



Short communication

## Investigation of transport numbers in yttrium doped bismuth niobates

M. Małys<sup>a,\*</sup>, M. Hołdyski<sup>a</sup>, F. Krok<sup>a</sup>, W. Wróbel<sup>a</sup>, J.R. Dygas<sup>a</sup>, C. Pirovano<sup>b</sup>, R.-N. Vannier<sup>b</sup>, E. Capoen<sup>b</sup>, I. Abrahams<sup>c</sup><sup>a</sup> Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662 Warszawa, Poland<sup>b</sup> Equipe de Chimie du Solide, UCCS, Unité de Catalyse et Chimie du Solide, CNRS UMR 8181, USTL-ENSCL, BP 90 108, 59652 Villeneuve d'Ascq Cedex, France<sup>c</sup> Centre for Materials Research, School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, UK

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## ABSTRACT

A study of ionic transference numbers in fluorite-based doped bismuth oxides of general formula  $\text{Bi}_{3.5}\text{Nb}_{1-x}\text{Y}_x\text{O}_{7.75-x}$  ( $0.0 \leq x \leq 0.8$ ) measured using a modified EMF method is presented. The modified method appears to yield transference numbers that are more consistent with the observed behaviour in a.c. impedance spectra compared to classical EMF methods. The results show that niobium-rich compositions have a significant electronic contribution to total conductivity at lower temperatures, but that at elevated temperatures above ca. 600 °C the electronic contribution is negligible. Yttrium doping yields almost pure ionic conductors at all temperatures studied. This is explained with reference to structural features in terms of a disruption of electronic conduction pathways.

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## 1. Introduction

The development of materials for modern electrochemical devices, such as solid oxide fuel cells (SOFCs), gas sensors and oxygen generators requires precise determination of transport properties under specific conditions. Solid electrolytes for SOFCs and oxygen pumps should exhibit high oxide ion conductivity, with negligible electronic contribution. In contrast, interconnection materials for these applications require almost pure electronic conductivity, whereas electrode materials need both electronic and ionic conductivity to be high. Therefore, in assessing the potential of materials for use in such devices, it is extremely important to determine both electronic and ionic contributions to total conductivity.

The highest oxide ion conductivity of any known material is exhibited by the defect fluorite structured  $\delta$ -phase of  $\text{Bi}_2\text{O}_3$ , with a conductivity value of ca.  $1 \text{ S cm}^{-1}$  at temperatures above 730 °C [1]. However, this phase is only stable over a narrow temperature range and much work has been carried out on the stabilisation of this phase to lower temperatures through cation substitution [2–5]. Niobium substitution of bismuth in  $\text{Bi}_2\text{O}_3$  results in a number of very interesting ordered fluorite phases closely related to the highly conducting  $\delta$ - $\text{Bi}_2\text{O}_3$  phase [6–8]. Unfortunately, super-valent cation substitution of  $\text{Bi}^{3+}$  inevitably leads to a reduction in

oxide ion vacancies, the main charge carrier in these systems, with a resultant reduction in ionic conductivity. A double substitution approach can be adopted to increase vacancy concentration and hence ionic conductivity. We have investigated double substitution in  $\text{Bi}_2\text{O}_3$  in the  $\text{Bi}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ - $\text{Nb}_2\text{O}_5$  ternary system with detailed structural and electrical investigations of the pseudo-binary systems  $\text{Bi}_3\text{YO}_6$ - $\text{Bi}_3\text{NbO}_7$  [9] and  $\text{Bi}_{3.5}\text{YO}_{6.75}$ - $\text{Bi}_{3.5}\text{NbO}_{7.75}$  [10]. Both these systems exhibit full solid solution ranges, with a fluorite type structure maintained throughout. Superlattice ordering of the cubic fluorite subcell is evident in niobium-rich compositions even at high temperatures. This ordering disappears at higher levels of Y substitution and is replaced by diffuse scattering in neutron diffraction profiles characteristic of short-range ordering. Our investigations of the defect structure in these systems revealed that non-linear thermal expansion of the cubic lattice parameter and non-Arrhenius behaviour of total electrical conductivity at elevated temperatures are correlated with subtle changes in the oxide ion distribution.

Different research groups over several decades have tried to determine the electronic and ionic contributions to total conductivity in bismuth niobates. The ionic transference number ( $t_0$ ) of  $\text{Bi}_3\text{NbO}_7$  was determined using the traditional electromotive force (EMF) method [11] and the reported  $t_0$  values were surprisingly low ( $t_0 < 0.2$ ) at temperatures below 500 °C. However, the accuracy of the EMF method depends strongly on the electrode polarisation resistance of the concentration cell used, especially at lower temperatures. Indeed, Kharton and Marques [12] recently discussed the problems associated with electrode polarisation resistance and

\* Corresponding author. Tel.: +48 22 234 8216; fax: +48 22 628 2171.  
E-mail address: [malys@mech.pw.edu.pl](mailto:malys@mech.pw.edu.pl) (M. Małys).

its influence on  $t_0$ . The Wagner polarisation method has also been applied in the determination of transference numbers in  $\text{Bi}_3\text{NbO}_7$  [13]. Interestingly, both ionic and electronic conductivity were found to be higher in the tetragonal phase of  $\text{Bi}_3\text{NbO}_7$  (Type-III) than in the pseudo-cubic phase (Type-II), at comparable temperatures.

A modified EMF method under external load resistance conditions has been developed [12,14,15], which has enabled significant improvements in the accuracy of values of the electronic contribution to total conductivity in certain systems. This method has already been successfully applied in the determination of transference numbers in bismuth niobates with low levels of substitution (Bi:Nb molar ratio ranging from 5.25:1 to 19:1), where pseudo-cubic  $\delta$ -phase type structures are observed [16]. The investigated materials were found to be predominantly ionic conductors with oxygen ion transference numbers greater than 0.90 in the temperature range 580–680 °C.

The aim of the present work was to investigate charge transport properties of the double substituted system  $\text{Bi}_{3.5}\text{Nb}_{1-x}\text{Y}_x\text{O}_{7.75-x}$  ( $0.0 \leq x \leq 0.8$ ) using the modified EMF method proposed by Gorelov [14] and Kharton and Marques [12].

## 2. Experimental

### 2.1. Preparations and general characterisation

Polycrystalline samples of  $\text{Bi}_{3.5}\text{Nb}_{1-x}\text{Y}_x\text{O}_{7.75-x}$  ( $0.0 \leq x \leq 0.8$ ) and  $\text{Bi}_4\text{NbO}_{8.5}$ , were prepared by conventional solid-state methods, with appropriate amounts of precursors:  $\text{Bi}_2\text{O}_3$  (Aldrich, 99.9%),  $\text{Y}_2\text{O}_3$  (Aldrich, 99.99%) and  $\text{Nb}_2\text{O}_5$  (Aldrich, 99.9%). Starting mixtures were ground in ethanol using a planetary ball mill. The dried mixtures were heated initially at 740 °C for 24 h, then cooled, reground and pelletised. Pellets (10 mm in diameter and about 4 mm thick for impedance measurements and 15 mm in diameter and 1 mm thick for transference number measurements) were pressed isostatically at a pressure of 400 MPa, then sintered at 900 °C for 10 h. Sintered pellets were slowly cooled in air to room temperature over a period of approximately 12 h. Phase purity was confirmed using X-ray powder diffraction on a Philips X'Pert X-ray diffractometer using nickel filtered  $\text{Cu K}\alpha$  radiation ( $\lambda_1 = 1.54056 \text{ \AA}$  and  $\lambda_2 = 1.54439 \text{ \AA}$ ).

### 2.2. Electrochemical and electrical measurements

Total conductivity was determined by a.c. impedance spectroscopy using a Solartron 1255/1286 system in the frequency range 1 Hz to 500 kHz. Platinum electrodes were sputtered by cathodic discharge.

Pellets used for transference number measurements had their surfaces mirror-polished using successive SiC papers up to 4000 grit and were sputtered with either platinum or gold electrodes on both sides by cathodic discharge. The transference numbers were measured using the concentration cell  $\text{O}_2$  ( $p\text{O}_2 = 1.01 \times 10^5 \text{ Pa}$ ); Pt or Au||oxide|Pt or Au;  $\text{O}_2$  ( $p\text{O}_2 = 0.21 \times 10^5 \text{ Pa}$ ) by the Gorelov EMF method [14], with external load resistance simulating the effect of enhanced electronic conductivity. The prepared pellet was introduced between two mullite tubes and sealed using Pyrex glass rings. Experiments were carried out between 450 °C and 750 °C at intervals of ca. 50 °C, after 12 h of stabilisation at each temperature. Leakage was monitored by measuring the trace oxygen content in the isolation chamber. The gas flows were fixed at  $2.5 \text{ cm}^3 \text{ s}^{-1}$ .

The modification of the EMF method proposed by Gorelov [14] and later well described by Kharton and Marques [12] lies in the addition of an external resistance ( $R_{\text{ext}}$ ), which simulates the effect of enhanced electronic conductivity. The modified method also makes the assumption that overpotential at the electrode-

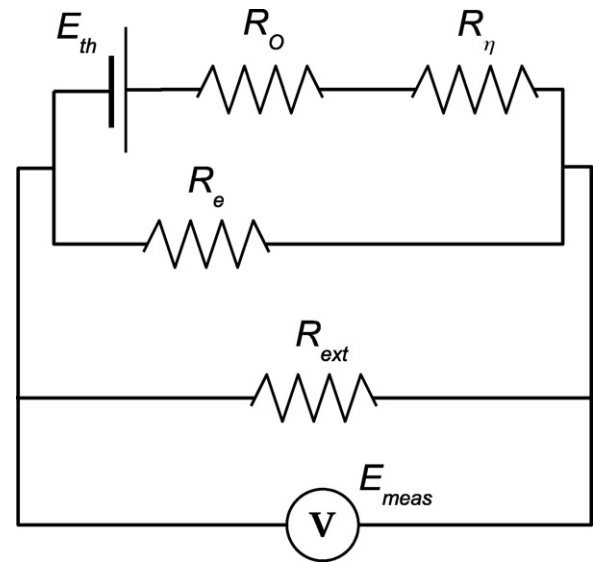


Fig. 1. Equivalent circuit describing modified EMF method with external load  $R_{\text{ext}}$ .

electrolyte interface ( $\eta$ ) is linearly dependent on current ( $I$ ), therefore polarisation resistance  $R_\eta$  can be defined as

$$R_\eta = \frac{\eta}{I} \quad (1)$$

The cell voltage is measured under open and closed circuit conditions as a function of external resistance  $R_{\text{ext}}$ . The corresponding equivalent circuit (Fig. 1) yields the following equation:

$$\frac{E_{\text{meas}}}{E_{\text{th}}} - 1 = (R_0 + R_\eta) \left( \frac{1}{R_e} + \frac{1}{R_{\text{ext}}} \right) \quad (2)$$

where  $E_{\text{meas}}$  and  $E_{\text{th}}$  are the voltages measured and calculated from the Nernst equation respectively and  $R_0$  and  $R_e$  are the resistances associated with ionic and electronic conductivity respectively. The dependence ( $E_{\text{th}}/E_{\text{meas}} - 1$ ) versus  $1/R_{\text{ext}}$  should be linear with a slope of  $(R_0 + R_\eta)$ :

$$\frac{E_{\text{meas}}}{E_{\text{th}}} - 1 = A \left( \frac{1}{R_{\text{ext}}} \right) + B \quad (3)$$

$$R_e = \frac{A}{B} \quad (4)$$

where  $A$  and  $B$  are regression parameters. The oxygen transference number can thus be obtained from

$$t_0 = 1 - \frac{R_{\text{bulk}}}{R_e} \quad (5)$$

where  $R_{\text{bulk}}$  is the bulk resistance as derived from a.c. impedance spectroscopy measurements made on the sample. The linear dependence of  $(E_{\text{th}}/E_{\text{meas}} - 1)$  versus  $1/R_{\text{ext}}$ , described in Eq. (3), was monitored and values of  $R_{\text{ext}}$  were adjusted from 1  $\Omega$  to 4 k $\Omega$  according to experimental conditions.

## 3. Results and discussion

X-ray diffraction patterns collected for all studied compositions confirmed each of the samples was phase pure and exhibited Bragg peaks that could be indexed on a cubic cell of dimension ca. 5.5  $\text{\AA}$  in space group  $Fm\bar{3}m$ . It should be noted that neutron diffraction studies on the  $\text{Bi}_{3.5}\text{Nb}_{1-x}\text{Y}_x\text{O}_{7.75-x}$  system revealed that niobium-rich compositions ( $x \leq 0.2$ ) show superlattice reflections, consistent with a Type-II incommensurately ordered phase and therefore these phases are technically pseudo-cubic, whereas for higher values of  $x$  a fully disordered  $\delta$ - $\text{Bi}_2\text{O}_3$  type cubic phase is observed [10].

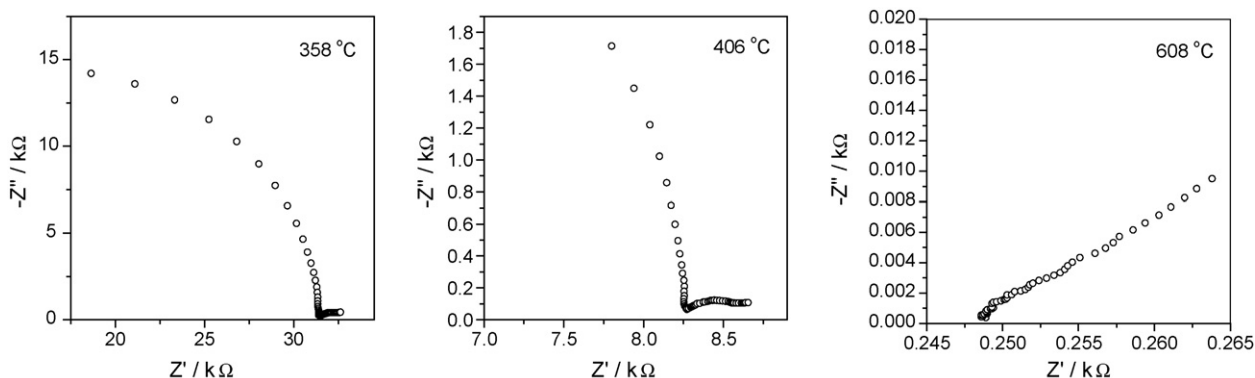


Fig. 2. Example impedance spectra for  $\text{Bi}_{3.5}\text{NbO}_{7.75}$ .

Impedance spectra for  $\text{Bi}_{3.5}\text{NbO}_{7.75}$  at low temperatures (Fig. 2) are dominated by a well-developed broad semicircle attributable to dispersions of bulk and grain boundaries. At the lowest temperatures studied, an additional small semicircle is observed at low frequencies, which terminates on the real axis. This feature is associated with electron transfer at the electrodes, encompassing charge polarisation at the electrode–electrolyte interface, and has previously been described by Wang et al. in  $\text{Bi}_3\text{NbO}_7$  [13]. At higher temperatures impedance spectra show diffusive tails associated with the blocking electrode, a feature characteristic of predominantly ionic conductivity. Similar features were observed in the impedance spectra of  $\text{Bi}_4\text{NbO}_{8.5}$  [17]. These features are therefore indicative of an electronic contribution to total conductivity at low temperatures in the pure niobium compositions. In contrast, the impedance spectra of the yttrium doped samples show diffusive tails throughout the temperature range studied, consistent with predominantly ionic conductivity even at low temperatures.

Transference number measurements for  $\text{Bi}_{3.5}\text{NbO}_{7.75}$  performed using the modified EMF method are compared with values from the classical EMF procedure in Fig. 3. The classical EMF method generally gives significantly lower values for the oxide ion transference number than the modified method. This difference may be attributed to the difficulties that the classical method has in accounting for polarisation resistances. Indeed, Kharton and Marques [12] comment that  $\text{Bi}_2\text{O}_3$ -based electrolytes show significant deviations from the classical method due to their enhanced surface activity leading to higher polarisation resistances. The results from

the modified EMF method confirm a significant electronic contribution to total conductivity in  $\text{Bi}_{3.5}\text{NbO}_{7.75}$  at lower temperatures. This electronic contribution decreases with increasing temperature and above ca. 600 °C conductivity is essentially purely ionic.

Transference number measurements for the yttrium doped samples using the modified EMF method reveal almost pure ionic conductivity over the entire temperature range studied (Fig. 4). This conclusion was also reached by Meng et al. [11] using the classical EMF method. They reported the  $(\text{Bi}_2\text{O}_3)_{0.75}(\text{Y}_2\text{O}_3)_x(\text{Nb}_2\text{O}_5)_{0.25-x}$  system to exhibit pure ionic conduction. Details of the thermal behaviour of the transference numbers for the yttrium doped samples are given in Fig. 5. The results show a general increase in  $t_0$  with increasing yttrium content.

Fig. 6 shows Arrhenius plots of total conductivity for  $\text{Bi}_{3.5}\text{NbO}_{7.75}$ . The plot can be interpreted as possessing two linear regions, one at low temperatures and one at high temperatures with a transition region around 600 °C. The corresponding activation energies,  $\Delta E_{\text{LT}}$  and  $\Delta E_{\text{HT}}$  respectively, are  $\Delta E_{\text{LT}} = 1.03$  eV and  $\Delta E_{\text{HT}} = 1.18$  eV for  $\text{Bi}_{3.5}\text{NbO}_{7.75}$ . Also shown in Fig. 6 are the individual ionic ( $\sigma_i$ ) and electronic ( $\sigma_e$ ) contributions to total conductivity. The observed transition in the Arrhenius plots of total conductivity appears to correlate well with the observed changes in  $t_0$  as seen in Fig. 4. These results suggest that in these compositions in the lower temperature region below ca. 600 °C a significant part of the total conductivity is associated with an electronic contribution which results in a lowering of the activation energy, whereas at higher temperatures, the higher activation energy reflects the predominantly ionic nature of total conductivity. Interestingly, a change in

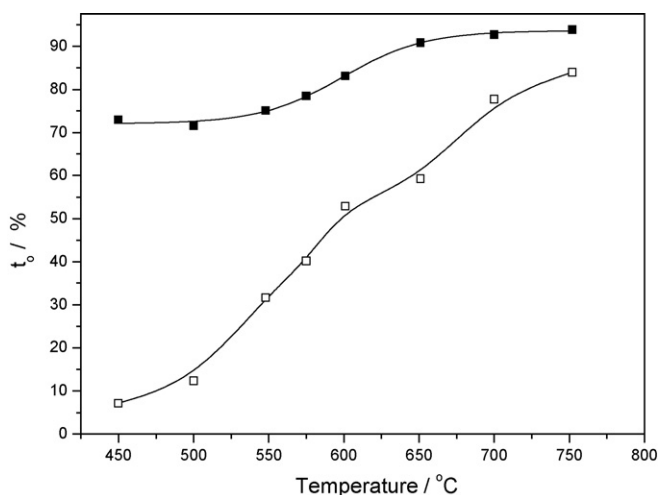


Fig. 3. Comparison of ionic transference numbers measured by the modified (■) and the classical EMF (□) methods for  $\text{Bi}_{3.5}\text{NbO}_{7.75}$ .

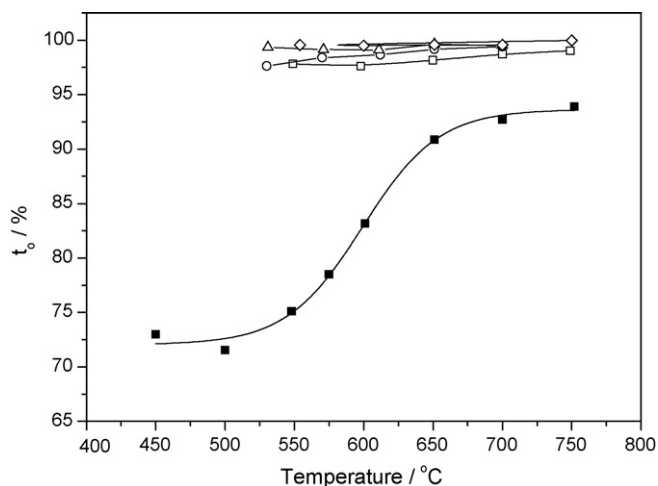


Fig. 4. Thermal dependence of ionic transference number in compositions of  $\text{Bi}_{3.5}\text{Nb}_{1-x}\text{Y}_x\text{O}_{7.75-x}$ . (■)  $x = 0.0$ , (□)  $x = 0.2$ , (○)  $x = 0.4$ , (△)  $x = 0.6$ , (◇)  $x = 0.8$ .

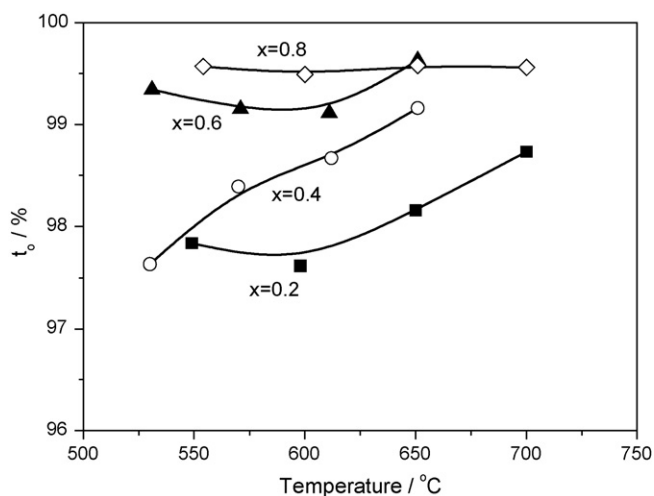


Fig. 5. Detail of thermal dependence of ionic transference number in  $\text{Bi}_{3.5}\text{Nb}_{1-x}\text{Y}_x\text{O}_{7.75-x}$ .

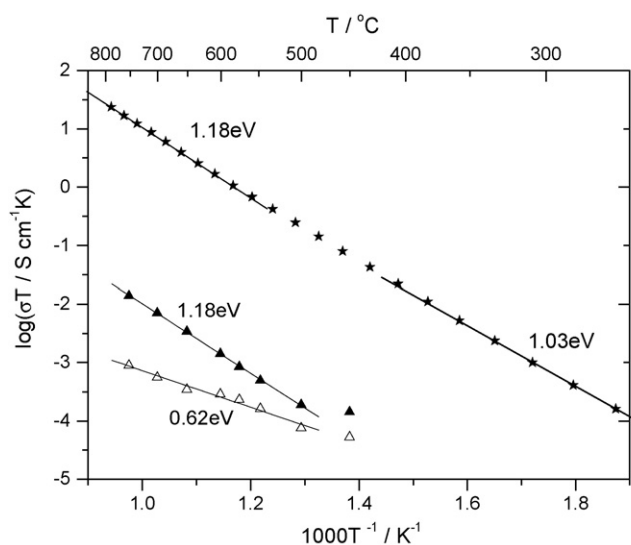


Fig. 6. Arrhenius plots for  $\text{Bi}_{3.5}\text{NbO}_{7.75}$  showing total conductivities ( $\sigma_{\text{tot}}$ ,  $\star$ ) as well as ionic ( $\sigma_i$ ,  $\blacktriangle$ ) and electronic ( $\sigma_e$ ,  $\triangle$ ) contributions and corresponding activation energies.

high temperature activation energy in the yttrium doped samples is also observed [10], but in these cases the values of  $\Delta E_{\text{HT}}$  are lower than the corresponding low temperature values. We have previously associated this with subtle thermally and compositionally dependent changes in the oxide ion distribution [9].

The observed changes in transference number with composition and temperature can be rationalised by considering the structures of these fluorite-based phases. The superlattice ordering of the Type-II incommensurate phase is believed to be associated with ordering of niobate polyhedra [18,8]. Several structural motifs based on pyrochlore type ordering of niobate polyhedra were suggested by Tang and Zhou [18] in Type-II bismuth niobates studied by electron diffraction, while later work by Ling [8] suggested that the chain motif dominates. More recently our neutron diffraction

studies of the related Type-II tantalum composition  $\text{Bi}_3\text{TaO}_7$  [19] have also indicated clustering of dopant octahedra consistent with the chain motif. In the studied compositions niobium is nominally in the  $d^0$  pentavalent oxidation state. However, under the standard synthetic conditions employed in this work, it is likely that a small degree of reduction occurs to give low concentrations of  $\text{Nb}^{4+}$  ions, which provide the electronic charge carriers. Therefore, electronic conduction presumably involves a hopping mechanism along the niobate chains. Doping with yttrium or increasing the Bi:Nb ratio effectively shortens the chains and thus limits long-range electronic conduction through disruption of the conduction pathway.

#### 4. Conclusions

Our results suggest that the modified EMF method yields a more realistic approximation to ionic transference numbers in doped bismuth oxides, which appears to be more consistent with observed features in a.c. impedance spectra. In niobium-rich bismuth niobates, a significant electronic contribution to total conductivity is observed at lower temperatures, which diminishes above ca. 600 °C to yield almost pure ionic conductivity. This appears to be correlated with observed changes in the activation energy of total conductivity. Electronic conduction is believed to be associated with the presence of low concentrations of  $\text{Nb}^{4+}$  cations located in chains of niobate polyhedra, with electron hopping along the chains. Disruption of the chains through yttrium doping or increasing the Bi:Nb ratio results in a dramatic decrease in electronic conductivity yielding almost pure ionic conductors.

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