

Ordering effect on the electrical properties of stoichiometric Ba₃CaNb₂O₉-based perovskite ceramics



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ABSTRACT

Cation ordering is the most common phenomenon detected in A₃B'B''₂O₉-based complex perovskites. Some important physical features of this system are due to the B-site ordering at long and short range. For microwave applications as filters and resonators, the 1:2 order is more appropriate. Otherwise, the oxygen vacancies and 1:1 order are considered the main factors behind the excellent performance of nonstoichiometric A₃B'_{1+x}B''_{2-x}O_{9-δ}-based ceramics as proton conductors. Until now, however, there are no available reports regarding the isolated effects of B-site ordering at long range on the electrical properties of stoichiometric systems. This work reports the preparation of 1:1 and 1:2 ordered Ba₃CaNb₂O₉ ceramics. Here, we combine the Raman scattering and group-theory calculations to distinguish the fingerprints of the 1:1 and 1:2 orders. The electrical properties of the ordered Ba₃CaNb₂O₉ are analyzed in terms of a phenomenological model based on the parallel combination of a resistor, constant phase element, and capacitor. In particular, the conductivity relaxation ascribed to the grains is due to the oxygen vacancies. Besides, we found that the 1:1 order increases the *dc* conductivity compared to the 1:2 order.

1. Introduction

In the past decades, compounds based on ordered complex perovskites with the chemical formula A₃B'B''₂O₉ [A = Ba²⁺ or Sr²⁺; B' = Mg²⁺, Ca²⁺ or Zn²⁺; B'' = Nb⁵⁺ or Ta⁵⁺] have attracted considerable attention owing to their very low loss and high proton conductivity, making them suitable for microwave devices [e.g. filters, resonators, antennas] [1], and electrolyte membranes for proton conducting solid oxide fuel cells [2]. In the former case, three parameters should be taken into account to improve the device performance: high dielectric permittivity enabling the miniaturization, low loss for good selectivity, and near zero temperature coefficient of permittivity providing a thermally stable device [3]. In the latter case, high proton conductivity and good chemical stability are desired capabilities to design new hydrogen and humidity sensors [4], chemical reactors for reforming of methane [5] and ammonia generation [6], and fuel cells [7]. In the perovskite structure, the protonic defects are usually due to the dissociative adsorption of water and/or hydrogen [8], in agreement with the next reactions [in Kröger-Vink notation]:



where the protons are attached to oxide ions forming the OH⁻ groups, with defect notation (OH)_O[•] [9].

Particularly, the nonstoichiometric perovskite-structured Ba₃Ca_{1+x}Nb_{2-x}O_{9-δ} exhibited an appropriate chemical stability under water and CO₂ atmospheres at high temperatures for *x* = 0.18 (BCN18) [10]. Nevertheless, its proton conductivity is low compared to the well-studied simple perovskites containing rare-earth-doped alkaline earth based cerates and zirconates [11,12]. Some strategies to enhance the proton conductivity of BCN18 without deteriorating its chemical stability have been reported, mainly focusing the generation of oxygen vacancies [≡ V_O^{••}]. The Thangadurai group has studied the partial replacement of Ba by K on A-site and Ti substitution for Nb in the stoichiometric Ba₃CaNb₂O₉ [13,14]; The Fanglin Chen group has reported the effects of Ce and Y doping on the Ca and Nb ions in complex perovskite Ba₃Ca_{1.18}Nb_{1.82}O_{9-δ} proton conductor [7,15]. In all cases, the nonstoichiometry leads to a formation of oxygen vacancies and a modification in the B-site ordering from 1:2 to 1:1 type [16]. In the 1:2 ordered systems, the Ca and Nb cations are alternately distributed in the sequence –Ca–Nb–Nb–Ca–Nb–Nb– along the [111]_c direction of the parent cubic cell [17]. In the 1:1 order, the 4b

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sites are occupied by Nb, whereas the 4a ones possess a randomly distribution of Ca and Nb: $\frac{2}{3}\text{Ca} + \frac{1}{3}\text{Nb}$ [18]. For microwave uses, the obtention of low loss $\text{A}_3\text{B}'\text{B}''_2\text{O}_9$ -based dielectrics is related to the 1:2 order [19–21]. To the best of our knowledge, however, there are no available reports regarding the isolated effects of B-site ordering on the electrical properties of stoichiometric $\text{Ba}_3\text{CaNb}_2\text{O}_9$ -based ceramics.

In this paper, we synthesized the 1:1 and 1:2 ordered $\text{Ba}_3\text{CaNb}_2\text{O}_9$ -based ceramics to probe the role of B-site ordering on their electrical properties, seeking to elucidate the ordering contribution to the dc conductivity and dielectric permittivity. As reported by many authors [22–24], the combination of both the complex impedance and complex electric modulus formalisms is an important tool to probe the conductivity relaxation in several materials, including conducting glasses, solid electrolytes, electroceramics, and so on. In particular, the electric modulus [$\mathbf{M}(\omega) \equiv 1/\epsilon^*(\omega) = \text{Re}(\mathbf{M}) + j\text{Im}(\mathbf{M})$] minimizes the occurrence of low frequency phenomena, such as the electrode polarization, parasite capacitance, and double layer formation, making such a formalism more appropriate to study the bulk contribution to the electrical response [25]. Besides, the signatures of order-disorder phenomena in ordered complex perovskites have been investigated using X-ray diffraction and Raman spectroscopy, mainly focusing on the fingerprints of short and long range ordering at B-site [26,27]. Such techniques will be used here to identify the ordering and then its role on the electrical properties of stoichiometric $\text{Ba}_3\text{CaNb}_2\text{O}_9$ -based ceramics.

2. Experimental procedures

2.1. Preparation of samples

$\text{Ba}_3\text{CaNb}_2\text{O}_9$ [here after: BCNO] ceramics were prepared by solid-state reaction route under air atmosphere using a stoichiometric mixture of high purity BaCO_3 [Alfa Aesar; 99.80%], CaCO_3 [Alfa Aesar; 99.95%], and Nb_2O_5 [Alfa Aesar; 99.90%]. Such precursors were homogenized in a nylon jar containing isopropyl alcohol and zirconia cylinders during 24 h. The slurry was dried and subsequently calcined at 1573 K for 2 h. After milling, the BCNO powder was mixed with a binder solution of PVB-polyvinyl butyral [~ 3 wt%], pressed into cylindrical pellets [D ~ 6 mm \times H ~ 2 mm] by uniaxial [15 MPa] and isostatic [300 MPa] cold pressing. To obtain 1:1 and 1:2 ordered ceramics, such green pellets were sintered in air by following the conditions listed in Table 1, yielding to dense ceramics with at least $\sim 92\%$ of relative density.

2.2. Characterization of samples

Powder X-ray diffraction patterns [pXRD] were recorded by a

Table 1

List of sintering condition, relative density, average grain size, A_{1g} peak positions, and electrical parameters of the 1:1 and 1:2 ordered BCNO ceramics.

Long range order	1:1	1:2
Sintering condition	1863 K for 2 h	1773 K for 32 h
Relative density, %	97 \pm 1	92 \pm 1
Average grain size, μm	2.8 \pm 0.6	1.4 \pm 0.5
Space group	<i>Fm-3m</i> (225)	<i>P-3m1</i> (164)
Crystallographic card	ICDD#49-0425	ICSD#162758
A_{1g} [1:1] peak position, cm^{-1}	765	750
A_{1g} [1:2] peak position, cm^{-1}	827	818
Geometrical factor λ , mm^{-1}	56.8	34.1
σ_g , 10^{-9} ($\Omega \text{ mm}$) $^{-1}$ (at 723 K)	34.9	4.63
ϵ_g (at 723 K)	53.7	40.3
α (at 723 K)	0.547	0.611
R_g , G Ω (at 723 K)	1.63	7.37
C_g , pF (at 723 K)	8.4	10.5
Activation energy E_a , eV	1.62 \pm 0.02	1.71 \pm 0.01
τ_a , ppm K $^{-1}$	-225	-143

Rigaku Rotaflex RU-200B diffractometer [50 kV and 100 mA; Cu-K α radiation $\lambda = 1.5406$ Å; Bragg-Brentano θ -2 θ geometry] over a 2 θ range from 10° to 100° with a step size of 0.02° and step time of 1 s. Raman spectra at room temperature were recorded using a *Jobin-Yvon* T64000 triple monochromator with an LN $_2$ cooled CCD detector. A backscattering geometry was employed with a 488 nm line of an argon laser [Coherent INNOVA 70C] as an excitation source. The 1800 grooves mm^{-1} grating was chosen to keep the resolution below 1 cm^{-1} . Raman spectra were further corrected by the Bose-Einstein thermal factor prior to the fitting by the Lorentzian profiles [28], including a baseline subtraction. The microstructures were probed by an Inspect F50 field-emission scanning electron microscope [FEI, Netherlands] operating at 5 kV equipped with an energy dispersive X-ray spectrometer (EDX). Additional information on the microstructural properties is available in the [Supplementary material data](#). The Archimedes principle was taken into account to obtain the bulk density of the ceramic samples using distilled water as an immersion liquid.

Measurements of impedance spectroscopy (IS) were performed in the frequency range from 0.5 Hz to 1 MHz using a Solartron frequency response analyzer [FRA model 1260] coupled with a dielectric interface Solartron [model 1296]. For this purpose, the pellet surfaces were painted with platinum paste (Pt), and then fired at 973 K for 1 h to remove its polymeric component and get good quality ceramic/electrode contact. The ac voltage of ~ 1 V was defined after signal/noise tests, and considering the ohmic behavior of the system. The temperature dependence of the electrical properties of BCNO ceramics was acquired using a homemade furnace in the range from ~ 300 to 840 K under air atmosphere. Firstly, the thermal spectra of the permittivity [at 10 kHz, 100 kHz, and 1 MHz] were obtained in this temperature range, during the controlled cooling with rate of 2 K min^{-1} . Next, the complex impedance spectra [$\mathbf{Z}^* = \text{Re}(\mathbf{Z}) + j\text{Im}(\mathbf{Z}) \equiv \lambda\rho$; λ is the geometrical factor in units of mm^{-1}] were acquired in the range between ~ 660 and 840 K, taking temperature plateaus with dwell time around 30 min in order to ensure a stable temperature (or isotherm) during the frequency sweep. The spectral data were further analyzed and adjusted using the ZView software 2.9c [29].

3. Results and discussion

3.1. Cation ordering at B-site

In this paper, we adjusted the synthesis conditions for obtaining fully disordered, 1:1 and 1:2 ordered BCNO samples. The disordered state takes place during the powder sample preparation, where Ca^{2+} and Nb^{5+} cations are randomly distributed at the B-site in $\text{Ba}(\text{Ca},\text{Nb})\text{O}_3$ composition. Such a crystal structure belongs to the cubic space group *Pm-3m* [lattice constant: a_0] without octahedral tilting [$\mathbf{a}^0\mathbf{a}^0\mathbf{a}^0$ in Glazer notation] [30], and its pXRD pattern is illustrated in Fig. 1(a). The ordered state can be achieved at high temperature through the sintering process [31], see details in Table 1. By monitoring the sintering, the 1:1 and 1:2 ordering types were obtained for the BCNO ceramics. In both cases, a superstructure is formed from the disordered cubic cell, leading to an increase in the unit cell volume [32]. The signature of this phenomenon can be detected in Fig. 1(b) through the superlattice X-ray Bragg reflections. Since the sizes and valences of Ca^{2+} and Nb^{5+} are found to be different, their Wyckoff sites should contain distinct local properties depending on the Ca–O and Nb–O bond distances. This fact explains the appearance of the superlattice peaks at lower diffraction angles, labeled as (111) $_c$, (001) $_h$ and (100) $_h$ [21,33]. The detection of those superlattice reflections is an evidence for the long range 1:1 and 1:2 orderings in the BCNO ceramics [34].

In the $\text{Ba}_3\text{CaNb}_2\text{O}_9$ -like system, the (001) $_h$ and (100) $_h$ superlattice peaks come from the $-\text{Ca}-\text{Nb}-\text{Nb}-\text{Ca}-\text{Nb}-\text{Nb}-$ stacking sequence (1:2) along the [111] $_c$ planes of the simple cubic cell [disordered system *Pm-3m*], leading to a trigonal cell with the lattice parameters $a_h \approx \sqrt{2}a_0$ and $c_h \approx \sqrt{3}a_0$ [space group: *P-3m1* or *D $_{3d}^3$*] [33]. However,

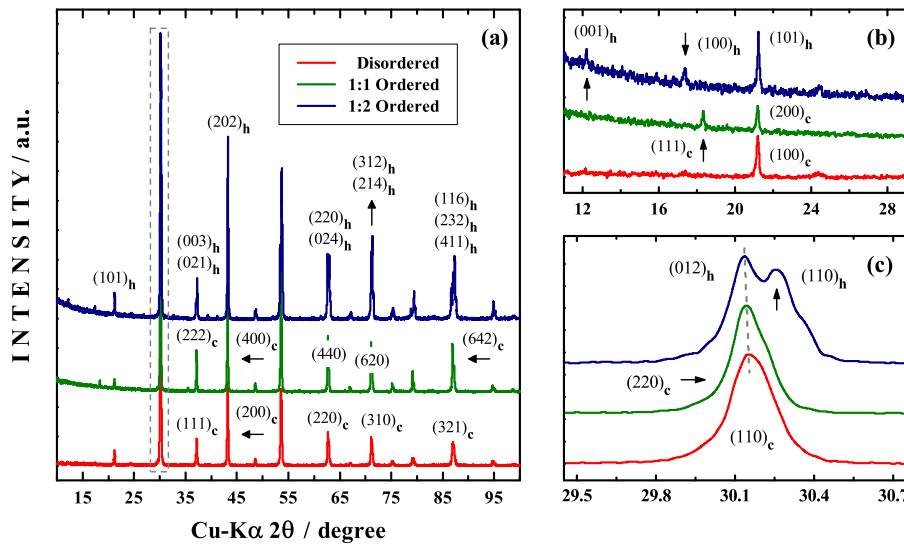


Fig. 1. (a) Powder X-ray diffraction patterns of disordered, 1:1 and 1:2 ordered BCNO samples at room temperature; (b) superlattice X-ray Bragg reflections at lower diffraction angles; (c) peak splitting process, namely (110)_c → (220)_c → (012)_h + (110)_h, owing to the trigonal cell formation.

Table 2

Factor group analysis for the crystal structures addressed in this work ($\Gamma_T = \Gamma_{Ac} \oplus \Gamma_{Si} \oplus \Gamma_{IR} \oplus \Gamma_R$).

Ion	Wyckoff site	Symmetry	Irreducible representation
Disordered cubic: O_h^1 ; $Fm-3m$; #221; $\alpha^0\alpha^0\alpha^0$			
Ba ²⁺	1b	O_h	F_{1u}
Ca ²⁺ /Nb ⁵⁺	1a	O_h	F_{1u}
O ²⁻	3d	D_{4h}	$2F_{1u} \oplus F_{2u}$
Γ_T	$4F_{1u} \oplus F_{2u}$		
Γ_{Ac}	F_{1u}		
Γ_{Si}	F_{2u}		
Γ_{IR}	$3F_{1u}$		
Γ_R	0		
1:1 Cubic: O_h^5 ; $Fm-3m$; #225; $\alpha^0\alpha^0\alpha^0$			
Ba ²⁺	8c	T_d	$F_{1u} \oplus F_{2g}$
Ca ²⁺ /Nb ⁵⁺	4a	O_h	F_{1u}
Nb ⁵⁺	4b	O_h	F_{1u}
O ²⁻	24e	C_{4v}	$A_{1g} \oplus E_g \oplus F_{1g} \oplus F_{2g} \oplus 2F_{1u} \oplus F_{2u}$
Γ_T	$A_{1g} \oplus E_g \oplus F_{1g} \oplus 2F_{2g} \oplus 5F_{1u} \oplus F_{2u}$		
Γ_{Ac}	F_{1u}		
Γ_{Si}	$F_{1g} \oplus F_{2u}$		
Γ_{IR}	$4F_{1u}$		
Γ_R	$A_{1g} \oplus E_g \oplus 2F_{2g}$		
1:2 Trigonal: D_{3d}^3 ; $P-3m1$; #164; $\alpha^0\alpha^0\alpha^0$			
Ba ²⁺	1b	D_{3d}	$A_{2u} \oplus E_u$
Ba ²⁺	2d	C_{3v}	$A_{1g} \oplus A_{2u} \oplus E_g \oplus E_u$
Ca ²⁺	1a	D_{3d}	$A_{2u} \oplus E_u$
Nb ⁵⁺	2d	C_{3v}	$A_{1g} \oplus A_{2u} \oplus E_g \oplus E_u$
O ²⁻	3f	C_{2h}	$A_{1u} \oplus 2A_{2u} \oplus 3E_u$
O ²⁻	6i	C_s	$2A_{1g} \oplus A_{1u} \oplus A_{2g} \oplus 2A_{2u} \oplus 3E_g \oplus 3E_u$
Γ_T	$4A_{1g} \oplus A_{2g} \oplus 5E_g \oplus 2A_{1u} \oplus 8A_{2u} \oplus 10E_u$		
Γ_{Ac}	$A_{2u} \oplus E_u$		
Γ_{Si}	$A_{2g} \oplus 2A_{1u}$		
Γ_{IR}	$7A_{2u} \oplus 9E_u$		
Γ_R	$4A_{1g} \oplus 5E_g$		

such a composition may also be indexed based on the face-centered cubic structure with cell dimension $a_F \approx 2a_0$ [space group: $Fm-3m$ or O_h^5], leading to the (111)_c superlattice Bragg reflection [18]. In this case, the stacking sequence (1:1) has the following rule [35]: $-(\frac{2}{3}Ca + \frac{1}{3}Nb)-Nb-(\frac{2}{3}Ca + \frac{1}{3}Nb)-Nb-$. It means that there is at least one crystallographic site with a random cation distribution (4a site): the so-called random site model. Fig. 1(c) displays a peak splitting process, namely (110)_c → (220)_c → (012)_h + (110)_h, owing to the trigonal cell

formation. Therefore, at this point, it can be concluded that we have prepared two ceramic samples with well-defined long range 1:1 and 1:2 orderings, respectively. Then, one can expect different physical properties coming from these two ordering types. In order to probe how the structural ordering at short and long range impacts the Raman spectra of BCNO samples at room temperature, the group theory analysis for the crystal structures addressed here are reported in Table 2. In this theoretical approach, the number and symmetries of the optical active modes can be estimated, based on the occupied Wyckoff sites within the crystalline structure [36].

For the fully disordered Ba(Ca,Nb)O₃ structure, no Raman-active modes should be observed in the first order Raman spectrum. Otherwise, 4 [$2F_{2g} \oplus E_g \oplus A_{1g}$] and 9 [$5E_g \oplus 4A_{1g}$] Raman-active modes are expected to appear in the first order Raman spectra of 1:1 and 1:2 ordered samples, respectively. Fig. 2(a) displays the Raman spectra acquired at room temperature for the disordered [powder], 1:1 and 1:2 ordered [ceramics] samples. For the 1:2 ceramic, the number of detected peaks agrees well with those predicted by the factor-group analysis. Particularly, the bands at 135, 250, 280 and 610 cm⁻¹ are fingerprints of the trigonal unit cell [33,37]. The internal modes of NbO₆ octahedra are located at 355, 410 and 818 cm⁻¹. The low wavenumber peaks at 85 and 90 cm⁻¹ are called the external modes concerning the vibrations of Ba²⁺ ions against O²⁻ anions. For the 1:1 ceramic, the broad bands at ~ 90, 300, 550 and 800 cm⁻¹ are assigned to F_{2g} , F_{2g} , E_g , and A_{1g} modes [38]. Besides, the last mode concerns the breathing vibration of the oxygen octahedra. For the disordered sample, however, its Raman spectrum containing at least 11 bands more closely resembles that of the 1:2 ceramic. It means that the disordered sample has a 1:2 order at short range, since the superlattice reflections did not appear in its pXRD pattern in Fig. 1(b). As accepted in recent literature, in this situation there are domain regions with 1:2 order embedded in a disordered cubic matrix [average space group: $Pm-3m$ or O_h^1] [39]. Similar model was taken into account to assign the first order Raman spectra of Pb₃MgNb₂O₉-based relaxor ferroelectrics, but considering the domain regions with 1:1 order instead of 1:2 order [40]. Further work should be carried out in order to account for the short range features in BCNO.

It is worth mentioning that the A_{1g} mode in the wavenumber range 700–900 cm⁻¹ is very sensitive to the cation ordering at B-site [26,41]. Such a mode denotes a breathing type vibration of oxygen atoms, being its wavenumber dependent on the B–O and O–O bond strengths [42]. Therefore, the A_{1g} mode properties such as wavenumber, width and intensity should reflect the B-site order changes [43]. Fig. 2(b) shows

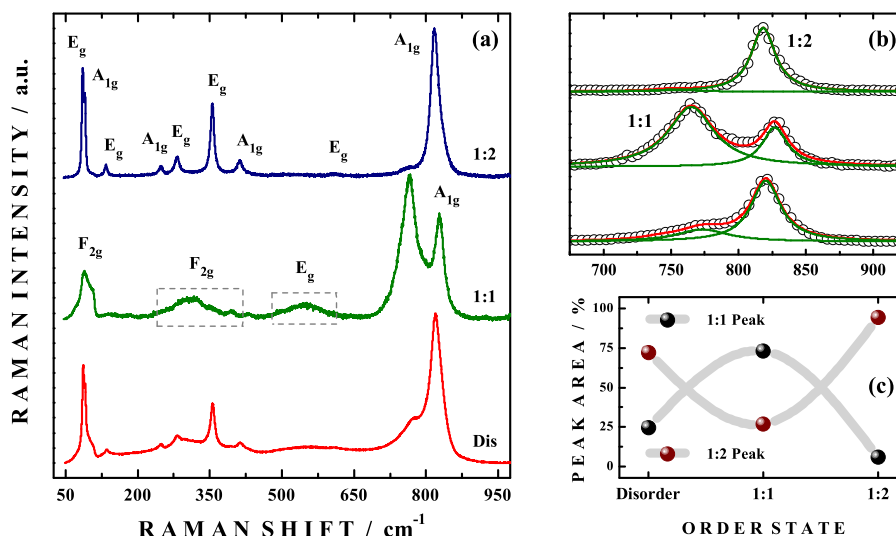


Fig. 2. (a) Raman spectra at room temperature for the disordered, 1:1 and 1:2 ordered samples; (b) the black open circles denote experimental data and red/green lines are the fitted spectrum using Lorentzian profiles; (c) dependence of the 1:1 and 1:2 peak areas with the order state.

the A_{1g} peak fitting procedure for the disordered, 1:1 and 1:2 ordered samples. A stronger peak can be noticed at 818 cm^{-1} with a weak shoulder at 750 cm^{-1} in the 1:2 sample spectrum. Otherwise, such a shoulder becomes more intense and shifts to higher wavenumber (at 765 cm^{-1}) for the 1:1 sample. For the disordered one, the band at 773 cm^{-1} behaves like a shoulder again. Since we have checked the long range order in the 1:1 and 1:2 ceramic samples, it can be further concluded that the A_{1g} modes at ~ 760 and 820 cm^{-1} are fingerprints of the 1:1 and 1:2 cation ordering in the $\text{Ba}_3\text{CaNb}_2\text{O}_9$ system, respectively. Fig. 2(c) displays the dependence of the perceptual area of 1:1 and 1:2 peaks on the order state. In this sense, the 1:2 ceramic should contain large 1:2 ordered domains and 1:1 domain boundary, as recently demonstrated by Ma et al. for the $\text{Ba}_3(\text{Co,Zn,Mg})\text{Nb}_2\text{O}_9$ perovskites [44]. On the contrary, the existence of large 1:1 ordered domain should better describe the Raman spectrum of 1:1 ceramic, with some regions containing short range 1:2 order, since we have detected a mode at 827 cm^{-1} . Next, the impedance spectroscopy is applied to probe the role of the B-site cation ordering in the *ac* conductivity and permittivity of the $\text{Ba}_3\text{CaNb}_2\text{O}_9$ -based perovskite ceramics. Here, we are interested in exploring the effect of order state in the electrical properties of BCNO dense ceramics, and particularly the contributions ascribed to the grains [or bulk].

3.2. Electrical conductivity and dielectric properties

For a comparative analysis, Fig. 3 shows (a) the thermal spectra of the permittivity, derived from the 10 kHz, 100 kHz and 1 MHz capacitance data, and (b) the Nyquist plot [or Cole-Cole: $-\text{Im}(\rho)$ vs. $\text{Re}(\rho)$] at $\sim 723\text{ K}$ for BCNO ceramics. The permittivity values are found to be different for the 1:1 and 1:2 ordered ceramics, and decreased with increasing temperature. It should be noticed that only one well-resolved semicircle for each sample appeared in the Nyquist plot of Fig. 3(b). Fig. 3(c) and (d) illustrate the resistivity spectra of the 1:1 and 1:2 ceramics at selected temperatures, respectively. There is no evidence of a second contribution ascribed to the grain boundary and/or electrode polarization. Such effects are usually detected as spikes in low frequency part of the Nyquist plot [45]. In order to describe the complex resistivity of our samples, we used a phenomenological model based on a parallel combination of a resistor (R_g), constant phase element (CPE), and capacitor (C_g), see in Fig. 4. Here, the R_s element takes into account the resistance coming from the measuring system. Hernández, Masó, and West have proposed this circuit model to improve the fitting procedure of the conductivity spectra of solid

electrolytes and electroceramics [ionic and electronic conductors] [46]. In practice, such a model introduces a limiting high frequency value (ϵ_g) in the real permittivity spectra. From Fig. 3, there is a good agreement between experimental data and simulated curves.

Table 3 summarizes a comparison among three circuit models, namely: $R_g||C_g$, $R_g||CPE$, and $R_g||CPE||C_g$. For parallel combination of a resistor and capacitor ($R_g||C_g$), a non-dispersive behavior is expected, since $\text{Re}(\sigma) = \sigma_g$ and $\text{Re}(\epsilon) = \epsilon_g$ [23]. Otherwise, the electrical response of real systems is better described by considering their dispersive features, and particularly $\text{Re}(\sigma) \sim \omega^\alpha$ and $\text{Re}(\epsilon) \sim \omega^{\alpha-1}$ [47]. In both models containing CPE, the real conductivity exhibits the same dependency. Otherwise, the real permittivity provides a limiting value (ϵ_g) at high frequencies only for the $R_g||CPE||C_g$ model. Owing to its accuracy we have employed this model to obtain valuable information on the electrical response of the ceramic samples addressed in this work. It is worth mentioning that the CPE introduces the dispersion behavior to take into account the Jonscher's Universal Dielectric Response (UDR) [48]. At each temperature, the real and imaginary parts of the complex resistivity were fitted by the $R_g||CPE||C_g$ model, as depicted in Fig. 5(a) and (c) for the 1:1 and 1:2 ceramic samples, respectively. Regarding the CPE, two parameters should be adjusted, and particularly its pseudo-capacitance Q and the dimensionless factor α ($0 < \alpha < 1$) [49]. The CPE impedance is expressed as follows:

$$Z_{CPE} = \frac{1}{Q(j\omega)^\alpha}. \quad (3)$$

The peak in the imaginary part of resistivity indicates a relaxation frequency associated to a conductivity relaxation time τ_σ , in which $\omega_m\tau_\sigma = 1$. Such a process can also be seen in the imaginary part of electric modulus [$M(\omega)$] of Fig. 5(b) and (d). Both peaks are found to be almost symmetrical in the frequency range from 1 Hz to 10^4 Hz. Furthermore, the relaxation frequencies are temperature dependent, and define a thermally-activated process. From Fig. 6, such an effect can be more clearly observed through the contour map of the imaginary part of electric modulus as a function of temperature. Indeed, the conductivity relaxation frequency ($f_m = \omega_m/2\pi$) increases with increasing temperature for both BCNO ceramics. Fig. 7(a) and (c) represent the dispersion behavior ($\sim \omega^\alpha$) of the real conductivity spectra at selected temperatures. As mentioned earlier, each spectrum contains a low frequency plateau ascribed to the *dc* conductivity σ_g ($= \lambda/R_g$). These values are found to be different for the 1:1 and 1:2 ceramic samples. Such quantities are also sensitive to changes in temperature, being defined as a thermally-activated process [50]. In order to analyze

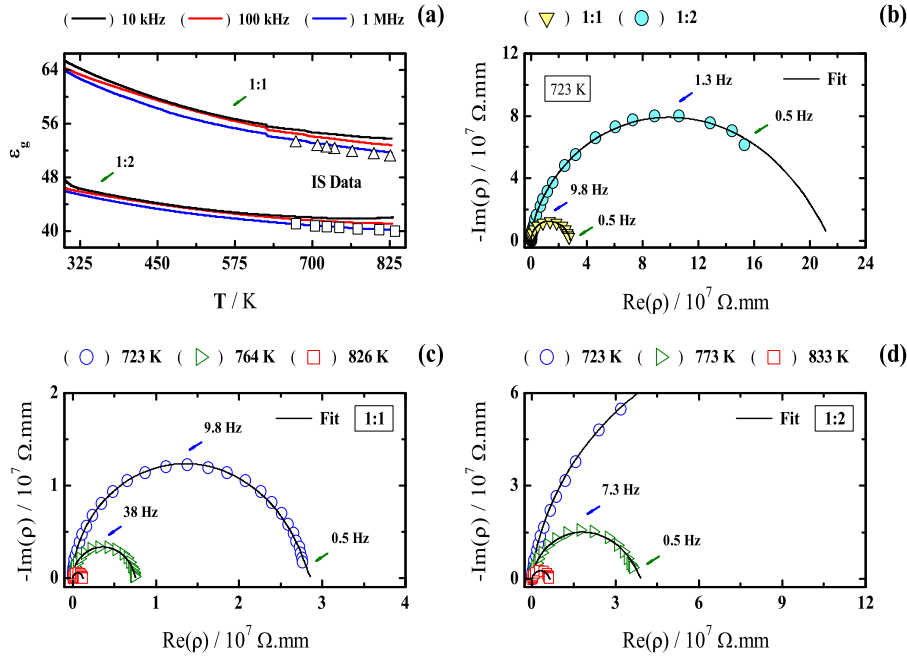


Fig. 3. (a) Thermal spectra of the dielectric permittivity, derived from the 10 kHz, 100 kHz and 1 MHz capacitance data; (b) the Nyquist plot $[-\text{Im}(\rho)$ vs. $\text{Re}(\rho)]$ at ~ 723 K for the 1:1 and 1:2 ordered BCNO ceramics. The resistivity spectra of the 1:1 (c) and 1:2 (d) ordered ceramics at selected temperatures. There is no evidence of a second contribution coming from the grain boundary and/or electrode polarization.

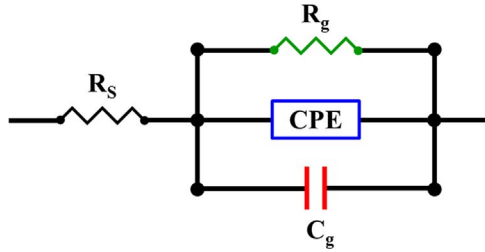


Fig. 4. A phenomenological model based on a parallel combination of resistor (R_g), constant phase element (CPE), and capacitor (C_g). The R_s element denotes the resistance coming from the measuring system.

the temperature dependence of the dc conductivity and relaxation frequency (f_m), we have plotted in Fig. 7(b) and (d) the reciprocal temperature dependence of those quantities for the 1:1 and 1:2 ceramics, respectively. In both cases, the general trend of the curves suggested an Arrhenius-like behavior, as follows:

$$\sigma_g T = A_\sigma \exp\left(-\frac{E_\sigma}{kT}\right), \quad (4)$$

$$f_m T = B_f \exp\left(-\frac{E_f}{kT}\right). \quad (5)$$

From these equations, one can find the macroscopic activation energies: ~ 1.6 eV [1:1] and 1.7 eV [1:2]. It should be noticed that the activation energies derived from dc conductivity and relaxation fre-

quency exhibited almost the same value [$E_\sigma \approx E_f$], denoting an ionic-hopping mechanism [here oxygen vacancies: $V_{O^{2-}}$] to the electrical conduction in the 1:1 and 1:2 ceramics [51]. Indeed, the magnitude of the activation energy determined here agrees well with those reported for ionic conductor ceramics [52].

Concerning the real part of dielectric permittivity, it was detected a low frequency dispersion ($\sim \omega^{\alpha-1}$) followed by a plateau at high frequencies associated with the limiting value $\epsilon_g (= \lambda C_g)$. This value is temperature dependent as we have demonstrated in Fig. 3(a). In the temperature range between ~ 660 and 840 K, the temperature coefficient of permittivity [τ_ϵ in units of ppm K^{-1}] was calculated, in accordance with the next equation:

$$\tau_\epsilon = \frac{1}{\epsilon_{g,i}} \frac{\Delta \epsilon_g}{\Delta T}, \quad (6)$$

so that $\epsilon_{g,i}$ is the high frequency permittivity at around 660 K. From Table 1, one should note different values for the temperature coefficient τ_ϵ depending on the long range order. Besides, the negative value for τ_ϵ denotes its decrease with increasing temperature. We should highlight the occurrence of a good agreement between the permittivity data at 100 kHz or 1 MHz and permittivity ϵ_g values obtained by fitting complex resistivity spectra to the $R_g || \text{CPE} || C_g$ circuit model.

From Table 1, it is reasonable to postulate that the difference in both dc conductivity and permittivity stems from the ordering type of the crystal structure. In light of the Brick-Layer model, extrinsic properties such as grain size and grain boundary thickness are only decisive to modulate the electrical response coming from the grain

Table 3

Complex impedance, real part of electrical conductivity, real part of dielectric permittivity, and conductivity relaxation time for the parallel circuit models addressed in this work.

Circuit model	$Z(\omega)$	$\text{Re}(\sigma)$	$\text{Re}(\epsilon)$	τ_σ
$R_g C_g$	$\frac{R_g}{1 + j\omega R_g C_g}$	σ_g	ϵ_g	$R_g C_g$
$R_g \text{CPE}$	$\frac{R_g}{1 + (j\omega)^\alpha R_g Q}$	$\sigma_g + \lambda Q \cos\left(\frac{\alpha\pi}{2}\right) \omega^\alpha$	$\lambda Q \sin\left(\frac{\alpha\pi}{2}\right) \omega^{\alpha-1}$	$(R_g Q)^{\frac{1}{\alpha}}$
$R_g \text{CPE} C_g$	$\frac{R_g}{1 + j\omega R_g C_g + (j\omega)^\alpha R_g Q}$	$\sigma_g + \lambda Q \cos\left(\frac{\alpha\pi}{2}\right) \omega^\alpha$	$\epsilon_g + \lambda Q \sin\left(\frac{\alpha\pi}{2}\right) \omega^{\alpha-1}$	$\approx R_g C_g$

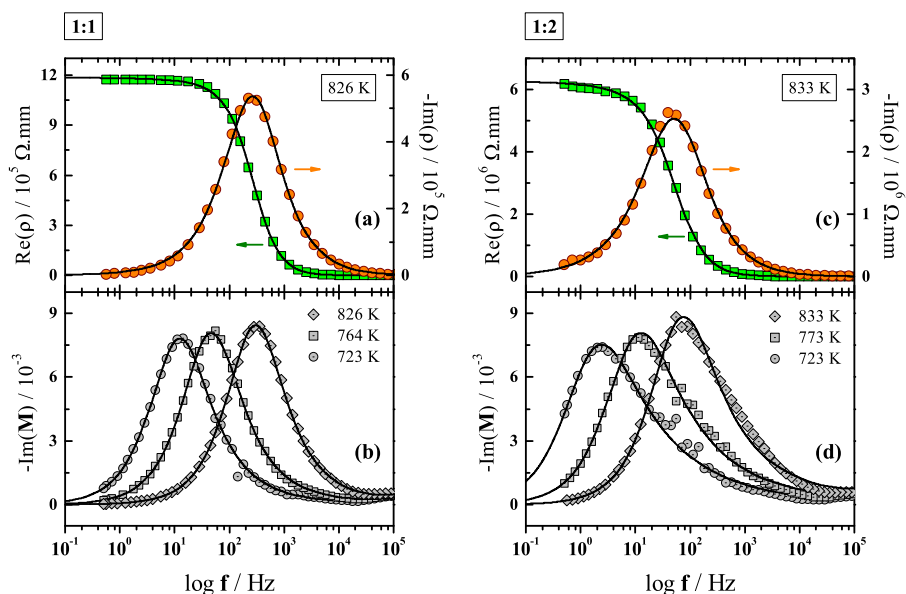


Fig. 5. The real and imaginary parts of the complex resistivity of the 1:1 (a) and 1:2 (c) ordered ceramics. The imaginary parts of the electric modulus spectra of the 1:1 (b) and 1:2 (d) ceramics. There is a good agreement between experimental data and simulated curves.

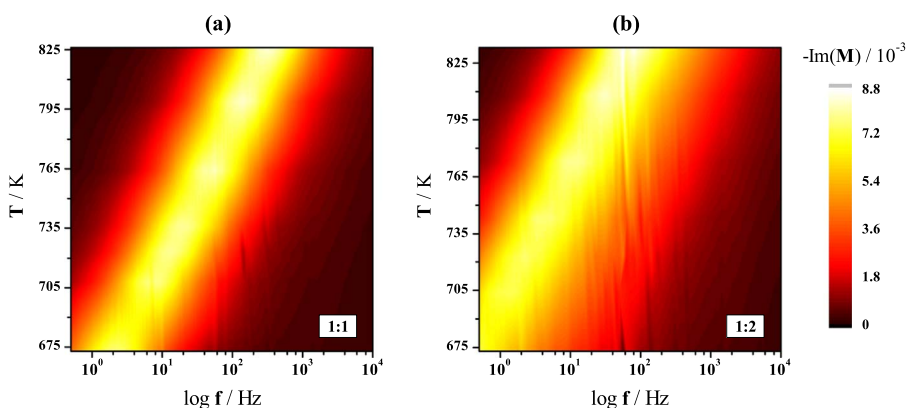


Fig. 6. The contour maps of the imaginary part of electric modulus as a function of temperature for the 1:1 (a) and 1:2 (b) ordered BCNO ceramics. The relaxation frequencies are temperature dependent, and defining a thermally-activated process.

boundaries [53]. In this way, intrinsic factors should better describe the electrical properties of the grains, including the cation ordering. For the $A_3B'B''_2O_9$ -like compounds, the 1:1 order yields a disorder at 4a site with a random distribution: ($\frac{2}{3}Ca + \frac{1}{3}Nb$). In a qualitative view, this disorder may lead to an anharmonicity of the crystal lattice, and then increasing the dielectric loss ($\tan \delta$). The electrical conductivity is sensitive to the dielectric loss changes, as predicted by the following identity:

$$Re(\sigma) = \omega(\tan \delta)Re(\epsilon). \tag{7}$$

The earlier assumption is based on the results reported in the literature concerning the dependence of dielectric loss on disorder in $A_3B'B''_2O_9$ perovskites. In general, an increased dielectric loss is expected for systems containing a local disorder at B-site. Here, our results have illustrated that the disorder effects modify the conductivity relaxation process in the grains (or bulk) of the $Ba_3CaNb_2O_9$ -based ceramics.

In the literature, BCNO systems have been investigated for possible applications as proton conductor for solid oxide fuel cells [7,15]. As we have demonstrated, the 1:2 ordered $Ba_3CaNb_2O_9$ depicts an insulator behavior at temperatures below ~ 673 K [$\sigma_g < 10^{-10} (\Omega \text{ mm})^{-1}$]. Concerning the 1:1 ordered BCNO, its dc conductivity is always higher than that of 1:2 ceramic. To further improve the conductivity,

nonstoichiometric must be taken into account as reported for the $Ba_3Ca_{1+x}Nb_{2-x}O_{9-\delta}$ system. In this material, two processes take place with the substitution of Ca^{2+} for Nb^{5+} : oxygen vacancy generation and gradual transition from 1:2 trigonal to 1:1 cubic [16,54]. From the defect chemistry point of view, the formation of oxygen vacancies is designated by the next reaction [in Kröger-Vink notation]:



Based on atomistic simulations, Ruiz-Trejo et al. have concluded that the oxygen migration along NbO_6 octahedra is most preferred in comparison with CaO_6 octahedra, since the migration energies [~ 1 eV] for oxygen jumps along the edges of NbO_6 octahedra are less than those energies [~ 2 eV] for jumps along the edges of CaO_6 units [55].

Interestingly, the reported values between 0.70 and 0.92 eV suggest that the proton migration along NbO_6 occurs in the $Ba_3Ca_{1+x}Nb_{2-x}O_{9-\delta}$ ceramics [56]. In this system, a percolation path of NbO_6 octahedra accounts for the increase in the proton conductivity until $x = 0.18$. For $x > 0.18$, an increased activation energy is observed, and then a decrease in the dc conductivity despite the high concentration of oxygen vacancies [14,54]. From our results above, we can conclude that the 1:1 ordering enhances the dc conductivity of stoichiometry BCNO system. Based on the macroscopic activation energies between

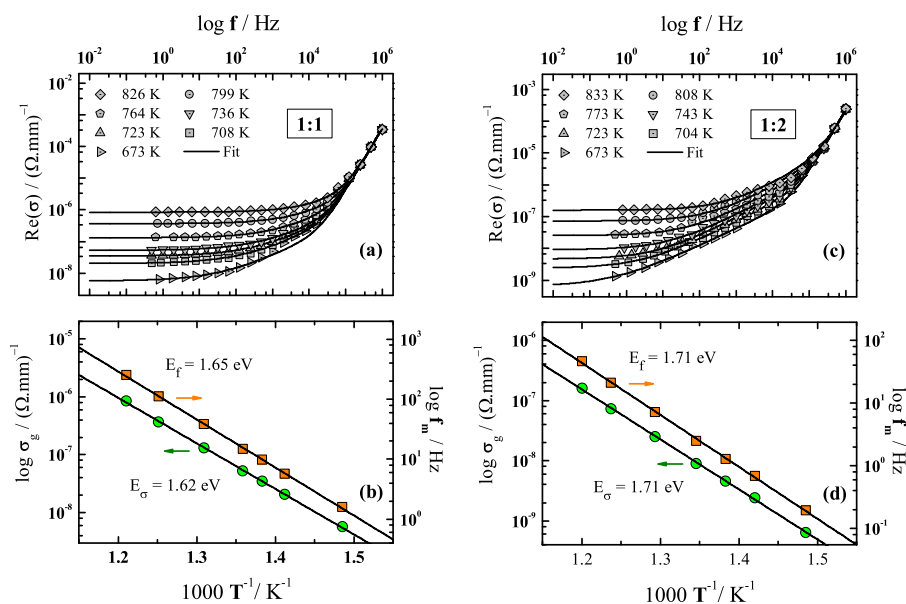


Fig. 7. The dispersion behavior ($\sim \omega^{-2}$) of the real conductivity spectra at selected temperatures of the 1:1 (a) and 1:2 (c) ordered BCNO ceramics. The reciprocal temperature dependences of both dc conductivity (σ_{dc}) and relaxation frequency (f_m) of the 1:1 (b) and 1:2 (d) ordered BCNO ceramics.

1.62 [1:1] and 1.71 eV [1:2], a more complex oxygen migration along both CaO_6 and NbO_6 units should take place in the 1:1 and 1:2 ordered BCNO ceramics investigated in the present work.

4. Conclusions

In short, we have investigated the 1:1 and 1:2 ordered $\text{Ba}_3\text{CaNb}_2\text{O}_9$ -based perovskite ceramics prepared by conventional solid state method. Our main goal in this paper was to probe the role of B-site ordering at long range on the electrical properties of stoichiometric $\text{Ba}_3\text{CaNb}_2\text{O}_9$ ceramics. The synthesis conditions were adjusted for obtaining 1:1 and 1:2 ordered BCNO. The ordered structures could be detected by the occurrence of superlattice X-ray reflections at lower 2θ angles, being an evidence for the long range order. A combination of Raman scattering and factor-group analysis was promising to detect the fingerprints of the 1:1 and 1:2 ordering through the A_{1g} modes at ~ 760 and 820 cm^{-1} . We have used a circuit model based on a parallel combination of a resistor, constant phase element, and a capacitor to describe the complex resistivity spectra of our ceramics. The conductivity relaxation coming from the grain is ascribed to the oxygen vacancies. From our results here, we have argued that the 1:1 order enhances the dc conductivity compared to the 1:2 ordered BCNO.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ceramint.2017.07.133.

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