Ba$_6$CoNb$_9$O$_{30}$ and Ba$_6$FeNb$_9$O$_{30}$: Two New Tungsten-Bronze-Type Ferroelectrics.

Centrosymmetry of Ba$_{5.2}$K$_{0.8}$U$_{2.4}$Nb$_{7.6}$O$_{30}$ at 300 K

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Abstract

Ba$_6$CoNb$_9$O$_{30}$ and Ba$_6$FeNb$_9$O$_{30}$ in space group $P4bm$ are shown to satisfy the structural criteria for ferroelectricity. Ba$_6$CoNb$_9$O$_{30}$ undergoes a diffuse phase transition at 660 (11) K, as observed calorimetrically, in addition to a dielectric permittivity anomaly with an onset temperature of 685 (10) K. The demonstration of dielectric hysteresis at room temperature under the application of a varied DC field reaching a maximum of \( \pm 300 \text{kV m}^{-1} \), corresponding to a spontaneous polarization of \( 1.2 (5) \times 10^{-2} \text{C m}^{-2} \), provides unambiguous verification that it is a new ferroelectric. Ba$_6$FeNb$_9$O$_{30}$ also undergoes a diffuse phase transition at 605 (16) K, with a dielectric anomaly at 583 (5) K, and exhibits dielectric hysteresis at room temperature under a varied DC field ranging to \( \pm 310 \text{kV m}^{-1} \) corresponding to a spontaneous polarization of \( 2.2 (5) \times 10^{-2} \text{C m}^{-2} \); it too is demonstrably a new ferroelectric. Although Ba$_{5.2}$K$_{0.8}$U$_{2.4}$Nb$_{7.6}$O$_{30}$ has also been reported in space group $P4bm$, all atomic displacements from the corresponding centrosymmetric positions are less than their refined root-mean-square thermal or static amplitudes. Such an arrangement is likely to be thermodynamically unstable. Either its space group has been incorrectly assigned, and reinvestigation will show the space group is $P4/mbm$, or the structural refinement is incomplete.

1. Introduction

Analysis of the 209 entries for the 128 different materials reported in the June 1995 version of the Inorganic Crystal Structure Database (Bergerhoff & Brown, 1987) under point group $4mm$ led to the structural prediction of 43 new and eight previously known ferroelectrics (Abrahams, 1996). Among these predictions are the three title materials with tungsten-bronze-type structure listed under space group $P4bm$. The structure of Ba$_6$CoNb$_9$O$_{30}$ was determined by Lehmann & Müller-Buschbaum (1981) (hereafter LMB); that of Ba$_6$FeNb$_9$O$_{30}$ by Brandt & Müller-Buschbaum (1986) (hereafter BMB); and that of Ba$_{5.2}$K$_{0.8}$U$_{2.4}$Nb$_{7.6}$O$_{30}$ by Saine (1988). A standard reference compilation of ferroelectric materials by Nakamura (1990) contains many known and possible ferroelectrics crystallizing in the tungsten-bronze-type structure with a variety of space groups. However, neither Ba$_6$CoNb$_9$O$_{30}$ nor Ba$_{5.2}$K$_{0.8}$U$_{2.4}$Nb$_{7.6}$O$_{30}$ is listed as ferroelectric although Ba$_6$FeNb$_9$O$_{30}$ is reported by Nakamura (1990) to be orthorhombic, with a unit cell four times larger than BMB's, and with permittivity anomalies at 133 and 570 K. The present study reports structural, calorimetric, dielectric permittivity and dielectric hysteresis data that verify the predicted ferroelectric property in Ba$_6$CoNb$_9$O$_{30}$ and Ba$_6$FeNb$_9$O$_{30}$ together with structural evidence that Ba$_{5.2}$K$_{0.8}$U$_{2.4}$Nb$_{7.6}$O$_{30}$ is most likely centrosymmetric at room temperature.

2. Crystal structure and ferroelectricity in Ba$_6$CoNb$_9$O$_{30}$

2.1. Preparation of Ba$_6$CoNb$_9$O$_{30}$

The method described by LMB to prepare Ba$_6$CoNb$_9$O$_{30}$ did not give a product with X-ray powder pattern matching that generated by the LAZY-PULVERIX program (Yvon, Jeitschko & Parthé, 1977) on the basis of the reported unit cell and crystal structure. However, the procedure used by BMB to prepare Ba$_6$FeNb$_9$O$_{30}$, in which Co is substituted for Fe and stoichiometric proportions of Nb$_2$O$_5$ (99.99% pure), CoC$_2$O$_4$.2H$_2$O (96% pure, determined locally) and BaCO$_3$ (99.98% pure), all from Aldrich, are finely ground, mixed, then contained in a Pt crucible and heated in a CM Furnaces Model 1706 furnace under computer control, was successful. After 5 d at 1625 K followed by annealing for 2 d at 775 K, transparent dark yellow (no. 88, NBS Circular 553 Supplement, 1964) single crystals grew from the mix with maximum dimensions \( \approx 1 \text{mm} \), together with crystal aggregates exhibiting a deep reddish-brown (no. 41) coloration. The observed and calculated X-ray powder patterns matched excellently. Unit-cell dimensions from three different single crystals confirmed the identity, with crystal (1) having \( a = 12.605 (2) \), \( c = 4.0063 (5) \); crystal (2) \( a = 12.609 (4) \), \( c = 4.007 (1) \); and crystal (3)
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Table 1. Atomic coordinates for Ba₆CoNb₉O₃₀ at room temperature, hypothetical z' coordinates and polar Δz displacements in Å

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>z'</th>
<th>Δz</th>
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<tr>
<td>Ba1</td>
<td>2(a)</td>
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</tr>
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<td>O3</td>
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<td>0.345</td>
<td>0.008</td>
<td>0.466</td>
<td>0.136</td>
</tr>
<tr>
<td>O4</td>
<td>4(c)</td>
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<td>0.782</td>
<td>0.500</td>
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</tr>
<tr>
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<td>0.069</td>
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<td>0.141</td>
<td>0.069</td>
<td>0.500</td>
<td>0</td>
</tr>
</tbody>
</table>

a = 12.589, c = 4.009 Å in space group P4/bm. Δz = (z – z')c; s.u.'s of atomic coordinates not given by authors.

2.2. Atomic displacements and predicted Tc from the hypothetical paraelectric structure

The atomic coordinates determined by LMB are given in Table 1 in addition to the z' coordinates expected in the paraelectric space group P4/mmb and the corresponding Δz displacement by each atom from its higher symmetry position along the polar direction. The largest Δz magnitude in Table 1 is Δz(Co/Nb1) = 0.176 Å. LMB did not report atomic displacement parameters (ADPs) for Ba₆CoNb₉O₃₀ beyond noting that Uiso(Ba2) is relatively large, nor were uncertainties given [values of B quoted in the literature are replaced throughout this report by Uiso(Ba2) = (B/8π²)¹/² as recommended by Trueblood et al., 1996]. However, ADPs for Ba₆FeNb₉O₃₀ are reported by BMB; apart from Uiso(Ba2) = 0.141 Å, all other r.m.s. thermal or static atomic displacements are less than 0.098 Å. Assuming comparable magnitudes in Ba₆CoNb₉O₃₀, these displacements are less than four corresponding values of Δz in Table 1. Ba₆CoNb₉O₃₀ hence satisfies the structural criteria for ferroelectricity (Abrahams, 1988).

The Co/Nb1 octahedron contains two Co/Nb1–O1 and four Co/Nb1–O3 bonds. The mean z coordinate of this oxygen octahedron is [0.027 + 1.027 + (4 x 0.466)]/6 = 0.4863 and the difference between it and the z coordinate of Co/Nb1, i.e. Δz(Co/Nb1), is then 0.5438 – 0.4863 or 0.231 Å. Assuming the uncertainties in Ba₆CoNb₉O₃₀ are identical to those reported in Ba₆FeNb₉O₃₀, see Table 2, then σ(Δz(Co/Nb1)) = 0.066 Å. The resulting value of Tc(Co/Nb1), from the Abrahams, Kurtz & Jamieson (1968) relationship (hereafter AKJ) is 1060 (520) K rather than the 620 K given by Abrahams (1996). It may be noted that the Co/Nb1–O1 distances quoted by LMB are 2.037 and 1.972 Å, whereas their coordinates in Table 1 correspond to 2.072 and 1.937 Å; the z coordinate of either O1 or Co/Nb1 appears to be in error by 0.011. The Nb2 octahedron contains two Nb2–O2, one Nb2–O3, one Nb2–O4 and two Nb2–O5 bonds; the mean z coordinate of its oxygen octahedron is thus [0.026 + 1.026 + 0.466 + 0.500 + (2 x 0.500)]/6 = 0.5030. The value of Δz(Nb2) = 0.02 (6) Å, hence the predicted AKJ value of Tc is only 8 (105) K and may be disregarded.

Additional numerical inconsistencies between atomic coordinates and interatomic distances are present in LMB's report. The possibility of typographic error leads to wider uncertainty in the predicted Curie temperature. The Ba₆CoNb₉O₃₀ diffraction data have been remeasured (Weakley, 1996) but problems with subsequent refinement remain unresolved.

3.3. Calorimetry

A broad endothermic maximum, characteristic of a diffuse phase transition (see §7.2) at Tc = 660 (11) K, is observed in a Perkin–Elmer Differential Scanning Calorimeter Model DSC-7 on heating Ba₆CoNb₉O₃₀ at a rate of 10 K min⁻¹. This Curie temperature value is the average of 14 separate measurements based on several different preparations and samplings. The associated entropy change, ΔS, is difficult to estimate but has a maximum of 8 J mol⁻¹ K⁻¹ with an average of 5 (4) J mol⁻¹ K⁻¹. A single exothermic anomaly with ΔS approaching 70 (4) J mol⁻¹ K⁻¹ has been observed at 605 K on cooling, suggestive of a transformation from a metastable state to a phase with lower free energy. This large entropy change may be attributable to translational invariance losses associated with substitutional disorder of Co atoms in the B sites, see §7.1, in addition to the possible ‘hopping’ of Co atoms at the transition. The calorimetric results are not independent of prior thermal treatment.
3.2. Dielectric permittivity

Permittivity measurements were made under computer control. An EG&G Princeton Applied Research Model 5210 Lock-in Amplifier provided signal generation over a wide frequency range in addition to phase angle measurement. The circuit included the sample and a reference capacitor of approximately equal value. Samples of dimension ~13 mm diameter and ~2 mm thick were pressed at ~1 GPa and sintered at 1585 K for 24 h, followed by cooling at 10 K h⁻¹. Silver ink (Englehard-CLAL, 1995) electrodes about 10.5 mm diameter were applied to both major faces, leaving an unelectroded frame to eliminate the possibility of fringing fields. The sample holder, modelled on a design of Ravez (1995) as used by Abrahams, Ravez, Simon, Reller & Oswald (1995), was installed in the programmable furnace described in §2.1. The permittivity at 0.1, 1, 10 and 100 kHz remains constant on heating to 685 (10) K whereupon it abruptly starts increasing. The rate of increase is lower at each successively higher frequency. The onset temperature is consistent with the results of §3.1.

3.3. Dielectric hysteresis

Hysteresis measurements were made under computer control as in §3.2. Known DC voltage increments from a Spellman High Voltage Model SL1PN10 supply, with ΔV typically 50 or 100 V, are successively applied to the sample reaching a maximum $V_{\text{max}}$; $-\Delta V$ increments are then applied until $-V_{\text{max}}$ is reached. Additional $+\Delta V$ increments return the sample through zero applied field to $V_{\text{max}}$, thereby completing the cycle and allowing it to be repeated. The voltage across a storage capacitor, approximating the capacitance of the sample, is read at each increment by the Keithley Model 6517 Electrometer to give the charge produced on the sample. A resistor in parallel with the storage capacitor allows for losses due to sample conductivity. Ceramic samples of $\text{Ba}_6\text{CoNb}_9\text{O}_{30}$ at room temperature clearly exhibit hysteresis in fields ranging to a maximum of ±300 kV m⁻¹, as shown in Fig. 1. The spontaneous polarization, $P_s$, may be estimated from Fig. 1, despite the less-than-saturated hysteresis loop, by extrapolation of the almost linear section of the loop at highest field to the polarization axis, giving $P_s \approx 1.2 (5) \times 10^{-2}$ C m⁻² at room temperature, see §§5.3 and 8.

3.4. Ferroelectricity in $\text{Ba}_6\text{CoNb}_9\text{O}_{30}$

The structural prediction of ferroelectricity (Abrahams, 1996) in $\text{Ba}_6\text{CoNb}_9\text{O}_{30}$ is verified by the calorimetric observation of a diffuse phase transition at 660 (11) K, see §3.1; a dielectric anomaly at 685 (10) K, see §3.2; and the exhibition of dielectric hysteresis at room temperature with a spontaneous polarization of $1.2 (5) \times 10^{-2}$ C m⁻², see §3.3.

4. Crystal structure and ferroelectricity in $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$

4.1. Preparation of $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$

The method reported by BMB (cf. §2.1), in which stoichiometric proportions of $\text{Nb}_2\text{O}_5$ (99.99% pure), $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (99.99% pure) and $\text{BaCO}_3$ (99.7% pure), all from Aldrich, are thoroughly mixed, placed in a Pt crucible, heated to 1625 K in air for 5 d, then subjected to an anneal time of 2 d at 775 K, results in the growth of grey yellowish-brown (no. 80, NBS Circular 553 Supplement, 1964) crystals with maximum dimensions of 0.5 mm. An excellent match was obtained between the resulting experimental and calculated X-ray powder diffraction patterns using BMB's structure by use of the LAZY-PULVERIX program (Yvon et al., 1977).

4.2. Atomic displacements and predicted $T_c$ from hypothetical paraelectric structure

The atomic coordinates reported by BMB, the $z'$ coordinates excepted in the paraelectric space group $P4/mmb$, and the corresponding displacement along the polar direction by each atom from its hypothetical higher symmetry position are presented in Table 2. The largest such displacement is 0.141 Å, hence $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ satisfies the structural criteria for ferroelectricity. BMB report the Fe atom to be distributed over both 2(b) and 8(d) Wyckoff positions occupied by the two independent Nb atoms. The Fe1/Nb1 octahedron contains two Fe1/Nb1–O1 and one Fe1/Nb1–O3 bonds, hence the mean oxygen octahedron value of $z = (0.031 + 1.031 + (4 \times 0.494))/6 = 0.5063$. The displacement $\Delta z(\text{Fe1}/\text{Nb1})$ is thus $0.5353 - 0.5063 = 0.1 (7)$ Å, corresponding to $T_c(\text{Fe1}/\text{Nb1}) = 270 (220)$ K on the basis of the AKJ relationship, rather than the 360 K given by Abrahams (1996). The Fe2/Nb2 octahedron contains two Fe2/Nb2–O2, one Fe2/Nb2–O3, one Fe2/Nb2–O4 and two Fe2/Nb2–O5 bonds, hence
this oxygen octahedron has a mean value of 
\[ z = \frac{0.021 + 1.021 + 0.494 + 0.469 + (20.5)}{6} = 0.5008. \] 
The resulting \( \Delta z (\text{Fe}2/\text{Nb}2) \) is 0.4919 – 0.5008, 
\textit{i.e.} 0.04(6) Å. The corresponding value of \( T_c \) from 
\( \Delta z (\text{Nb}2) \) is only 25 (165) K and may be neglected. The 
predicted value of \( T_c \) from either independent Fe/Nb atom 
is below room temperature, although that from 
Fe1/Nb1 has a large uncertainty; both predicted \( T_c \) and 
space group assignment are consistent with the results in 
§5 but the former would be more reliable with higher-
accuracy atomic positions.

5. Calorimetric and dielectric measurement of 
\( \text{Ba}_6\text{FeNb}_9\text{O}_{30} \)

5.1. Calorimetry

Heating \( \text{Ba}_6\text{FeNb}_9\text{O}_{30} \) under the conditions of §3.1

gives rise to a broad endothermic maximum similar to 
that produced by \( \text{Ba}_6\text{CoNb}_9\text{O}_{30} \) and similarly char-
acteristic of a diffuse phase transition at \( T_c = 605 (16) \) K, 
see also §7. The estimated maximum associated entropy 
change \( \Delta S \) is 5 J mol\(^{-1}\) K\(^{-1}\), with an average of 
3(2) J mol\(^{-1}\) K\(^{-1}\). Several small but irreproducible 
exothermic thermal anomalies, with \( \Delta S < 0.1 \) J mol\(^{-1}\) K\(^{-1}\), are observable below \( T_c \) in some calorimetric runs, 
see §7.2.

5.2. Dielectric permittivity

Samples prepared as in §3.2, with comparable dimensions, led to the dielectric permittivity results at 
100 Hz shown in Fig. 2; the dielectric anomaly remains 
readily observable over the frequency range 50–1000 Hz 
at about the same temperature. The peak at 583 (5) K

closely matches an earlier report by Ismailzade, 
Huseynov, Sultanov & Hajiyev (1976) who found a 
permittivity maximum in \( \text{Ba}_6\text{FeNb}_9\text{O}_{30} \) at \( \sim 570 \) K but
reported the material to have orthorhombic symmetry, 
see Table 4.

5.3. Dielectric hysteresis

A typical polarization hysteresis loop in 
\( \text{Ba}_6\text{FeNb}_9\text{O}_{30} \), measured with maximum DC fields of 
\( \pm 310 \) kV m\(^{-1}\), is shown in Fig. 3. The spontaneous 
polarization may be estimated from 
Fig. 3 as \( 2.2 (5) \times 10^{-2} \) C m\(^{-2}\) at room temperature, see 
§§3.3 and 8.

5.4. Ferroelectricity in \( \text{Ba}_6\text{Nb}_9\text{O}_{30} \)

The prediction of ferroelectricity in \( \text{Ba}_6\text{FeNb}_9\text{O}_{30} \) by 
structural analysis (Abrahams, 1996) is confirmed by the 
calorimetric observation reported in §5.1 of a diffuse 
phase transition at 605 (16) K, by a dielectric anomaly at 
583 (5) K, see §5.2, and by the exhibition of dielectric 
hysteresis at room temperature with a spontaneous 
polarization of \( 2.2 (5) \times 10^{-2} \) C m\(^{-2}\), see §5.3.

6. Centrosymmetric \( \text{Ba}_{5.2}\text{K}_{0.8}\text{U}_{2.4}\text{Nb}_{7.6}\text{O}_{30} \)

6.1. Reported structure

An examination of the atomic coordinates reported by 
Saine (1988), see Table 3, indicates no atom in 
\( \text{Ba}_{5.2}\text{K}_{0.8}\text{U}_{2.4}\text{Nb}_{7.6}\text{O}_{30} \) is further than 0.122 Å from 
the position it would occupy if the space group were 
P4/mbm. This maximum departure from cen-
trosymmetry is by the U1/Nb1 atom in Wyckoff position 
2(b), with a reported root-mean-square (r.m.s.) magni-
tude \( U_{1/2} = 0.148 \) Å. The range, of \( U_{1/2} \) for the 
remaining atoms is 0.127 – 0.156 Å, with \( \Delta z < U_{1/2} \) 
for each atom. If the \( U_{1/2} \) magnitudes reported were 
correct, the atomic arrangement would be thermo-
dynamically unstable since its energy would be mini-
mized by a transformation to the centrosymmetric phase 
as is the case for ferroelectric crystals at or above their 
ferroelectric–paraelectric phase-transition temperature.
The most likely space group at room temperature in that case would be $P4/mbm$. However, disorder in the content of both $A$ and $B$ sites, see §7.2, together with the wide range in scattering between $U$ and $O$, led to difficulties in refinement.

If the space-group assignment and reported coordinates were correct, then the mean $z$ coordinate for the $U1/Nb1$ oxygen octahedron would be $[0.0013 + 1.0013 + (4 \times 0.4843)]/6 = 0.4900$, for a displacement $\Delta z(U1/Nb1)$ of 0.5304 $- 0.4900$, i.e. 0.04 $\AA$, with corresponding predicted $T_c(U1/Nb1)$ of 525 (150) K. Similarly, $\Delta z(U2/Nb2)$ would be 0.04 $\AA$ with a predicted $T_c(U2/Nb2)$ of only 32 (75) K, and hence negligible. Until redetermination of the crystal structure settles the space-group choice, the presumption of centrosymmetry must be favored as noted by Marsh (1995), particularly in view of odds estimated as no better than about 1 in 12 (Abrahams et al., 1997) against a given inorganic crystal possessing a polar axis.

### 7. The ferroelectric tungsten-bronze-type oxides

#### 7.1. General

All known ferroelectric-tungsten-bronze-type oxide ferroelectrics listed by Nakamura (1990) crystallize either in the tetragonal system, with structure comparable to that of the three present materials and $a \approx 12.6, c \approx 4.0 \AA$, or in one of several closely related variants within the orthorhombic system. If the latter applies, then the orthorhombic $a$ and $b$ axes may be almost identical at $\sim 12.6 \AA$ or either or both axes may be $n^{2/12}$ multiples ($n = 1,2$) of this basic value. The $c$ axis may also be doubled in length. Among the orthorhombic space groups reported are $Bb2_m, Bm2m$ and $Pba2$; the space group of many family members at ambient temperatures has not yet been definitively assigned, see Table 4. Each known ferroelectric-tungsten-bronze-type oxide undergoes a transition to a centrosymmetric phase at a higher temperature. Further investigation is necessary to determine which of the unassigned tungsten-bronze-type oxides may be ferroelectric, with potential device value.

The basic framework formed by the NbO$_6$, TiO$_6$ or TaO$_6$ octahedra in the ferroelectric tetragonal tungsten bronzes has been described by Abrahams, Jamieson & Bernstein (1971). With general chemical formula $(A1)_{x}(A2)_yC_d(B1)_z(B2)_wO_{30}$, the $A1$ atom in the Wyckoff $2(a)$ site is twelve-coordinated, the $A2$ ($4c$) and $C$ ($4c$) sites are nine-coordinated and both $B1$ ($2b$) and $B2$ ($8d$) sites are six-coordinated. In the two present ferroelectric materials, both $A1$ and $A2$ sites are reported to be fully occupied by Ba, the $C$ site remaining vacant; in Ba$_6$CoNb$_9$O$_{30}$ the Co$^{3+}$ ion has been assigned to the $B1$ site, see Table 1, whereas in Ba$_6$FeNb$_9$O$_{30}$ the Fe$^{3+}$ ion was assigned to both $B1$ and $B2$ sites, see Table 2. Further investigation of this difference in assignment may be justified. Both 3$d^{10}$ ions have radii about 0.1 $\AA$ less than that of Nb$^{5+}$, opening opportunities for long-range order variations among the $B$ site occupancies that may lead to the diffuse phase transitions observed in the two materials, see also §7.2. In Ba$_6$K$_{0.8}$U$_2$4Nb$_{7.6}$O$_{30}$ the $A1$ site in addition to both $B1$ and $B2$ sites is described as disordered.

#### 7.2. Diffuse phase transition in tetragonal tungsten-bronze-type ferroelectrics

Phase-transition broadening, common in many solid solutions [see Lines & Glass (1977) for a review], often originates in structural disorder and compositional variations. Sharp phase transitions characteristic of systems with translational invariance are expected to broaden as the compositional disorder in a system increases, thereby leading to a degradation of the invariance. The degree of translational variance among $B$-site ions in Ba$_6$CoNb$_9$O$_{30}$ and Ba$_6$FeNb$_9$O$_{30}$ is likely to be a function of thermal annealing conditions. Departures from stoichiometry are possible in both materials and have not been investigated. The large exothermic entropy changes found are indicative of 'hopping' by the Co and Fe atoms among the $B$ sites at $T_c$. Diffuse phase transitions have been widely reported in such technologically important tetragonal tungsten-bronze-type ferroelectrics as Ba$_6$Sr$_5$Nb$_{10}$O$_{30}$ (BSN), Ba$_4$Na$_2$Li$_4$Nb$_{10}$O$_{30}$ (BNN) and K$_{6-x}$Li$_{4+x}$Nb$_{10+y}$O$_{30}$ (KLN), see Nakamura (1990). Cooling either Ba$_6$CoNb$_9$O$_{30}$ or Ba$_6$FeNb$_9$O$_{30}$ rapidly from high temperatures occasionally produces an exotherm which may be attributable to the resulting range of compositional disorder among the Co or Fe atoms and subsequent formation of a free energy barrier between the high temperature $P4/mmb$ and the stable $P4bnm$ phases. The resulting thermal spread in specific heat and permittivity
maxima observed on heating leads to an extended range in Curie temperature.

8. Spontaneous polarization
Calorimetric and dielectric verification of the structurally predicted property of ferroelectricity in $\text{Ba}_6\text{CoNb}_9\text{O}_{30}$ and $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ (Abrahams, 1996), is provided in §8.3 and 5. The measured values of $P_s$ in these two materials, however, are among the lowest reported for tungsten-bronze-type oxide ferroelectrics. Values of $P_s$ collated by Nakamura (1990) range from $45 \times 10^{-2} \text{ C m}^{-2}$ for $\text{Pb}_2\text{RbNb}_3\text{O}_{15}$ to $0.1 \times 10^{-2} \text{ C m}^{-2}$ for ceramic $\text{NaCsEuNb}_3\text{O}_{15}$; the next-largest reported value of $P_s$ is $15 \times 10^{-2} \text{ C m}^{-2}$ for $\text{Ba}_4\text{BiO}_{33}\text{R}_5\text{O}_{15}$. Lack of saturation in either the $\text{Ba}_6\text{CoNb}_9\text{O}_{30}$ or the $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ hysteresis loops indicates the values measured on these ceramic samples are too low. Ferroelectrics such as the tungsten-bronze-type oxides, in which the major atomic displacements undergone as the spontaneous polarization is reversed are parallel to the polar axis, have been classified as one-dimensional ferroelectrics (Abrahams & Keve, 1971). A characteristic of all such materials reported prior to 1971 was their range in $P_s$ from $\sim 25$ to $\sim 75 \times 10^{-2} \text{ C m}^{-2}$. Neglecting the value of $P_s$ in ceramic $\text{NaCsEuNb}_3\text{O}_{15}$ as also too low due to unsaturated hysteresis, the minimum in the ferroelectric tungsten-type oxides may be taken as no lower than $\sim 15 \times 10^{-2} \text{ C m}^{-2}$. Remeasurement using single crystals and higher electric fields is expected to increase the two present measured values of $P_s$.

9. Magnetic spin ordering
The nominal presence of $3d^{3+}$ ions in $\text{Ba}_6\text{CoNb}_9\text{O}_{30}$ and $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ opens the possibility of magnetic spin ordering and potential coupling with the ferroelectricity. Ismailzade et al. (1976) measured the magnetic susceptibility of $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ between 80 and 300 K and reported an effective magnetic moment of $4.3 \mu_B$, consistent with the presence of $\text{Fe}^{3+}$ ions. A change in slope of the inverse magnetic susceptibility at $\sim 110$ K, and the corresponding negative Curie constant, suggests an antiferromagnetic interaction below room temperature. Magnetic spin ordering has not been reported at higher temperatures, hence coupling with ferroelectric ordering appears unlikely.

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Note added in proof: Following acceptance of the present paper, we became aware of work by Krainik, Isupov, Bryzhina & Agranovskaya (1964) in which $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ was reported to have crystal lattice parameters $a = 17.95$, $b = 17.95$ and $c = 7.98$ Å (confirming a report by Ismailzade, 1963), with a dielectric anomaly maximum at 133 K and a poorly-formed hysteresis loop observable at 77 K. The latter assumed the tetragonal symmetry at room temperature to be characteristic of the paraelectric phase. We have not investigated $\text{Ba}_6\text{FeNb}_9\text{O}_{30}$ at low temperatures.

References