

RbCa₂Nb₃O₁₀ from X-ray powder data

Zhen-Hua Liang,^{a,b} Kai-Bin Tang,^{a,b*} Qian-Wang Chen^b
and Hua-Gui Zheng^a

^aDepartment of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China, and ^bDepartment of Nanomaterials and Nanochemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Correspondence e-mail: kbtang@ustc.edu.cn

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Key indicators: powder X-ray study; $T = 298$ K; mean $\sigma(\text{Nb}-\text{O}) = 0.003$ Å; R factor = 0.035; wR factor = 0.053; data-to-parameter ratio = 9.2.

Rubidium dicalcium triniobate(V), RbCa₂Nb₃O₁₀, has been synthesized by solid-state reaction and its crystal structure refined from X-ray powder diffraction data using Rietveld analysis. The compound is a three-layer perovskite Dion–Jacobson phase with the perovskite-like slabs derived by termination of the three-dimensional CaNbO₃ perovskite structure along the *ab* plane. The rubidium ions (*4/mmm* symmetry) are located in the interstitial space.

Related literature

For the synthesis of RbCa₂Nb₃O₁₀, see: Dion *et al.* (1981). For related three-layer Dion–Jacobson analogues, see: CsCa₂Nb₃O₁₀ (Dion *et al.*, 1984); RbSr₂Nb₃O₁₀ (Thangadurai *et al.*, 2001); KCa₂Nb₃O₁₀ (Fukuoka *et al.*, 2000). For the application of Dion–Jacobson phases, see: Thangadurai *et al.* (2001); Li *et al.* (2007); Ida *et al.* (2008); Compton & Osterloh (2009). For properties of RbCa₂Nb₃O₁₀, see: Thangadurai & Weppner (2001, 2004); Byeon *et al.* (2003).

Experimental

Crystal data

RbCa₂Nb₃O₁₀
 $M_r = 604.34$
Trigonal, *P4/mmm*
 $a = 3.85865$ (6) Å
 $c = 14.9108$ (3) Å
 $V = 222.01$ (1) Å³
 $Z = 1$

Cu $K\alpha$ radiation
 $T = 298$ K
Specimen shape: flat sheet
 $10 \times 15 \times 1$ mm
Specimen prepared at 1423 K
Particle morphology: plate-like,
white

Data collection

PANalytical X'pert PRO
diffractometer
Specimen mounting: packed powder
pellet

Specimen mounted in reflection
mode
Scan method: continuous
 $2\theta_{\min} = 10.0$, $2\theta_{\max} = 110.0^\circ$
Increment in $2\theta = 0.02^\circ$

Refinement

$R_p = 0.035$
 $R_{wp} = 0.053$
 $R_{exp} = 0.008$
 $S = 2.54$
Wavelength of incident radiation:
1.54178 Å
Profile function: pseudo-Voigt

238 reflections
26 parameters
Preferred orientation correction:
March–Dollase (Dollase, 1986)
AXIS 1 Ratio = 0.95964, $h = k = 0$,
 $l = 1$; correction range: min =
0.94007, max = 1.13156

Data collection: *X'pert Data Collector* (PANalytical, 2003); cell refinement: *GSAS* (Larson & Von Dreele, 2000) and *EXPGUI* (Toby, 2001); data reduction: *X'pert Data Collector*; method used to solve structure: coordinates taken from an isotypic compound (Thangadurai *et al.*, 2001); program(s) used to refine structure: *GSAS* and *EXPGUI*; molecular graphics: *VESTA* (Momma & Izumi, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2107).

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supplementary materials

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Comment

The Dion-Jacobson phase which was first discovered by Dion *et al.* (1981), has a general formula A'_n[A_{n-1}B_nO_{3n+1}], where A' is a monovalent ion, A is a divalent alkaline earth metal ion and B is a tetravalent or pentavalent transition metal ion. Related crystal structures of three-layer Dion-Jacobson phase have been reported for KCa₂Nb₃O₁₀ (Dion *et al.*, 1984), RbSr₂Nb₃O₁₀ (Thangadurai *et al.*, 2001), and KCa₂Nb₃O₁₀ (Fukuoka *et al.*, 2000). Although the three-layer Dion-Jacobson phase RbCa₂Nb₃O₁₀ was first synthesized by Dion *et al.* (1981), its crystal structure has not yet been reported. The structure of RbCa₂Nb₃O₁₀ has now been refined by the Rietveld method from powder diffraction data in the present communication.

The observed, calculated and intensities difference plots of the Rietveld refinement are shown in Fig. 1. There are some *00 l* preferential orientation which were often observed in the Rietveld refinement of the layered perovskites. Then we applied the March-Dollase option for a correction in the EXPGUI program and obtain the best result finally.

The structure of the compound is illustrated in Fig. 2. The structure consists of three layers of corner-sharing NbO₆ octahedra that run perpendicular to the *c* axis; adjacent sets of layers are staggered.

Table 1 shows refined interatomic distances and angles for the RbCa₂Nb₃O₁₀ structure. The octahedra forming the inner layer are less distorted with Nb—O distances ranging from 1.876 (7) to 1.92932 (3) Å (Table 2), which is typical for layered perovskites involving Nb(V). As it is well known in layered perovskites, the NbO₆ octahedra forming the outer layer of the slabs are characterized by off-centering of the Nb atoms, leading to four equal equatorial Nb—O distances within the perovskite layers [1.9663 (11) Å], a short Nb—O bond toward the interlayer spacing [1.650 (8) Å], and a long opposite Nb—O bond [2.379 (7) Å]. Such a distortion is quite similar to that encountered in homologous niobates and tantalates where the niobium shows an out-of-plane distortion, moving away from the more positively charged calcium towards the rubidium layer. Similar behavior has been observed in a number of d⁰ systems containing niobium, tantalum, and titanium. This has been attributed to a second-order Jahn-Teller effect. Concerning the interlayer, the rubidium ions are coordinated with eight terminal oxygen atoms to form the same eight Rb—O bonds [3.318 (4) Å]. These distances, as for the Ca—O bonds [2.560 (4)–2.9207 (22) Å] are close to those commonly observed in layered perovskites.

Experimental

RbCa₂Nb₃O₁₀ powders were prepared by a conventional solid state reaction described previously (Byeon *et al.*, 2003). All starting materials were of analytical grade and were used without further purification. Stoichiometric amounts of CaCO₃ and Nb₂O₅ with a 50% molar excess of Rb₂CO₃ were mixed together and heated in air at 1423 K for 24 h (heating rate 5 K/min). The calcination procedure was repeated one time after grinding to ensure a complete reaction. A 50% molar excess of Rb₂CO₃ was used in the reaction to offset the volatilization of the alkali oxides at the synthesis temperature. The products were washed thoroughly with distilled water to remove excess alkali oxides, and were then dried at 393 K overnight.

Refinement

All peaks of the XRD pattern could be indexed on a tetragonal cell and the systematic absences show simple tetragonal symmetry. The $P4/mmm$ crystal structure of $\text{RbSr}_2\text{Nb}_3\text{O}_{10}$ (Thangadurai *et al.*, 2001) was used as a starting model for the Rietveld refinement of the structure of $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$. The corresponding isotropic atomic displacement parameters of all oxygen atoms are constrained to be equal. The March-Dollase option in the EXPGUI program was applied to correct $00l$ preferential orientation which were often observed in the Rietveld refinement of the layered perovskites.

Figures

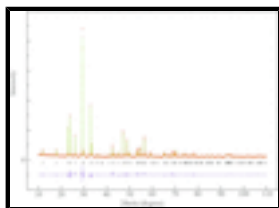


Fig. 1. Rietveld difference plot for the multi-phase refinement of $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$. The red crosses, and green and pink lines show respectively the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by black lines for the $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$ phase.

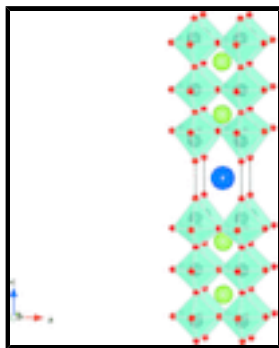


Fig. 2. The crystal structure of $\text{RbCa}_2\text{Nb}_3\text{O}_{10}$. blue octahedron show NbO_3 units with Nb^{5+} cations as black spheres and O^{2-} anions as red spheres. Large green spheres represent Ca^{2+} cations and large blue spheres Rb^+ cations.

Rubidium dicalcium triniobate(V)

Crystal data

$\text{RbCa}_2\text{Nb}_3\text{O}_{10}$

$M_r = 604.34$

Tetragonal, $P4/mmm$

Hall symbol: -P 4 2

$a = 3.85865$ (6) Å

$b = 3.85865$ (6) Å

$c = 14.9108$ (3) Å

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 222.009$ (7) Å³

$Z = 1$

$D_x = 4.520$ Mg m⁻³

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

$T = 298$ K

Specimen shape: flat sheet

$10 \times 15 \times 1$ mm

Specimen prepared at 1423 K

Particle morphology: plate-like, white

Data collection

PANalytical X'pert PRO
diffractometer

Scan method: continuous

Radiation source: sealed tube $T = 298$ K
 Monochromator: graphite $2\theta_{\min} = 10.01$, $2\theta_{\max} = 109.99^\circ$
 Specimen mounting: packed powder pellet Increment in $2\theta = 0.02^\circ$
 Specimen mounted in reflection mode

Refinement

Refinement on F^2 Profile function: pseudo-Voigt
 Least-squares matrix: full 26 parameters
 $R_p = 0.035$ $w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $R_{wp} = 0.053$ $(\Delta/\sigma)_{\max} = 0.020$
 $R_{exp} = 0.008$ Extinction correction: none
 Preferred orientation correction: March–Dollase
 (Dollase, 1986) AXIS 1 Ratio= 0.95964, $h = k = 0$,
 $l = 1$. Preferred orientation correction range: min =
 0.94007, Max = 1.13156
 $S = 2.54$
 Wavelength of incident radiation: 1.54178 Å

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Rb1	0.5	0.5	0.5	0.0433 (8)*
Ca1	0.5	0.5	0.14706 (19)	0.0281 (8)*
Nb1	0.0	0.0	0.0	0.0127 (6)*
Nb2	0.0	0.0	0.28537 (8)	0.0134 (5)*
O1	0.0	0.5	0.0	0.0716 (14)*
O2	0.0	0.0	0.1258 (5)	0.0716 (14)*
O3	0.0	0.5	0.2599 (4)	0.0716 (14)*
O4	0.0	0.0	0.3960 (6)	0.0716 (14)*

Geometric parameters (\AA , $^\circ$)

Rb1—O4	3.138 (4)	Ca1—O3	2.560 (4)
Rb1—O4 ⁱ	3.138 (4)	Ca1—O3 ⁱⁱ	2.560 (4)
Rb1—O4 ⁱⁱ	3.138 (4)	Ca1—O3 ^{viii}	2.560 (4)
Rb1—O4 ⁱⁱⁱ	3.138 (4)	Ca1—O3 ^{ix}	2.560 (4)
Rb1—O4 ^{iv}	3.138 (4)	Nb1—O1 ^x	1.929320 (30)
Rb1—O4 ^v	3.138 (4)	Nb1—O1	1.929320 (30)
Rb1—O4 ^{vi}	3.138 (4)	Nb1—O1 ^{xi}	1.929320 (30)
Rb1—O4 ^{vii}	3.138 (4)	Nb1—O1 ^{viii}	1.929320 (30)
Ca1—O1	2.9207 (22)	Nb1—O2	1.877 (7)
Ca1—O1 ⁱⁱ	2.9207 (22)	Nb1—O2 ^{xii}	1.877 (7)
Ca1—O1 ^{viii}	2.9207 (22)	Nb2—O2	2.379 (7)
Ca1—O1 ^{ix}	2.9207 (22)	Nb2—O3 ^x	1.9663 (11)
Ca1—O2	2.7468 (9)	Nb2—O3	1.9663 (11)
Ca1—O2 ⁱ	2.7468 (9)	Nb2—O3 ^{xi}	1.9663 (11)

supplementary materials

Ca1—O2 ⁱⁱ	2.7468 (9)	Nb2—O3 ^{viii}	1.9663 (11)
Ca1—O2 ⁱⁱⁱ	2.7468 (9)	Nb2—O4	1.650 (8)
O1 ^x —Nb1—O1	180.0	O1 ^{viii} —Nb1—O2 ^{xii}	90.0
O1 ^x —Nb1—O1 ^{xi}	90.0	O2—Nb1—O2 ^{xii}	180.0
O1 ^x —Nb1—O1 ^{viii}	90.0	O3 ^x —Nb2—O3	157.75 (32)
O1 ^x —Nb1—O2	90.0	O3 ^x —Nb2—O3 ^{xi}	87.87 (6)
O1 ^x —Nb1—O2 ^{xii}	90.0	O3 ^x —Nb2—O3 ^{viii}	87.87 (6)
O1—Nb1—O1 ^{xi}	90.0	O3 ^x —Nb2—O4	101.12 (16)
O1—Nb1—O1 ^{viii}	90.0	O3—Nb2—O3 ^{xi}	87.87 (6)
O1—Nb1—O2	90.0	O3—Nb2—O3 ^{viii}	87.87 (6)
O1—Nb1—O2 ^{xii}	90.0	O3—Nb2—O4	101.12 (16)
O1 ^{xi} —Nb1—O1 ^{viii}	180.0	O3 ^{xi} —Nb2—O3 ^{viii}	157.75 (32)
O1 ^{xi} —Nb1—O2	90.0	O3 ^{xi} —Nb2—O4	101.12 (16)
O1 ^{xi} —Nb1—O2 ^{xii}	90.0	O3 ^{viii} —Nb2—O4	101.12 (16)
O1 ^{viii} —Nb1—O2	90.0		

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

Fig. 1

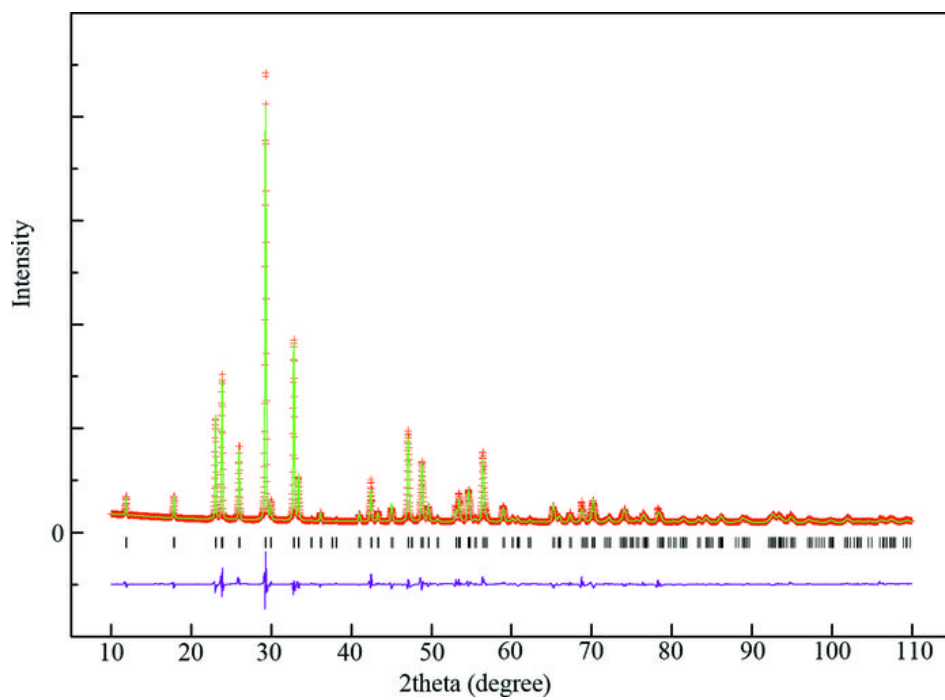


Fig. 2

