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Crystal structure analysis of Dion-Jacobson type oxide-ion conductors from high-resolution synchrotron X-ray diffraction

Wenrui ZHANG,* Kotaro FUJII and Masatomo YASHIMA**

Department of Chemistry, School of Science, Tokyo Institute of Technology, 2–12–1 W4–17 O-okayama, Meguro-ku, Tokyo, 152–8551, Japan

Oxide-ion conducting ceramics have attracted much attention due to their various applications such as solid oxide electrolysis cells (SOECs) and solid-oxide fuel cells (SOFCs). Herein, we report the crystal structure analysis of the oxide-ion conducting Dion-Jacobson phases $CsR_2Ti_2NbO_{10}$, which were analyzed using the synchrotron X-ray powder diffraction data.

1 Introduction

Oxide-ion conductors have attracted significant attention from both industrial and academic researchers due to their various applications in oxygen separation films, oxygen pumps, solid oxide electrolysis cells (SOECs) and solid-oxide fuel cells (SOFCs). The oxide-ion conductivity is strongly dependent on the crystal structure. Therefore, the crystal structure analysis of oxide-in conductors is important. In this work, the $CsR_2Ti_2NbO_{10}$ materials were prepared and their structural properties were investigated where *R* is rare earth element [1][2].

2 Experiments

The $CsR_2Ti_2NbO_{10}$ samples were synthesized by the solid-state reactions. High-purity (> 99.9%) of starting materials were mixed and ground as ethanol slurries and as dried powders for 1 h. 30 mol% excess amounts of Cs_2CO_3 was added to compensate the Cs loss during sintering process. The obtained mixtures were uniaxially pressed into pellets at about 100 MPa and subsequently sintered in air at 1150 °C for 12 h. After sintering, the pellets were cooled in air to room temperature. The heating and cooling rates were 5 °C min^{-1}. The processes were repeated 2 times.[3]

Parts of all the synthesized $CsR_2Ti_2NbO_{10}$ pellets were crushed and ground into powders to carry out Synchrotron X-ray powder diffraction (SXRD) at room temperature in air. High-angular-resolution synchrotron X-ray powder diffraction data of $CsR_2Ti_2NbO_{10}$ were obtained at room temperature using a multi-detector system installed at beam line 4B2 of the synchrotron facility PF, KEK, Tsukuba, Japan. The synchrotron X-ray wavelength was determined to be 1.197591(15) Å. The structure refinement was carried out using the SXRD data by the Rietveld method with the Z-Rietveld software.

3 Results and Discussion

All the reflections in the SXRD patterns of $CsR_2Ti_2NbO_{10}$ are indexed to a body-centered orthorhombic lattice, indicating the single orthorhombic Dion-Jacobson phase. In our work, Rietveld refinements of SXRD data of $CsR_2Ti_2NbO_{10}$ were successfully performed using an orthorhombic *Ima*2 Dion–Jacobson structure (**Figure 1**). The reliability factors in the Rietveld analysis are R_{wp} = 14.13 %, R_P = 11.73 %, R_B = 9.70 %, and R_F = 6.59 %. The refined lattice parameters of $CsR_2Ti_2NbO_{10}$ were *a* = 30.79823(8) Å, *b* = 5.4445759(4) Å, and *c* = 5.444647(16) Å. ICP-OES data also indicated that the cation ratio agreed well with the nominal cation ratio within 3 times of the standard deviation of the measured chemical composition.

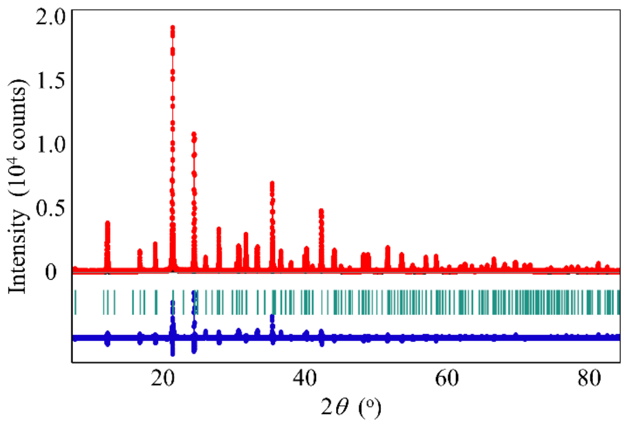

Figure 1 Rietveld pattern of SXRD data of $CsR_2Ti_2NbO_{10}$ at room temperature. Red marks and black solid line are experimental and calculated intensities, respectively. Green tick marks are Bragg peak positions of orthorhombic *Ima*2 Dion–Jacobson phase. The blue dots below the profile denote the difference pattern.

The average BVS values of Cs, *R*, Ti/Nb1, Ti/Nb2, O1, O2, O3, O4 and O5 atoms agree with their formal charges, which indicates the validity of the refined crystal structure. The structure of $CsR_2Ti_2NbO_{10}$ consists of perovskite-like [$R_2Ti_2NbO_{10}$] slabs and Cs layers, where a Cs layer separates the perovskite-like slabs, showing a Dion–Jacobson structure (**Figure 2**). The investigated structural properties of the oxide-ion conductor CsR_2Ti$_2$NbO$_{10}$ can help us to further understand the oxide ion diffusion pathways, which would develop the science and technology of Dion-Jacobson-type oxide-ion conductors.

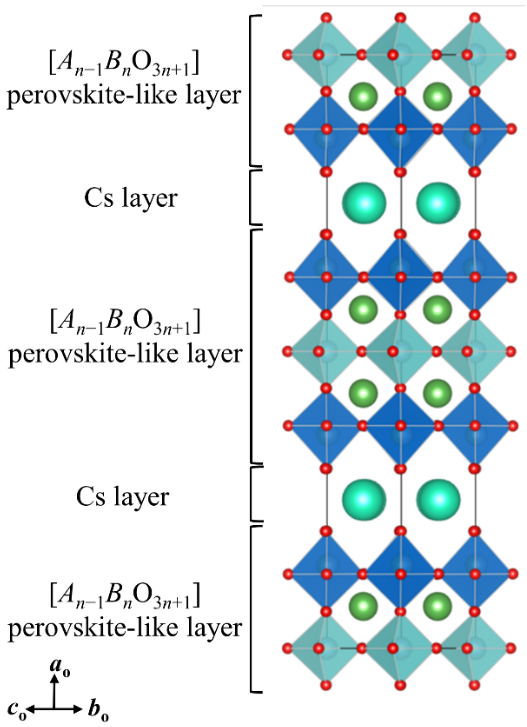

Figure 2 Refined crystal structure of CsR_2Ti$_2$NbO$_{10}$ at room temperature, which was obtained by Rietveld analysis of SXRD data.

References

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Research Achievements

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* zhang.w.ah@m.titech.ac.jp
** yashima@cms.titech.ac.jp