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

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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 Cs$_2$Ti$_2$NbO$_{10}$, 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-ion conductors is important. In this work, the Cs$_2$Ti$_2$NbO$_{10}$ materials were prepared and their structural properties were investigated where $R$ is rare earth element [1][2].

2 Experiments
The Cs$_2$Ti$_2$NbO$_{10}$ 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$_2$CO$_3$ 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 Cs$_2$Ti$_2$NbO$_{10}$ 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 Cs$_2$Ti$_2$NbO$_{10}$ 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 Cs$_2$Ti$_2$NbO$_{10}$ are indexed to a body-centered orthorhombic lattice, indicating the single orthorhombic Dion-Jacobson phase. In our work, Rietveld refinements of SXRD data of Cs$_2$Ti$_2$NbO$_{10}$ were successfully performed using an orthorhombic $Ima2$ Dion–Jacobson structure (Figure 1). The reliability factors in the Rietveld analysis are $R_p = 14.13 \%$, $R_B = 11.73 \%$, $R_B = 9.70 \%$, and $R_F = 6.59 \%$. The refined lattice parameters of Cs$_2$Ti$_2$NbO$_{10}$ 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](https://example.com/image1.png)

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 Cs$_2$Ti$_2$NbO$_{10}$ 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 Cs$_2$Ti$_2$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 Cs$_2$Ti$_2$NbO$_{10}$ at room temperature, which was obtained by Rietveld analysis of SXRD data.

References

Research Achievements

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