Synthesis and structural ordering of nano-sized Ba$_3$B$'$Nb$_2$O$_9$ (B$'$ = Ca and Zn) powders

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Abstract

In this work we investigated the phase formation and structural ordering of Ba$_3$B$'$Nb$_2$O$_9$ (B$'$ = Ca and Zn) perovskite powders obtained by a modified polymeric precursor route using X-ray powder diffraction and Raman spectroscopy. We obtained single phase complex perovskites at 900 °C. Williamson-Hall analysis and scanning electron microscopy showed that the powders have crystallites and particles of nanometric size.

Keywords: Soft chemical method, Nanopowders, Raman spectroscopy, Structural ordering, Scanning electron microscopy

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1. Introduction

Ba$_3$B$'$B$''$$_2$O$_9$-type perovskites (B$'$ = Mg, Ca, Zn, Ni, Co, or Cd; B$''$ = Nb and Ta) are materials widely employed as resonators and filters for wireless communication technologies due mainly to their high permittivities and low dielectric losses in the spectral range of micro- and millimeter-waves [1-11]. Some of these materials are also applied as non-lead based ferroelectric/relaxor ceramics [12-14], high temperature

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proton conductors for fuel cells [15, 16], and photocatalysts which split water into H\(_2\) and O\(_2\) under ultraviolet light irradiation [17, 18].

These oxides belong to the family of complex perovskites, being classified into disordered and ordered, depending on the degree of ordering of B’ and B’’ ions. The disordered structure adopts a cubic unit cell with space group \(Pm\bar{3}m\) (no. 221), in which B’ and B’’ ions are randomly distributed. Otherwise, the ordered structure has a trigonal unit cell that belongs to the space group \(P\bar{3}m1\) (no. 164) induced by distortion along the \(\langle 111 \rangle\) direction of the cubic cell [19, 20].

In recent years, several works demonstrated that the structural ordering drives the physical and chemical properties of Ba\(_3\)B’B’’\(_2\)O\(_9\)-type perovskites. For example, the features of optical polar phonons and dipole interactions carry on the high permittivity of ordered Ba\(_3\)ZnNb\(_2\)O\(_9\), being very sensitive to the local disorder [21, 22]. Meanwhile, the protonic conductors based on the non stoichiometric series Ba\(_3\)Ca\(_{1-x}\)Nb\(_{2-x}\)O\(_{9-\delta}\) proved that their reductions are strongly influenced by calcium excess, and consequently by the disorder [15]. Ordered ceramics are usually prepared by high temperature solid state reaction of the starting oxides, being required long steps of heat treatment. Therefore, there is a need for new routes that would enable synthesis of both ordered and disordered materials at relatively low temperatures, mainly of applied materials as devices that require low co-firing temperatures.

Raman spectroscopy is a powerful tool to probe the ordering features in complex perovskites based on their phonon properties, as described in Refs. [23, 24, 25, 26, 27]. For example, the crystal structures and phonons of \((\text{Ba}_{1-x}\text{Sr}_x)(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\) solid solutions were studied using this technique together X-ray powder diffraction, probing a phase transition for samples with strontium excess [28]. Also, the evolution of the structural ordering in Ba\(_3\)CaNb\(_2\)O\(_9\) ceramics were well probed by Raman spectroscopy [29]. Usually, the vibrational spectra of complex perovskites are predicted in agreement with group-theoretical formalism, where there is a very close correlation between spectroscopic and ordering features [30, 31, 32, 33].

This work investigates the structural ordering of Ba\(_3\)CaNb\(_2\)O\(_9\) (BCN) and Ba\(_3\)ZnNb\(_2\)O\(_9\) (BZN) complex perovskites using powders prepared by a modified polymeric precursor route. We probed the structural features using the X-ray powder diffraction associated to the Rietveld refinement.
analysis, scanning electron microscopy, and Raman spectroscopy. Our main aims were to evaluate the single phase formation and structural ordering induced by the calcining process.

2. Material and methods

2.1. Chemicals and materials

The compounds barium nitrate (Ba(NO\(_3\))\(_2\), Sigma-Aldrich Co.), calcium citrate tetrahydrate (Ca\(_3\)(C\(_6\)H\(_5\)O\(_7\))\(_2\)-4H\(_2\)O, Ecibra), zinc nitrate (Zn(NO\(_3\))\(_2\), Sigma-Aldrich Co.), ammonium complex of niobium (NH\(_4\)H\(_2\)[NbO(C\(_2\)O\(_4\))]\(_3\)-3H\(_2\)O, CBMM), ethylene glycol (C\(_2\)H\(_6\)O\(_2\), Merck), and citric acid (C\(_6\)H\(_8\)O\(_7\)-H\(_2\)O, Proquímico) were used as starting materials to obtain polymeric precursors. All the reagents had pa grade and they were used as acquired. Distilled water was used throughout the experiments and the heat treatments were carried out in a conventional furnace.

2.2. Preparation of powders

The samples were prepared using a modified polymeric precursor (MPP) route based on the Pechini method [34]. The precursors based on barium and zinc were obtained in accordance with the following steps. First, the aqueous solutions of nitrate and citric acid were mixed in a molar ratio of 1:3 metal-citric acid, and kept under stirring between 60 and 70 °C. Then, ethylene glycol was added to metal-citric acid aqueous solution in a mass ratio of 1:1 in relation to citric acid. The procedures used to prepare the calcium polymeric precursors were similar to that employed for the barium and zinc precursors. To obtain niobium polymeric precursor, niobium hydroxide (Nb(OH)\(_5\)) was precipitated by stirring an aqueous solution of ammonium complex of niobium until pH ≈ 9 in a thermal bath at 0 °C. Niobium hydroxide was separated from oxalate ions using vacuum filtering and then it was washed with water at 40 °C. Thus, citric acid and ethylene glycol were added to the niobium hydroxide solution.

In the mixing process of the polymeric precursors, the precursors were kept at the same pH value to avoid precipitation. To determine the amount of each precursor required to obtain the correct chemistry stoichiometry, gravimetric analysis at 900 °C for 1h were employed. After, the precursors of barium, calcium (zinc), and niobium were mixed to produce the polymeric precursor of BCN (BZN). After, these precursors were heated between 80
and 90 °C to form a polyester, which had high viscosity and glassy aspect. The polyesters were treated thermally at 400 °C for 2 h to obtain black porous powders. These powders were grounded using an agate mortar. Finally, the grounded powders were calcined at 500, 700, 900, 1100, and 1300 °C for 2h in covered alumina crucibles to obtain BCN and BZN samples.

2.3. Characterization of powders

The crystalline structure of BCN and BZN powders were characterized by X-ray powder diffraction (XRPD) using a Brucker D8 Advance with CuKα radiation (λ = 0.15406 nm) in the 2θ range between 10 and 100° with a step size of 0.02° and a total exposure time of 10 h. The XRPD patterns were compared with data from Inorganic Crystal Structure Database (ICSD, FIZ Karlsruhe and NIST). The powder morphology and particle size were observed and estimated using a scanning electron microscopy (SEM—Jeol 6360LV) operated at 20 kV of an accelerating voltage. The Raman spectroscopy measurements were recorded in the wavenumber range between 120 and 1000 cm\(^{-1}\) using an iHR550 Horiba scientific spectrometer coupled to an Olympus microscope model BX-41. A He-Ne laser (632.8 nm, 10 mW) was used to excite the Raman signal of the samples. The backscattering geometry was employed to acquire the scattered light, which were collected in an air-cooled Synapse CCD detector. The spectral resolution was kept lower than 2 cm\(^{-1}\) using an 1800 grooves/mm grating in the spectrometer. All measurements were performed at room temperature.

2.4. Data analysis

The DBWS-9807 free software was employed to refine the BCN and BZN structures. The Rietveld refinement method was used to calculate the structural parameters using the Pseudo-Voigt function in the refinement for profile fitting [35, 36, 37, 38]. The crystallite size (\(D\)) and microstrain (\(\epsilon\)) were calculated using the Williamson-Hall (HW) analysis [39], in which both parameters are deconvoluted in the full width at half maximum (FWHM, \(\beta\)) of the diffraction peak according to the following equation

\[
\frac{\beta \cos \theta}{\lambda} = \frac{k}{D} + \frac{4\epsilon}{\lambda} \sin \theta,
\]

where \(\lambda\) is the wavelength of incident radiation, \(k\) is a dimensionless shape factor with typical value of about 0.9, and \(\beta\) is corrected for the instrumental
broadening, as follows

\[ \beta = \sqrt{\beta_{\text{expt}}^2 - \beta_{\text{inst}}^2}. \]  

In this method, \( \beta_{\text{expt}} \) is the measured broadening and \( \beta_{\text{inst}} \) is the instrumental broadening using the Cagglioti parameters \((U,V,W)\) [40]. Here, \( \beta_{\text{inst}} \) was obtained from a plate of sintered corundum \((\text{Al}_2\text{O}_3, \text{NIST SRM 1976})\). Details on the HW analysis are given elsewhere [41, 42].

The deconvolutions of the Raman spectra were performed using Lorentzian peak functions to determine the wavenumber position \((\omega_0, \text{cm}^{-1})\) and the full width at half maximum (FWHM, cm\(^{-1}\)) of each peak [43]. All spectra were divided by the Bose-Einstein thermal factor [44].

3. Results and discussion

In our investigation we studied the phase formation, structure, ordering and morphology of the BCN and BZN powder calcined at different temperatures. In next sections we discuss each one of these samples’ characteristics.

3.1. Formation and structural features

The composition and phase purities of the BCN and BZN powders calcined for 2 h at different temperatures were investigated by XRPD. The XRPD patterns obtained are shown in Fig. [1]. As can be observed, for both BCN and BZN powders, are indexed by the trigonal structure with space group \( \text{P} \bar{3} \text{m} \) (no. 164, \( D_{3d}^3 \)), in agreement with ICSD no. 162758 [45, 46] and ICSD no. 157044 [47, 48], respectively. The refined parameters for BCN and BZN powders calcined at 1300 °C for 2 h are listed in Table [1].

Diffraction peaks corresponding to the secondary phase of barium niobate phase \( \text{BaNb}_2\text{O}_6 \) were clearly observed for powders calcined at 500 and 700 °C. These peaks are marked with diamond symbols in Fig. [1]. It is outstanding that the single phase was already obtained at 900 °C. This shows the marked availability of our method to obtain good ceramics at low temperatures, mainly because the temperature is lower than 1000 °C, which is wanted to produce low temperature co-fired ceramic (LTCC) devices. Also, it is important to point out that it is hard to prepare materials with complex structures like these perovskites, mainly when MPP is used as synthesis route [49].

MPP usually provides low size crystallites. Thus it is interesting to determine our samples’ size and the microstrain, which measures the defor-
mation in the crystallites due to the small size because of surface energies. The crystallite size and microstrain values of the BCN and BZN powders calcined for 2 h at 1300 °C were investigated by WH analyses, which are shown in Fig. [2]. The low fluctuations of the straight lines indicate low dispersion in crystallite size $D$ and microstrain values $\epsilon$. For BCN powders, $D$ obtained was 65.8 nm and $\epsilon$ was about 0.00123, while $D$ is 67.5 nm and $\epsilon$ was about 0.00126 for BZN powders, showing that both, BCN and BZN powders calcined at 1300 °C for 2 h, have crystallites of nanometric size.

We also probed the microstrain values using the program STRAIN (available in Bilbao Crystallographic Server). In this program, it is provided two initial unit cells: the undeformed and deformed cells. With basis on these two cells it calculates the linear strain tensor (LST) and its corresponding eigenvalues based on the expansion or contraction of the undeformed structure with relation to the deformed structure [50, 51]. Here, the undeformed structures were taken from Refs. [46, 47] for crystallites with micrometric size, which we considered relaxed. Table 1 summarizes some structural parameters of our undeformed structures and results obtained using the STRAIN program. The positive signal of eigenvalue $\epsilon_a$ indicates a lattice expansion in $ab$-plane, while negative signal of $\epsilon_c$ suggests a lattice contraction in $c$-axis of the trigonal unit cell, see Table 2. By comparison with the microstrain values, the eigenvalues of LST show that the effect of lattice strain in BCN and BZN crystallites is larger along $ab$-plane, showing that the partially ordered trigonal structure deforms mainly in $a$- and $b$-axes.

3.2. Ordering features

From XRPD patterns it can be estimated the degree of ordering at long-range in materials [52]. If the cations $B^\prime 2^+$ and $Nb^5+$ are randomly distributed, then the structure is fully disordered. In this case, the pattern should be indexed by the cubic structure that belongs to the space group $Pm\bar{3}m$ (no. 221, $O^{h}_{1}$). Otherwise, if the cations $B^\prime 2^+$ and $Nb^5+$ are alternately distributed in the form ($\cdots B^\prime$−$Nb$−$Nb$−$B^\prime$−$Nb$−$Nb$−$\cdots$) in (111) direction of the cubic cell, then the structure is fully ordered and this distribution produces characteristic reflections of the trigonal lattice that belongs to the space group $Pm\bar{3}1$ (no. 164, $D^{12}_{3d}$). [20]. However, it is important to note that complex perovskites may have different values of degree of ordering, where the lattice assumes a partially ordered trigonal structure, in which $B^\prime$ and Nb ions can exchange their Wyckoff positions, as described
in Refs. [24, 29, 53, 54]. Nevertheless, the indices of planes in the XRPD pattern can still be indexed by the trigonal structure as we have indexed in Fig. 1 and showed in previous section. Hence, we assume that BCN and BZN structures have a partial ordering. In addition, our $R_{wp}$ values are similar for refinements performed using other partially ordered structures, see Refs. [46, 55].

As discussed previously, Raman spectroscopy is a powerful tool to probe the ordering features in complex perovskites once their phonon properties are based on the site occupation. Fig. 3 shows the Raman spectra obtained for BCN and BZN powders calcined at different temperatures for 2 h. It is clear that there are significant changes in the Raman spectra of these powders when the calcining temperature is increased. We also note that the Raman bands near 800 cm$^{-1}$ become narrower and more intense. This behavior is associated to the structural ordering, as we discuss in more details next.

According to the group-theoretical prediction, the fully ordered trigonal structure with 15 atoms in its primitive unit cell exhibits 30 phonons, whose distributions are as follows [46, 47]: one Ba ion occupies 1$a$ site and two others are at 2$d$ sites, giving $\Gamma_{Ba} = A_{1g} \oplus E_g \oplus 2A_{2u} \oplus 2E_u$; the $B'$ ion (in our case, $B' = Ca, Zn$) located at 1$b$ site, for which $\Gamma_{B'} = A_{2u} \oplus E_u$; two Nb ions are at 2$d$ sites, such that $\Gamma_{Nb} = A_{1g} \oplus E_g \oplus A_{2u} \oplus E_u$; six O ions are at 6$i$ sites and three others are at 3$e$ sites, giving $\Gamma_{O} = 2A_{1g} \oplus A_{2g} \oplus 3E_g \oplus 2A_{1u} \oplus 4A_{2u} \oplus 6E_u$. $A$ modes are non degenerate and $E$ modes are doubly degenerate, the subscripts $g$ and $u$ indicate the parity property under inversion operation in centrosymmetric crystals, and the symmetry and number of phonons are based on the irreducible representation of the group factor $\bar{3}m (D_{3d})$ [56, 57]. After subtracting the silent ($\Gamma_{Silent} = 2A_{1u} \oplus A_{2g}$) and acoustic ($\Gamma_{Acoustic} = A_{2u} \oplus E_u$) phonons, we expect 9 zone-center Raman-active phonons and 16 zone-center infrared phonons for both BCN and BZN lattices at room temperature, in agreement with the following distributions:

$$\Gamma_{Raman} = 4A_{1g} \oplus 5E_g,$$

$$\Gamma_{IR} = 7A_{2u} \oplus 9E_u.$$  

Otherwise, one must observe an increase in the number of phonons for the partially ordered trigonal structure when there are exchanges in the non
equivalent positions of $B'$ and Nb ions \cite{3,5,30,31,58}. Indeed, the existence of $B'$ ions at $2d$ sites provides more 2 Raman-active and 2 IR-active phonons, while Nb ion at $1b$ site adds just 2 IR-active phonons, as summarized below

$$\Gamma_{B'|2d} = A_{1g} \oplus E_g \oplus A_{2u} \oplus E_u,$$

(5)

$$\Gamma_{Nb|1b} = A_{2u} \oplus E_u.$$

(6)

Hence, in partially ordered trigonal structure are expected 11 Raman- and 20 infrared-active phonons in the vibrational spectra. We employed this model to investigate the structural ordering process under different calcining temperatures in BCN and BZN powders.

From the deconvolution showed in Fig. 4, it was observed 12 and 14 peaks in the Raman spectra of BCN and BZN powders calcined at 1300 °C for 2 h. The measured spectra of BCN and BZN was compared with the Raman-active phonons calculated in Refs. \cite{29,59}, as summarized in Table 3. There is an excellent agreement between the measured and calculated values for the symmetric stretching mode of BCN near 821 cm$^{-1}$. Furthermore, the difference in wavenumber between the measured and calculated data is no more than 25 cm$^{-1}$ for each mode of BZN. The phonons that are directly related with the fully ordered trigonal structure are recognized in the range between 130 and 305 cm$^{-1}$ (see peak nos. 1, 3, and 4 of BCN and peak nos. 2, 4 and 5 of BZN). Also, it can be observed the extra phonons in the Raman spectra of BCN and BZN at, respectively, 615.9 and 523.7 cm$^{-1}$, which are also connected with the fully ordered structure \cite{31,59,60}. Besides, some peaks attributed to defects in our samples (DM), and baseline effect in the deconvolution process (FLB) were identified \cite{30,31}. These defect modes are usual in ceramic materials \cite{61}.

Since the modes $A_{1g}^{(3)}$ and $A_{1g}^{(4)}$ are related to breath-vibrations of oxygen octahedron, and the modes $E_{1g}^{(3)}$ and $E_{1g}^{(4)}$ are connected to twisting breath-vibrations of oxygen octahedron \cite{28,31,60}, the vibrations of oxygens at 6i sites are strongly influenced by $B'$ ions occupation at $2d$ sites in the partially ordered structure due to the different strength between Ca–O bond, Zn–O bond and Nb–O bond. This behaviour is corroborated through the occurrences of the peak nos. 9 and 11 in the BCN spectra and peak nos. 11 and 13 in the BZN spectra, in agreement with the model described in Eqs. \cite{5} and \cite{6}. Indeed, the ratios between the wavenumbers of
peak nos. 9–10 (0.92) and 11–12 (0.94) are, respectively, 4.3% and 2.1% less than the estimated value (0.96) based on the charge-mass relationship \( \frac{q_{Ca}/m_{Ca}}{q_{Nb}/m_{Nb}} \). Hence, the peak nos. 9 and 11 correspond to the Raman-active phonons of Ca ions at 2d sites, as described in Ref. [29]. However, the Zn–O bond not simply follows the charge-mass relationship. Instead, the dipole interaction should be take account to explain the correct attribution of BZN measured modes due mainly to the strong covalent bond between Zn and O which is related to the zinc 3d orbital [59, 60, 63]. In this sense, we further suggest that peak nos. 11 and 13 correspond to the Raman-active phonons of Zn ions at 2d sites. The ratios between the wavenumbers of peak nos. 11–10 (1.10) and 13–12 (1.01) show that our assumption is correct. Thus, the structural ordering process can be probed by analyzing the evolutions of these measured peaks, as depicted in Fig. 5. We observed that some peaks become stronger, and others become weaker in the wavenumber range between 650 and 950 cm\(^{-1}\), when calcining temperature is increased. The peak no. 12 intensifies with increasing calcining temperatures. On the other hand, the intensities of peak nos. 11 (BCN) and 13 (BZN) decrease with increasing calcining temperatures, and thus structural ordering. This behaviour allows us to estimate the degree of ordering at long-range using Raman spectroscopy [23, 30, 64, 65].

In this sense, we used the ratio of peak intensities designated by \( \Psi_{B'}(Nb) \) and expressed as follows

\[
\Psi_{Ca}(Nb) = \frac{I_{11}(12)}{I_{11} + I_{12}},
\]

\[
\Psi_{Zn}(Nb) = \frac{I_{13}(12)}{I_{13} + I_{12}}.
\]

If the ratio \( \Psi_{Nb} \) is equal to one, then Nb ions are located at 2d sites and B’ ion locates at 1b site. For partially ordered structure, the ratio \( \Psi_{B'} \) is non null in accordance with Eq. [5] [29]. As can be seen in Table 4, there is a progressive increase in ratio \( \Psi_{Nb} \) with increasing the calcining temperatures, showing that modes \( A_{1g}^{(4)} \) are highly sensitive to change in the structural ordering. Finally, the most ordered nano-sized BCN and BZN powders are that calcined for 2 h at 1300 °C, for which the ratios \( \Psi_{Ca} \) and \( \Psi_{Zn} \) are equal to 0.25 and 0.21, respectively. Also, we can monitor the structural ordering process by monitoring the behaviour of phonons provided from B’ ions (in our case, B’ = Ca, Zn) at 2d sites.
The wavenumber position and FWHM calculated from peak deconvolutions confirmed the role of mode $A_{1g}^{(4)}$ to probe the structural ordering process, and we present these parameters in Fig. 6. Clearly, the wavenumber position of the mode $A_{1g}^{(4)}$ increases with increasing calcining temperatures, while FWHM decreases with the temperature increase up to 1300 °C. This trend indicates a successive increase in the structural ordering because widest (narrower) peak corresponds to shorter (longer) phonon lifetime and thus more (less) interaction with phonons, in light of the following expression

$$\tau = \frac{1}{\pi c \gamma}, \quad (9)$$

where $c$ is the velocity of light, and $\tau$ is the phonon lifetime. This equation is based on the energy uncertainty relationship [66, 67, 68]. Therefore, a narrower FWHM suggests a little damping effect in the lattice vibrations, and thus a most ordered structure.

3.3. Morphological features

Fig. 7 depicts the SEM micrographs of BCN and BZN powders calcined for 2 h at 900 °C. SEM micrographs show that BCN and BZN powders treated thermally at 900 °C exhibit a large quantity of agglomerated particles. We also observe the formation of blocks and necks in Figs. 7(a) and 7(c) for BCN and BZN, respectively. The random aggregation process between small particles implied in the formation of a sphere- and ellipsoid-like morphologies, as shown in Figs. 7(b) and 7(d).

The size distributions determined from SEM micrographs depicted in Figs. 7(b) and 7(d) are shown in Fig. 8. The average particle sizes of BCN and BZN powders calcined at 900 °C for 2 h are approximately 100 nm. In addition, the deviations in the particle size distributions can be attributed to the inhomogeneous particles formation due mainly to the synthesis process, which contains a large amount of organic composition that must be obliterated to produce pure oxides. These analyses complement the results discussed from WH analysis.

4. Conclusions

A modified polymeric precursor route was used to produce $\text{Ba}_3B'\text{Nb}_2\text{O}_9$ ($B' = \text{Ca}$ and $\text{Zn}$) powders. We employed the X-ray powder diffraction and Raman spectroscopy to evaluate the crystal structure, ordering and phonon
behaviours for different calcining temperatures. It was observed that these polycrystals have a partially ordered structure, which it belongs to the trigonal space group $P\overline{3}m1$ (no. 164). Single phases were at as low temperatures as $900\, ^\circ C$ and the most ordered powders are that calcined for 2h at $1300\, ^\circ C$. The Williamson-Hall analysis revealed that powders calcined at $1300\, ^\circ C$ for 2h had nanometric size in the range of $60–70$ nm, being deformed mainly in $a$- and $b$-axes of the trigonal lattice. The SEM micrographs indicated that the average particle sizes of powders calcined at $900\, ^\circ C$ for 2 h are approximately 100 nm, with spherical and ellipsoidal morphologies, besides they showed some inhomogeneity.

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Figure captions

Fig. 1. XRPD patterns of BCN and BZN powders calcined at 700, 900, 1100, and 1300 °C for 2 h. The indices of planes are indexed in agreement with the trigonal structure that belongs to space group $P\overline{3}m1$ (no. 164). The brown diamond symbols indicate the barium niobate phase.

Fig. 2. Williamson-Hall analyses of BCN and BZN powders calcined for 2 h at 1300 °C. The dotted lines are the adjusted functions, see also Table 2.

Fig. 3. Raman spectra of the BCN and BZN powders calcined at 700, 900, 1100, and 1300 °C for 2 h, whose bands near 800 cm$^{-1}$ become more intense and narrower when the calcining temperature is increased. This fact is associated to the structural ordering process.

Fig. 4. Deconvolutions of the Raman spectra of BCN (a) and BZN (b) powders calcined for 2 h at 1300 °C, where the number on each Lorentzian peak function represents the phonons observed, see also Table 3.

Fig. 5. Deconvolutions of the Raman spectra of BCN (a) and BZN (b) powders calcined at different temperatures for 2 h only in the wavenumber range between 650 and 950 cm$^{-1}$.

Fig. 6. Wavenumber position and full width at half maximum of the mode $A_{4g}^{(4)}$ in function of the calcining temperature. The decrease of FWHM is associated to the structural ordering process when the calcining temperature is increased.

Fig. 7. SEM micrographs of BCN (a)-(b) and BZN (c)-(d) powders calcined for 2 h at 900 °C, in which the particles present morphology with spherical and ellipsoidal forms. A log-normal distribution describes the counting of crystallite sizes.

Fig. 8. The particle size distributions of BCN and BZN powders calcined for 2 h at 900 °C. Both average particle sizes are approximately 100 nm.
Figure 2:
Figure 3:
Figure 6:
Figure 8:
Table 1: Structural parameters of BCN and BZN powders refined using X-ray powder diffraction data.

| Chemical formula | Ba$_3$CaNb$_2$O$_9$ | Ba$_3$ZnNb$_2$O$_9$ |
|------------------|---------------------|---------------------|
| Space group, Z    | P3m1; 3             | P3m1; 3             |
| a, Å             | 5.9154(6)           | 5.7900(2)           |
| c, Å             | 7.2625(9)           | 7.0967(5)           |
| $\gamma$, °      | 120                 | 120                 |
| V, Å$^3$         | 220.090             | 206.040             |
| Ba$_2$ z (2d)    | 0.6760              | 0.6743              |
| O$_1$ x (6i)     | 0.2142              | 0.2114              |
| O$_1$ z (6i)     | 0.3288              | 0.3116              |
| Density, g/cm$^3$| 5.897               | 6.345               |
| D, nm            | 65.84 ± 4.27        | 67.47 ± 4.56        |
| $\epsilon \times 10^3$ | 1.2255 ± 0.0728    | 1.2552 ± 0.0726     |
| Caglioti parameters (U,V,W) | 0.282876, -0.105603, 0.064551 | 0.092537, -0.054572, 0.046780 |
| $R_p$, $R_{wp}$, $R_{exp}$, % | 7.37, 9.81, 5.90 | 8.37, 10.71, 5.85 |
Table 2: Lattice parameters of BCN and BZN cells considered as undeformed structures and employed in program STRAIN. The eigenvalues of linear strain tensor (LST) are also presented.

| Chemical formula | Lattice parameters | Eigenvalues of LST |
|------------------|--------------------|--------------------|
|                  | a, Å               | c, Å               | γ, ° | Ref. | $\epsilon_a \times 10^3$ | $\epsilon_c \times 10^3$ |
| $\text{Ba}_3\text{CaNb}_2\text{O}_9$ | 5.9037(7)          | 7.2636(3)          | 120  | [46] | 1.992                 | -0.139                |
| $\text{Ba}_3\text{ZnNb}_2\text{O}_9$ | 5.78207(6)         | 7.09731(11)        | 120  | [47] | 1.375                 | -0.079                |
Table 3: Wavenumbers of measured phonons of BCN and BZN structures with respective attribution. We have also compared the measured (expt.) and calculated (calc.) data [29, 59].

| Peak no. | \( \omega_0 \) (expt.) | \( \omega_0 \) (calc.) | Attrib. | Peak no. | \( \omega_0 \) (expt.) | \( \omega_0 \) (calc.) | Attrib. |
|----------|------------------------|------------------------|---------|----------|------------------------|------------------------|---------|
|          |                        |                        |         |          |                        |                        |         |
| Ba\(_3\)Ca\(_2\)Nb\(_2\)O\(_9\) | | | | | | |
| 1        | 136.6                  | 62.0                   | \( E_g^1 \) | 1        | 144.6                  | 100.8                  | \( A_{1g}^1 \) |
| 2        | 148.9                  | DM\(^a\)               |          | 2        | 163.9                  | 160.13                 | \( E_g^2 \) |
| 3        | 241.5                  | 241.2                  | \( A_{1g}^2 \) | 3        | 212.7                  | DM\(^a\)               |          |
| 4        | 280.0                  | 250.7                  | \( E_g^3 \) | 4        | 267.5                  | 264.7                  | \( A_{1g}^2 \) |
| 5        | 309.8                  | FLB\(^b\)              |          | 5        | 301.1                  | 276.9                  | \( E_g^3 \) |
| 6        | 353.5                  | 305.8                  | \( E_g^4 \) | 6        | 360.4                  | FLB\(^b\)              |          |
| 7        | 408.3                  | 356.8                  | \( A_{1g}^3 \) | 7        | 374.9                  | 360.9                  | \( E_g^4 \) |
| 8        | 517.4                  | DM\(^a\)               |          | 8        | 394.0                  | DM\(^a\)               |          |
| 9        | 564.6                  | \( E_g^5 \)            |          | 9        | 432.6                  | 409.5                  | \( A_{1g}^3 \) |
| 10       | 615.9                  | 658.9                  | \( E_g^5 \) | 10       | 523.7                  | 529.9                  | \( E_g^5 \) |
| 11       | 772.9                  | \( A_{1g}^4 \)         |          | 11       | 578.4                  |                        |          |
| 12       | 820.5                  | 827.7                  | \( A_{1g}^4 \) | 12       | 783.7                  | 770.9                  | \( A_{1g}^4 \) |
| 13       |                        |                        |          | 13       | 795.8                  |                        |          |
| 14       |                        |                        |          | 14       | 814.6                  | DM\(^a\)               |          |

\(^a\) DM: defect mode and \(^b\) FLB: floating base line.
Table 4: The ratio of peak intensities calculated from BCN and BZN powders calcined at 700, 900, 1100, and 1300 °C for 2h.

| Temperature, °C | Ba$_3$CaNb$_2$O$_9$ | Ba$_3$ZnNb$_2$O$_9$ | Ba$_3$CaNb$_2$O$_9$ | Ba$_3$ZnNb$_2$O$_9$ |
|----------------|--------------------|--------------------|--------------------|--------------------|
| 700            | 0.61               | 0.31               | 0.39               | 0.69               |
| 900            | 0.47               | 0.33               | 0.53               | 0.74               |
| 1100           | 0.41               | 0.26               | 0.59               | 0.78               |
| 1300           | 0.25               | 0.22               | 0.75               | 0.79               |