Virtually extinction-free single-crystal diffraction using small crystals  
- Superstructure of triclinic LiCa₂Nb₃O₁₀ -

Nobuo ISHIZAWA¹, Reiko YAMASHITA¹, Satoru KUZE¹, Masato HAYATSU¹, Katsumi SUDA¹,  
Barbara ETSCHMANN², Douglas DU BOULAY¹, Shuji OISHI², James HESTER³  
and Shunji KISHIMOTO⁴

¹ Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan,  
² Faculty of Engineering, Shinshu University, Nagano 380-8553, Japan,  
³ ANST, Menai, NSW 2234, Australia, ⁴ KEK-PF, Tsukuba, Ibaraki 305-0801, Japan.

Introduction  
The layered perovskite-type ACa₂Nb₃O₁₀ compounds with A=Li, Na, K, Rb, and Cs have recently attracted  
attention because of their properties such as superconductivity and photocatalytic behaviours  
for overall water splitting. Though the aristotype structure of ACa₂Nb₃O₁₀ has tetragonal symmetry, detailed analyses  
based on single-crystal X-ray diffraction suggest lower symmetries. The crystals are generally difficult to grow in  
large scale suitable for single-crystal diffraction, and are often accompanied by the twinning and poor crystallinity.  
These difficulties had left the system out of detailed structural studies using conventional X-ray sources.

Experimental  
A crystal of approximately 60x46x25 µm² was chosen from a number of crystal fragments for the SR experiment.  
Diffraction data were obtained using a horizontal-type four-circle diffractometer at beam line [1]. Vertically polarised X-rays of 0.75008 (2) Å were used with an  
eight-channel avalanche photodiode detector [2]. The detection efficiency was approximately 75% at this  
wavelength. Since the dynamic range of the detector exceeds 10⁸ cps, neither attenuator nor absorber was used for  
data collection. The recorded maximum count rate for the present crystal was approximately 1.4x10⁶ cps for 020.  
The determination of cell dimensions assuming a triclinic cell revealed a significant though small offset for β while  
no significant offsets from orthogonality for α and γ: α = 5.4809 (3) Å, β = 5.4804 (3) Å, γ = 26.5533 (16) Å, α=  
89.999 (4)°, β = 90.245 (4)°, γ = 89.999 (5)°. This superstructure has a doubled unit cell volume with respect to  
the tetragonal aristotype. The intensity statistics of the parity groups suggested that there were no systematic  
absences for hkl except for 0k0 with k odd. Therefore the crystal was assumed to have monoclinic P2₁ symmetry  
until the final stage of structure solution and refinement.

After the structure was solved with P2₁, however, it was difficult to eliminate the possibility of inversion centres  
completely, because only the Li and several O atom positions were displaced more than three standard  
uncertainties from the centrosymmetric positions. The monoclinic space groups containing mirrors were  
excluded by the geometrical problems they would involve for octahedral rotation. Therefore, triclinic P-1 symmetry  
was tested finally. It was revealed that the P-1 model is superior to P2₁ in all senses. The major reason for the  
removal of the twofold screw symmetries lies in the interlayer structure, i.e., positional shifts of the lightest Li  
atoms and their distribution among the available sites. The extinction correction was unnecessary in all  
calculations.

Results  
Because of the space problem, all structural figures were eliminated in this report. Readers may refer to the  

The corner-linked NbO₆ octahedra are rotated relative to each other by approximately 10° about axes parallel to  
<110>. The dominant rotation axes align parallel within a slab, while they are flipped by 90° in adjacent slabs. As a  
result, the slabs are geometrically related by 4₂ pseudo symmetry along c. Adjacent slabs are joined together by  
Li atoms. There are twice as many sites as Li atoms, providing the variety of population at these Li sites. The  
fivefold Li1 and Li2 sites have populations approximately twice as large as the fourfold Li3 and Li4 sites. The 2:1  
ratio in the occupancies of the Li sites is suggestive of a possible long-range modulation with a tripled c axis  
periodicity, though the present X-ray study revealed no such modulation along c. It is possible that a longer  
ameaning time would allow such a modulation to develop in the present crystal.

Virtually extinction-free single crystal diffraction experiments to obtain accurate deformation density  
distributions in various inorganic compounds are also being carried out using the program 99G190. Several  
outcomes are given in the references [4-5].

References  

* nishizawa@n.cc.titech.ac.jp