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Raman signatures of monoclinic distortion in \((\text{Ba}_{1-x}\text{Sr}_x)_3\text{CaNb}_2\text{O}_9\) complex perovskites

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Octahedral tilting is the most common distortion process observed in centrosymmetric perovskite compounds. Indeed, crucial physical properties of this oxide stem from the tilt of BO\(_6\) rigid octahedra. In microwave ceramics with perovskite-type structure, there is a close relation between the temperature coefficient of resonant frequency and the tilt system of the perovskite structure. However, in many cases, limited access facilities are needed to assign correctly the space group, including neutron scattering and transmission electron microscopy. Here, we combine the Raman scattering and group theory calculations to probe the structural distortion in the perovskite \((\text{Ba}_{1-x}\text{Sr}_x)_3\text{CaNb}_2\text{O}_9\) solid solution, which exhibits a structural phase transition at \(x \geq 0.7\), from \(\text{D}_{3h}^2\) trigonal to \(\text{C}_{2h}\) monoclinic cell. Both phases are related by an octahedral tilting distortion (a\(^{a/b}b^*\) in Glazer notation). Low-temperature Raman spectra corroborate the group-theoretical predictions for \(\text{Sr}_3\text{CaNb}_2\text{O}_9\) compound because 36 modes detected at 25 K agree well with the 42 (25A\(_g\) @ 17B\(_g\)) predicted ones. Copyright © 2017 John Wiley & Sons, Ltd.

Keywords: ordered perovskites; octahedral tilting; crystal structure; group theory; monoclinic

Introduction

It is well established that the compounds crystallizing in the perovskite structure \((\text{ABO}_3)\) display an enormous technological and scientific importance in solid-state physics and chemistry.\(^{[1,2]}\) Due to their ability to accommodate a large variety of cations at A and B sites, several physical properties may emerge from this feature, including ferroelectricity, piezoelectricity, superconductivity, ionic conductivity, half-metallic conductivity, multifunctionality, and ferromagnetism.\(^{[3,4]}\) With a correct chemical design, the parameters of each property can be tuned to improve their performance as sensors, transducers, capacitors, photovoltaic cells, electrolytes for fuel cell, magnetic memories, catalysts, or dielectric resonators.\(^{[5-7]}\) From a structural point of view, the substitution at the A or B sites can provide two interesting phenomena in centrosymmetric perovskite structures, namely, octahedral tilting and B-site cation ordering.\(^{[8,9]}\) In the first case, cooperative tilts of BO\(_6\) rigid octahedra should occur to accommodate a smaller A site cation in the cuboctahedral cavity.\(^{[10]}\) In the second one, two distinct cations, B’ and B”, yield an ordered pattern and then induce a superstructure formation. As a consequence, these processes modify the overall symmetry of the crystalline structure from the simple cubic perovskite (aristotype cell: O\(_h^1\) or Pm-3m). In this cell, the octahedral tilting leads to the hetotype structures including the most common orthorhombic phase (D\(_{2h}^2\) or Pnma).\(^{[11,12]}\)

Particularly, the octahedral tilting and B-site cation ordering are promising in the case of the dielectric resonator devices for microwave applications.\(^{[13,14]}\) In the last decades, such devices have been applied successfully in the telecommunication fields, including millimeter waves, base station, and mobile phones.\(^{[15]}\) For high performance, the microwave dielectric ceramics should present a high dielectric permittivity (\(\varepsilon_r\)), low dielectric loss (tan \(\delta \sim 10^{-4}\)), and near zero-temperature coefficient of resonant frequency (\(\tau_r\)). By using the chemical design, for instance, it is possible to improve the dielectric loss at microwave by controlling the B-site cation ordering at long range.\(^{[16]}\) On the other hand, a temperature-stable device can be achieved by inducing the octahedral tilting.\(^{[17,18]}\) Both approaches are frequently employed to obtain desired microwave parameters in the 1:2 ordered perovskite, with the chemical formula \(\text{A}_3^2\text{B}^{2+}\text{B}^{4+}\text{O}_9\) \((\text{A} = \text{Ba, Sr, Ca; B}’= \text{Ca, Mg, Co, Zn; B}” = \text{Ta, Nb})\). In its undistorted state, such a structure adopts a trigonal unit cell belonging to the \(\text{D}_{3h}^2\) space group, with an alternate distribution of the B-site cations along the <11\(\tau\)> cubic cell direction.\(^{[9]}\)

Recently, we have reported in the \(\text{Ba}_3\text{CaNb}_2\text{O}_9\) compound that the dielectric loss is related to the 1:2 ordered domain amount in the crystallite. Also, we have argued that the origin of its high \(\tau_r\) value stems from the structural instabilities associated with the onset of an octahedral tilt transition.\(^{[19]}\) In this sense, Sr\(^{2+}\) is selected as the A-site substituent cation for the \(\text{Ba}_3\text{CaNb}_2\text{O}_9\) perovskite. Thus, on the basis of ionic radii,\(^{[20]}\) the strontium...
ion may introduce distortions in the crystalline structure. In this paper, we synthesized the (Ba1−xSr2x)CaNb2O6 solid solution to probe possible distortion induced by the octahedral tilting (CaO6 and NbO6 units). As far as we know, there are no available reports on the structural features concerning this system. Furthermore, Raman spectroscopy is applied to detect the local structure disturbance induced by symmetry lowering. As reported by many authors, the combination of Raman scattering and factor-group analysis is an important tool to investigate the structural changes in perovskites and related compounds through the optical phonon behavior at the first-Brillouin zone ($q \approx 0$). This approach will be used here to assign our Raman results.

Experimental details

All polycrystalline samples were prepared by using the conventional solid-state synthesis method under air atmosphere. We aimed to synthesize the solid solution investigated here (hereafter: BCN–SCN system). Stoichiometric amounts of BaCO3 (Alfa Aesar: 99.80%), SrCO3 (Sigma Aldrich: 99.90%), CaCO3 (Alfa Aesar: 99.95%), and Nb2O5 (Alfa Aesar: 99.90%) were weighed and homogenized in a nylon jar containing isopropyl alcohol and zirconia cylinders for 24 h. After a drying procedure at 373 K, the mixture was thermally treated at 1573 K for 2 h and then ground to obtain fine powders.

X-ray powder diffraction patterns (XRPDs) were acquired by a Rigaku Rotaflex RU-200B diffractometer (Bragg–Brentano 0–20 geometry; Cu-Kα radiation $\lambda = 1.5406$ Å; 50 kV and 100 mA) over a 20 range from 10° to 100° with a step size of 0.02° (step time of 1 s). Raman spectra were collected in a backscattering geometry by a Jobin-Yvon T64000 triple monochromator with an LN2 cooled charge-coupled device camera and a 1800 grooves mm−1 holographic grating (resolution ≤ 1 cm−1). An Olympus microscope is attached to the spectrometer, and the Raman signals were excited by a 514 nm line of an argon laser (Coherent, Innova 70C). The excitation source was kept below ~2 mW and recorded after a drying procedure at 373 K, the mixture was thermally treated at 1573 K for 2 h and then ground to obtain fine powders.

Glazer notation and group theory analysis

In this work, we will describe the octahedral tilting process in perovskite by using a notation designed by Glazer. Each tilt system depends on the BO6 octahedral rotations about the axes of the so-called aristotype unit cell (an undistorted structure). Such a notation has the following representation: a'b'c', where the letters represent the tilt magnitude about the x, y, and z orthogonal axes, respectively. The # symbol denotes no tilt (# = 0), antiphase (# = −), and in-phase octahedral tilting (# = +) in neighboring layers. Therefore, the aristotype perovskite is designated by a'a'a'0 in Glazer notation. In the 1:2 ordering, the undistorted structure belongs to the trigonal D3d space group (P-3m1; #164), for which 9 (4A1g ⊗ 5Eg) Raman active phonons are expected. Table 1 summarizes the factor group analysis for the crystal structures discussed in this paper, where letters A and B denote the nondegenerate modes, while letter E represents the doubly degenerate ones. The subscripts g (gerade) and u (ungerade) are the parity under inversion operation in centrosymmetric crystals. Particularly, we are interested in distorted structure with 1:2 ordering at the B site derived from antiphase tilting process. Table 1 also depicted the site symmetries (Wyckoff positions) and the corresponding vibrational modes for the crystalline structures addressed here.

Results and discussion

The XRPD patterns of the (Ba1−xSr2x)CaNb2O6 ($x = 0.0, 0.3, 0.5, 0.7, 0.9$, and 1.0) system are illustrated in Fig. 1(a). Within the detection limit of the X-ray diffraction technique, no phase segregation was noticed in the full-range composition. The end-members of the BCN–SCN system were indexed in accordance with the ICSD#162758 and ICDD#17-0174 cards, respectively, for the BCN and SCN systems. Those cards are related to a trigonal crystal structure belonging to the D3d space group (P-3m1; #164) with one chemical formula per cell, in which the Ca2+ and Nb5+ ions feature an ordering behavior, occupying the 1a and 2d Wyckoff sites. The earlier work is derived from the disordered cubic cell within the Q1c space group, as a consequence of rhombohedral distortion along the $\cdot 111_2$ cubic direction, which provides the following lattice parameters for the resulting trigonal cell: $a_0 = \sqrt{2}a$, and $c_0 = \sqrt{3}a$ ($a_0$ is the cubic lattice constant). Because the Sr2+ ion has a lower ionic radius than that for the Ba2+ ion, one can expect the d-spacing shifting behavior. Indeed, a shifting is noticed with increasing strontium content in Fig. 1(b), resulting in a decrease of the unit cell volume, as shown in Fig. 1(c).

Some diffraction peaks at the 20 region from 10° to 25° start to appear for $x \geq 0.7$. At the same time, an extra peak at 20 ~36.5° becomes more intense, being indexed as ½(3 1 1) of the theoretical density of the (Ba1−xSr2x)CaNb2O6 compositions. Here, the theoretical density was calculated from the XRPD data. The linear trend of both curves can be regarded as a signature of the solid solution formation in the system under investigation. Also, there is a good agreement between the earlier reported densities for BCN and SCN systems) and those obtained in this work.

Nagai et al. proposed that the antiphase tilting of both MgO6 and TaO6 octahedra changed the space group of the (Ba1−xSr2x)MgTa2O6 compounds from trigonal (D3d) to monoclinic (C2/m; A2/n or C2/c; #15). Another evidence of this phase transition comes from the (2 0 2), peak splitting into two counterparts indexed as (2 4 2) and (2 4 2) reflections from the monoclinic phase. This behavior was not noticed here for the (2 0 2) peak [Fig. 1(b)], although a slight increase in its intensity occurred for $x \geq 0.9$. According to Goldschmidt, the distortion and structural stability of the perovskite structures can be predicted by using the
Table 1. Factor group analysis for the crystal structures addressed in this work ($\Gamma_T = \Gamma_Ac \oplus \Gamma_{Si} \oplus \Gamma_{IR} \oplus \Gamma_R$). Abbreviations: Ac, acoustic; Si, silent; IR, infrared; R, Raman

<table>
<thead>
<tr>
<th>Ion</th>
<th>Wyckoff site</th>
<th>Symmetry</th>
<th>Irreducible representation</th>
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<tbody>
<tr>
<td>Ba$^{2+}$</td>
<td>1b</td>
<td>D$_{3d}$</td>
<td>A$_{2u}$ ⊕ E$_u$</td>
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<tr>
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<td>2d</td>
<td>C$_{3v}$</td>
<td>A$<em>{1g}$ ⊕ A$</em>{2g}$ ⊕ E$_g$ ⊕ E$_u$</td>
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<tr>
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<td>D$_{3d}$</td>
<td>A$_{2u}$ ⊕ E$_u$</td>
</tr>
<tr>
<td>Nb$^{5+}$</td>
<td>2d</td>
<td>C$_{3v}$</td>
<td>A$<em>{1g}$ ⊕ A$</em>{2g}$ ⊕ E$_g$ ⊕ E$_u$</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>3f</td>
<td>C$_{2h}$</td>
<td>A$<em>{1g}$ ⊕ 2A$</em>{2u}$ ⊕ 3E$_u$</td>
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<tr>
<td>O$^{2-}$</td>
<td>6i</td>
<td>C$_{5}$</td>
<td>2A$<em>{1g}$ ⊕ A$</em>{1u}$ ⊕ A$<em>{2g}$ ⊕ 2A$</em>{2u}$ ⊕ 3E$_u$ ⊕ 3E$_i$</td>
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<td>$\Gamma_{IR}$</td>
<td>18A$_{2u}$ ⊕ 27B$_8$</td>
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<tr>
<td>$\Gamma_R$</td>
<td>25A$_{2u}$ ⊕ 17B$_8$</td>
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Monoclinic: C$_{12}$; A2/m; #12; a$^+$.b$^-$.b$^-$

$\Gamma_T$ | 2A$_{2g}$ ⊕ A$_{1u}$ ⊕ B$_g$ ⊕ 2B$_g$ |
| $\Gamma_{Ac}$ | 2A$_{2g}$ ⊕ A$_{1u}$ ⊕ B$_g$ ⊕ 2B$_g$ |
| $\Gamma_{Si}$ | 2A$_{2g}$ ⊕ A$_{1u}$ ⊕ B$_g$ ⊕ 2B$_g$ |
| $\Gamma_{IR}$ | 2A$_{2g}$ ⊕ A$_{1u}$ ⊕ B$_g$ ⊕ 2B$_g$ |
| $\Gamma_R$ | 2A$_{2g}$ ⊕ A$_{1u}$ ⊕ B$_g$ ⊕ 2B$_g$ |

so that $R_{Ba}$, $R_{Si}$, $R_{Ca}$, $R_{Nb}$, and $R_{O}$ are the ionic radii of Ba (1.61 Å; CN = 12), Sr (1.44 Å; CN = 12), Ca (1.00 Å; CN = 6), Nb (0.64 Å; CN = 6), and O (1.35 Å; CN = 2), taken from the Shannon's table.$^{[20]}$ The calculated $t$ value was around 0.992 for BCN, which decreases linearly until 0.935 for SCN. It means that the BCN–SCN may experience a phase transition as the Sr$^{2+}$ substitution increases.

Hence, one can expect a distorted 1:2 structure for SCN rather than the undistorted D$_{3d}$ cell for BCN.$^{[31]}$ To investigate those structural changes in more detail, Raman scattering measurements were collected in all samples of the BCN–SCN solid solution at room temperature, as discussed next.

Raman spectra of the (Ba$_{1-x}$Sr$_x$)$_3$CaNb$_2$O$_9$ solid solution are displayed in Fig. 2(a). In the spectrum of BCN ($x = 0.0$), the peaks at 85 and 90 cm$^{-1}$ are assigned to E$_g$ and A$_{1g}$ external modes, respectively. The bands centered at 413 and 820 cm$^{-1}$ denote the internal modes concerning the stretching and breathing motions of NbO$_6$ octahedra. The twisting breath mode of oxygen octahedron occurs at 355 cm$^{-1}$ with E$_g$ symmetry. The peaks

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appearing at approximately 135, 250, 280, and 610 cm\(^{-1}\) can be attributed to the D\(_{3d}\) trigonal structure.\(^{[19]}\) Two remaining bands are due to the 1:1 domain boundary in the crystalline structure, as elucidated by Blasse \(\text{et al.}\)\(^{[35]}\). Such bands are allowed when the crystallites exhibit the accumulation of antisite defects, defining the antiphase boundary defects.\(^{[5]}\) It is clear that this phenomenon occurred in the full-range composition. Recently, Ma \(\text{et al.}\) analyzed the boundary regions of 1:2 ordered domain in Ba\(_3\)(Co, Zn, Mg)Nb\(_2\)O\(_9\) perovskites by using high-resolution transmission electron microscopy technique, detecting an extra stabilized ordered structure in these regions.\(^{[36]}\) In practice, it means that there are two well-defined zones in the crystallites containing 1:1 (domain boundary) and 1:2 (domain) orders at B site. Therefore, we should expect the fingerprints of each region in the Raman spectra at room temperature.

Fig. 2(b) illustrates the effect of strontium content on the peak parameters ascribed to the 1:1 and 1:2 regions, respectively. One can note the redshift behavior of the intense oxygen breathing \(\text{A}_{1g}\) mode ranging from 820 ($x = 0.0$) to 811 cm\(^{-1}\) ($x = 1.0$). The 1:2 peak area has a minimum value at $x = 0.5$, corresponding to a maximum one for the 1:1 peak area. Such a trend can be better visualized by the contour map in Fig. 3. As a whole, this phenomenon can be interpreted as follows: the Sr\(^{2+}\) incorporation leads to an increase in the domain boundary distribution until $x = 0.5$. From this value, a decrease in this boundary region was noticed. In a recent work, we found out that there is a dependence between the 1:1 peak parameters and the dielectric performance of the Ba\(_3\)CaNb\(_2\)O\(_9\)-based microwave ceramics. In particular, a decrease in the 1:1 peak intensity led to an improved quality factor.\(^{[19]}\) Azough \(\text{et al.}\) also reported that the high-quality factor...
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Stokes seminal work describing the group–subgroup relationships for \(A_1B_1B_2^0O_6\) possible phases.\(^{29,30}\) From the untitled trigonal phase \((D_{3d}; \text{a}_1\text{a}_1\text{a}_1^\prime \text{ in Glazer notation})\), five derived structures can be obtained directly from the octahedral tilting process, namely, \(C_{3h}\) \((P-3; \#147); \text{a}_1\text{a}_1\text{a}_1^\prime\), \(C_{3h}\) \((C2/m; \#12); \text{a}_1\text{b}_1\text{b}_1\), \(C_{3h}\) \((P2_1/c; \#14); \text{a}_1\text{a}_2\text{c}_2^\prime\), \(C_{3h}\) \((A2/m; \#12); \text{a}_1\text{b}_1\text{b}_1\text{ b}_1\), and \(D_{3d}\) \((P-3c1; \#165); \text{a}_1\text{a}_1\text{a}_1\text{ a}_1\text{ a}_1\text{ a}_1\). As one can see, only two of them are ascribed as an antiphase (out-of-phase) octahedral rotation with a negative superscript. An antiphase rotation usually appears in perovskites with a negative value for the temperature coefficient of resonance frequency \(\tau_T\).\(^{17}\) Such a parameter denotes the thermal stability of the dielectric resonator for applications in microwave circuitry.\(^{39}\) Therefore, the monoclinic \(A2/m\) and trigonal \(P-3c1\) phases should better describe the crystalline structure of \(Sr_9\text{CaNb}_2\text{O}_9\) composition. By using the method of factor group analysis\(^{27}\) we calculated the distribution of the zone-center vibrational modes in terms of the respective representations of \(C_{3h}\) and \(D_{3d}\) point groups, as listed in Table 1.

In this sense, \(42 (25A_{1g} \oplus 17 B_{2g})\) Raman active modes are expected to be detected for the monoclinic structure, while \(20 (6A_{1g} \oplus 14E_g)\) Raman active phonons are allowed for the trigonal space group. Otherwise, 29 bands in the SCN Raman spectrum were noticed at room temperature, as depicted in Fig. 4. This result can eliminate the trigonal system \(\text{a}_1\text{a}_1\text{a}_1\text{ a}_1\text{ a}_1\text{ a}_1\) in Glazer notation) in the description of the SCN structure. However, low-temperature Raman spectra were collected in order to solve overlapping bands from the thermal effect, and the results are shown in Fig. 5. Also, the spectra were acquired in the ranging from 25 to 300 K and then corrected by the Bose–Einstein thermal factor \([n(h\nu, T) + 1]^{-1}\).\(^{39}\) The bands in the wavenumber interval 65–515 cm\(^{-1}\) are clearly more detectable, leading to 36 modes at approximately 25 K. Such a result agrees more closely with the 42 ones predicted for the \(C_{3h}\) monoclinic system \(\text{a}_1\text{b}_1\text{b}_1\text{ b}_1\text{ b}_1\text{ b}_1\) in Glazer notation, being our finding similar to

\((Q \times f)\) depends on the removal of domain boundaries in single domain grains (or crystallites) of \(\text{Ba}_y\text{MgTa}_x\text{O}_9\) ceramics.\(^{37}\) Therefore, we can predict that the \(Sr^{2+}\) cations at the A site modify not only the thermal stability (i.e., \(\tau_T\) parameter) but also the dielectric loss at microwave.

Unlike the BCN sample, there are an increased number of Raman bands in the SCN spectrum, as depicted in Figs 4(a) and 4(b). Our results are in accordance with those reported for \(Sr_9\text{MgNb}_2\text{O}_9\) perovskites.\(^{32}\) Dias et al. showed that the \(Sr_9\text{MgNb}_2\text{O}_9\) system can be indexed as a monoclinic cell belonging to the \(C_{3h}\) space group \((A2/m; \#12)\). This assumption is based on the Howard and

\[\text{Figure 3.}\] 1:1 and 1:2 ordered regions: The contour plot of the Sr content dependence of the Raman spectra in high wavenumber region. The \(Sr^{2+}\) incorporation leads to an increase in the domain boundary distribution until \(x = 0.5\). The vertical dashed line is a guide for the eye. [Colour figure can be viewed at wileyonlinelibrary.com]

\[\text{Figure 4.}\] Comparison between trigonal and monoclinic phases: Raman spectra for the \(\text{Ba}_9\text{CaNb}_2\text{O}_9\) and \(\text{Sr}_9\text{CaNb}_2\text{O}_9\) compounds in the wavenumber regions: (a) 65–465 cm\(^{-1}\) and (b) 490–840 cm\(^{-1}\), showing an increased number of bands in the strontium-based system; see Tables S2 and S3. [Colour figure can be viewed at wileyonlinelibrary.com]

\[\text{Table 1.}\] Dependence of the Raman spectra on the respective representations of the zone-center vibrational modes for the monoclinic space group \((A2/m; \#12)\). The vertical dashed line is a guide for the eye. [Colour figure can be viewed at wileyonlinelibrary.com]
that reported for Sr$_2$MgNb$_2$O$_8$.

Because the internal modes of NbO$_6$ octahedron usually appear at $\nu > 550$ cm$^{-1}$, we should not expect more than two bands in this interval (modes at 613 and 812 cm$^{-1}$). The remaining band centered at 776 cm$^{-1}$ comes from the domain boundary, as previously mentioned.

According to Howard et al.,

the C$_{2h}^1$ monoclinic structure for the Sr$_2$CaNb$_2$O$_8$ system has three Sr$^{2+}$ at 4$i$ positions, two Ca$^{2+}$ located at 2$a$ and 2$d$ sites, two Nb$^{5+}$ at 4$i$ positions, and six oxygen anions distributed at 4$i$ (3O$_1$) and 8$j$ (3O$_2$) Wyckoff sites. Its unit cell has the dimensions $a\sqrt{3} \times \sqrt{2} \times \sqrt{6}$ relative to the edge of the ABO$_3$ simple cubic perovskite. Otherwise, a more distorted structure is expected to crystallize when Sr$^{2+}$ are replaced by Ca$^{2+}$ cations. Indeed, Levin et al. concluded that the Ca$_2$Nb$_2$O$_8$=Ca$_2$CaNb$_2$O$_8$ perovskite can be indexed as a monoclinic cell belonging to the C$_{2h}^1$ space group ($P2_1/c$; #14: b b c’ in Glazer notation).

Besides the antiphase rotation, this structure has an in-phase octahedral tilting with the cell dimensions $\sqrt{6} \times \sqrt{2} \times 3\sqrt{2}$ relative to the edge of the cubic perovskite. Fu et al. also employed the previous monoclinic unit cell to describe the crystalline structure of the Ca$_2$MgB$_2$O$_6$ (B” = Nb and Ta) complex perovskite ceramics.

**Conclusions**

In summary, we have investigated the (Ba$_{1-x}$Sr$_x$)$_2$CaNb$_2$O$_8$ solid solution obtained by conventional solid-state method. Our main goal in this work was to introduce a structural transition by replacing Ba$^{2+}$ cations with Sr$^{2+}$. A combination of Raman spectroscopy and factor group analysis was necessary to detect the symmetry lowering process in Sr-rich samples ($x \geq 0.7$). Based on Howard and Stokes work, we argued that the monoclinic structure within the C$_{2h}^1$ space group is an appropriate choice to describe the unit cell of Sr$_2$CaNb$_2$O$_8$. Such a monoclinic cell is directly obtained from the aristotype D$_{3d}$ trigonal cell after an octahedral tilting distortion ($a’b’b’$ in Glazer notation). Indeed, low-temperature Raman spectra were employed to corroborate the group-theoretical predictions, and a total of 36 peaks were fitted at 25 K in comparison with the 42 (25A$_g$ $\oplus$ 17B$_g$) predicted ones. As a result, we believe that the highlight of this paper lies in the understanding of the structural distortion induced by octahedral tilting process in the (Ba$_{1-x}$Sr$_x$)$_2$CaNb$_2$O$_8$ solid solution, and then this result can encourage future studies in similar systems.

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Supporting information

Additional Supporting Information may be found online in the supporting information tab for this article.