

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

^aDepartment of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China, and ^bDepartment of Nanomaterial and Nanochemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, 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 $\sigma(\text{La}-\text{O}) = 0.003$ 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 isotopic 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).

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supplementary materials

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Rietveld refinement of KLaTiO₄ from X-ray powder data

B.-C. Zhu and K.-B. Tang

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 KLaTiO₄ we report here is a $n = 1$ member of this family. Isotypic crystal structures have been reported for NaLnTiO₄ ($Ln = La, Pr, Nd, Sm, Eu, Gd, Y$ and Lu; Toda *et al.*, 1996a) in the space group $P4/nmm$.

Schaak & Mallouk (2001) reported the KLnTiO₄ ($Ln = La, Nd, Sm, Eu, Gd, Dy$) 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 KLnTiO₄ ($P4/nmm$; Schaak & Mallouk, 2001) and NaLnTiO₄ ($P4/nmm$; Toda *et al.*, 1996a) as starting models for Rietveld refinement of KLaTiO₄. 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 NaLnTiO₄ compounds have tetragonal symmetry for $Ln = La-Nd$, while an orthorhombic symmetry is observed for $Ln = Sm-Lu$ and Y (Nishimoto *et al.*, 2006). We can infer that a similar situation might be present for KLnTiO₄ compounds. We ascribe the difference in symmetry between KLaTiO₄ 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 KLaTiO₄ 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. KLaTiO₄ easily decomposes at high temperature and is converted into the three-layer Ruddlesden-Popper phase K₂La₂Ti₃O₁₀. This phenomenon is also found in during preparation of NaLaTiO₄ reported by Toda *et al.* (1996b). Therefore we modified the reaction conditions on the basis of the preparation of NaLaTiO₄ 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 KLaTiO₄. It consists of a single layer of corner-sharing distorted TiO₆ octahedra extending parallel to (001). The layers are separated by alternating layers of K⁺ and La³⁺ cations along [001]. The TiO₆ 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 La³⁺ cations are distorted KO₉ and LaO₉ polyhedra, each with $4mm$ symmetry.

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.

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.

Figures

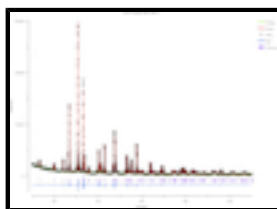


Fig. 1. Rietveld difference plot for the refinement of KLaTiO_4 .

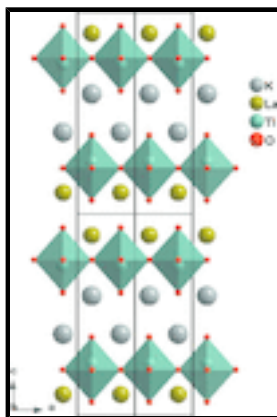


Fig. 2. The crystal structure of KLaTiO_4 in a projection along $[010]$.

Potassium lanthanum titanate

Crystal data

KLaTiO_4

$M_r = 289.90$

Tetragonal, $P4/nmm$

Hall symbol: -p 4a 2a

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

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

$Z = 2$

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

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

$T = 298 \text{ K}$

white

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

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

Specimen preparation: Prepared at 1223 K

Data collection

PANalytical X'pert PRO
diffractometer

Data collection mode: reflection

Radiation source: sealed tube
graphite

Scan method: continuous

Specimen mounting: packed powder pellet

$2\theta_{\min} = 9.872^\circ$, $2\theta_{\max} = 109.815^\circ$, $2\theta_{\text{step}} = 0.017^\circ$

Refinement

Refinement on F^2

Excluded region(s): none

Least-squares matrix: full

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(pte) = 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

$R_p = 0.046$

60 parameters

$R_{wp} = 0.068$

0 restraints

$R_{\text{exp}} = 0.046$

$w = 1/[\sigma^2(F_o^2) + (0.0677P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$R(F^2) = 0.04713$

$(\Delta/\sigma)_{\max} = 0.01$

$\chi^2 = 2.220$

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

5880 data points

Preferred orientation correction: March-Dollase AX-IS 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)*

supplementary materials

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 (Å, °)

K1—O1 ⁱ	3.065 (4)	La1—O1 ⁱⁱⁱ	2.5295 (32)
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	2.5295 (32)	Ti1—O1 ^x	1.9635 (12)
La1—O1	2.5295 (32)	Ti1—O2 ^{vii}	1.775 (9)
La1—O1 ⁱⁱ	2.5295 (32)	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}	158.96 (27)
O2—K1—O2 ^{vi}	94.34 (18)	O3 ^v —La1—O3 ^{vi}	158.96 (27)
O2—K1—O2 ^{vii}	94.34 (18)	O3 ^v —La1—O3 ^{vii}	88.09 (5)
O2 ^{iv} —K1—O2 ^v	89.672 (27)	O3 ^{vi} —La1—O3 ^{vii}	88.09 (5)
O2 ^{iv} —K1—O2 ^{vi}	89.672 (27)	O1—Ti1—O1 ^{ix}	156.05 (33)
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}	89.672 (27)	O1—Ti1—O2 ^{vii}	101.97 (16)
O2 ^{vi} —K1—O2 ^{vii}	89.672 (27)	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	156.05 (33)
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) $-y+3/2, x, z$.

Fig. 1

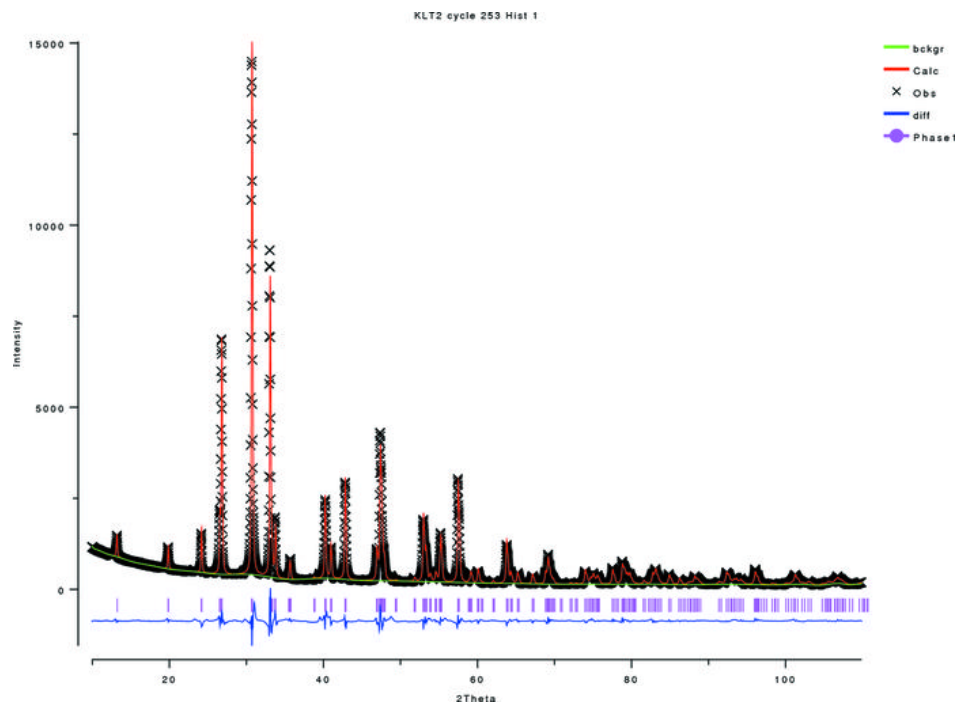


Fig. 2

