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Effect of non-isoelectronic cation substitution on lattice parameters of barium sodium niobate

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Ceramic samples of $Ba_2NaNb_5O_{15}$, with the cations selectively substituted by Gd or Cr, showed that the changes in their orthorhombic lattice parameters *a*, *b*, and *c* were linearly correlated to each other. The changes in lattice parameters in the *a*, *b*, and *c* directions occurred proportionally in the ratio of 2.5 : 3.27 : 1.0.

1. Introduction

Barium sodium niobate has a tungsten bronze structure [1]. In this structure, NbO_6 octahedra are connected by corner oxygen ions with each oxygen shared by two niobium ions. The Nb to O ratio is therefore 1:3. In the (001) plane, the NbO_6 octahedra link together into rings of 3, 4 and 5 octahedra. The sites enclosed by rings of 3, 4, and 5 octahedra are given the site symbols γ, α and β, respectively. Each unit cell contains ten formula units of $Ba_2NaNb_5O_{15}$. In the unit cell of $Ba_2NaNb_5O_{15}$ all the α and β are completely occupied. Two α sites are occupied by Na and four β sites are occupied by Ba; all four γ-sites are vacant. In this structure, ten NbO_6 octahedra in each unit cell require ten positive ionic charges by the modifying A type ($A^+A_2^{2+}Nb_5O_{15}$) cations. $Ba_2NaNb_5O_{15}$ is orthorhombic at room temperature and transforms to a tetrahedral modification at 260° C, becoming paraelectric at the curie temperature of 560° C.

The present investigation is to study the effects of substituted cations of different ionic sizes and electronic structures on the lattice parameters of $Ba_2NaNb_5O_{15}$. The substituted cations in our study are Gd^{3+} (ionic radius = 0.97 Å) and Cr^{3+} (ionic radius = 0.63 Å). The ionic radius of Gd^{3+} is between the ionic radii of Ba^{2+} (ionic radius = 1.34 Å) and Na^+ (ionic radius = 0.94 Å). On the other hand, the ionic radius of Cr^{3+} is smaller than ionic radii of both Ba^{2+} and Na^+. Substitutions of Gd^{3+} or Cr^{3+} were made at 0.05 mole and 0.1 mole. Two kinds of substitution were made in this study. In one case, an atom-for-atom substitution was made so that the electrical neutrality was maintained by the addition of oxygen ions and these compositions are called anion-compensated, such as those listed as Type A and Type C of cation substitution in Table I. In the other case, substitution was made such that the oxygen stoichiometry and the electrical neutrality were maintained by the cation substitutions. These compositions are called cation-compensated, such as those listed as Types B and D in Table I. This paper reports on the effect of these types of Gd^{3+} or Cr^{3+} ion substitutions on the lattice parameters of $Ba_2NaNb_5O_{15}$.

2. Experimental procedures

(a) Sample preparation: Conventional ceramic processing was used to prepare the niobate samples.

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TABLE I Nominal compositions for the gadolinium and chromium doped barium sodium niobates

Code number	Formula	Type of substitution
Single crystal S.C.	$Ba_2NaNb_5O_{15}$	
Gd-doped samples		
Gd–A1	$Ba_{1.9}NaGd_{0.1}Nb_5O_{15.05}$	A
Gd–A2	$Ba_2Na_{0.9}Gd_{0.1}Nb_5O_{15.10}$	A
Gd–A3	$Ba_{1.95}Na_{0.95}Gd_{0.1}Nb_5O_{15.075}$	A
Gd–B1	$Ba_{1.9}Na_{1.05}Gd_{0.05}Nb_5O_{15}$	B
Gd–B2	$Ba_2Na_{0.9}Gd_{0.03}Nb_5O_{15}$	B
Gd–B3	$Ba_{1.95}Na_{0.95}Gd_{0.05}Nb_5O_{15}$	B
Gd–B4	$Ba_{1.85}NaGd_{0.1}Nb_5O_{15}$	B
Gd–B5	$Ba_2Na_{0.7}Gd_{0.1}Nb_5O_{15}$	B
Gd–B6	$Ba_{1.9}Na_{0.9}Gd_{0.1}Nb_5O_{15}$	B
Cr-doped samples		
Cr–A1	$Ba_{1.9}NaCr_{0.1}Nb_5O_{15.05}$	C
Cr–A2	$Ba_2Na_{0.9}Cr_{0.1}Nb_5O_{15.1}$	C
Cr–A3	$Ba_{1.95}Na_{0.95}Cr_{0.1}Nb_5O_{15.075}$	C
Cr–B1	$Ba_{1.9}Na_{1.05}Cr_{0.05}Nb_5O_{15}$	D
Cr–B2	$Ba_2Na_{0.9}Cr_{0.03}Nb_5O_{15}$	D
Cr–B3	$Ba_{1.95}Na_{0.95}Cr_{0.05}Nb_5O_{15}$	D

X-ray diffraction technique was used to insure the completeness of the chemical reactions.

(b) Lattice parameter measurements: X-ray measurements were made on powdered samples using a G.E. XRD-5 diffractometer. A precise determination of the orthorhombic lattice parameters, a, b, and c from the X-ray powder data was done, based on the Vogel and Kempter method [4]. The Vogel and Kempter method employs the convergent iterative procedure. A computer program on this method was kindly supplied to us by Dr Charles P. Kempter of Las Alamos Scientific Laboratory.

3. Results

The measured lattice parameters a, b and c, and from them, the unit cell volumes V, of sixteen niobate compounds (including the single crystal data by Barnes [5]) are tabulated in Table II. It was found that, within the accuracies of these lattice parameter data, linear correlations exist between the lattice parameters. These linear relationships can be expressed as follows:

$$\begin{pmatrix} 1 & -0.76 & 0 \\ 0 & 1 & 3.27 \\ -0.4 & 0 & 1 \end{pmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} 4.2 \\ 4.59 \\ -3.06 \end{bmatrix} \qquad (1)$$

From Equation 1, lattice parameters can be calculated from any other measured lattice parameter values. The calculated lattice parameters are listed in Table II. Standard deviations between the measured and calculated a, b, and c values are found to be 0.054, 0.038, and 0.014 Å, respectively. They are less than the accuracy of the data. The correlation coefficients for these linear fits are 0.920, 0.905, and 0.975, respectively.

From these linear correlations between lattice parameters, it is obvious that the orthorhombic unit cell volume V can be approximated to a linearly correlation to the cubic power of any one lattice parameter. It was found that

$$V = 14.9c^3 + 294.0 \qquad (2)$$

Calculated unit cell volumes, by the use of Equation 2, are also listed in Table II. Standard deviations are found to be 3.61 Å^3 for Equation 2. Correlation coefficient for the linear fit of Equation 2 with the data was found to be 0.925.

4. Discussion

These linear correlation relationships in Equations 1 and 2 show that the changes in the directions of orthorhombic lattice parameters a, b, and c in the cation-substituted barium sodium niobates occurred proportionally in the ratios of 2.5 : 3.27 : 1.0, within standard errors of less than 0.3%. These ratios hold true apparently for both Gd- and Cr-substitutions, as well as the anion- and cation-compensated substitutions (types A, B, C, and D).

Francombe [8] showed that from the geometry of the tetragonal bronze-type structure with its regular grouping of NbO_6 octahedra into 3-, 4-, and 5-numbered rings, the distance $a/\sqrt{10}$ is equivalent to the corner-to-corner diameter of an

TABLE II Measured and calculated lattice parameters and unit cell volumes for the Gd- and Cr-substituted $Ba_2NaNb_5O_{15}$

Sample no.	Measured values				Calculated values			
	Lattice parameters† (Å)			Cell volume V(Å^3)	Lattice parameters (Å)			Cell volume V(Å^3)§
	a	b	c		a‡	b‡	c‡	
S.C.*	17.59182 ±0.00001	17.62560 ±0.00005	3.99491 ±0.00000	1238.69	17.587	17.653	3.977	1244.56
Gd–A1	17.59 ±0.03	17.61 ±0.03	3.974 ±0.004	1230.71	17.535	17.585	3.976	1229.71
Gd–A2	17.39 ±0.01	17.48 ±0.08	3.92 ±0.01	1191.96	17.403	17.411	3.896	1192.77
Gd–A3	17.42 ±0.07	17.48 ±0.06	3.93 ±0.01	1195.78	17.418	17.431	3.908	1196.90
Gd–B1	17.61 ±0.08	17.63 ±0.09	3.97 ±0.01	1233.33	17.533	17.582	3.984	1229.01
Gd–B2	17.59 ±0.03	17.60 ±0.04	3.971 ±0.004	1229.92	17.528	17.575	3.976	1227.60
Gd–B3	17.55 ±0.02	17.58 ±0.02	3.953 ±0.002	1219.27	17.482	17.516	3.960	1214.96
Gd–B4	17.69 ±0.06	17.71 ±0.05	3.99 ±0.01	1250.96	17.583	17.647	4.016	1243.20
Gd–B5	17.65 ±0.05	17.65 ±0.05	3.997 ±0.01	1245.36	17.593	17.660	4.000	1246.05
Gd–B6	17.63 ±0.04	17.67 ±0.06	3.99 ±0.01	1242.63	17.570	17.631	3.992	1239.64
Cr–A1	17.60 ±0.02	17.62 ±0.04	3.985 ±0.004	1235.66	17.563	17.621	3.980	1237.51
Cr–A2	17.58 ±0.03	17.61 ±0.01	3.972 ±0.006	1229.46	17.530	17.578	3.972	1228.30
Cr–A3	17.53 ±0.04	17.57 ±0.02	3.961 ±0.007	1220.20	17.503	17.542	3.952	1220.56
Cr–B1	17.53 ±0.04	17.58 ±0.02	3.974 ±0.005	1224.55	17.535	17.585	3.952	1229.71
Cr–B2	17.56 ±0.04	17.58 ±0.02	3.978 ±0.005	1227.88	17.545	17.598	3.964	1232.54
Cr–B3	17.58 ±0.02	17.59 ±0.01	3.978 ±0.002	1230.20	17.545	17.598	3.972	1232.54
Standard deviation σ					±0.054	±0.038	±0.014	±3.61

* Single crystal data [5].

† The lattice parameters were fitted to an orthorhombic structure. They differ, therefore, greatly from the lattice parameters given by Iwasaki and his co-workers [6, 7], who fitted to only a tetragonal structure. Their data gave lattice parameters a in the range of 12.4 Å, and c in the range 3.9 Å.

‡ From Equation 1.

§ From Equation 2.

octahedron, or to the shortest Nb–Nb separation in the (0 0 1) plane.

The distance c is the Nb–Nb spacing between layers of NbO_6 octahedra. Therefore, when there is a constant ratio of $\Delta a/\Delta c$ as in Equation 1, it signifies that there is a constant ratio of changes in the Nb–Nb distances in the (0 0 1) plane and in the c-axis, due to the Gd- and Cr-substitutions to barium sodium niobates.

The niobate samples used in this study were synthesized by the conventional ceramic processes. Prolonged heating at 1200° C in excess of twenty-four hours rendered these samples susceptible to nonstoichiometry. Barns and Carruthers [9] made a study of the lithium tantalate single crystal stoichiometry. Their results showed that X-ray lattice parameters changed nearly monotonically with the mole percent of Li_2O in lithium tantalate ($LaTaO_3$). Within acceptable ranges of standard deviations, their X-ray lattice parameters a, and c can also be linearly correlated. A preliminary study [10] with the use of X-ray electron microprobe established the nonstoichiometry in some of the niobate samples used in this study. It is, therefore, surmized that the linear correlations in the orthorhombic lattice parameters of cation-substituted barium sodium niobates are the direct results of non-stoichiometry in our samples. Conversely, the X-ray lattice parameters, as measured, can serve as accurate indicators for the chemical compositions, and therefore the non-stoichiometry, of the barium sodium niobate samples with small amount of non-isoelectronic substitutions of cations such as Gd and Cr.

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