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Rietveld refinement of KLaTiO_4 from X-ray powder dataBai-Chuan Zhu^a and Kai-Bin Tang^{a,b*}

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Key indicators: powder X-ray study; $T = 298$ K; mean $\sigma(\text{La}-\text{O}) = 0.003$ Å; R factor = 0.046; wR factor = 0.068; data-to-parameter ratio = 98.0.

Potassium lanthanum titanate(IV), KLaTiO_4 , has been synthesized by conventional solid-state reaction. It crystallizes isotypically with the NaLnTiO_4 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Y}$ and Lu) family. Five of the six atoms in the asymmetric unit (one K, one La, one Ti and two O atoms) are situated on sites with $4mm$ symmetry, whereas one O atom has $2mm$ site symmetry. The crystal structure can be described as being composed of single layers of distorted corner-sharing TiO_6 octahedra extending parallel to (001). The layers are alternately separated by K^+ and La^{3+} cations along [001]. The coordination number of both K^+ and La^{3+} cations is nine, resulting in distorted KO_9 and LaO_9 polyhedra.

Related literature

For the isotypic NaLnTiO_4 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Y}$ and Lu) family, see: Toda *et al.* (1996a). Orthorhombic symmetry for other members of this family has been reported by Nishimoto *et al.* (2006). Decomposition products of NaLnTiO_4 were investigated by Toda *et al.* (1996b). For preparation by ion-exchange and structure analysis of KLnTiO_4 ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$) compounds, see: Schaak & Mallouk (2001). For hydrothermal preparation of similar compounds, see: Dairong *et al.* (1999). For crystallographic background, see: Howard (1982); Thompson *et al.* (1987).

Experimental

Crystal data

KLaTiO_4 $a = 3.84155$ (10) Å
 $M_r = 289.90$ $c = 13.4695$ (4) Å
 Tetragonal, $P4/nmm$ $V = 198.78$ (1) Å³

$Z = 2$
 Cu $K\alpha$ radiation, $\lambda = 1.54060$,
 1.54443 Å

$T = 298$ K
 flat sheet, 20×20 mm

Data collection

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

Data collection mode: reflection
 Scan method: continuous
 $2\theta_{\min} = 9.872^\circ$, $2\theta_{\max} = 109.815^\circ$,
 $2\theta_{\text{step}} = 0.017^\circ$

Refinement

$R_p = 0.046$
 $R_{wp} = 0.068$
 $R_{\text{exp}} = 0.046$
 $R(F^2) = 0.047$

$\chi^2 = 2.220$
 5880 data points
 60 parameters

Table 1

Selected bond lengths (Å).

K1—O1	3.065 (4)	La1—O3 ⁱ	2.7628 (12)
K1—O2	2.765 (9)	Ti1—O1	1.9635 (12)
K1—O2 ⁱ	2.7242 (7)	Ti1—O2 ⁱⁱⁱ	1.775 (9)
La1—O1	2.530 (3)	Ti1—O3 ⁱⁱⁱ	2.558 (7)
La1—O3 ⁱⁱ	2.339 (7)		

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $x, y, z + 1$; (iii) $-x + 1, -y + 1, -z + 1$.

Data collection: *X'pert Data Collector* (PANalytical, 2003); cell refinement: *GSAS* (Larson & Von Dreele, 2004) and *EXPGUI* (Toby, 2001); data reduction: *X'pert Data Collector*; method used to solve structure: coordinates taken from an isotypic compound (Toda *et al.*, 1996b); program(s) used to refine structure: *GSAS* and *EXPGUI*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2446).

References

- Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Dairong, C., Xiuling, J. & Ruren, X. (1999). *Mater. Res. Bull.* **34**, 685–691.
 Howard, C. J. (1982). *J. Appl. Cryst.* **15**, 615–620.
 Larson, A. C. & Von Dreele, R. B. (2004). *General Structure Analysis System (GSAS)*. Report LAUR 86-748. Los Alamos National Laboratory, New Mexico, USA.
 Nishimoto, S., Matsuda, M., Harjo, S., Hoshikawa, A., Kamiyama, T., Ishigaki, T. & Miyake, M. (2006). *J. Solid State Chem.* **179**, 1892–1897.
 PANalytical (2003). *X'pert Data Collector*. PANalytical BV, Almelo, The Netherlands.
 Schaak, R. E. & Mallouk, T. E. (2001). *J. Solid State Chem.* **161**, 225–232.
 Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *J. Appl. Cryst.* **20**, 79–83.
 Toby, B. H. (2001). *J. Appl. Cryst.* **34**, 210–213.
 Toda, K., Kameo, Y., Kurita, S. & Sato, M. (1996a). *J. Alloys Compd.* **234**, 19–25.
 Toda, K., Watanabe, J. & Sate, M. (1996b). *Mater. Res. Bull.* **31**, 1427–1435.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

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Rietveld refinement of KLaTiO_4 from X-ray powder data

Bai-Chuan Zhu and Kai-Bin Tang

S1. Comment

Layered perovskites that belong to the Ruddlesden-Popper $A'_2[A_{n-1}B_2O_{3n+1}]$ family (A' = alkali, A = alkaline earth or rare earth cation; B = transition metal cation) possess a variety of interesting properties, such as superconductivity, colossal magnetoresistance, ferroelectricity, as well as catalytic activity. The structure of KLaTiO_4 we report here is a $n = 1$ member of this family. Isotypic crystal structures have been reported for NaLnTiO_4 ($Ln = \text{La, Pr, Nd, Sm, Eu, Gd, Y}$ and Lu ; Toda *et al.*, 1996a) in the space group $P4/nmm$.

Schaak & Mallouk (2001) reported the KLnTiO_4 ($Ln = \text{La, Nd, Sm, Eu, Gd, Dy}$) family of compounds to crystallize in space group $Pbcm$, as determined from Rietveld refinements of X-ray powder data. We tested both $Pbcm$ and $P4/nmm$ space groups with the underlying structures KLnTiO_4 ($P4/nmm$; Schaak & Mallouk, 2001) and NaLnTiO_4 ($P4/nmm$; Toda *et al.*, 1996a) as starting models for Rietveld refinement of KLaTiO_4 . The results revealed the $P4/nmm$ model to be significantly better than the $Pbcm$ model. It is well-known that different rare earth elements can affect the crystal structure dramatically. In single layer Ruddlesden-Popper phase perovskites some studies reported that NaLnTiO_4 compounds have tetragonal symmetry for $Ln = \text{La—Nd}$, while an orthorhombic symmetry is observed for $Ln = \text{Sm—Lu}$ and Y (Nishimoto *et al.*, 2006). We can infer that a similar situation might be present for KLnTiO_4 compounds. We ascribe the difference in symmetry between KLaTiO_4 obtained through solid state reactions (tetragonal) and through ion-exchange (orthorhombic) to the different temperature treatment (higher temperatures for the solid state reaction route).

Other methods used to prepare KLaTiO_4 have been reported previously, like an ion exchange method by Schaak & Mallouk (2001) and a hydrothermal method by Dairong *et al.* (1999). To our knowledge, a solid state route to synthesize this compound and its detailed structure analysis based on Rietveld refinement from X-ray powder diffraction data has not been reported. KLaTiO_4 easily decomposes at high temperature and is converted into the three-layer Ruddlesden-Popper phase $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$. This phenomenon is also found in during preparation of NaLaTiO_4 reported by Toda *et al.* (1996b). Therefore we modified the reaction conditions on the basis of the preparation of NaLaTiO_4 and obtained a single phase product successfully.

Fig. 1 shows the observed difference plots (calculated, observed) of the Rietveld refinement.

Fig. 2 illustrates the structure of KLaTiO_4 . It consists of a single layer of corner-sharing distorted TiO_6 octahedra extending parallel to (001). The layers are separated by alternating layers of K^+ and La^{3+} cations along [001]. The TiO_6 octahedra ($4mm$ symmetry) are considerably distorted. They have four equal equatorial Ti—O distances [1.9635 (12) Å], one very short Ti—O distance [1.775 (9) Å] toward the K layer and a significantly longer Ti—O distance [2.558 (7) Å] towards the La layer. The corresponding coordination polyhedra around the K^+ and La^{3+} cations are distorted KO_9 and LaO_9 polyhedra, each with $4mm$ symmetry.

S2. Experimental

The sample was prepared by conventional solid-state reaction. The starting materials were KNO_3 , La_2O_3 and TiO_2 in a molar ratio of 2:1:2. An excess of KNO_3 (55 mol%) was added to compensate for the loss due to the volatilization of the potassium component. La_2O_3 was heated to 1173 K for 10 h prior to use to remove water and carbonate impurities. The mixture was then ground and calcined at 1223 K for 30 min.

S3. Refinement

The crystal structure of NaLaTiO_4 (Toda *et al.*, 1996b) in the spacegroup $P4/nmm$ was used as a starting model for the final Rietveld refinement of the KLaTiO_4 structure. Isotropic displacement parameters were used for all atoms. The March-Dollase option in the *EXPGUI* program (Toby, 2001) was applied to correct for preferential orientation along $[00l]$ which is often observed for such layered perovskites.

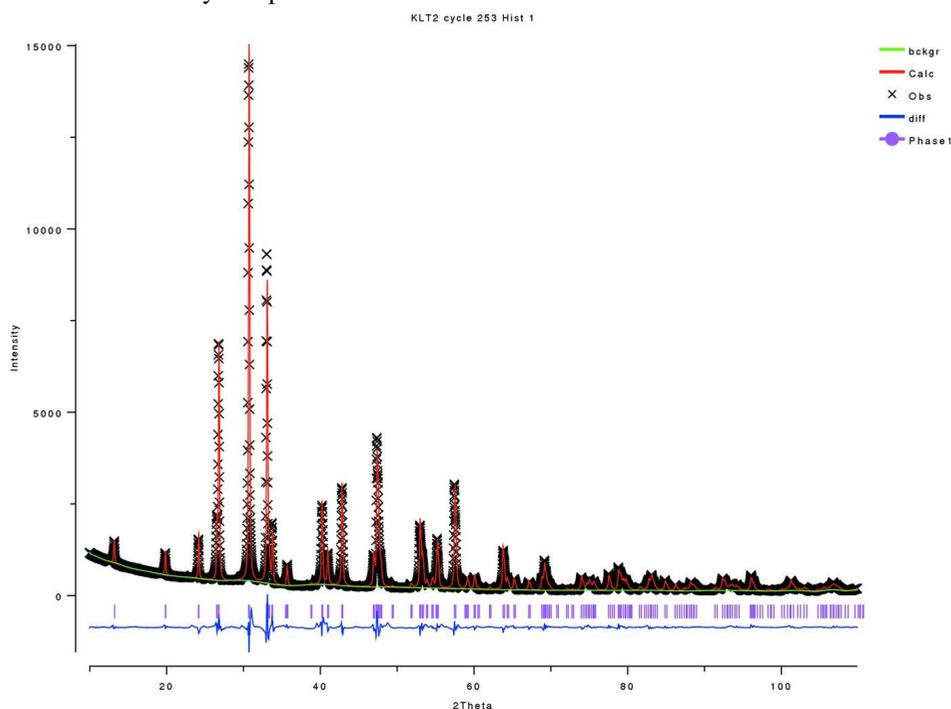


Figure 1

Rietveld difference plot for the refinement of KLaTiO_4 .

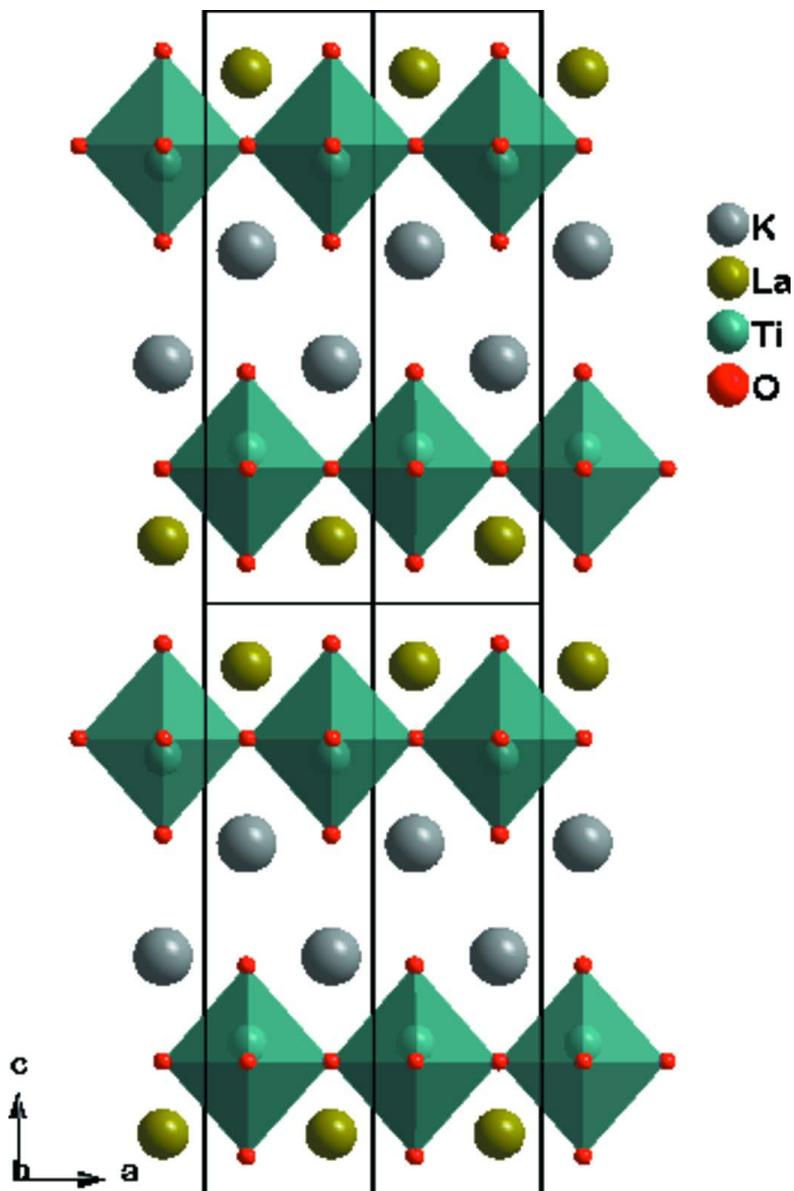


Figure 2

The crystal structure of KLaTiO_4 in a projection along $[010]$.

Potassium lanthanum titanate

Crystal data

KLaTiO_4

$M_r = 289.90$

Tetragonal, $P4/nmm$

Hall symbol: $-p\ 4a\ 2a$

$a = 3.84155(10)\ \text{\AA}$

$c = 13.4695(4)\ \text{\AA}$

$V = 198.78(1)\ \text{\AA}^3$

$Z = 2$

$D_x = 4.848\ \text{Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54060, 1.54443\ \text{\AA}$

$T = 298\ \text{K}$

white

flat sheet, $20 \times 20\ \text{mm}$

Specimen preparation: Prepared at 1223 K

Data collection

PANalytical X'pert PRO
diffractometer
Radiation source: sealed tube
Graphite monochromator

Specimen mounting: packed powder pellet
Data collection mode: reflection
Scan method: continuous
 $2\theta_{\min} = 9.872^\circ$, $2\theta_{\max} = 109.815^\circ$, $2\theta_{\text{step}} = 0.017^\circ$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R_p = 0.046$
 $R_{\text{wp}} = 0.068$
 $R_{\text{exp}} = 0.046$
 $R(F^2) = 0.04713$
 $\chi^2 = 2.220$
5880 data points
Excluded region(s): none
Profile function: CW Profile function number 2
with 18 terms Profile coefficients for Simpson's
rule integration of pseudovoigt function C.J.
Howard (1982). J. Appl. Cryst., 15, 615-620. P.
Thompson, D.E. Cox & J.B. Hastings (1987). J.
Appl. Cryst., 20, 79-83. #1(GU) = 0.000 #2(GV)
= -2.261 #3(GW) = -9.290 #4(LX) = 4.310
#5(LY) = 17.630 #6(trns) = 0.000 #7(asym) =
3.5282 #8(shft) = 0.0000 #9(GP) = 17.284
#10(stec) = 0.00 #11(ptec) = 0.00 #12(sfec) = 0.00
#13(L11) = 0.000 #14(L22) = 0.000 #15(L33) =
0.000 #16(L12) = 0.000 #17(L13) = 0.000
#18(L23) = 0.000 Peak tails are ignored where
the intensity is below 0.0010 times the peak
Aniso. broadening axis 0.0 0.0 1.0

60 parameters
0 restraints
 $w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.01$
Background function: GSAS Background
function number 1 with 36 terms. Shifted
Chebyshev function of 1st kind 1: 353.285 2:
-361.136 3: 220.846 4: -104.260 5: 61.8271 6:
-33.1030 7: 19.7877 8: -5.01446 9: 3.42337 10:
-3.14370 11: 0.340114 12: 2.15882 13:
-0.130836 14: -1.88421 15: 5.08631 16:
-1.48077 17: 4.42719 18: 2.91556 19:
-3.924060E-0220: 0.679453 21: 5.77738 22:
-2.47188 23: 3.81643 24: 3.21357 25: -4.71396
26: -1.63350 27: 0.665874 28: -7.16378 29:
-7.040150E-0230: 3.04932 31: -2.36381 32:
0.787399 33: 4.27144 34: -2.96952 35: 4.90415
36: 1.54599
Preferred orientation correction: March-Dollase
AXIS 1 Ratio = 0.96438 h = 0.000 k = 0.000 l =
1.000 Preferred orientation correction range:
Min = 0.94706, Max = 1.11492

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.25	0.25	0.5950 (2)	0.0278 (9)*
LA1	0.25	0.25	0.89446 (6)	0.0199 (4)*
Ti1	0.75	0.75	0.74203 (19)	0.0151 (7)*
O1	0.75	0.25	0.7723 (4)	0.0189 (17)*
O2	0.25	0.25	0.3897 (6)	0.039 (2)*
O3	0.25	0.25	0.0681 (5)	0.018 (2)*

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

K1—O1 ⁱ	3.065 (4)	La1—O1 ⁱⁱⁱ	2.530 (3)
K1—O1	3.065 (4)	La1—O3 ^{viii}	2.339 (7)
K1—O1 ⁱⁱ	3.065 (4)	La1—O3 ^{iv}	2.7628 (12)
K1—O1 ⁱⁱⁱ	3.065 (4)	La1—O3 ^v	2.7628 (12)
K1—O2	2.765 (9)	La1—O3 ^{vi}	2.7628 (12)
K1—O2 ^{iv}	2.7242 (7)	La1—O3 ^{vii}	2.7628 (12)
K1—O2 ^v	2.7242 (7)	Ti1—O1	1.9635 (12)
K1—O2 ^{vi}	2.7242 (7)	Ti1—O1 ^{ix}	1.9635 (12)

K1—O2 ^{vii}	2.7242 (7)	Ti1—O1 ⁱⁱⁱ	1.9635 (12)
La1—O1 ⁱ	2.530 (3)	Ti1—O1 ^x	1.9635 (12)
La1—O1	2.530 (3)	Ti1—O2 ^{vii}	1.775 (9)
La1—O1 ⁱⁱ	2.530 (3)	Ti1—O3 ^{vii}	2.558 (7)
O1 ⁱ —K1—O1	77.62 (13)	O1 ⁱ —La1—O3 ^v	65.85 (12)
O1 ⁱ —K1—O1 ⁱⁱ	52.61 (8)	O1 ⁱ —La1—O3 ^{vi}	130.30 (11)
O1 ⁱ —K1—O1 ⁱⁱⁱ	52.61 (8)	O1 ⁱ —La1—O3 ^{vii}	130.30 (11)
O1 ⁱ —K1—O2	141.19 (6)	O1—La1—O1 ⁱⁱ	64.95 (9)
O1 ⁱ —K1—O2 ^{iv}	59.94 (15)	O1—La1—O1 ⁱⁱⁱ	64.95 (9)
O1 ⁱ —K1—O2 ^v	59.94 (15)	O1—La1—O3 ^{viii}	130.59 (9)
O1 ⁱ —K1—O2 ^{vi}	112.52 (18)	O1—La1—O3 ^{iv}	130.30 (11)
O1 ⁱ —K1—O2 ^{vii}	112.52 (18)	O1—La1—O3 ^v	130.30 (11)
O1—K1—O1 ⁱⁱ	52.61 (8)	O1—La1—O3 ^{vi}	65.85 (12)
O1—K1—O1 ⁱⁱⁱ	52.61 (8)	O1—La1—O3 ^{vii}	65.85 (12)
O1—K1—O2	141.19 (6)	O1 ⁱⁱ —La1—O1 ⁱⁱⁱ	98.81 (17)
O1—K1—O2 ^{iv}	112.52 (18)	O1 ⁱⁱ —La1—O3 ^{viii}	130.59 (9)
O1—K1—O2 ^v	112.52 (18)	O1 ⁱⁱ —La1—O3 ^{iv}	65.85 (12)
O1—K1—O2 ^{vi}	59.94 (15)	O1 ⁱⁱ —La1—O3 ^v	130.30 (11)
O1—K1—O2 ^{vii}	59.94 (15)	O1 ⁱⁱ —La1—O3 ^{vi}	65.85 (12)
O1 ⁱⁱ —K1—O1 ⁱⁱⁱ	77.62 (13)	O1 ⁱⁱ —La1—O3 ^{vii}	130.30 (11)
O1 ⁱⁱ —K1—O2	141.19 (6)	O1 ⁱⁱⁱ —La1—O3 ^{viii}	130.59 (9)
O1 ⁱⁱ —K1—O2 ^{iv}	59.94 (15)	O1 ⁱⁱⁱ —La1—O3 ^{iv}	130.30 (11)
O1 ⁱⁱ —K1—O2 ^v	112.52 (18)	O1 ⁱⁱⁱ —La1—O3 ^v	65.85 (12)
O1 ⁱⁱ —K1—O2 ^{vi}	59.94 (15)	O1 ⁱⁱⁱ —La1—O3 ^{vi}	130.30 (11)
O1 ⁱⁱ —K1—O2 ^{vii}	112.52 (18)	O1 ⁱⁱⁱ —La1—O3 ^{vii}	65.85 (12)
O1 ⁱⁱⁱ —K1—O2	141.19 (6)	O3 ^{viii} —La1—O3 ^{iv}	79.48 (14)
O1 ⁱⁱⁱ —K1—O2 ^{iv}	112.52 (18)	O3 ^{viii} —La1—O3 ^v	79.48 (14)
O1 ⁱⁱⁱ —K1—O2 ^v	59.94 (15)	O3 ^{viii} —La1—O3 ^{vi}	79.48 (14)
O1 ⁱⁱⁱ —K1—O2 ^{vi}	112.52 (18)	O3 ^{viii} —La1—O3 ^{vii}	79.48 (14)
O1 ⁱⁱⁱ —K1—O2 ^{vii}	59.94 (15)	O3 ^{iv} —La1—O3 ^v	88.09 (5)
O2—K1—O2 ^{iv}	94.34 (18)	O3 ^{iv} —La1—O3 ^{vi}	88.09 (5)
O2—K1—O2 ^v	94.34 (18)	O3 ^{iv} —La1—O3 ^{vii}	159.0 (3)
O2—K1—O2 ^{vi}	94.34 (18)	O3 ^v —La1—O3 ^{vi}	159.0 (3)
O2—K1—O2 ^{vii}	94.34 (18)	O3 ^v —La1—O3 ^{vii}	88.09 (5)
O2 ^{iv} —K1—O2 ^v	89.67 (3)	O3 ^{vi} —La1—O3 ^{vii}	88.09 (5)
O2 ^{iv} —K1—O2 ^{vi}	89.67 (3)	O1—Ti1—O1 ^{ix}	156.1 (3)
O2 ^{iv} —K1—O2 ^{vii}	171.3 (4)	O1—Ti1—O1 ⁱⁱⁱ	87.53 (7)
O2 ^v —K1—O2 ^{vi}	171.3 (4)	O1—Ti1—O1 ^x	87.53 (7)
O2 ^v —K1—O2 ^{vii}	89.67 (3)	O1—Ti1—O2 ^{vii}	101.97 (16)
O2 ^{vi} —K1—O2 ^{vii}	89.67 (3)	O1 ^{ix} —Ti1—O1 ⁱⁱⁱ	87.53 (7)
O1 ⁱ —La1—O1	98.81 (17)	O1 ^{ix} —Ti1—O1 ^x	87.53 (7)
O1 ⁱ —La1—O1 ⁱⁱ	64.95 (9)	O1 ^{ix} —Ti1—O2 ^{vii}	101.97 (16)
O1 ⁱ —La1—O1 ⁱⁱⁱ	64.95 (9)	O1 ⁱⁱⁱ —Ti1—O1 ^x	156.1 (3)

O1 ⁱ —La1—O3 ^{viii}	130.59 (9)	O1 ⁱⁱⁱ —Ti1—O2 ^{vii}	101.97 (16)
O1 ⁱ —La1—O3 ^{iv}	65.85 (12)	O1 ^x —Ti1—O2 ^{vii}	101.97 (16)

Symmetry codes: (i) $x-1, y, z$; (ii) $-y+1/2, x-1, z$; (iii) $-y+1/2, x, z$; (iv) $-x, -y, -z+1$; (v) $-x, -y+1, -z+1$; (vi) $-x+1, -y, -z+1$; (vii) $-x+1, -y+1, -z+1$; (viii) $x, y, z+1$; (ix) $x, y+1, z$; (x) $-y+3/2, x, z$.