_{\text{eff}}/\text{mol Co}$ (μ_B)
x=0.0	4.78
x=0.2	5.06
x=0.3	4.72

electric charge carriers according to the hopping conduction mechanism [26].

Magnetic properties: magnetic data obtained for $x=0, 0.2,$ and 0.3 pyrochlore samples indicated qualitatively similar paramagnetic behavior with a weak para-ferromagnetic transition observed at 68 K for $x=0.2$ and 0.3 fractions (Fig. 8). Above 100 K, the inverse magnetic susceptibility was linear and that range was fitted to the Curie-Weiss law. The results are given in Table II. For all compounds, the extrapolation of the linear fits indicated small negative temperature intercepts [θ (K)], suggesting the presence of weak antiferromagnetic cooperative interactions. The observed effective magnetic moments ($\mu_{\text{eff}}/\text{mol Co}$), calculated from the slopes of the Curie-Weiss

fits were similar to those observed for other Co-containing pyrochlores [27] giving the range of values reported for high spin Co^{2+} ($4.6\text{-}5.2 \mu_B/\text{Co}$) [28].

CONCLUSIONS

A new solid solution of pyrochlore-type was synthesized with the chemical formula $\text{Bi}_{1.56-x}\text{Ca}_x\text{Sb}_{1.48}\text{Co}_{0.96}\text{O}_{7-\delta}$. The homogeneity domain existed until $x=0.3$ with a decrease in the lattice parameter. The electrical conductivity increased with the temperature and reached $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at 500 °C. Electronic conduction probably occurred in these compounds assigned, on the one hand, to the increase of the electrical conductivity with temperature and, on the other hand, to the elevated dielectric loss ($\tan\delta$). A paramagnetic behavior was observed with a para-ferromagnetic transition at $x=0.2$ and 0.3 fractions at low temperatures.

REFERENCES

- [1] M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, Prog. Solid State Chem. **15** (1983) 55.
- [2] J.C. Beam, A.G. Hehn, A.P. Grosvenor, J. Electron Spectrosc. Relat. Phenom. **234** (2019) 5.
- [3] M.J. Winiarski, T.M. McQueen, J. Solid State Chem. **278** (2019) 120898.
- [4] R.A.U. Rahman, D.E. Ruth, M. Ramaswamy, Ceram. Int. **46** (2020) 14346.
- [5] A. Bhuiyan, V. Wong, J.L. Abraham, R.D. Aughterson, L. Kong, R. Farzana, D.J. Gregg, C.C. Sorrell, Y. Zhang, P. Koshy, Mater. Chem. Phys. **273** (2021) 125058.
- [6] V.A. Vorotnikov, S.A. Belyakov, M.S. Plekhanov, A.Y. Stroeveva, A.S. Lesnichyova, O.M. Zhigalina, D.N. Khmelenin, A.V. Atanova, V.G. Basu, A.V. Kuzmin, Ceram. Int. **48** (2022) 35166.
- [7] L. Gao, K. Liang, Z. Liu, H. Chen, J. Zhang, J. Alloys Compd. **922** (2022) 165859.
- [8] J. Du, R. Liu, F. Wan, D. Li, J. Li, Y. Wang, Ceram. Int. **48** (2022) 33563.
- [9] S. Sun, Y. Xue, D. Yang, Z. Pei, L. Fang, Y. Xia, R. Ti, C. Wang, C. Liu, B. Xiong, Z. Fu, X. Yin, Chem. Eng. J. **448**

- (2022) 137580.
- [10] N.A. Zhuk, N.A. Sekushin, M.G. Krzhizhanovskaya, V.V. Kharton, *Solid State Ion.* **377** (2022) 115868.
- [11] H. Shao, L. Gao, K. Liang, H. Chen, Q. Ye, J. Zhang, *Mater. Sci. Eng. B* **277** (2022) 115571.
- [12] M. Sellami, A. Bekka, N. Bettahar, C. R. Chim. **8** (2005) 1129.
- [13] O.M. Detlef, W. Bahnemann, M. Wark, *Catal. Today* **225** (2014) 102.
- [14] E.S. Converse, G. King, J. Li, M.A. Subramanian, *Prog. Solid State Chem.* **68** (2022) 100378.
- [15] N.A. Zhuk, B.A. Makeev, M.G. Krzhizhanovskaya, R.I. Korolev, *Ceram. Int.* **49** (2023) 5496.
- [16] T.A. Vanderah, T. Siegrist, M.W. Lufaso, M.C. Yeager, R.S. Roth, J.C. Nino, S. Yates, *Eur. J. Inorg. Chem.* **23** (2006) 231.
- [17] M. Sellami, A. Bekka, N. Bettahar, V. Caignaert, N. Nguyen, C. R. Chim. **12** (2009) 276.
- [18] N. Benhadria, A. Elaziouti, N. Laouedj, M. Sellami, N. Bettahar, *Mater. Res. Bull.* **74** (2016) 491.
- [19] R.D. Shannon, *Acta Cryst. A* **32** (1976) 751.
- [20] M. Sellami, A. Bekka, N. Bettahar, N. Nguyen, C. R. Chim. **9** (2006) 1209.
- [21] P.J. Durrant, B. Durrant (Eds.), "General and inorganic chemistry", Longmans Green (1962).
- [22] H.W. Qiao, T.Q. Yang, Q.H. Xu, X. Yao, *Ferroelectrics* **356**, 8 (2007) 8.
- [23] H. Du, H. Wang, X. Yao, *Ceram. Int.* **30** (2004) 1383.
- [24] H.L. Du, X. Yao, *J. Electroceram.* **9**, 2 (2002) 119.
- [25] N.A. Zhuk, M.G. Krzhizhanovskaya, N.A. Sekushin, D.V. Sivkov, I.E. Abdurakhmanov, *J. Mater. Res. Technol.* **22** (2023) 1791.
- [26] C. Kaliyaperumal, S. Jayabalan, A. Sankarakumar, T. Paramasivam, *Solid State Sci.* **105** (2020) 106245.
- [27] M.K. Haas, R.J. Cava, M. Avdeev, J.D. Jorgensen, *Phys. Rev. B* **66** (2002) 94429.
- [28] R.L. Carlin, *Magnetochemistry*, Springer-Verlag, Berlin (1986).
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