Virtually extinction-free single-crystal diffraction using small crystals - Superstructure of triclinic $LiCa_2Nb_3O_{10}$ -

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Introduction

The layered perovskite-type $ACa_2Nb_3O_{10}$ 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 $ACa_2Nb_3O_{10}$ 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 μm^3 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) A 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 10^8 cps, neither attenuator nor absorber was used for data collection. The recorded maximum count rate for the present crystal was approximately $1.4x10^6$ 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: a = 5.4809 (3) Å, b = 5.4804 (3) Å, c = 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 $P2_1$ symmetry until the final stage of structure solution and refinement. After the structure was solved with $P2_1$, 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 $P2_1$ 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 reference [3] for further understanding.

The corner-linked NbO_6 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 4_2 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 annealing 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

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