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Incommensurate modulation of calcium barium niobate (CBN28 and Ce:CBN28)

Heribert A. Graetsch,[a]* Chandra Shekhar Pandey,[a] Jürgen Schreuer,[a] Manfred Burianek[b] and Manfred Mühlberg[b]

[a]Institut für Geologie, Mineralogie und Geophysik, Ruhr Universität Bochum, Universitätsstrasse 150, D-44801 Bochum, Germany, and [b]Institut für Kristallographie, Universität zu Köln, Germany

Correspondence e-mail:
heribert.graetsch@rub.de

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The incommensurately modulated crystal structures of $Ca_{0.28}Ba_{0.72}Nb_2O_6$ (CBN28) and $Ce_{0.02}Ca_{0.25}Ba_{0.72}Nb_2O_6$ (Ce:CBN28) were refined in the supercentred setting $X4bm(AA0,-AA0)$ of the 3 + 2-dimensional superspace group $P4bm(aa\frac{1}{2},-aa\frac{1}{2})$. Both compounds are isostructural with a tetragonal tungsten bronze-type structure. The modulation of CBN28 consists of a wavy distribution of Ba and Ca atoms as well as vacancies on the incompletely occupied Me2 site with 15-fold oxygen coordination. The occupational modulation is coupled with a modulation of the atomic displacement parameters and a very weak modulation of the positional parameters of Me2. The surrounding O atoms show strong displacive modulations with amplitudes up to *ca* 0.2 Å owing to the cooperative tilting of the rigid NbO_6 octahedra. The Me1 site with 12-fold coordination and Nb atoms are hardly affected by the modulations. Only first-order satellites were observed and the modulations are described by first-order harmonics. In Ce:CBN28 cerium appears to be located on both the Me2 and Me1 sites. Wavevectors and structural modulations are only weakly modified upon substitutional incorporation of 0.02 cerium per formula unit of calcium.

1. Introduction

$Ca_{1-x}Ba_xNb_2O_6$ crystals have interesting ferroelectric and electro-optic properties which promise technological applica-

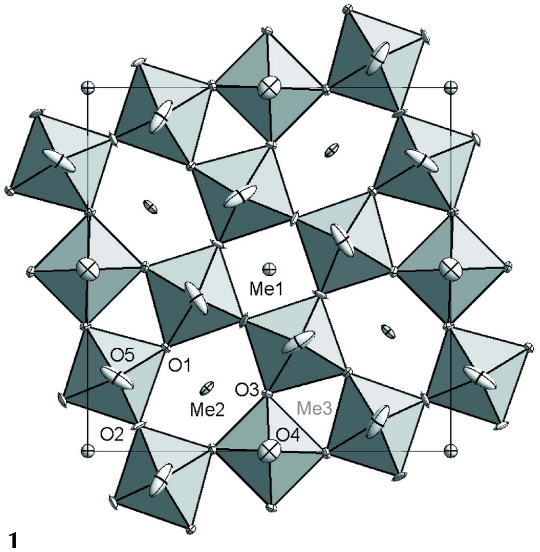

Figure 1
Average structure of tetragonal tungsten bronze type $Ca_{0.28}Ba_{0.72}Nb_2O_6$ projected along the *c* axis. The Nb atoms are located near the centres of the octahedra. The Me1 position is predominately occupied by calcium and the Me2 position predominately by barium (*cf.* Table 2). The Me3 site is not filled.

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Table 1
Experimental details.

For all structures: Tetragonal, $X4bm(AA0, -AA0)$, $Z = 10$. Experiments were carried out at 295 K with Mo $K\alpha$ radiation using an Xcalibur diffractometer with Saphhire2 CCD detector. Refinement was on 191 parameters.

	CBN28	Ce:CBN28
Crystal data		
Chemical formula	$Ca_{0.28}Ba_{0.72}Nb_2O_6$	$Ce_{0.02}Ca_{0.25}Ba_{0.72}Nb_2O_6$
Chemical formula weight	391.9	394.3
Centring	$0\ 0\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$	$0\ 0\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$
Modulation wavevectors	$\mathbf{q}_1 = 0.2942\ (9)\mathbf{a}^* + 0.2942\ (9)\mathbf{b}^*$ $\mathbf{q}_2 = -0.2942\ (9)\mathbf{a}^* + 0.2942\ (9)\mathbf{b}^*$	$\mathbf{q}_1 = 0.2875\ (7)\mathbf{a}^* + 0.2875\ (7)\mathbf{b}^*$ $\mathbf{q}_2 = -0.2875\ (7)\mathbf{a}^* + 0.2875\ (7)\mathbf{b}^*$
a, c (Å)	12.4529 (4), 7.9242 (6)	12.4596 (6), 7.9042 (6)
V (Å^3)	1228.84 (11)	1227.06 (13)
D_x (Mg m^{-3})	5.294	5.334
μ (mm^{-1})	10.58	10.77
Crystal size (mm)	0.19 × 0.18 × 0.12	0.18 × 0.17 × 0.17
Data collection		
Data collection method	φ and ω scans	φ and ω scans
Absorption correction	Analytical	Analytical
T_{min}, T_{max}	0.255, 0.426	0.223, 0.272
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	34 896, 3291, 2925	34 673, 3275, 2492
No. of main reflections all, obs	671, 668	669, 666
No. of satellites all, obs	2620, 2257	2606, 1826
R_{int}	0.025	0.024
Refinement		
$R[F^2 > 3\sigma(F^2)]$, wR, S	0.028, 0.041, 1.65	0.031, 0.039, 1.38
R, wR (observed main reflections)	0.0190, 0.0293	0.0230, 0.0306
R, wR (observed satellite reflections)	0.0556, 0.0690	0.0578, 0.0644
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.00, −1.00	1.65, −1.36
Extinction correction	B-C type 1 Gaussian isotropic (Becker & Coppens, 1974)	
Extinction coefficient	0.063 (3)	0.117 (3)
Inversion twin volume fractions	0.51 (2), 0.49 (2)	0.48 (3), 0.52 (3)
No. of restraints	2	3

Computer programs used: *JANA*2006 (Petříček *et al.*, 2006), *NADA* (Schönleber *et al.*, 2001), *CrysAlis Pro* (Oxford Diffraction, 2009), *DIAMOND*3.0 (Brandenburg & Putz, 2005).

tions for instance as holographic data storage. Doping with cerium can promote the photo-refractive effect (Baetzold, 1993).

The crystal structure of $Ca_{1-x}Ba_xNb_2O_6$ is of the incompletely filled tetragonal tungsten bronze (TTB) type (Bach & Liebertz, 1977). Corner-sharing octahedra form a framework leaving space for three types of cavities (Fig. 1). The Me1 site is coordinated by 12 O atoms, the Me2 site by 15 O atoms and the Me3 position by 9 O atoms in TTB (Jamieson *et al.*, 1968). The latter is not occupied and the Me1 and Me2 sites are incompletely filled by larger cations since there are two Me1 and four Me2 sites in the unit cell of the average structure for only five cations. The X-ray single-crystal diffraction patterns of $Ca_{0.28}Ba_{0.72}Nb_2O_6$ exhibit weak first-order satellite reflections in addition to the main reflections indicating the existence of a two-dimensional structural modulation as in isostructural $Sr_{1-x}Ba_xNb_2O_6$ with x ranging from ~ 0.25 to 0.75. The wavevectors are $\mathbf{q}_1 = \alpha\ \mathbf{a}^* + \alpha\ \mathbf{b}^* + \frac{1}{2}\ \mathbf{c}^*$ and $\mathbf{q}_2 = -\alpha\ \mathbf{a}^* + \alpha\ \mathbf{b}^* + \frac{1}{2}\mathbf{c}^*$ with $\alpha \simeq 0.3$. The incommensurate modulation was found to mainly affect the positions of the O atoms (Woike *et al.*, 2003; Surmin *et al.*, 2006). However, it was assumed that the modulation originates from a wave-like occupation of the large cation sites. The present study was undertaken in order to more accurately characterize the incommensurate modulation of $Ca_{0.28}Ba_{0.72}Nb_2O_6$ (CBN28) and $Ce_{0.02}Ca_{0.25}Ba_{0.72}Nb_2O_6$ (Ce:CBN28).

2. Experimental

2.1. Czochralski growth of CBN28 and Ce:CBN28

Single crystals of undoped CBN28 and cerium-doped Ce:CBN28 were grown with a Czochralski puller equipped with automatic diameter control (ADC) based on crystal weighing. The runs were carried out in air at 1713 K. Dispersion-hardened Pt-crucibles of 40 mm in diameter and 1.5 mm wall thickness were used. 250 g of $Ca_{0.28}Ba_{0.72}Nb_2O_6$ and 1 wt% CeO_2 were prepared from $CaCO_3$ (purum pa, Fluka), $BaCO_3$ (precipitated pure, Merck), CeO_2 (99.9%, Heraeus) and Nb_2O_5 (single-crystal grade, H.C. Starck) powders. After mixing and drying at 423 K for 6 h the powder was calcinated at 1523 K in air for 24 h and finally melted at 1723 K. The crucible was heated by an induction coil. To establish a moderate axial temperature gradient (10 K cm^{-1}) a double working coil was used, which heats the crucible and a platinum afterheater simultaneously. An additional platinum radiation shield was inserted to prevent heat loss and melt overheating. Deep red crystals of Ce:CBN28 oriented along [001] with dimensions up to 10 mm in diameter and 60 mm in length were grown with a translation rate of 0.75 mm h^{-1} and a rotation rate of 20 min^{-1}. Further details of the growth procedure were described by Burianek *et al.* (2007).

2.2. Chemical characterization

The chemical compositions were determined as $Ca_{0.279\,(2)}Ba_{0.720\,(4)}Nb_{2.000\,(1)}O_6$ and $Ce_{0.024\,(2)}Ca_{0.251\,(3)}Ba_{0.720\,(3)}Nb_{1.996\,(2)}O_6$ on carbon-coated thin sections with a Cameca SX-50 electron microprobe in wavelength dispersion mode. Beam conditions were 15 kV, 20 nA and a spot diameter of 1 µm. At least 30 analyses were taken at different points of each sample. Counting times of peak and background were 20 s. The following standards were used: andradite (Ca), barium glass, niobium metal and cerium (Pandey, 2010).

Table 2
Occupation of the Me1 and Me2 sites in %.

Site	Atom	CBN28	Ce:CBN28
Me2	Ba	88.21 (7)	88.01 (8)
Me2	Ca	5.53 (12)	0.48 (12)
Me2	Ce	–	1.53 (9)
Me2	Sum	93.74 (19)	90.0 (3)
Me1	Ba	2.61 (12)	4.30 (13)
Me1	Ca	58.81 (2)	61.9 (2)
Me1	Ce	–	2.91 (14)
Me1	Sum	62.4 (3)	69.1 (5)
	f.u.	$Ca_{0.2794\,(17)}Ba_{0.7201\,(11)}Nb_2O_6$	$Ce_{0.0239\,(13)}Ca_{0.2515\,(18)}Ba_{0.7213\,(11)}Nb_2O_6$

Average structure refined with *SHELXL*97 (Sheldrick, 2008); f.u.: formula units.

2.3. X-ray diffraction

The crystals selected for data collection were ground to a spherical shape in order to facilitate absorption corrections. The data was collected at room temperature on a four-circle kappa diffractometer (Xcalibur, Oxford Diffraction) equipped with a Saphire2 CCD area detector and an enhanced X-ray source. Mo $K\alpha$ radiation was obtained from a graphite monochromator. The sample-to-detector distance was 44.4 mm. One φ and 4 ω scans were recorded covering more than 95% of the reciprocal space at a resolution of 0.8 Å. Details of the data collection are listed in Table 1.[1] Data reduction, Lp correction and numerical absorption correction were carried out with the program *CrysAlis Pro* (Oxford Diffraction, 2009).

2.4. Refinement

The average structures were refined from the main reflections in the space group *P*4*bm* (No. 100) with the *SHELXL*97 (Sheldrick, 2008) program starting from the positional parameters of $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (Woike *et al.*, 2003). Two restraints for CBN28, and three for Ce:CBN28 were set on the site occupancy factors of the Me1 and Me2 sites so that the sum of the respective Ba, Ca and Ce atoms on both sites remains compatible with the chemical analyses. As the crystals were not poled, one parameter for the volume ratio of the inversion twinning was refined and one parameter for an empirical extinction correction.

The modulated structure has 3 + 2-dimensional superspace-group symmetry $P4bm(aa\frac{1}{2})000(-aa\frac{1}{2})000$ (No. 100.2.69.13 according to Stokes *et al.*, 2011). The refinements were undertaken with the program *JANA*2006 (Petříček *et al.*, 2006) using first-order satellites and main reflections. The supercentred setting $X4bm(AA0, -AA0)$ with centring in $0\,0\,\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$ was chosen in order to avoid the rational component of the modulation vector (*cf.* Woike *et al.*, 2003). This setting implies a doubling of the c lattice parameter with respect to the average structure. Individual anisotropic atomic displacement parameters and Fourier coefficients of positional modulations were varied for all atoms. For the Me2 site, refinements of modulations of the site occupancy and the atomic displacement parameters were found to be necessary. Refinements of atomic displacement parameter modulations of all cations slightly reduced the *R* values further. Three of the 38 additional parameters are larger than three sigma. Atomic displacement parameter modulations of the O atoms could not be successfully refined as the harmonic tensors of some O atoms did not remain positive in some regions along the wave-vector. The z parameter of Me2 was fixed in order to define the origin. One parameter for the twin domain ratio and an isotropic extinction parameter were also varied.

3. Results and discussion

The unit-cell volume of the cerium-substituted crystal is 0.15 (3)% smaller compared with the unit-cell volume of the undoped sample (Table 1). The reduction along the tetragonal **c** axis is 0.25 (2)%, whereas the **a** axis slightly expands by 0.05 (1)%. The small contraction of the unit-cell volume upon substitution of calcium by cerium seems to indicate that at least part of the cerium is incorporated as Ce^{4+} as the effective ionic radius of Ce^{3+} is virtually the same as in Ca^{2+} (Shannon, 1976). The wavelength of the modulation shows a slight increase of 2.4 (1)% in the cerium-doped sample. Inversion twinning is perfectly racemic in both investigated crystals within the limits of the estimated standard uncertainty (Table 1).

Free refinement of the site occupancy factors of the Me1 and Me2 sites of the average structure of CBN28 resulted in a composition of $Ca_{0.25}Ba_{0.75}Nb_2O_6$ in reasonable agreement with the chemical analysis ($Ca_{0.28}Ba_{0.72}Nb_2O_6$). The large cations are not evenly distributed over the Me1 and Me2 sites. Restrained refinements of CBN28 yielded occupancies of the

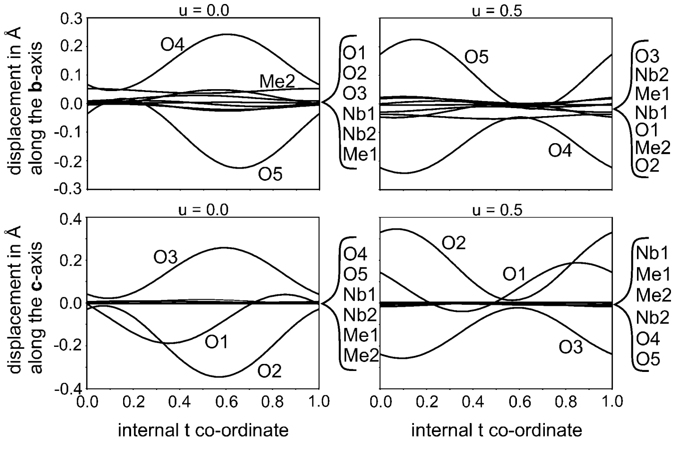

Figure 2
Deviations of the atoms from their average positions *versus* the internal t coordinate. The internal u coordinate is zero in both pictures on the left side and u = 0.5 on the right side.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: CK5044). Services for accessing these data are described at the back of the journal.

Table 3
Interatomic distances in modulated $Ca_{0.279}Ba_{0.720}Nb_2O_6$ and $Ce_{0.027}Ca_{0.249}Ba_{0.720}Nb_2O_6$.

Me2 and Me1 = Ba, Ca (and Ce for Ce:CBN28).

	$Me_{0.279}Me_{0.720}Nb_2O_6$			$Ce_{0.027}Me_{0.249}Me_{0.720}Nb_2O_6$		
Distance	Av.	Min.	Max.	Av.	Min.	Max.
Me2—O1$^{\mathrm{i}}$	2.861 (6)	2.832 (6)	2.919 (6)	2.842 (9)	2.810 (9)	2.900 (9)
Me2—O1$^{\mathrm{ii}}$	2.729 (6)	2.705 (6)	2.772 (6)	2.738 (9)	2.714 (9)	2.786 (9)
Me2—O2$^{\mathrm{i}}$	3.469 (7)	3.375 (7)	3.511 (7)	3.466 (9)	3.377 (9)	3.504 (9)
Me2—O2$^{\mathrm{ii}}$	3.234 (7)	3.151 (7)	3.340 (7)	3.248 (9)	3.153 (9)	3.351 (9)
Me2—O2$^{\mathrm{iii}}$	3.459 (7)	3.372 (7)	3.511 (7)	3.456 (9)	3.370 (9)	3.508 (9)
Me2—O2$^{\mathrm{iv}}$	3.262 (7)	3.182 (7)	3.306 (7)	3.268 (9)	3.187 (9)	3.313 (9)
Me2—O3$^{\mathrm{v}}$	2.966 (6)	2.837 (6)	3.102 (6)	2.954 (8)	2.828 (8)	3.082 (8)
Me2—O3$^{\mathrm{vi}}$	2.782 (6)	2.709 (6)	2.868 (6)	2.788 (8)	2.712 (8)	2.882 (8)
Me2—O3$^{\mathrm{vii}}$	2.917 (6)	2.821 (6)	3.117 (6)	2.904 (8)	2.812 (8)	3.097 (8)
Me2—O3$^{\mathrm{viii}}$	2.751 (6)	2.688 (6)	2.886 (6)	2.757 (8)	2.688 (8)	2.902 (8)
Me2—O4	3.068 (4)	2.892 (4)	3.174 (4)	3.070 (5)	2.885 (5)	3.182 (5)
Me2—O5$^{\mathrm{i}}$	3.257 (5)	2.850 (5)	3.536 (5)	3.256 (6)	2.822 (6)	3.565 (6)
Me2—O5$^{\mathrm{v}}$	3.357 (5)	3.106 (5)	3.770 (5)	3.353 (6)	3.107 (6)	3.773 (6)
Me2—O5$^{\mathrm{vii}}$	3.551 (5)	3.098 (5)	3.779 (5)	3.553 (6)	3.092 (6)	3.788 (6)
Me2—O5$^{\mathrm{iii}}$	3.155 (5)	3.079 (5)	3.309 (5)	3.154 (6)	3.075 (6)	3.316 (6)
⟨*Me2—O*⟩	*3.122*	*2.980*	*3.261*	*3.121*	*2.976*	*3.264*
Me1—O2$^{\mathrm{ix}}$, O2$^{\mathrm{x}}$, O2$^{\mathrm{vi}}$, O2$^{\mathrm{iv}}$	2.612 (7)	2.486 (7)	2.755 (7)	2.628 (9)	2.490 (9)	2.787 (9)
Me1—O2, O2$^{\mathrm{xi}}$,O2$^{\mathrm{v}}$, O2$^{\mathrm{iii}}$	2.951 (7)	2.617 (7)	3.266 (8)	2.921 (9)	2.589 (9)	3.228 (9)
Me1—O5, O5$^{\mathrm{xi}}$, O5$^{\mathrm{v}}$, O5$^{\mathrm{iii}}$	2.699 (5)	2.663 (5)	2.758 (5)	2.698 (6)	2.654 (6)	2.758 (6)
⟨*Me1—O*⟩	*2.755*	*2.589*	*2.927*	*2.750*	*2.579*	*2.925*
Nb1—O3	1.967 (6)	1.956 (6)	1.978 (6)	1.965 (9)	1.955 (9)	1.987 (9)
Nb1—O3$^{\mathrm{v}}$	1.971 (6)	1.956 (6)	1.979 (6)	1.968 (9)	1.957 (9)	1.975 (9)
Nb1—O3$^{\mathrm{vii}}$	1.971 (6)	1.955 (6)	1.978 (6)	1.966 (9)	1.951 (9)	1.981 (9)
Nb1—O3$^{\mathrm{xii}}$	1.970 (6)	1.957 (6)	1.979 (6)	1.971 (9)	1.960 (9)	1.981 (9)
Nb1—O4	1.820 (9)	1.807 (9)	1.829 (9)	1.838 (11)	1.820 (11)	1.849 (11)
Nb1—O4$^{\mathrm{xiii}}$	2.171 (9)	2.171 (9)	2.176 (9)	2.149 (11)	2.138 (11)	2.156 (11)
⟨*Nb1—O*⟩	*1.979*	*1.967*	*1.987*	*1.977*	*1.964*	*1.989*
Nb2—O1	2.003 (6)	1.994 (6)	2.024 (6)	2.004 (9)	1.985 (9)	2.032 (9)
Nb2—O2	1.965 (7)	1.945 (7)	1.989 (7)	1.968 (10)	1.942 (10)	1.991 (9)
Nb2—O2$^{\mathrm{x}}$	2.002 (7)	1.986 (7)	2.024 (7)	2.003 (10)	1.986 (10)	2.029 (9)
Nb2—O3	1.950 (6)	1.939 (6)	1.961 (6)	1.951 (9)	1.934 (9)	1.969 (9)
Nb2—O5	1.836 (8)	1.813 (8)	1.879 (8)	1.860 (11)	1.835 (11)	1.922 (11)
Nb2—O5$^{\mathrm{xiii}}$	2.170 (8)	2.145 (8)	2.210 (8)	2.140 (11)	2.112 (11)	2.197 (11)
⟨*Nb2—O*⟩	*1.988*	*1.971*	*2.015*	*1.988*	*1.966*	*2.024*

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $y, -x, z$; (iv) $y, -x, z+\frac{1}{2}$; (v) $-x, -y, z$; (vi) $-x, -y, z+\frac{1}{2}$; (vii) $-y+\frac{1}{2}, -x+\frac{1}{2}, z$; (viii) $-y+\frac{1}{2}, -x+\frac{1}{2}, z+\frac{1}{2}$; (ix) $x, y, z+\frac{1}{2}$; (x) $-y, x, z+\frac{1}{2}$; (xi) $-y, x, z$; (xii) $y+\frac{1}{2}, x+\frac{1}{2}, z$; (xiii) $x-1, y, z+\frac{1}{2}$.

Me1 and Me2 sites of 62.4 (3) and 93.74 (19)% (Table 2). Barium is mainly incorporated on the larger Me2 position (88.2%) and calcium (58.8%) mainly on the Me1 site. The niobium sites at the centres of the octahedra are fully occupied. The restrained refinement of the cerium-doped crystal indicates that cerium is probably built in on both sites [1.57 (9)% on Me2 and 2.91 (14)% on Me1]. The occupancies of the Me1 and Me2 sites are slightly changed with respect to the undoped crystal [69.1 (5)% on Me1 and 90.0 (3)% on Me2 (Table 2)]. No indications were found for the incorporation of cerium on niobium sites neither from refinement of the site occupation factors nor from the average Nb—O distances (Table 3), as could be expected from the larger radius of cerium (1.01 of Ce^{3+} and 0.87 of Ce^{4+} in octahedral coordination compared with 0.64 Å of Nb^{5+}; Shannon, 1976).

The atomic displacement ellipsoids of the O atoms are anomalously elongated in the average structure either perpendicular (O4 and O5) or parallel (O1, O2 and O3) to the tetragonal **c** axis. All O atoms turned out to be positionally modulated, indicating that the large atomic displacement parameters of the average structure contain a static contribution from the displacive modulations in addition to the thermal vibrations of the atoms. O5 and O4 show the largest amplitudes of the positional modulation of 0.2 Å perpendicular to the tetragonal **c** axis and almost no displacement in the direction of the **c** axis, whereas the amplitudes are largest (up to 0.2 Å) parallel to the **c** axis for O3, O2 and O1 (Fig. 2). The displacive modulations of the O atoms are similar to those reported for KNSBN60 (Surmin *et al.*, 2006).

The Me1 site, like both sites of the Nb atoms, is not strongly affected either by positional (see supplementary material) or occupational modulations. As a consequence, the variation of the bond-valence sum of calcium on the Me1 position is much smaller than that of barium on the Me2 position (Fig. 3). The

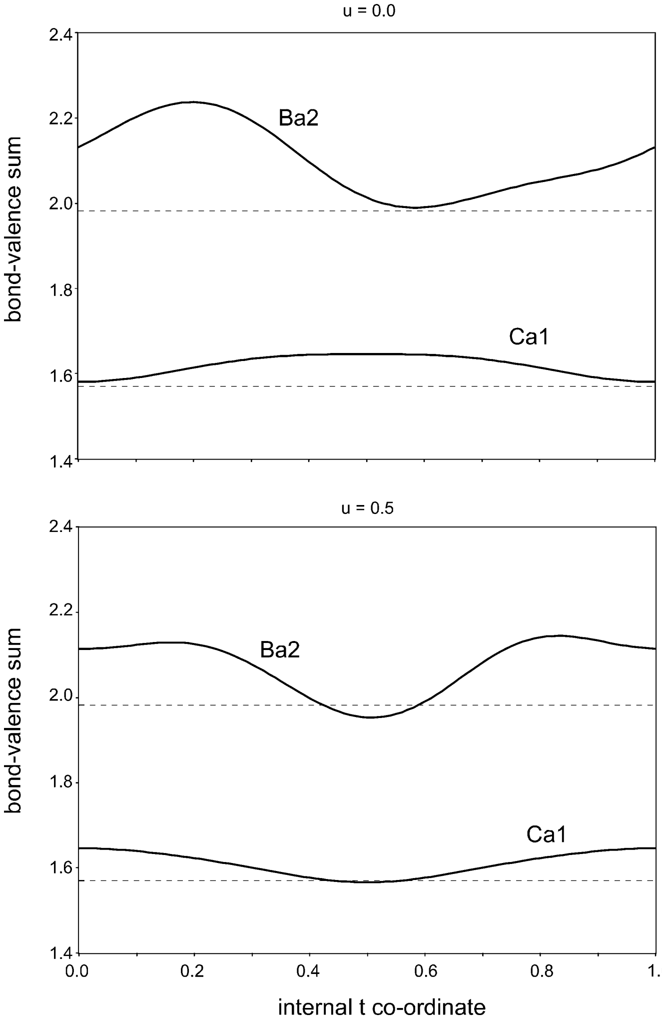

Figure 3
Variation of the bond-valence sum of Ca on the Me1 position and Ba on the Me2 position as a function of the internal *t* coordinate with *u* = 0 and *u* = 0.5. The dashed lines represent the values for an unmodulated average structure.

NbO_6 octahedra are rather stiff with only small variations of the Nb—O distances along the modulation vector (Table 3), but are cooperatively tilted with changes of the inter-octahedral Nb—O—Nb angles of up to ~ 24° (Fig. 4).

A modulation of the occupation of the Me2 site with a small variation of ~ 2% was found together with a very small positional modulation (amplitudes of ~ 0.008 Å perpendicular and ~ 0.006 Å parallel to the *c* axis, Table 4 and Fig. 5). The atomic displacement parameters of Me2 are also modulated (see supplementary material). The modulations seem to be coupled to each other. There is a reciprocal relationship between the modulations of the site occupancy factors and the largest atomic displacement parameters U^{11} (and also U^{22}). Large occupancies correspond to small values of U^{11} and *vice versa*. The positional displacements perpendicular to the **c** axis are either large or small, where the Me2 site occupancy factor changes slope from high to low values (Fig. 5).

Table 4
Amplitudes of the occupational modulation waves of the Me2 site.

Harmonic, $\mathbf{q}_1$, $\mathbf{q}_2$	$Ca_{0.279}Ba_{0.720}Nb_2O_6$	$Ce_{0.023}Ca_{0.249}Ba_{0.720}Nb_2O_6$
Sin,1,0	0.0013 (10)	0.0069 (13)
Cos,1,0	0.0020 (10)	0.0025 (12)
Sin,0,1	0	0
Cos,0,1	−0.0090 (10)	−0.0169 (12)

These observations can possibly be understood by a common origin of the modulations. A wave-like occupation of the Me2 site could be expected to show less thermal vibrations where occupied by heavy barium or cerium cations rather than by calcium or even left vacant. Similarly, the NbO_6 octahedra might be expected to be more strongly tilted (Figs. 4 and 6) where the Me2 sites are vacant or occupied by a smaller cation leading to the rather large positional modulation of the O atoms. The small amplitude of the occupational modulation function at the Me2 site indicates that the wave-like order might not be perfect, although no significant diffuse intensity was observed by X-ray diffraction. Doping with cerium does not appear to significantly affect the modulations.

The Nb atoms are displaced along the **c** axis away from the centres of their coordination octahedra which is considered to be a major cause of the spontaneous electric polarization of ferroelectric TTB (Jamieson *et al.*, 1968). Both symmetrically independent Nb atoms are shifted to the same direction (Fig. 6). The Nb—O distances along the **c** axis differ by 0.36 (2) and

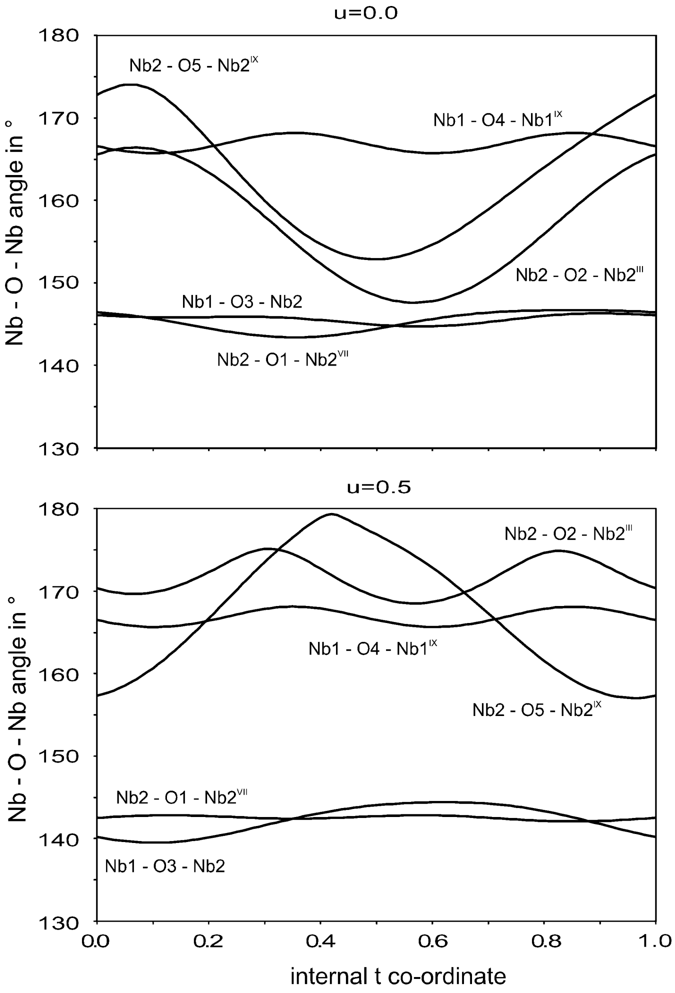

Figure 4
Variation of the inter-octahedral Nb—O—Nb angles along the internal *t* coordinate for *u* = 0 and *u* = 0.5. For symmetry codes see Table 3.

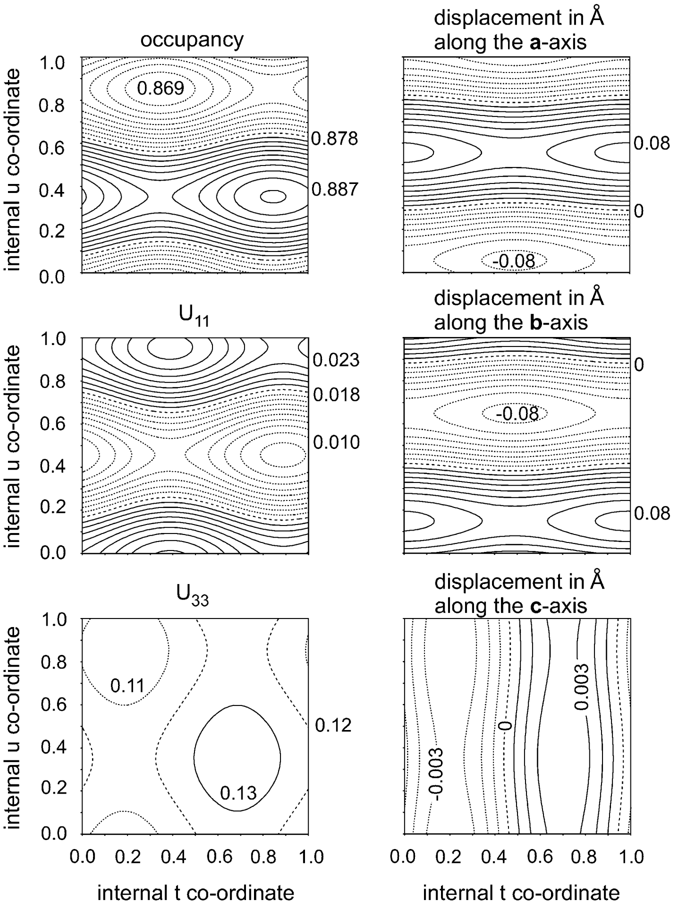

Figure 5
Two-dimensional representations of the variations of occupation by Ba^{2+}, positional and atomic displacement parameters of the Me2 site as functions of the internal *t* and *u* coordinates. Values larger than the average are plotted as solid contours, smaller values as dotted lines.

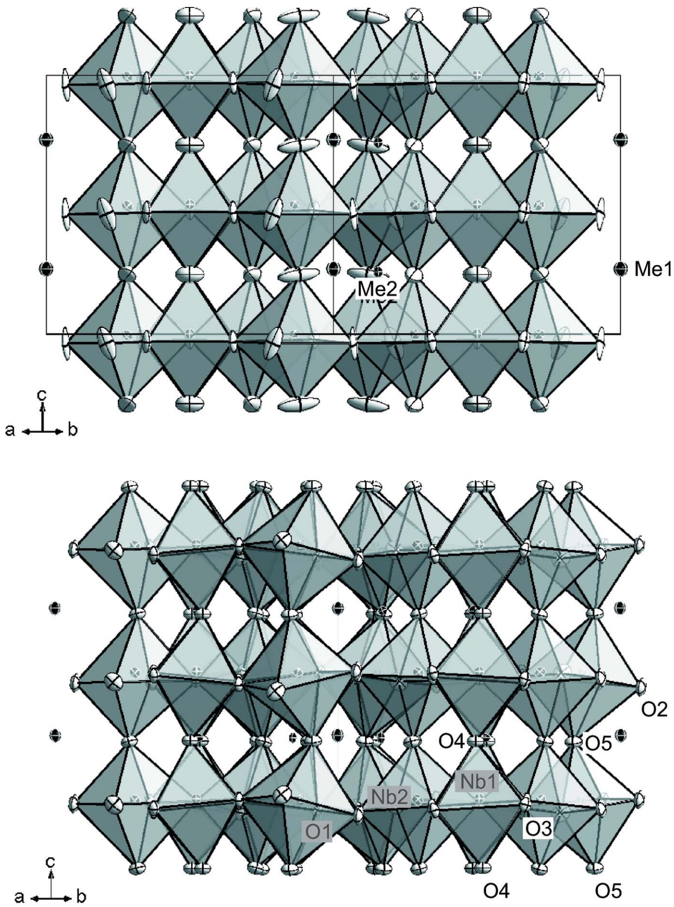

Figure 6
Modulated (bottom) and average (top) structure of tetragonal tungsten bronze type $Ca_{0.28}Ba_{0.72}Nb_2O_6$ projected along the [110] direction. Only a portion of the modulated structure corresponding to the size of the unit cell of the average structure is shown.

0.33 (1) Å for the pairs of Nb1—O4/Nb1—O4^{xiii} and Nb2—O5/Nb2—O5^{xiii} distances of CBN28 (Table 3). The differences are slightly smaller for Ce:CBN28. The differences between the longest and smallest Nb—O distances are hardly affected by the displacive modulations of the apical O4 and O5 atoms. The O1, O2 and O3 atoms forming the equatorial square of the NbO_6 octahedra, however, are strongly involved in positional modulations along the **c** axis. This results in slight shifts of the centres of negative charges so that the electric dipole moment can vary along the modulation vector.

4. Conclusions

The incompletely filled large cation site Me1 [62.4 (3)%] of TTB is predominately occupied by Ca^{2+} [58.81 (2)%] in CBN28 and to a much lesser extent by Ba^{2+} [2.61 (12)%]. The less incompletely occupied Me2 site [93.74 (19)%] mainly contains Ba^{2+} [88.21(7)%] and only a minor amount of Ca^{2+} [5.53 (12)%]. The Me2 site shows an occupational modulation which has previously not been found with isostructural SBN possibly due to the smaller scattering contrast between Sr^{2+} and Ba^{2+} than between Ca^{2+} and Ba^{2+}. The density modulation on the Me2 site is coupled to a small positional modulation with an amplitude of ~ 0.01 Å and a modulation of the atomic displacement parameters. Furthermore, the modulations of the Me2 site appear to induce a displacive modulation of the adjacent O atoms with amplitudes up to 0.2 Å so that the rigid NbO_6 octahedra are cooperatively tilted from their average positions. The Me1 site houses less foreign incorporation and shows hardly any modulation.

The structural modulations persist at temperatures above the transition from the ferroelectric to the paraelectric state (Schneck *et al.*, 1981; Graetsch *et al.*, 2011) so that it might be assumed that the modulations do not disappear until the temperature is high enough to enable enhanced diffusion of the cations. This could finally destroy the wave-like ordered occupation of the Me2 site and the associated displacive modulations of the neighbouring O atoms.

Cerium seems to be built in on both large cation sites {Me1 [2.91 (14)%] and Me2 [1.53 (9)%]} replacing part of the calcium ions in Ce:CBN. The small amount of incorporated cerium does not significantly influence the structural modulations.

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