

# Crystal Structure of a Layered Perovskite Niobate $\text{KCa}_2\text{Nb}_3\text{O}_{10}$

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The crystal structure of a layered perovskite niobate  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  was investigated through single-crystal X-ray analysis. The niobate crystallized in the orthorhombic system  $Cmcm$  with lattice constants of  $a = 3.8802(9) \text{ \AA}$ ,  $b = 29.508(6) \text{ \AA}$ ,  $c = 7.714(1) \text{ \AA}$ ,  $V = 883.2(2) \text{ \AA}^3$ . The final refinement using the 908 independent reflections converged into  $R = 4.1\%$ , and  $R_w = 4.7\%$ . The structure of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  was composed of triple-layered perovskite slabs, potassium ions being situated between the slabs. The adjacent perovskite slabs, stacking along the  $c$  axis, were mutually displaced with a displacement vector of  $\bar{a}/2$ . The potassium ions were coordinated by six oxygen atoms to form two short and four long bonds. Apparent disordering was observed in the equatorial oxygen sites of the central niobium atoms in the triple perovskite slabs. © 2000 Academic Press

**Key Words:** layered perovskite niobate.

## INTRODUCTION

Layered perovskite niobates formulated with  $A\text{Ca}_2\text{Nb}_3\text{O}_{10}$ , where  $A$  is an alkali metal, are members of the Dion–Jacobson-type oxides (1). In these niobates, the  $A$  atoms are sandwiched between  $\text{Ca}_2\text{Nb}_3\text{O}_{10}$  perovskite slabs composed of corner-sharing  $\text{NbO}_6$  octahedra and Ca ions. Although the structure of the Cs analogue was well defined by single-crystal analysis (2), the structures of the other niobates were estimated from the studies of the reciprocal unit cells by Dion *et al.* (1).

These niobates form intercalation compounds with alkali metals and alkylammonium ions (3, 4). The alkali metal intercalation compounds are particularly interesting, because the niobates change from an electrical insulator to a metal by the electron doping of the niobate layers; the resulting compounds belong to the Ruddlesden–Popper series  $AA'_x\text{Ca}_2\text{Nb}_3\text{O}_{10}$  ( $A'$ , intercalated alkali metal). Recently, we have reported the superconductivity of the lithium-intercalated  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  with a transition temperature ( $T_c$ ) of 6 K (5). It was prepared by the intercalation of lithium into  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  using an *n*-butyllithium

solution in hexane. Similar superconductivity was also reported by Takano *et al.* for the same intercalation compound (6, 7). The electric band structure of this superconductor is an important subject for understanding of superconductivity of this system (8, 9), but the precise structure is required for the calculation.

In the present paper, we describe the synthesis of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  single crystals and determination of its crystal structure. The crystal system for this compound was reported to be tetragonal (1), but our single-crystal analysis showed that it had an orthorhombic unit cell. The difference of the structure from the other Dion–Jacobson series niobates will be discussed.

## EXPERIMENTAL

Single crystals of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  were prepared by the following method. A mixture of reagent-grade  $\text{K}_2\text{SO}_4$ ,  $\text{CaSO}_4$ , and  $\text{Nb}_2\text{O}_5$  with a mole ratio of  $\text{K}:\text{Ca}:\text{Nb} = 10:2:3$  was well ground in an agate mortar. The mixture was heated in a platinum crucible at  $1300^\circ\text{C}$  for 1 week, and then slowly cooled to  $1100^\circ\text{C}$  at a rate of  $4^\circ\text{C}/\text{h}$ , followed by rapid cooling to room temperature. The excess  $\text{K}_2\text{SO}_4$  was used as flux and removed by washing with water. The obtained colorless crystals were characterized as the desired niobate  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  by using powder X-ray diffraction.

Many crystals showed twinning or stacking faults. Single crystals suitable for structural analysis were selected by using a four-circle X-ray diffractometer (Rigaku AFC-7R). In the unit cell determination, it was found that the crystal had an orthorhombic unit cell with  $a = 3.8802(9) \text{ \AA}$ ,  $b = 29.508(6) \text{ \AA}$ , and  $c = 7.714(1) \text{ \AA}$  as the fundamental unit cell. A superstructure existed along the  $a$  axis with a dimension twice as large as the fundamental cell. The intensity data collection was, therefore, performed on each unit cell. All measurements were made on an AFC-7R diffractometer with monochromatized  $\text{MoK}\alpha$  radiation. The data collection for the superlattice showed that the intensities for superspots were very weak compared to those for main spots. The averaged intensity  $|F_o|^2$  for the superspots

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(having  $h = \text{odd indices}$ ) was 3.9 and the average for the main spots was 13.3 in the  $2\theta < 50^\circ$  region. Only 20% of the measured superspots were observed ( $F > 3\sigma(F)$ ), while 40% were observed for main spots. The weakness of the superspots indicates that the displacement of atoms or occupational deviations along the  $a$  axis is very small in the superlattice. We tried to perform the structural analysis for the superlattice using all reflections including the superspots. The possible space groups derived from the extinction conditions were  $Pbca$ ,  $Pmca$ , and  $P2_1ca$ . However, we could not obtain good results; anisotropic thermal parameters for some atoms sites became nonpositive definite in the refinement. We therefore performed the structural analysis on the fundamental unit cell.

## RESULTS

The space group of the fundamental cell was determined to be  $Cmcm$ . The positional parameters for niobium, calcium, and potassium were determined by the direct method (MULTAN88 (10, 11)). The positional parameters for oxygen atoms were determined by Fourier techniques. The structure was finally refined by full-matrix least-squares analysis using the Rigaku TeXsan program (12). The last cycle of the refinement converged at  $R = 0.041$  and  $R_w = 0.047$ . Anisotropic thermal parameters were adopted for each atom. A summary of the refinement of KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> is given in Table 1. Positional parameters and main interatomic distances are listed in Tables 2 and 3.

As shown in Fig.1, the structure of KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> is composed of two dimensional triple perovskite slabs

**TABLE 1**  
Crystallographic Data for KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>

Space group	$Cmcm$ (No.63)
$a$ (Å)	3.8802(9)
$b$ (Å)	29.508(6)
$c$ (Å)	7.714(1)
$V$ (Å <sup>3</sup> )	883.2(2)
$Z$	4
$T$ (K) of data collection	300
Crystal size (mm)	0.12 × 0.10 × 0.04
Diffractometer	Rigaku AFC7R
Radiation (graphite monochromated)	MoK $\alpha$ 0.7107 Å
Collection region	$0 \leq h \leq 9$ $0 \leq k \leq 46$ $0 \leq l \leq 12$
$2\theta$ limit	$5^\circ \leq 2\theta \leq 70^\circ$
No. of used reflections	908
with $ F_o  > 3\sigma( F_o )$	
No. of variable parameters	61
$R$ , $R_w^a$	0.041, 0.047
Residual densities (e Å <sup>-3</sup> ) (Max./Min.)	1.39/−1.12

$$^a R = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}, R_w = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2} \right]^{1/2} (w = 1/\sigma(F_o)^2).$$

**TABLE 2**  
Atomic Parameters and Anisotropic Thermal Vibration Parameters for KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> with Standard Deviations in Parentheses

Atom	$x$	$y$	$z$	$B_{eq}$
Nb1	0	0	0.5	0.47(2)
Nb2	0	0.14381(2)	0.5045(1)	0.43(1)
Ca1	0.5	0.0736(1)	0.75	1.72(7)
Ca2	0.5	0.0751(1)	0.25	1.19(6)
K	0	0.2580(1)	0.25	1.60(6)
O1 <sup>a</sup>	0.131(3)	0.0117(4)	0.75	0.6(2)
O2 <sup>a</sup>	0.5	0.003(1)	0.555(2)	4.2(4)
O3	0	0.0637(2)	0.459(1)	4.4(2)
O4	0.5	0.1295(3)	0.507(1)	1.9(1)
O5	0	0.1205(3)	0.75	0.7(2)
O6	0	0.1390(3)	0.25	1.4(2)
O7	0	0.2024(2)	0.5376(9)	1.8(2)

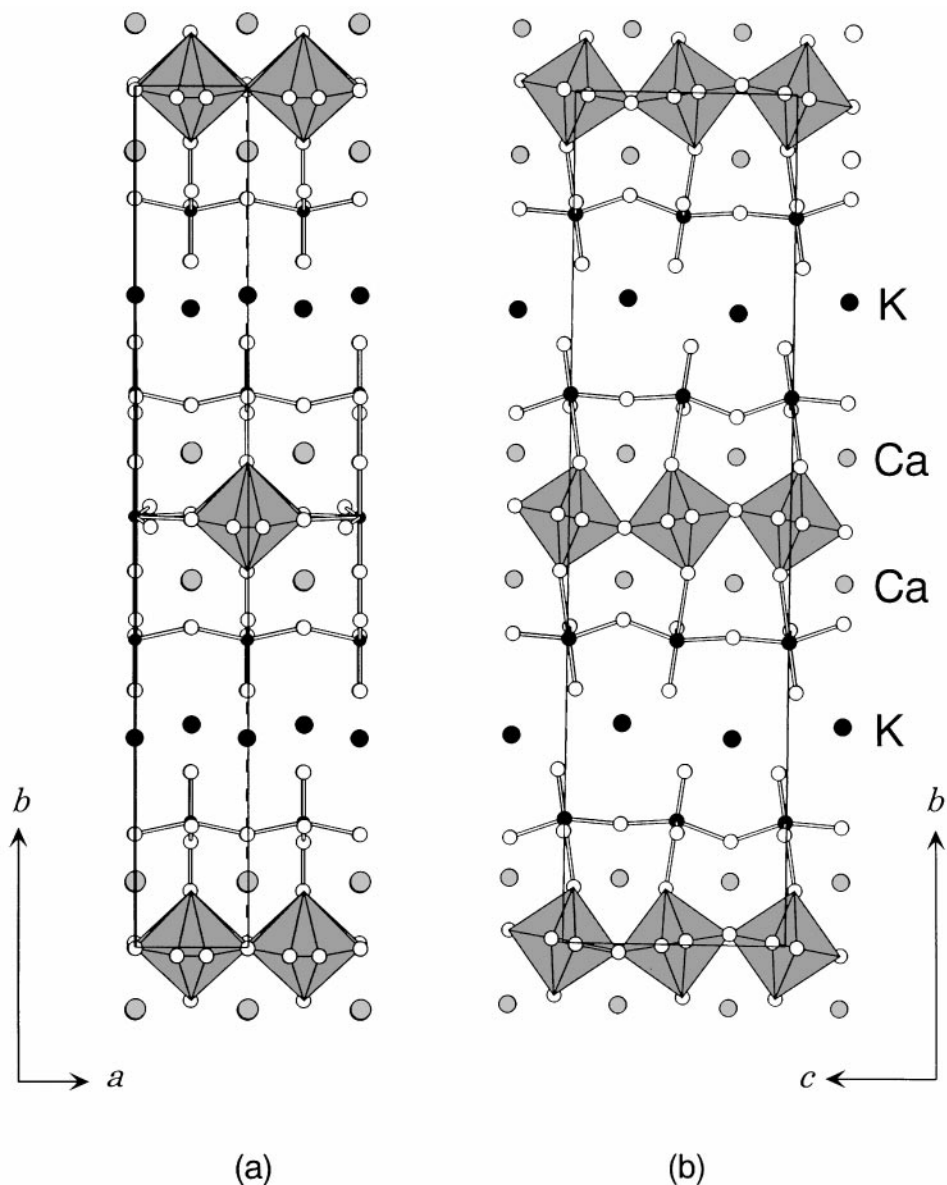
  

$U_{ij} \times 100$						
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Nb1	0.69(4)	0.44(4)	0.66(4)	0	0	0.06(5)
Nb2	0.50(3)	0.50(3)	0.63(3)	0	0	−0.01(3)
Ca1	0.8(1)	1.1(1)	4.6(2)	0	0	0
Ca2	1.2(1)	2.0(2)	1.3(1)	0	0	0
K	1.9(2)	2.0(2)	2.2(2)	0	0	0
O1	1.4(6)	0.9(5)	0.1(4)	0.3(5)	0	0
O2	1.9(7)	13(2)	1.2(8)	0	0	−3(1)
O3	16(1)	0.3(3)	0.9(4)	0	0	0.1(3)
O4	1.0(3)	4.7(5)	1.7(4)	0	0	0.7(5)
O5	1.9(5)	0.5(4)	0.5(4)	0	0	0
O6	3.6(7)	1.2(5)	0.5(4)	0	0	0
O7	5.6(6)	0.1(2)	1.2(4)	0	0	0.0(2)

<sup>a</sup> Half occupation (disordered atoms).

between which the potassium ions are sandwiched. The adjacent perovskite slabs are stacked along the  $b$  axis with a displacement vector of  $\bar{a}/2$  (Fig.1b). The potassium ions are coordinated with six terminal oxygen atoms to form two short K–O bonds of 2.759 Å and four long bonds of 2.796 Å.

Bonds between niobium and terminal oxygen atoms are not parallel to the  $b$  axis to avoid conflict with the potassium ions. As shown in Fig.2, this displacement of the terminal oxygen atoms from the ideal perovskite structure resulted in longer K–O bonds with the two nearest oxygen atoms and four shorter K–O bonds with the second nearest oxygen atoms than in the case where the terminal oxygen atoms are in the positions of the ideal perovskite structure. The terminal oxygen atoms are displaced along the  $c$  direction as illustrated in Fig.2. The lattice constant of the  $c$  axis is therefore 2 times as large as that of the  $a$  axis. Owing to the displacement, the NbO<sub>6</sub> octahedra forming the outer layer of the perovskite slabs lean in the  $c$  direction



**FIG. 1.** The crystal structure of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  projected upon the  $a$ - $b$  plane (a) and the  $b$ - $c$  plane (b) on the basis of the fundamental unit cell. Small filled and open circles represent niobium and oxygen atoms, respectively. Large filled circles represent potassium and calcium atoms. The inner octahedra of the perovskite slabs are shown by the polyhedra. The equatorial oxygen atoms of the inner octahedra are apparently disordered.

(see Fig. 1b). The tilting of the outer  $\text{NbO}_6$  octahedra in turn tilts the inner  $\text{NbO}_6$  octahedra, which made the zigzag connection of  $\text{NbO}_6$  octahedra along the  $b$  axis. The two-dimensional  $\text{NbO}_2$  plane in the inner perovskite slabs is corrugated along the  $c$  direction (Fig. 1b). No significant displacement can be seen along the  $a$  axis (Fig. 1a), but this may not indicate that the inner octahedra do not rotate about the  $c$  axis. The inner  $\text{NbO}_6$  octahedra of  $\text{CsCa}_2\text{Nb}_3\text{O}_{10}$  rotate about all three axes (2). Figure 3 shows the thermal ellipsoids for all atoms viewed along the

$c$  axis of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ . The large thermal vibrational motions along the  $a$  or  $b$  axis for O2 and O3 sites, which compose the inner  $\text{NbO}_6$  octahedra, suggest the rotation about the  $c$  axis. This niobate has a superstructure along the  $a$  axis and the large thermal motions seem to be caused by this superstructure. The detailed structural features could be revealed after the structure analysis of the super lattice.

The bond distance between the niobium and the terminal oxygen atom is  $1.748 \text{ \AA}$ , while the bond length between the niobium and the oxygen atom that is in the opposite site

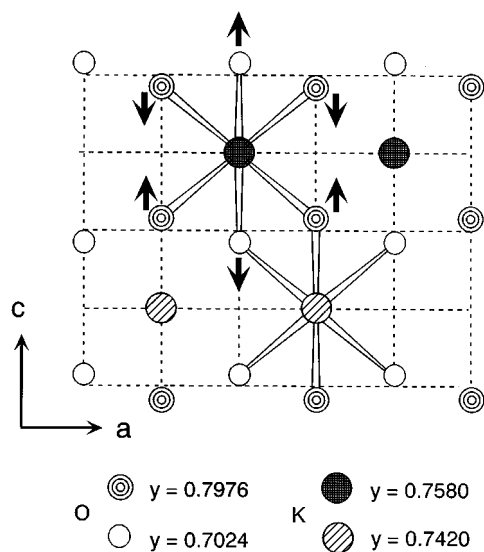
**TABLE 3**  
Bond Distances in  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$

Nb(1)–O(1)	2.024(4) Å × 2	Ca(2)–O(1)	2.94(1) Å × 2
–O(2)	1.989(3) Å × 2	–O(1)	3.54(1) Å × 2 <sup>a</sup>
–O(3)	1.905(7) Å × 2	–O(2)	2.76(4) Å × 2
		–O(2)	3.17(3) Å × 2 <sup>a</sup>
Nb(2)–O(3)	2.389(7) Å	–O(3)	2.546(5) Å × 4
–O(4)	1.985(2) Å × 2	–O(4)	2.547(9) Å × 2
–O(5)	2.015(3) Å	–O(6)	2.704(7) Å × 2
–O(6)	1.968(1) Å		
–O(7)	1.748(6) Å		
Ca(1)–O(1)	2.32(1) Å × 2	K–O(7)	2.759(7) Å × 2
–O(1)	3.05(1) Å × 2 <sup>a</sup>		2.795(5) Å × 2
–O(2)	2.56(3) Å × 2		2.796(5) Å × 2
–O(2)	3.27(2) Å × 2 <sup>a</sup>		
–O(3)	2.980(6) Å × 4		
–O(4)	2.501(9) Å × 2		
–O(5)	2.383(6) Å × 2		

<sup>a</sup> Bond distances with the other (farther) disordered atoms

against the terminal oxygen atom is 2.389 Å. The formation of such short and long Nb–O distances is commonly observed in Nb(V) compounds. The Nb–O distances for the inner octahedra range from 1.90 to 2.02 Å, indicating that the coordination environment for the niobium (Nb(1)) in the inner octahedra is more isotropic than that for the niobium (Nb(2)) in the outer octahedra.

In the refinement of the fundamental cell, the sites for oxygen atoms were determined by using differential Fourier



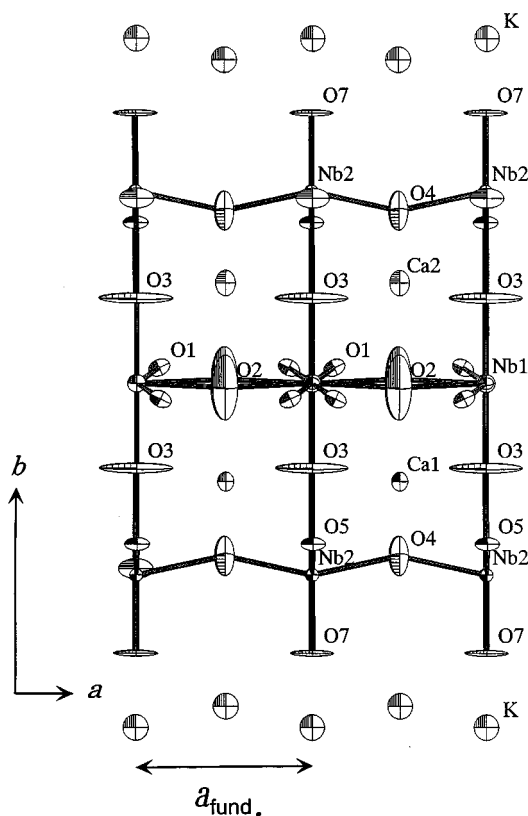
**FIG. 2.** Schematic illustration of the bondings between potassium ions (large circles) and terminal oxygen atoms (small circles) viewed down along the  $b$  axis. The positions for the terminal oxygen atoms of the ideal perovskite structure are at the intersecting points of the broken lines. Arrows show the displacement directions.

maps, and it was found that the  $\text{Nb}(1)\text{O}_6$  octahedra have a disorder in the equatorial oxygen sites, O1 and O2. The positions of these oxygen atoms projected along the  $b$  axis are illustrated in Fig. 4a. The positions of O1a–O1b and O2a–O2b sites are close to each other and the sites are not occupied simultaneously. The occupational parameters for these atoms are 1/4 (corresponding to 50% filled).

The apparent disordering may be caused by the use of the fundamental unit cell rather than the actual superstructure. The twisting of an  $\text{NbO}_6$  octahedron about the  $b$  axis results in the twisting of the next  $\text{NbO}_6$  octahedra in the opposite direction as shown in Fig. 4b. If the superstructure of this compound as shown in Fig. 4b is solved,  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  may be understood as an ordered structure. The fundamental structure is the superimposition of the two regular octahedra, the  $\text{Nb}(\text{O}_a)_4$  set and the  $\text{Nb}(\text{O}_b)_4$  set. The rotation angle ( $\frac{1}{2}\angle\text{O1a-Nb1-O1b}$ ) of  $15^\circ$  for the O(1) atom from the ideal perovskite structure is in good agreement with the angle ( $\frac{1}{2}\angle\text{O2a-Nb1-O2b}$ ) of  $13^\circ$  for the O(2) atom.

## DISCUSSION

In a series of Dion–Jacobson–type niobates represented as  $A\text{Ca}_2\text{Nb}_3\text{O}_{10}$ , where  $A$  is Li, Na, K, Rb, and Cs, only



**FIG. 3.** Crystal description of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  in the thermal ellipsoid mode viewed along the  $c$  axis.

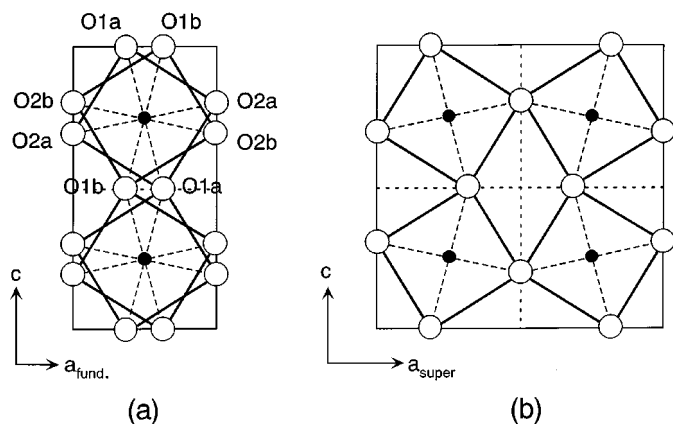


FIG. 4. Arrangement of the inner  $\text{NbO}_6$  octahedra in the triple perovskite slabs of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  projected along the  $b$  axis for (a) the fundamental unit cell and (b) the superstructure, where  $a_{\text{fund.}} = a_{\text{super}}/2$ . Solid and open circles represent niobium and equatorial oxygen atoms, respectively.

$\text{CsCa}_2\text{Nb}_3\text{O}_{10}$  was previously studied by single-crystal X-ray analysis (2). Single-crystal structure analysis for the other niobates has not been published. The present study of  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  is the second example. The  $a$  axis for the potassium compound is half of that for the cesium compound. The two structures,  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$  and  $\text{CsCa}_2\text{Nb}_3\text{O}_{10}$ , are different mainly in the stacking of the perovskite slabs as suggested by Dion *et al.* (1). In  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ , the adjacent perovskite slabs are mutually displaced by the displacement vector of  $\vec{a}/2$ , while the slabs in  $\text{CsCa}_2\text{Nb}_3\text{O}_{10}$  are not displaced and are stacked in register. Owing to the difference, different coordination environments for the interlayer alkali cations occur in these compounds.

Local structures around different types of alkali cations are illustrated in Fig. 5, in which the potassium ion is coordinated by six oxygen atoms, and the cesium ion is coordinated by eight oxygen atoms. The average bond lengths between the alkali cations and oxygen atoms are 2.78 and 3.17 Å for the K and Cs compounds, respectively. The Cs compound has a larger coordination number and larger bond lengths than the K compound. The stacking manner of the  $\text{Ca}_2\text{Nb}_3\text{O}_{10}$  slabs depends on the size of the interlayer cations.

The stacking manner and the coordination number for the  $\text{ACa}_2\text{Nb}_3\text{O}_{10}$  series compounds are summarized in Table 4. The rubidium analogue has a lattice constant half those for the other niobates (1) along the stacking direction. The lattice constant corresponds to the thickness of one perovskite slab, which results in the  $\text{Ca}_2\text{Nb}_3\text{O}_{10}$  slabs in the rubidium compound being in register like those in the cesium analogue (Fig. 5a). The rubidium ions must be therefore in eight-coordinated sites. In the compounds with much smaller ions such as  $\text{Na}^+$  and  $\text{Li}^+$ , another type of stacking

of the perovskite slabs was observed. According to the studies by Dion *et al.* (1), adjacent perovskite slabs in the  $\alpha$ -type  $\text{NaCa}_2\text{Nb}_3\text{O}_{10}$  are mutually displaced with the displacement vector of  $(\vec{a} + \vec{b})/4$ , where the  $a$  and  $b$  axes are involved in the perovskite plane because this compound belongs to the tetragonal crystal system. The schematic representation of these compounds is presented in Fig. 5c. This stacking pattern provides tetrahedral sites for the sodium ions. In the polytype  $\beta$ - $\text{NaCa}_2\text{Nb}_3\text{O}_{10}$ , the sodium ion has a different

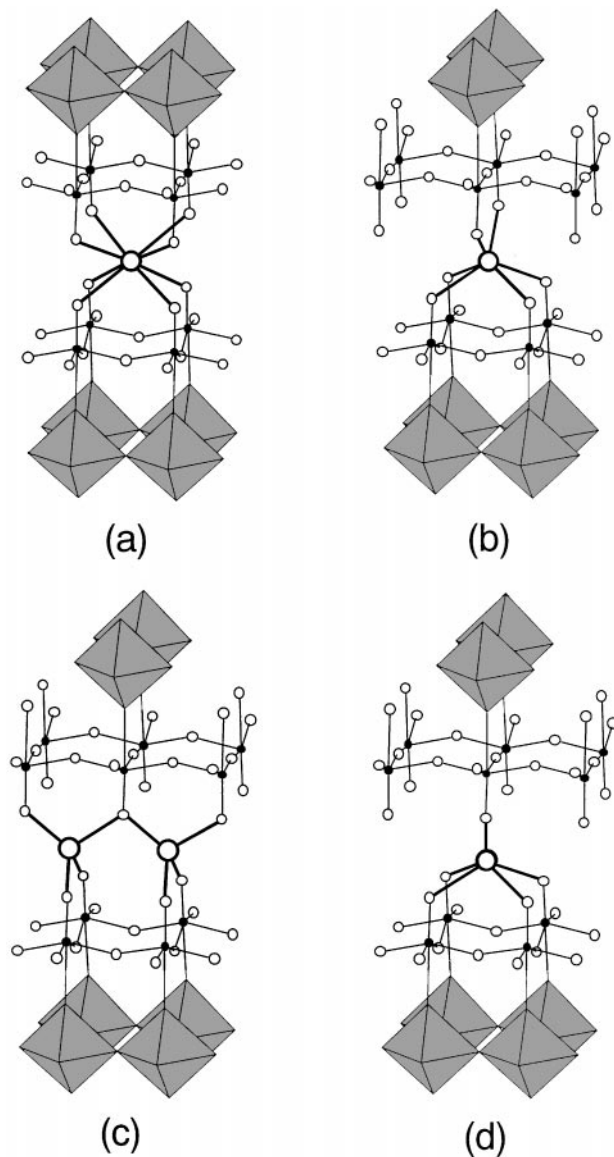


FIG. 5. Schematic representation of the local structures around alkali metal cations in (a) Cs- and  $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$ , (b)  $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ , (c)  $\text{LiCa}_2\text{Nb}_3\text{O}_{10}$  and  $\alpha$ - $\text{NaCa}_2\text{Nb}_3\text{O}_{10}$ , and (d)  $\beta$ - $\text{NaCa}_2\text{Nb}_3\text{O}_{10}$ . Large open circles are alkali cations, and small open and filled circles are oxygen and niobium atoms, respectively. The cesium and rubidium ion are coordinated with eight oxygen atoms and the potassium ion is coordinated with six oxygen atoms.

**TABLE 4**  
**Space Group, Lattice Constants, Displacement Vector, and Coordination Number of Alkali Cations in ACa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> Series Compounds**

Compounds	Crystal system	Lattice constants			Displacement vector	Coordination number	Ref.
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)			
NaCa <sub>2</sub> Nb <sub>3</sub> O <sub>10</sub> $\alpha$ -form	Tetra.	7.740(8)	—	28.58(1)	( <i>a</i> + <i>b</i> )/4	4	1
NaCa <sub>2</sub> Nb <sub>3</sub> O <sub>10</sub> $\beta$ -form	Tetra.	7.730(3)	—	28.978(8)	( <i>a</i> + <i>b</i> )/4	5	1
KCa <sub>2</sub> Nb <sub>3</sub> O <sub>10</sub> <sup>a</sup>	Ortho.	3.8802(9)	7.714(1)	29.508(6)	<i>a</i> /2	6	This work
RbCa <sub>2</sub> Nb <sub>3</sub> O <sub>10</sub>	Tetra.	7.725(2)	—	14.909(5)	0	8	1
CsCa <sub>2</sub> Nb <sub>3</sub> O <sub>10</sub>	Ortho.	7.740(2)	7.746(2)	30.185(3)	0	8	2

<sup>a</sup> For comparison, the unit cell parameters for *b* and *c* are exchanged

arrangement from that of the  $\alpha$ -type compound, as shown in Fig. 5d. The perovskite slab has the same displacement vector as the  $\alpha$  form but the coordination number of sodium ions is 5. Evidently, the interlayer cations with large ionic radii have a tendency to have larger coordination numbers, which gives rise to a variety of stacked structures.

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#### REFERENCES

1. M. Dion, M. Ganne, and M. Tournoux, *Mater. Res. Bull.* **16**, 1429 (1981).
2. M. Dion, M. Ganne, and M. Tournoux, *Rev. Chim. Miner.* **21**, 92 (1984).
3. A. J. Jacobson, J. T. Lewandowski, and J. W. Johnson, *J. Less-Common Metals* **116**, 137 (1986).
4. A. J. Jacobson, J. T. Lewandowski, and J. W. Johnson, *Mater. Res. Bull.* **25**, 679 (1990).
5. H. Fukuoka, T. Isami, and S. Yamanaka, *Chem. Lett.* 703 (1997).
6. Y. Takano, S. Takayanagi, S. Ogawa, T. Yamadaya, and N. Mori, *Solid State Commun.* **103**, 215 (1997).
7. Y. Takano, H. Taketomi, H. Tsurumi, T. Yamadaya, and N. Mori, *Physica B*, 237 (1997).
8. R. Rousseau, M. J. Palaćin, P. G. Romero, and E. Canadell, *Inorg. Chem.* **35**, 1179 (1996).
9. I. Hase and Y. Nishihara, *Phys. Rev.* **58**, R1707 (1998).
10. T. Debaedemaeker, C. Tafe, and M. M. Woolfson, *Acta Crystallogr.* **A41**, 286 (1985).
11. T. Debaedemaeker, C. Tafe, and M. M. Woolfson, *Acta Crystallogr.* **A44**, 353 (1988).
12. TeXsan: Single Crystal Structure Analysis Software, Ver. 1.6, Molecular Structure Corp. The Woodlands, TX, 77381, 1993.
13. D. Brown, in "Structure and Bonding in Crystals" (M. O'Keeffe and A. Navrotsky, Eds.), Chap. 14. Academic Press, New York, 1981.