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High-temperature synchrotron X-ray powder diffraction study of the orthorhombic-tetragonal phase transition in lanthanum titanate perovskite $La_{0.68}(Ti_{0.95},Al_{0.05})O_3$

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Introduction

Doped $La_{2/3}TiO_3$ compounds have double perovskite-type structure and exhibit excellent electrical and dielectric properties. Thermal expansion and temperature dependence of lattice parameters are important factors in designing the components of solid oxide fuel cells. Conventional X-ray diffractometer produces double wavelengths of $K\alpha_1$+$K\alpha_2$, and broad diffraction peaks with asymmetric shape, which lead inaccuracy in determining the peak positions and thus lattice parameters. Here, we have used synchrotron X-ray diffraction technique, having higher angular resolution and simple peak shape (no $K\alpha_2$ peak) compared with conventional X-ray diffractometry, to determine precise lattice parameters of $La_{0.68}(Ti_{0.95},Al_{0.05})O_3$ as a function of temperature and to investigate the phase transition temperature.

Experiments

To obtain higher angular resolution as possible with good counting statistics, we performed synchrotron X-ray powder diffraction experiments for $La_{0.68}(Ti_{0.95},Al_{0.05})O_3$ at the beam line BL-3A at the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. A monochromatized 1.37852(6) Å X-ray was used for high-temperature diffraction experiments. To improve the angular resolution a Si (111) analyzer crystal was installed between the sample and the scintillation counter. The angular resolution $\Delta d/d$ was estimated to be 0.0002 from the peak width for the standard CeO_2 powders where d is the lattice spacing.

Results and discussion

Figure 1a shows the conventional laboratory-based X-ray powder diffraction profile for 004, 020 and 200 reflections of $La_{0.68}(Ti_{0.95},Al_{0.05})O_3$ measured at 200°C. The splitting into 020 and 200 reflections was not so clear in the conventional diffraction profile. On the contrary, the corresponding split was clear for the synchrotron X-ray powder diffraction profile measured at the same temperature (Fig. 1b). This clear splitting is ascribed to (1) much narrower peak width and to (2) no splitting as $K_{\alpha1}$ and $K_{\alpha2}$. The full width at half maximum for 020 synchrotron X-ray diffraction peak 0.0209(6) deg. was much narrower than that obtained by the conventional diffractometer, 0.119(5) deg. Therefore, the resultant unit-cell parameters estimated by the synchrotron diffraction technique had smaller error bars: a=3.85926(3), b=3.87045(4) and c=7.77595(5) Å, comparing with those by the conventional diffractometer: a=3.8600(2), b=3.8711(1) and c=7.7731(2) Å. These results indicate that the present synchrotron X-ray powder diffraction technique is very powerful to decompose the peaks with very small difference in peak positions, compared with the conventional laboratory-based X-ray powder diffraction method. The unit-cell parameters a, b and c increased with an increase of temperature. Unit-cell parameter a increased considerably compared with b parameter, resulting that these two parameters became closer continuously with an increase of temperature and that coincided at 350 ± 2°C. The c/a ratio was almost independent of temperature, while the b/a decreased continuously with an increase of temperature and became unity at 350°C. Unit-cell parameters determined from the data measured on heating exhibited fairly good agreements with those measured on cooling. Taking account into the results, (I) Good agreement between the unit-cell parameters obtained from the heating and cooling data, (II) Continuous change in unit-cell parameters with temperature, the orthorhombic-tetragonal phase transition is strongly suggested to be continuous and reversible.

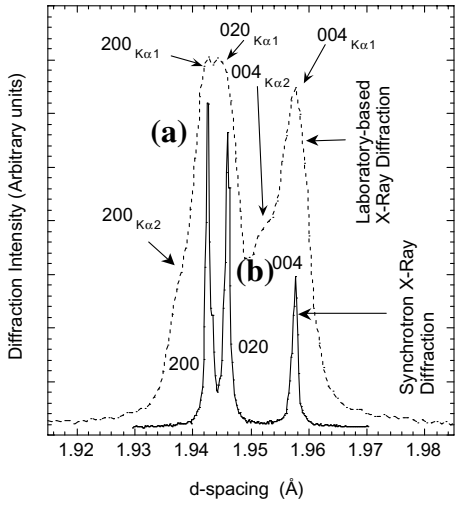

Fig.1. Comparison between synchrotron and conventional X-ray diffraction profile of 004, 020 and 200 reflection peaks of $La_{0.68}(Ti_{0.95}Al_{0.05})O_3$. The lattice spacing d value in the horizontal axis was obtained from the diffraction angle 2θ by using Bragg's equation $\lambda = 2d \sin\theta$ where the values λ =1.54056 Å and λ=1.37852 Å were used for the conventional and synchrotron data, respectively.

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