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Structure and Antiferroelectric Properties of Cesium Niobate, Cs<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub>

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## Abstract

The compound cesium niobate,  $\text{Cs}_2\text{Nb}_4\text{O}_{11}$ , is an antiferroelectric, as demonstrated by double hysteresis loops in the electric-field versus polarization plot. The crystal structure refinement by X-ray diffraction at both 100 and 297 K shows it to have a centrosymmetric structure in point group  $m\bar{3}m$  and orthorhombic space group  $Pnna$ , which is consistent with its antiferroelectric behavior. The 100-K data is reported herein. The lattice is comprised of niobium-centered tetrahedra and octahedra connected through shared vertices and edges; cesium atoms occupy channels afforded by the three-dimensional polyhedral network. The critical field for onset of ferroelectric behavior in a single-crystal sample is 9.5 kV/cm.

Keywords: Structure, X-ray Diffraction, Antiferroelectricity

## 1. Introduction

Cesium niobate (or CNO), which has the chemical formula  $\text{Cs}_2\text{Nb}_4\text{O}_{11}$ , was first reported as a component of the  $\text{Cs}_2\text{O}/\text{Nb}_2\text{O}_5$  phase diagram by Reisman and Mineo in 1961 [1], and the crystal structure was subsequently refined in the polar point group  $\text{mm}2$  and noncentrosymmetric space group  $\text{Pnn}2$  by Gasperin in 1981 [2]. Kharitonova et al. studied its physical properties [3] and reported it to have a ferroelectric-type phase transition at  $164^\circ\text{C}$  with little temperature hysteresis, from which they surmised the transition to be second-order. It has also recently been reported to be a photocatalyst for the decomposition of water [4].

As part of our on-going investigation into ferroelectrics and high-dielectric materials, we embarked on a project to further investigate the reported ferroelectric transition and explain its origin. In the course of this project, we confirmed the transition at  $165^\circ\text{C}$  from the temperature dependence of complex capacitance, impedance, and polarized Raman spectra of a single-crystal sample [5]. Upon examination of the room-temperature hysteresis, however, we were surprised to observe a double hysteresis loop indicative of an antiferroelectric rather than the single loop indicative of a ferroelectric material.

Ferroelectricity requires a noncentrosymmetric structure in a polar point group, but antiferroelectricity requires a nonpolar point group. The reported structure of CNO in space group  $\text{Pnn}2$  (and polar point group  $\text{mm}2$ ) would therefore be incorrect if CNO were antiferroelectric.

Because of these conflicting results, we sought to resolve the matter by conducting a second harmonic generation (or SHG) experiment. A second harmonic can only be produced from noncentrosymmetric materials and can be viewed as a necessary result of such materials. The results of the SHG experiment were negative, so we decided to determine the actual

structure and space group through our own single-crystal refinement, which is reported herein along with the antiferroelectric hysteresis results. Crystal structure refinement at 100 K and room temperature showed the material to be in the nonpolar point group  $mmm$  and space group  $Pnna$ .

## 2. Experimental

### X-ray Diffraction and Structure Refinement

Large single crystals of CNO were grown from the binary system using the flux method, the details of which have been described elsewhere [3]. From a larger crystal mass, we cut a block-shaped single crystal with dimensions 0.07 x 0.12 x 0.17 mm and mounted it on a 20-micron Hampton CryoLoops for subsequent X-ray diffraction data collection. Geometry and intensity data were obtained at 100 K and 297 K on a Bruker diffractometer equipped with a SMART Apex CCD area detector and Oxford Cryosystems 700 cooler [6]. Both data sets yielded the same results, and only the 100-K data and refinement are reported herein. Radiation was monochromatic Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ). Data were collected with the  $\omega$ -scan method.

Data were processed with the SAINT+ program [7] for reduction and cell refinement. Multi-scan absorption corrections were applied to data sets by the SADABS program [8]. The structure was solved by direct methods and refined using SHELXTL [9]. Systematic absences (including that for the  $a$ -glide) unambiguously indicated space group  $Pnna$ . All atoms were refined with anisotropic displacement parameters. Crystal data and refinement results are listed in Table 1. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: [crysdata@fiz.karlsruhe.de](mailto:crysdata@fiz.karlsruhe.de)) on quoting the depository number CSD ###.

## Ferroelectric Hysteresis

Electric-field dependence of polarization was measured with a Radiant Technology Precision LC ferroelectric tester with a Trek signal amplifier. Gold films were sputtered on a single crystal as electrodes on both faces normal to the *c* axis, which is the polarization axis. The electric field applied was  $-12.5$  to  $12.5$  kV/cm and 1 Hz.

## 3. Results

Atomic coordinates and isotropic thermal coefficients for the 100-K refinement are shown in Table 2. A view of the structure is shown in Fig. 1.

The structural motif of CNO in our refinement is very similar to that reported in reference 2, though in a different space group. The structure is comprised of niobium-centered tetrahedra and octahedra connected through shared vertices and edges. Cesium atoms occupy channels afforded by the three-dimensional polyhedral network. The structure is of a type derived from pyrochlore, as has already been reported [2].

Average tetrahedral Nb–O bond distances are  $1.85 \pm 0.04$  Å, and average octahedral Nb–O bond distances are  $2.00 \pm 0.12$  Å. These values compare well with the expected values of 1.88 and 2.04 Å, respectively, derived from the ionic radii reported by Shannon [10]. The polyhedra are fairly regular: tetrahedral bond angles range from 106.8 to 110.6°, and octahedral bond angles for adjacent atoms range from 74.6 to 105.5°, with most within a few degrees of the ideal. The cesium atoms are twelve and ten-coordinate with average Cs–O bond distances of  $3.50 \pm 0.22$  Å and  $3.35 \pm 0.27$  Å, respectively. These are slightly larger than the expected values of 3.28 and 3.21 Å. Table 3 lists some selected bond distances and angles.

Fig. 2 displays the electric-field dependence of polarization at room temperature for CNO. It clearly exhibits double hysteresis loops, which are the basic characteristics of an antiferroelectric material. Generally, an antiferroelectric crystal has a zero net switchable dipole moment due to the antiparallel alignment of elementary dipoles in its unit cell [11]. When the external electric field is weak, the induced polarization is proportional to the field and exhibits no macroscopic polarization hysteresis. When the electric field exceeds a threshold value, called the critical field, the crystal becomes ferroelectric and the polarization displays hysteresis with respect to the field. A hysteresis loop also forms in the negative field, the two loops being associated with antiparallel dipoles in adjacent unit-cell sublattices. From the hysteresis loops in Fig. 2, we deduce the critical field to be 9.5 kV/cm for CNO.

#### 4. Discussion

The symmetry considerations of ferroelectricity have been described by Zheludev [12], to which we direct the interested reader for a more thorough treatment. What follows herein is a short summary of these considerations and how they pertain to our experimental results.

Ferroelectric materials must have structures in one of the ten polar point groups, i.e., those with a unique polar axis. These point groups are 1, 2, m, mm2, 3, 3m, 4, 4mm, 6, and 6mm. Antiferroelectric materials, in contrast, must be in one of the eleven centrosymmetric, nonpolar point groups:  $\bar{1}$ , 2/m, mmm,  $\bar{3}$ ,  $\bar{3}m$ , 4/m, 4/mmm, m $\bar{3}$ , m $\bar{3}m$ , 6/m, and 6/mmm. (We also note that while the symmetry considerations are requirements for the respective ferroelectric properties, they are not sufficient for the property to occur.)

In accordance with the preceding symmetry considerations, the structure for CNO reported in the literature (i.e., in point group mm2 and space group Pnn2) could be correct if the

material were a ferroelectric though not if it were an antiferroelectric. It is therefore crucial to examine the crystallographic evidence as to which point group and space group is correct. We assert that the correct point group is mmm and the correct space group is Pnna. Our reasons are as follows.

First, the systematic absences from our two data sets are the same as the literature report except that ours also include absences for an a-glide plane, i.e.,  $hk0, h = 2n + 1$ . The only space group possible with such a combination is Pnna (no. 52) in point group mmm.

Second, when we attempted to refine the structure in Pnn2, the refinement would not converge and the thermal ellipsoids became non-positive definite. Nonsensical thermal ellipsoids are frequently due to choosing an incorrect space group [13], as we believe was done in the previous structure report.

Third, the literature structure reports tetrahedral Nb–O bond lengths that vary from 1.74 to 1.93 Å while in our structure the same bond lengths are 1.817 to 1.884 Å, a more narrow distribution. Regular bond lengths and angles are a major factor in the evaluation of the “correctness” of a structure, along with such refinement criteria as residuals and goodness of fit, so the structure reported herein is superior in this regard as well.

Finally, the presence of certain physical properties, such as pyroelectricity or second harmonic generation, are conclusive proofs for certain structural aspects of materials. For example, *lack* of a second harmonic generation may be due to a very small nonlinear coefficient in a noncentrosymmetric space group rather than the actual presence of a center of symmetry, but the *presence* of a second harmonic generation is proof for a noncentrosymmetric structure. In the case of CNO, the presence of the antiferroelectric hysteresis requires the structure to be in a nonpolar point group (such as mmm) and a space group derived therefrom.

Antiferroelectricity (as well as ferroelectricity) is partially due to long-range interactions between microscopic dipoles created by atomic displacements within the lattice. Usually, a group theoretical treatment can be applied to obtain local distortions about a particular Wyckoff position within a crystal lattice, which would allow one to determine the atomic displacements that produce the antiferroelectric phase from the paraelectric phase. We shall describe this treatment, as well as the high-temperature paraelectric structure of CNO (which has not yet been refined), in a separate report.

The study of antiferroelectricity in solid materials is fairly sparse, and the number of reported solid-state antiferroelectrics few, although antiferroelectricity in liquid crystals is a field of growing interest because of their ability to switch rapidly between three stable states in optical displays [14]. Some examples of solid-state antiferroelectric materials studied recently include  $\text{Sr}_9\text{In}(\text{PO}_4)_7$  [15],  $\text{BaFCl}$  [16], and  $\text{PbZrO}_3$  [17], the last of which has been studied extensively, along with solid solutions pertaining thereto. CNO is thus a noteworthy addition to the field of study.

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Table 1

Crystallographic data for Cs<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub>.

Formula mass (amu)	813.46
Space group	Pnna (No. 52)
a (Å)	7.46660(10)
b (Å)	28.9047(4)
c (Å)	10.48570(10)
V (Å <sup>3</sup> )	2263.02(5)
Z	8
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	4.775
Temperature (K)	100(2)
Crystal dimensions (mm)	0.16 x 0.12 x 0.07
Radiation	Graphite monochromated Mo K $\alpha$ , $\lambda = 0.71073$ Å
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	10.336
Transmission factors	0.2886-0.5315
2 $\theta$ limits	2.82° $\leq$ 2 $\theta$ (Mo K $\alpha$ ) $\leq$ 55.98°
Data collected	-9 < h < 9, -38 < k < 38, -13 < l < 13
No. of data collected	28,176
No. of unique data	2728
R <sub>int</sub>	0.0300
No. of variables	156
R(F) for F <sub>o</sub> <sup>2</sup> > 2 $\sigma$ (F <sub>o</sub> <sup>2</sup> )	0.0172
R <sub>w</sub> (F <sub>o</sub> <sup>2</sup> )	0.0473
Goodness of fit	1.118
( $\Delta\rho$ ) <sub>max</sub> , ( $\Delta\rho$ ) <sub>min</sub> (e Å <sup>-3</sup> )	0.941, -0.849

Table 2

Atomic coordinates and equivalent isotropic displacement parameters for Cs<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub>.

atom	Wyckoff position	x	y	z	U <sub>eq</sub> (Å <sup>2</sup> ) <sup>a</sup>
Cs(1)	8e	0.7552(1)	0.1924(1)	0.1230(1)	0.014(1)
Cs(2)	8e	0.7522(1)	0.0756(1)	0.3535(1)	0.010(1)
Nb(1)	4c	¼	0	0.2312(1)	0.005(1)
Nb(2)	4d	0.2401(1)	¼	¼	0.006(1)
Nb(3)	8e	0.2455(1)	0.1253(1)	0.2613(1)	0.005(1)
Nb(4)	8e	0.5015(1)	0.0613(1)	0.0018(1)	0.005(1)
Nb(5)	8e	0.5164(1)	0.1883(1)	0.4887(1)	0.005(1)
O(1)	8e	0.0615(3)	0.0998(1)	0.1335(2)	0.008(1)
O(2)	8e	0.0650(3)	0.1368(1)	0.3778(2)	0.007(1)
O(3)	8e	0.0645(3)	0.2335(1)	0.3749(2)	0.007(1)
O(4)	8e	0.2493(2)	0.0517(1)	0.3298(2)	0.007(1)
O(5)	8e	0.2481(2)	0.1844(1)	0.1859(2)	0.007(1)
O(6)	8e	0.4525(3)	0.0002(1)	0.1241(2)	0.006(1)
O(7)	8e	0.4392(3)	0.1002(1)	0.1330(2)	0.008(1)
O(8)	8e	0.4362(3)	0.1365(1)	0.3761(2)	0.007(1)
O(9)	8e	0.4365(3)	0.2340(1)	0.3727(2)	0.007(1)
O(10)	8e	0.7508(2)	0.0529(1)	0.0514(2)	0.008(1)
O(11)	8e	0.7529(2)	0.1854(1)	0.4352(2)	0.007(1)

<sup>a</sup> U<sub>eq</sub> is defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor.

Table 3

Selected bond distances and angles for Cs<sub>2</sub>Nb<sub>4</sub>O<sub>11</sub>; < > indicates the average bond length.

bond	distance (Å)	bond	distance (Å)
Nb(1)–O(4)	1.817(2) x 2	Nb(4)–O(1)	1.858(2)
Nb(1)–O(6)	1.884(2) x 2	Nb(4)–O(6)	2.214(2)
< Nb(1)–O >	1.85 ± 0.04	Nb(4)–O(6)	2.240(2)
Nb(2)–O(3)	1.913(2) x 2	Nb(4)–O(7)	1.837(2)
Nb(2)–O(5)	2.013(2) x 2	Nb(4)–O(10)	1.948(2)
Nb(2)–O(9)	2.005(2) x 2	Nb(4)–O(10)	1.968(2)
< Nb(2)–O >	1.98 ± 0.05	< Nb(4)–O >	2.01 ± 0.18
Nb(3)–O(1)	2.056(2)	Nb(5)–O(1)	2.074(2)
Nb(3)–O(2)	1.849(2)	Nb(5)–O(1)	1.971(2)
Nb(3)–O(4)	2.247(2)	Nb(5)–O(1)	1.998(2)
Nb(3)–O(5)	1.881(2)	Nb(5)–O(1)	1.892(2)
Nb(3)–O(7)	2.105(2)	Nb(5)–O(1)	1.855(2)
Nb(3)–O(8)	1.892(2)	Nb(5)–O(1)	2.125(2)
< Nb(3)–O >	2.01 ± 0.16	< Nb(5)–O >	1.96 ± 0.10
bonds	angle (°)		
O(4)–Nb(1)–O(4)	110.62(13)		
O(4)–Nb(1)–O(6)	109.83(8) x 4		
O(6)–Nb(1)–O(6)	106.81(13)		

## Figure Captions

Fig. 1 View of the CNO structure along the a axis. Large atoms are Cs, small atoms are O.

Fig. 2 Electric-field dependence of polarization for CNO at room temperature.