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The *R*-3 distortion in $LaAlO_3$ derivatives

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Introduction

It has been reported that the crystal structure of $(1-x)LaAlO_3$-$xSrTiO_3$ system adopts the space group *R*-3*c* in the range $0 \leq x < 0.8$ [1]. On the other hand, the far infrared reflective spectral analysis on the Sr and Ti doped $LaAlO_3$ ceramics [2] revealed new phonon modes which do not exist in the pure $LaAlO_3$, suggesting a possible difference in symmetry for the Sr and Ti codoped $LaAlO_3$ compared with the pure $LaAlO_3$. The present study was undertaken to reinvestigate the symmetry and structure of the $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ single crystals [3] with nominal compositions x=0.005 and 0.20.

Experimental

Prior to the synchrotron X-ray experiments, preliminary data were collected at room temperature by the single-crystal CCD diffractometer using Mo Kα radiation. Since the rhombohedral distortion of the crystals from the cubic symmetry were so small, a careful treatment was necessary to choose the true 3-fold axis from the four possible orientations [4].

Synchrotron diffraction experiments were carried out using the horizontal-type four-circle diffractometer at beamline 14A, PF-KEK [5]. Vertically polarized X-rays were monochromatized with the Si (111) double crystal monochromater. The wavelength of the X-rays was calibrated using the Si standard crystal. The eight-channel avalanche photodiode detector was used for the photon counting. Neither absorbers nor attenuators were used owing to the wide dynamic range of the detector with a linearity up to 10^8 counts per second [6]. Data were collected for the crystal x=0.005 at 120 K and 297 K, and for the crystal x=0.20 at 300 K. Data reduction and the refinements of structure parameters were carried out using Xtal program package.

The reciprocal sections reconstructed from the CCD frame images, and the ω-2θ step scan profiles using SR, indicated a presence of reflections which are not allowed in the space group *R*-3*c*. An example of the 221 profile in rhombohedral setting is shown in Fig. 1. This fact indicates that the *c*-glide plane is missing in the crystal. The possible space groups are limited to *R*3 and *R*-3 with the Laue class -3, and *R*32, *R*3*m*, and *R*-3*m* with the Laue class -3m.

The present crystals presumably belong to the *R*-3 symmetry which accommodates two crystallographically independent octahedral sites B1 and B2 with different octahedral volumes. The larger octahedral B1 site is occupied by both the Al and Ti atoms whereas the smaller B2 site is occupied exclusively by Al atoms in the crystal x=0.005. This site preference became indistinguishable in the crystal x=0.20, and Ti was found at both sites with almost equal population. The changes in B1-O-B2 bond angle and the population of Ti at B1 and B2 sites are, supposedly, highly correlated with the dielectric properties of the $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ solid solution crystals with 0<x<0.5.

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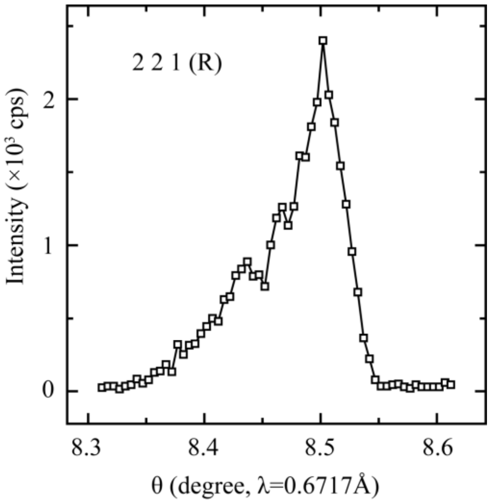

Fig. 1. The 221 diffraction profile of the $(1-x)LaAlO_3$-$xSrTiO_3$ crystal with x=0.005 in rhombohedral setting.

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