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Disorder-induced symmetry lowering in Ba(Y$_{1/2}$Nb$_{1/2}$)O$_3$ ceramics probed by Raman spectroscopy

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This work investigates the evolution of the crystal structure of microwave-hydrothermal synthesized Ba(Y$_{1/2}$Nb$_{1/2}$)O$_3$ powders as a function of firing temperature by Raman spectroscopy. The samples were produced at 200 °C and fired at temperatures ranging from 600 to 1600 °C. Raman spectra were obtained at room temperature for all samples and the results showed that materials fired at 1600 °C exhibited tetragonal ($I4/m$ or C_{4h}^5) structure, whereas those fired at lower temperatures exhibited the triclinic ($P\bar{1}$ or C_i^1) structure. The results were compared with those observed for ceramics obtained by conventional solid-state methods. It is believed that the lowering of the symmetry verified in materials fired below 1600 °C is a consequence of the local disorder of Y^{+3} and Nb^{+5} ions in octahedral sites. Copyright © 2008 John Wiley & Sons, Ltd.

INTRODUCTION

Mobile phones are dominating the telecommunication markets around the world. These devices are associated with base stations that connect cell to cell via antennas. Each base station contains hundreds of microwave resonators employed to carry signals and filter spurious signals and sidebands.[1] For high-selectivity applications (narrow bandwidth), ceramic materials such as Ba(RE$_{1/2}$Nb$_{1/2}$)O$_3$ (RE = rare-earth elements, In or Y) complex perovskites can be used as dielectric resonators. These compounds have been studied in the past by many research groups in attempts to understand their crystal structure as a function of chemical substitution, which is intimately related to their performance in service. Only very recently conclusive results on this subject were achieved by using X-ray diffraction (XRD) as well as Raman and Fourier-transform infrared spectroscopies.[2] In this respect, the polar optical phonons determine the high-frequency dielectric response, which in turn depends on the sample structure (intrinsic contributions) together with extrinsic contributions coming from space charges, domain walls and imperfections linked to the sample morphology.[2–5]

Thus, these ceramic materials are very sensitive to the processing conditions (powder synthesis and sintering), which affect directly the three key properties for applications as dielectric resonators: permittivity, temperature coefficient of the resonant frequency, and dielectric loss.

There is increasing interest in evaluating new methods for the synthesis of microwave materials.[6] Hydrothermal methods present the highest technological potential to prepare materials in environmentally friendly conditions, producing ultrafine, crystalline powders in a single step.[3–8] In previous works, Dias *et al.*[4,5] showed that Ba(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ complex perovskites with different long-range order parameters (critical for minimum dielectric losses) could be obtained by heating the samples at increasing temperatures, starting from the hydrothermal powders produced under mild temperatures. For these samples, the Raman spectra did not show any structural change, but exhibited an increasing degree of ordering through the narrowing of the phonon modes for increasing heating temperatures. For Ba(RE$_{1/2}$Nb$_{1/2}$)O$_3$ materials, tetragonal, orthorhombic, and monoclinic symmetries are reported in the literature, depending upon the chemistry involved. It is suggested that the difference in the crystal symmetry is due to a small tilting in the octahedra (anti-phase or in-phase), which is sometimes difficult to determine or quantify by conventional XRD procedures.[2]

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A previous work in $Ba(Y_{1/2}Nb_{1/2})O_3$ ceramics, which is a member of the $Ba(RE_{1/2}Nb_{1/2})O_3$ family, showed that the fully ordered ceramic produced by conventional solid-state route exhibits a tetragonal structure.[2] This conclusive result was possible only through the comparative analysis between XRD and Raman scattering. Although the structure of fully ordered samples is well established, no information regarding the structure of $Ba(Y_{1/2}Nb_{1/2})O_3$ ceramics from powders obtained at mild temperatures is available. Also, the heating effects on the crystal structure from lower temperatures up to the sintering temperatures frequently employed in conventional routes are unknown. In view of that, this work expands the previous one (Ref. 2) by studying $Ba(Y_{1/2}Nb_{1/2})O_3$ ceramics, henceforth BYN, synthesized through the microwave-hydrothermal method and fired at different temperatures. The goal is to investigate the structural evolution by XRD and Raman spectroscopy, besides group theory tools, and therefore to contribute to a better understanding of the crystalline structure of BYN as a function of heating temperature.

EXPERIMENTAL

$BaCl_2 \cdot 2H_2O$ (> 99.9%, Fluka-Switzerland), $YCl_3 \cdot 6H_2O$ (>99.9%, Fluka-Switzerland) and $NH_4H_2(NbO(C_2O_4)_3) \cdot 3H_2O$ (>99%, CBMM-Brazil) were used as the starting materials. The salts were dissolved separately in deionized water (18.2 MΩ cm) and mixed in stoichiometric proportions. The niobium ammonium oxalate was previously treated with a NaOH solution maintained at pH > 13 and washed. After mixing, precipitation occurred and the pH was controlled and adjusted to 13.5. Microwave-hydrothermal syntheses were performed using a Milestone MLS-1200 MEGA microwave digestion system (100 mL teflon-lined flasks, 2.45 GHz).[3] The syntheses occurred at 200 °C in 2 h, and the resulting powders were repeatedly washed with deionized water and dried at 80 °C. The materials were fired in air (conventional furnace) at temperatures ranging from 600 to 1600 °C, for 2 h.

XRD analyses were carried out in a Philips PW1710 diffractometer with graphite-monochromated Cu Kα radiation (40 kV, 30 mA, Ni filtered) in the 15–100° 2θ range (0.01° 2θ step size and 5 s/step). A scanning electron microscope (SEM-JEOL 5410) was employed to study the morphological features of the BYN powders after processing. Micro-Raman scattering spectra were collected at room temperature using a triple-monochromator Dilor XY spectrometer, equipped with a liquid-N_2-cooled charge-coupled-device detector and an Olympus microscope (100× objective). The measurements were carried out in the backscattering geometry using the 415.6, 488 or 632.8 nm lines of an argon-krypton ion or a helium−neon laser as excitation sources. The accumulation times were typically 10 collections of 20 s and the spectral resolution was better than 2 cm^{-1}. Better results were obtained for the helium−neon laser line.

RESULTS AND DISCUSSION

Crystalline, single-phase BYN perovskite powders were produced after microwave-hydrothermal processing at 200 °C (ICDD card # 24–1042). Figure 1 shows the morphological features of the microwave-hydrothermal-processed samples as obtained (Fig. 1(a)), and after firing at 600, 800, 1000, 1200 and 1400 °C (Fig. 1(b) to (f)). Large, needle-shaped (*ca* 50 μm long) and very fragile (under manipulation) materials were produced, as previously reported for the complex $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics.[3] Fig. 1 also shows that the solid-state sintering starts above 1000 °C (Fig. 1(d–f)), with the presence of solid contacts (bridges) between the needles. Figure 2 presents the results from the XRD analysis for the materials fired at different temperatures (800, 1000, 1200 and 1600 °C). As can be seen, the ceramics remain in single phase after firing without any secondary phases or impurities. All materials were indexed as cubic (ICDD 24–1042), although some faint peaks could be interpreted as indication of a lower symmetry, particularly the tetragonal phase $I4/m$.[2] The inset in Fig. 2 shows in detail the superstructure (111) peak, observed only in the sample fired at 1600 °C, which indicates that this sample presents a fully ordered B-site arrangement.[9,10]

Despite this particular (111) peak, no additional information could be obtained from the diffractograms shown in Fig. 2. Thus, it was concluded that XRD analysis was not able to distinguish any significant difference between the structures of our fired samples. Barnes *et al.*[9] studied BYN ceramics by neutron diffraction and XRD techniques and obtained 'nearly equivalent' goodness-of-fit parameters for both cubic ($Fm\bar{3}m$) and tetragonal ($I4/m$) structures. Studying similar samples by Raman spectroscopy, Dias *et al.*[2] showed that a tetragonal ($I4/m$, C_{4h}^5) structure is compatible with the observed phonon modes for samples sintered at high temperatures. For BYN materials, the tolerance factor can be determined by:

$$t = \frac{R_{Ba} + R_O}{\sqrt{2}\left[\left(\dfrac{R_Y + R_{Nb}}{2}\right) + R_O\right]} \tag{1}$$

where R_{Ba}, R_Y, R_{Nb} and R_O are the ionic radii of Ba, Y, Nb and O ions, respectively. A tolerance factor of 0.986 was calculated, which means that the NbO_6 and YO_6 octahedra are slightly tilted and Ba ions (located in the A-site) have enough space for vibrations. On the basis of previous results in $Ba(Mg_{1/3}Nb_{2/3})O_3$ ceramics,[4] it is believed that the BYN samples fired at temperatures below 1600 °C could present a more distorted (or even lower-symmetry) structure in their pseudo or nearly cubic lattices. In order to investigate that, we carried out Raman spectroscopic measurements in all BYN ceramics aiming to analyze the evolution of the phonon modes, probing potential lattice distortions and the resulting changes in crystal structures. Differently to XRD, where local disorder is observed through the average scattering
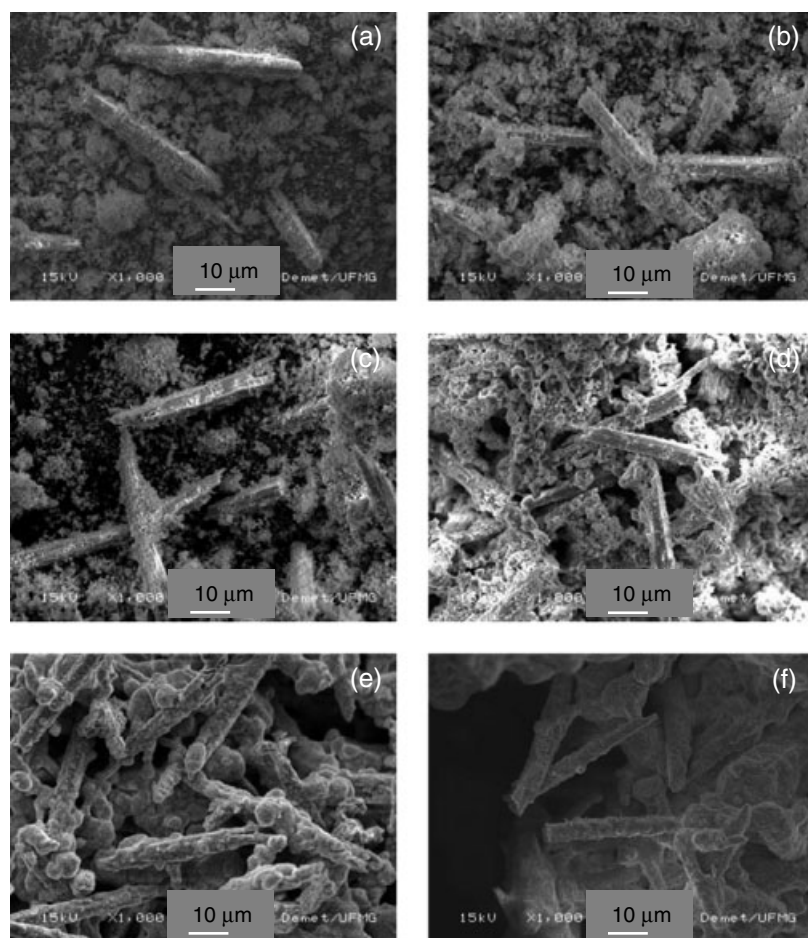
Figure 1. SEM photographs for the powders after microwave-hydrothermal processing (a) and fired at (b) 600 °C; (c) 800 °C; (d) 1000 °C; (e) 1200 °C; and (f) 1400 °C.

factors, the vibrational spectra are affected not only by the distribution of the atomic species but also by the different atomic interactions.

As mentioned above, BYN ceramics were described as belonging to the C_{4h}^5 ($I4/m$) group, with four motifs per unit cell ($Z = 4$) but only two for the primitive one ($Z_p = 2$). In this structure, Ba atoms occupy $4d$ sites (S_4 symmetry), Y and Nb ions occupy respectively $2a$ and $2b$ sites (C_{4h} symmetry), and the oxygen atoms are in $8h$ (C_s symmetry) and $4e$ (C_4 symmetry) sites. Then, using the site group method of Rousseau *et al.*[11] it is possible to obtain the following distribution of the phonon modes at the Brillouin zone center in the irreducible representations of the C_{4h} point group:

$$\Gamma = 3A_g + 5A_u + 3B_g + B_u + 3E_g + 6E_u \qquad (2)$$

Excluding the acoustic ($A_u + E_u$) and silent (B_u) modes, 18 optical vibrational modes remain, 9 being Raman active ($3A_g + 3B_g + 3E_g$) and 9 infrared active ($4A_u + 5E_u$). While the Raman-active modes are only due to vibrations of Ba and O atoms (A_g, B_g and E_g), the infrared active phonons include the vibrations of ions in the B-sites (Y^{+3} and Nb^{+5} ions for

A_u and E_u vibrational modes).[2,4,5] However, for complex perovskites with 1:1 ordering, infrared measurements fail to study crystal structures because of the proximity of transverse and longitudinal phonons, which makes difficult the identification and assignment of the modes.[2]

Micro-Raman spectroscopic investigations were carried out in samples fired in temperatures ranging from 600 to 1600 °C. Figure 3 presents the spectra for the microwave ceramics fired at (a) 800, (b) 1000, (c) 1200 and (d) 1600 °C. For the samples fired at 1600 °C (Fig. 3(d)), nine bands are clearly identified, in good agreement with conventional solid-state-reacted BYN materials presented in a previous work.[2] The fitting parameters, wavenumbers and full-width at half maxima (FWHM) are given in Table 1. We noticed that our microwave-hydrothermal BYN presents narrower Raman bands (about 30%) than the sample produced by conventional routes (Ref. 2), also displayed in Table 1 for comparison (both materials were fired at 1600 °C). This result indicates longer phonon lifetimes for the microwave-hydrothermal samples, probably due to their reduced structural defects or disorder. In view of the microwave
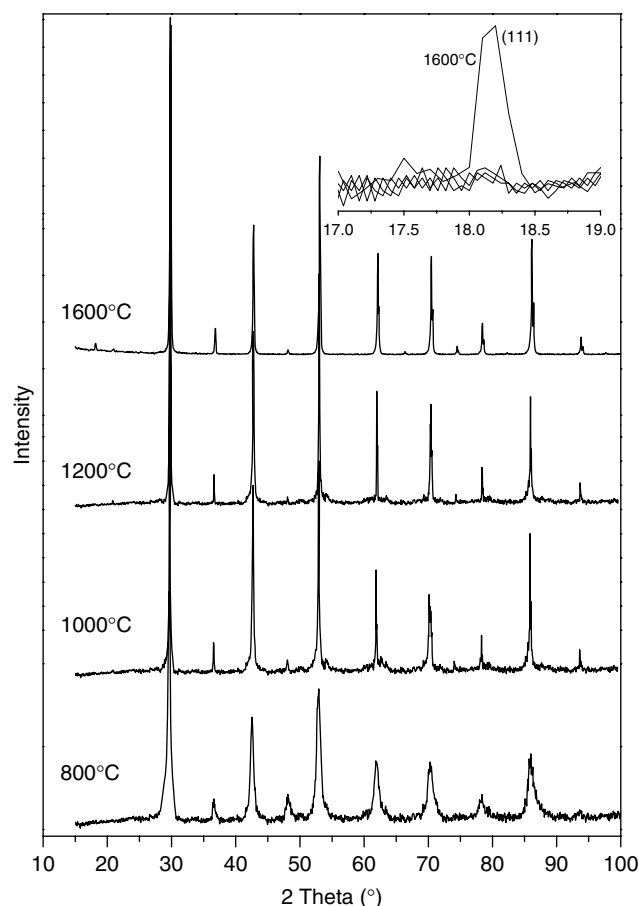
Figure 2. XRD for the samples produced by microwave-hydrothermal processing and fired at (a) 800 °C; (b) 1000 °C; (c) 1200 °C; and (d) 1600 °C.
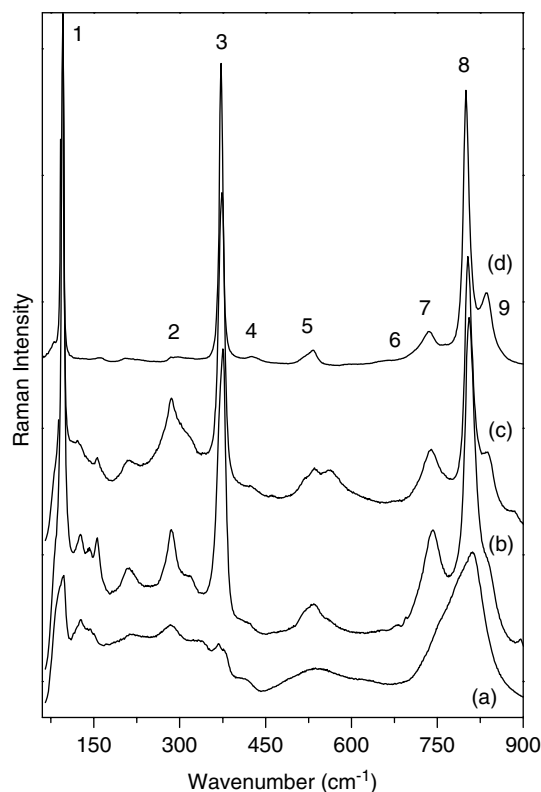

Figure 3. Raman spectra for the BYN ceramics fired at (a) 800 °C; (b) 1000 °C; (c) 1200 °C; and (d) 1600 °C. Numbers indicate the bands observed for the sample fired at 1600 °C.

applications, this is an interesting result, since narrower phonon modes would indicate larger quality factors for the hydrothermal BYN, as previously discussed by our research group in recent publications.[2,4,5,12] It was observed that BYN samples fired at lower temperatures exhibited a higher number of broader phonon modes, which could be due to lattice distortions indicating lower-symmetry structures. Thus, for samples fired at temperatures lower than 1600 °C,

Table 1. Raman fitting parameters (in cm^{-1}) for the BYN ceramics fired at 1600 and 800 °C. The numbers correspond to those shown in Figs 3 and 4

| Band | Microwave-hydrothermal (1600 °C) | | Conventional solid-state (1600 °C) (Ref. 2) | | Band | Microwave-hydrothermal (800 °C) | |
	Wavenumber	FWHM	Wavenumber	FWHM		Wavenumber	FWHM
1	95	3	102	3	1	95	13
2	299	35	305	57	2	124	26
3	372	6	380	7	3	146	43
4	426	21	434	36	4	211	87
5	534	18	537	23	5	284	76
6	716	25	716	30	6	337	49
7	734	22	743	26	7	373	31
8	800	10	809	12	8	417	27
9	837	22	843	27	9	533	107
					10	614	78
					11	771	69
					12	812	42

a careful analysis was conducted to examine the possible origins for the observed behavior.

Figure 4 shows the Raman spectrum of the BYN ceramic fired at 800 °C fitted by using Lorentzian lines. Broad bands can be visualized, in a larger number than expected for BYN materials with tetragonal structure (in fact, 12 bands were identified in Fig. 4). The fitting parameters (wavenumbers and FWHM) are also shown in Table 1. Comparing the bands identified in Fig. 4 for the sample fired at 800 °C with those for ceramics fired at 1600 °C (Fig. 3), one can observe that the peaks are weakened and broadened. Besides the nine predicted modes for tetragonal BYN ceramics, samples fired below 1600 °C present three additional bands. These bands could originate from local symmetry breaking or from the activation of infrared or silent modes due to the B-site disorder.[7,12] The last hypothesis was investigated by accessing the additional material published in Ref. 2. Infrared modes (TO/LO branches) appear around 117/138, 215/285, 317/398 and 528/713 cm^{-1}. These wavenumbers, valid for the solid-state sample studied in Ref. 2, do not match with those presented in Table 1 (microwave-hydrothermal BYN fired at 800 °C, last column), showing that the infrared modes were not activated in our BYN samples fired below 1600 °C.

The intensities and wavenumbers of all modes varied with the sintering temperature, indicating that the Raman
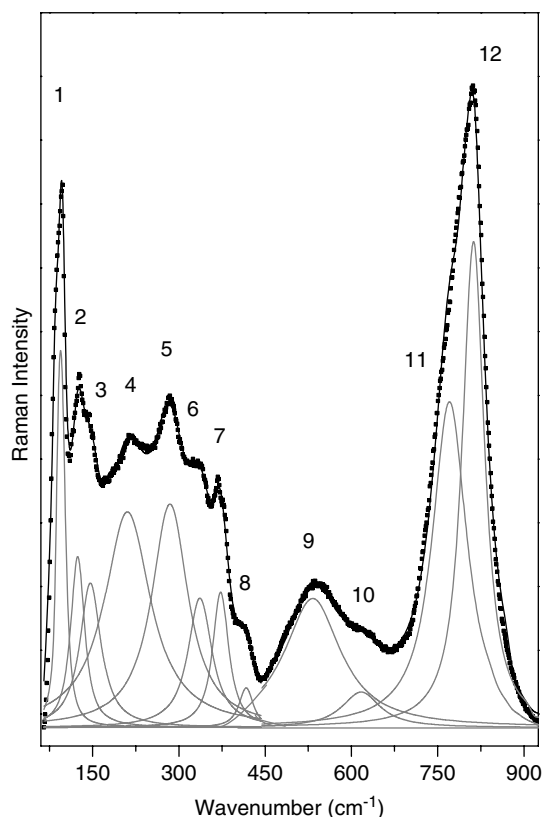

Figure 4. Raman spectroscopic data (squares) for the sample fired at 800 °C. Fitting (black line) was carried out by a sum of Lorentzian lines (gray lines).

spectra are sensitive to the changes produced by the annealing of the samples. Therefore, the hypothesis of a structural change at lower firing temperatures was investigated by Raman spectroscopy. The data obtained for the sample fired at 800 °C (Fig. 4) was studied in detail at the light of the group-theory approach. For this sample, our assumption is that a distorted, tilted perovskite with lower symmetry than the tetragonal structure occurs. It is well known that perovskites of the A$_2$BB'O$_6$-type present 1 : 1 B-site cation ordering and, in the absence of octahedral tilting, belongs to the parent $Fm\bar{3}m$ space-group symmetry.[13] For these materials, it has been shown by group-theory methods that 11 different structures are possible as a consequence of lowering the symmetry by octahedral tilting.[13] The possible group-subgroup relationships were obtained and are used in the present work to describe the phase transformation in the Ba$_2$YNbO$_6$ system. Starting from the space group $Fm\bar{3}m$ (cubic, untilted), the derived subgroups by loss of symmetry elements (due to possible octahedral tiltings) are $Pn\bar{3}$, $P4_2/nnm$, $P4/mnc$, $I4/m$, $C2/m$ and $R\bar{3}$.[11] Among the six subgroups listed above, only the tetragonal space group $I4/m$ describes the BYN ceramics fired at 1600 °C, as previously discussed here and in Ref. 2.

The space group $I4/m$ ($a^0a^0c^-$) in turn is correlated (by group-subgroup relationships) with the subgroups $P4_2/n$ (C_{4h}^4, tetragonal), $C2/c$ (C_{2h}^6, monoclinic) and $P\bar{1}$ (C_i^1, triclinic).[13] The first subgroup includes two additional in-phase tilting ($a^+a^+c^-$), while the third subgroup presents two additional anti-phase tilting ($a^-b^-c^-$). On the other hand, the subgroup $C2/c$ presents only one additional in-phase distortion ($a^0b^+c^-$). Lufaso et al.[14] showed that the structures $C2/c$ and $P4_2/n$ hold only when multiple cations are present in A-site, which does not apply for our BYN ceramics. Moreover, by using the site group method of Rousseau et al.[11] one would expect a total of 24 Raman-active bands for the monoclinic $C2/c$ structure, and 35 bands for the tetragonal $P4_2/n$ space group, which are much higher than the 12 observed bands for our materials. These results demonstrated that both $P4_2/n$ and $C2/c$ structures are not compatible with our system.

Again, Lufaso et al.[14] showed that the space group $P\bar{1}$ (with $Z = 2$) is possible for a single A-site cation. Besides, the results of Howard et al.[13] for a group-subgroup relationship between tetragonal and triclinic structures lead us to consider this possibility for a lower-symmetry structure for BYN ceramics fired below 1600 °C. For a factor-group analysis, the atomic positions must be considered and Wyckoff symbols for BYN materials in the triclinic group would be as follows: the Ba atoms should occupy three 4i sites of general C_1 symmetry, Y and Nb ions would sit on 2a and 2g positions (C_i symmetry), and the oxygen atoms would be in three 4i sites (C_1 symmetry). Then, using the site-group method of Rousseau et al.[11] it is possible to obtain the Raman active phonon modes at the Brillouin zone center for this C_i^1 point group: $\Gamma_R = 12A_g$ (12 Raman bands are expected

for this group). As can be visualized in Fig. 4, the spectrum for the BYN samples fired at 800 °C was fitted with 12 Lorentzian lines, in perfect agreement with the present assumption.

Ayala *et al.*[15] and Oliveira *et al.*[16] studied different pyrochlores ($CsInMgF_6$ and $NaCaMg_2F_7$) by spectroscopic techniques. For these materials, a large number of vibrational bands were observed, which could not be explained by factor-group analyses for the cubic structures determined by single-crystal XRD. For both fluorides, a disorder-induced symmetry lowering was responsible for the observed phonon mode behaviors. In a deeper analysis, the symmetry lowering mechanism in the pyrochlore family originates from the loss of the equivalence of neighboring polyhedra in the disordered network. In the present work, a similar situation holds for samples fired at temperatures below 1600 °C. On the basis of our XRD results, we can assume that partially disordered BYN ceramics are formed at lower temperatures (no superlattice reflections were observed in samples fired below 1600 °C). If some B-cation disorder occurs, it is important to analyze the first-neighbor coordination of the atomic species in order to understand the effect of the disorder on the BO_6 octahedra and on the local symmetry. Indeed, oxygen atoms always surround Y^{+3} and Nb^{+5} ions and their coordination octahedra are not affected by B-site occupational disorder. However, the first neighbors of the oxygen atoms are always the partially disordered Y^{+3} and Nb^{+5} ions. As a consequence, disorder-induced symmetry breakdown results only from these sites.

As explained above for a tetragonal $I4/m$ structure, oxygen anions are located at sites with C_4 and C_s symmetries, while Ba atoms present the S_4 symmetry. Any disorder in the B-sites leads to a complete loss of the symmetry elements, which reduces their symmetries to C_1 (or absence of symmetry). The loss of symmetry elements of Ba and O ions is, of course, accompanied by small displacements of these ions from their original atomic positions and, then, to additional octahedral tiltings. Therefore, although the first neighbors of Nb^{+5} and Y^{+3} maintain the local inversion symmetry, the C_4 symmetry element of their sites is lost by the octahedral tiltings. It is worth noticing that C_{4h} groups are formed by the tensorial product of C_4 and C_i groups.[17] The disorder-induced loss of the C_4 element by the ions of BYN would then lead the system to the lower symmetry group C_i, in agreement with the Raman features discussed above. Therefore, we conclude that BYN ceramics fired at low temperatures present a highly distorted structure, as a result of stresses due to B-site disorder. These stresses destroy the symmetry element C_4 observed in the tetragonal $I4/m$ phase. The remaining symmetry element (C_i) agrees well with the spectra observed towards a $P\bar{1}$ space group. The more symmetric tetragonal phase will be achieved only by increasing the order of the material by heating it at very high temperatures.

CONCLUSIONS

Raman spectroscopy was employed to study the optical phonons of BYN ceramics as a function of the firing temperature. The samples were produced by microwave-hydrothermal method at 200 °C and fired at temperatures from 600 to 1600 °C. XRD showed that all samples are cubic or nearly cubic in symmetry, while Raman spectra indicated that a structural change occurred in ceramics fired in temperatures below 1600 °C. Lower-symmetry structures were investigated in the light of the group theory analysis. Ceramics obtained at 1600 °C showed nine Raman active bands, in perfect agreement with theoretical predictions and previous works for a tetragonal ($I4/m$) structure. The results indicate that Raman spectra are sensitive to the variations produced by the annealing of the samples. Materials fired below 1600 °C exhibit rather a structure belonging to the $P\bar{1}$ space group, with 12 Raman active bands. It is believed that the local disorder verified in ceramics fired at temperatures lower than 1600 °C suppresses the C_4 symmetry operation and transforms the $I4/m$ group into its $P\bar{1}$ subgroup. Group theory analysis based on this $P\bar{1}$ subgroup gives the correct number of observed vibrational bands observed through Raman spectroscopy.

REFERENCES

1. Reaney IM, Iddles D. *J. Am. Ceram. Soc.* 2006; **89**: 2063.
2. Dias A, Khalam LA, Sebastian MT, Paschoal CWA, Moreira RL. *Chem. Mater.* 2006; **18**: 214.
3. Dias A, Ciminelli VST. *Chem. Mater.* 2003; **15**: 1344.
4. Moreira RL, Matinaga FM, Dias A. *Appl. Phys. Lett.* 2001; **78**: 428.
5. Dias A, Bijumon PV, Sebastian MT, Moreira RL. *J. Appl. Phys.* 2003; **94**: 3414.
6. Byrappa K, Yoshimura M. *Handbook of Hydrothermal Technology*. William Andrew Publishing: New York, 2001.
7. Rabenau A. *Angew. Chem. Int. Ed.* 1985; **24**: 1026.
8. Adam D. *Nature* 2003; **421**: 571.
9. Barnes PW, Lufaso MW, Woodward PM. *Acta Crystallogr.* 2006; **B62**: 384.
10. Molodetsky I, Davies PK. *J. Eur. Ceram. Soc.* 2001; **21**: 2587.
11. Rousseau DL, Bauman RP, Porto SPS. *J. Raman Spectrosc.* 1981; **10**: 253.
12. Dias A, Ciminelli VST, Matinaga FM, Moreira RL. *J. Eur. Ceram. Soc.* 2001; **21**: 2739.
13. Howard CJ, Kennedy BJ, Woodward PM. *Acta Crystallogr.* 2003; **B59**: 463.
14. Lufaso MW, Barnes PW, Woodward PM. *Acta Crystallogr.* 2006; **B62**: 397.
15. Ayala AP, Paschoal CWA, Guedes I, Paraguassu W, Freire PTC, Mendes Filho J, Moreira RL, Gesland J-Y. *Phys. Rev.* 2002; **B66**: 214105.
16. Oliveira EA, Guedes I, Ayala AP, Gesland J-Y, Ellena J, Moreira RL, Grimsditch M. *J. Solid State Chem.* 2004; **177**: 2943.
17. Tinkham M. *Group Theory and Quantum Mechanics*. McGraw-Hill: New York, 1964.