

Powder Neutron Diffraction Study of Layered Perovskite, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$

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層状ペロブスカイト $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ の粉末中性子回折による構造決定

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Crystal structure of a layered perovskite, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, was determined by the Rietveld refinement method for a powder neutron diffraction pattern. The compound crystallizes a monoclinic system with a space group $P2_1/m$ (No. 11) and lattice parameters of $a = 0.77418(6)$ nm, $b = 0.77073(6)$ nm, $c = 1.4859(1)$ nm, $\beta = 97.51(1)^\circ$.

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1. Introduction

In recent years, the layered perovskite series containing an alkali metal ion such as $M[A_{n-1}B_nO_{3n+1}]$ (M = alkali metal; A = alkaline earths and rare earths; B = Nb and Ta)^{1),2)} have been actively studied as photocatalysts,^{3),4)} ionic conductors,^{5),6)} superconductors^{7),8)} and phosphors.^{9),10)} This phase has recently been dubbed the Dion–Jacobson series. The layered perovskite compound, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, is a typical example for the Dion–Jacobson series. Dion et al. indexed the X-ray patterns of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ on the basis of a tetragonal unit cell. More recently the crystal structure of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was described with a tilting of NbO_6 octahedron in an orthorhombic system.¹¹⁾ However, many weak superlattice peaks were neglected in the refinement based on the orthorhombic symmetry. The validity of each structure model was not clear up at present. Since neutron beams interact more strongly with nuclei than do X-rays, neutron diffraction is more useful than X-ray diffraction for determining oxygen positions. By the neutron diffraction study, we found that the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ actually crystallizes in a monoclinic system in disagreement with a recent report.

2. Experimental

The layered perovskite, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, was prepared by a conventional solid state reaction. The starting materials were K_2CO_3 , CaCO_3 and Nb_2O_5 . An excess amount of K_2CO_3 (50 mol%) was added to compensate for loss due to the evaporation of potassium component. Excess potassium carbonate can also act as a reactive flux. The reactants were ground, pelletized and then fired in an open alumina crucible. The mixture was heated for 12 h at 1073 K, subsequently calcined for another 4–24 h at 1273–1573 K. The product was washed with distilled water to remove excess alkaline component and air-dried at room temperature. The product does not exist in any hydrous form even when the compound is washed with water. We performed neutron powder diffraction experiments on the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, of Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research

Institute (JAERI), Tokai.¹²⁾ An incident neutron wavelength λ was 0.18207(7) nm. The fine powder sample was enclosed in a cylindrical vanadium vessel. The data were collected on thoroughly ground powders by a multi-scanning mode in the 2θ range from 3° to 153° with a step width of 0.1° . The powder pattern obtained was indexed with the aid of the computer program CELL.¹³⁾ Rietveld structure refinement was carried out with the program RIETAN2000.¹⁴⁾

3. Results and discussion

Fukuoka et al. indexed their XRD pattern for single crystal $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ based on an orthorhombic ($Cmcm$) unit cell with $a = 0.38802(9)$ nm, $b = 2.9508(6)$ nm, $c = 0.7714(1)$ nm.¹¹⁾ First, the orthorhombic model based on the space group $Cmcm$ as suggested in Ref. 11 was checked. However, the refinement gave rather poor R -factors ($R_{wp} = 12.85\%$, $R_p = 9.70\%$, $R_e = 3.45\%$, $R_1 = 7.81\%$ and $R_f = 4.14\%$). **Figure 1** shows the powder neutron diffraction pattern of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$. All of the reflections could be assigned as a monoclinic and not orthorhombic symmetry. Possible space groups were monoclinic $P2_1/m$ (No. 11) or Pm (No. 6). High symmetry $P2_1/m$ was adopted in this study. The model structure was derived from the orthorhombic one.¹¹⁾ The positional para-

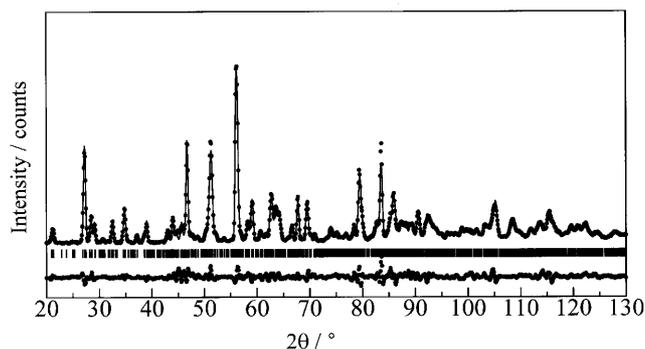


Fig. 1. Powder neutron fitting pattern of layered perovskite, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$.

meters and temperature factors are listed in **Table 1**. Selected bond distances are presented in **Table 2**. $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ has a monoclinic unit cell with space group $P2_1/m$. The unit cell parameters are: $a=0.77418(6)$ nm, $b=0.77073(6)$ nm, $c=1.4859(1)$ nm, $\beta=97.51(1)^\circ$ and $Z=4$. The R -factors of refinement are $R_{\text{wp}}=9.44\%$, $R_p=7.10\%$, $R_e=3.41\%$, $R_I=2.69\%$ and $R_F=1.23\%$.

The crystal structure of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ is illustrated in **Fig. 2**. The calcium cation is located in the perovskite intralayer site and the potassium cation in the interlayer site. The adjacent perovskite layers are stacked with a displacement by $1/2$ along only one direction within the layer plane. The stacking feature of the perovskite layer is similar to that of the tantalate compound, $\text{KCa}_2\text{Ta}_3\text{O}_{10}$.¹⁵⁾ The crystal structure of monoclinic model is essentially analogous as that of previously reported structure proposal.^{1),11)} The reduction in symmetry arises from subtle tilting of NbO_6 , which was not detected by X-ray diffraction data. The neutron diffraction study provides clear

evidence for rotation about the three axes with octahedral twisting. Therefore, the potassium cations are also displaced slightly from the ideal positions. Octahedral tilting reduces the symmetry of the A-site cation coordination environment and results in a change in A–O bond lengths. In addition, the tilting of the octahedra changes the angles and distances along the Nb–O–Nb bonds. Recent precise structural study of related layered perovskites, $\text{LiCa}_2\text{Nb}_3\text{O}_{10}$ and $\text{NaCa}_2\text{Nb}_3\text{O}_{10}$ also indicate such symmetry reductions based on the octahedral tilting.^{16),17)} These structural changes affect the optic and electrical properties drastically. Our precise structure model will contribute toward calculating band structure for theorists.

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Table 1. Positional Parameters and Temperature Factors of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$

Atoms	site	x	y	z	B/Å ²	
Ca1	2e	0.220(6)	0.25	0.847(2)	1.3(6)	
Ca2	2e	0.283(6)	0.25	0.154(3)	1.3(6)	(= Ca1)
Ca3	2e	0.678(4)	0.25	0.872(2)	0.09(56)	
Ca4	2e	0.799(5)	0.25	0.149(2)	0.09(56)	(= Ca3)
K1	2c	0.384(8)	0.75	0.465(3)	1.6(6)	
K2	2c	0.868(7)	0.75	0.492(2)	1.6(6)	(= K1)
Nb1	2a	0.0	0.0	0.0	0.15(9)	
Nb2	2b	0.5	0.0	0.0	0.15(9)	(= Nb1)
Nb3	4f	0.429(2)	-0.004(1)	0.7152(9)	0.15(9)	(= Nb1)
Nb4	4f	0.925(2)	0.013(1)	0.7110(9)	0.15(9)	(= Nb1)
O1	4f	0.505(2)	-0.033(2)	0.871(1)	0.6(4)	
O2	4f	0.406(4)	0.017(3)	0.595(1)	2.4(4)	
O3	4f	0.684(3)	-0.012(2)	0.730(1)	0.5(3)	
O4	2e	0.459(4)	0.250	0.751(2)	0.7(4)	
O5	2e	0.426(6)	0.75	0.725(2)	2.0(3)	
O6	2e	0.424(3)	0.25	0.986(1)	0.7(4)	(= O4)
O7	4f	0.245(4)	-0.053(1)	-0.020(1)	2.0(3)	(= O5)
O8	4f	-0.008(3)	-0.052(2)	0.870(1)	0.6(3)	
O9	4f	0.919(3)	0.047(2)	0.594(1)	0.6(3)	
O10	4f	0.182(3)	0.026(2)	0.752(1)	0.008(5)	
O11	2e	-0.065(4)	0.25	0.767(2)	1.0(6)	
O12	2e	0.931(5)	0.75	0.718(2)	2.0(3)	(= O5)
O13	2c	0.027(4)	0.25	0.972(1)	0.4(5)	

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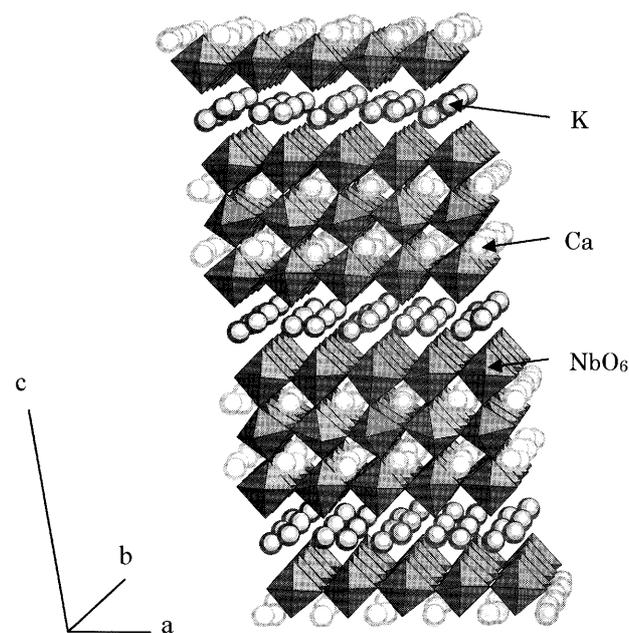


Fig. 2. Crystal structure of layered perovskite, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$.

Table 2. Bond Distance of NbO_6 Octahedral in Layered Perovskite, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$

Bond	Bond distance (nm)	Bond	Bond distance (nm)
Nb1–O7 (×2)	0.198(4)	Nb2–O1 (×2)	0.190(3)
Nb1–O8 (×2)	0.194(3)	Nb2–O6 (×2)	0.200(1)
Nb1–O13 (×2)	0.1999(9)	Nb2–O7 (×2)	0.201(4)
Nb3–O1	0.236(3)	Nb4–O3	0.190(4)
Nb3–O2	0.175(3)	Nb4–O8	0.239(3)
Nb3–O3	0.200(3)	Nb4–O9	0.174(3)
Nb3–O4	0.204(2)	Nb4–O10	0.195(3)
Nb3–O5	0.188(1)	Nb4–O11	0.195(2)
Nb3–O10	0.209(3)	Nb4–O12	0.205(1)

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