A New Structure Family of Oxide-Ion Conductors Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$

Mg$_3$TeO$_6$-type Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ has been found as a new structure family of oxide-ion conductors, by bond-valence-based-energy (BVE) calculations for 147 tin (Sn)-containing compositions [1]. Electrical conductivity measurements and the optical band gap suggested that the dominant carrier of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ is oxide ions. Synchrotron X-ray powder diffraction data of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ taken at the BL-4B2 beamline at 300 and 1273 K were successfully analyzed with the Mg$_3$TeO$_6$-type structure. BVE calculations using the refined crystal structure of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ at 1273 K strongly suggested three-dimensional oxide-ion diffusion. [This article is reproduced from Ref. [1] with permission from The Royal Society of Chemistry.]

Oxide-ion conducting ceramics are important materials, because they can be used in solid oxide fuel cells (SOFCs), batteries, catalysts, gas sensors and oxygen separation membranes. Since most of the researches on oxide-ion conductors are limited to a small number of structure families such as fluorite- and perovskite-type structures, the discovery of a new structure family of oxide-ion conductors would assist the development of materials science and solid state ionics. In the present work, we found that Mg$_3$TeO$_6$-type Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ is a good candidate for an oxide-ion conductor among Sn (tin)-containing oxides. We used the bond-valence method, which is quite fast for calculating the energy landscapes of a test ion in crystal structures [2, 3]. Sn^{4+} has the d^{10} electronic configuration. Since there are many reports of oxide-ion conductors containing d^{10}

electronic configuration cations, such as Ga^{3+} and Ge^{4+}, there are expected to be undiscovered oxide-ion conductors in Sn-containing oxides. There are 119 structure types of oxides containing Sn as an essential element in the inorganic crystal structure database. We selected at least one composition for each structure type and carried out BVE calculations. Finally, we calculated BVE for 147 compositions. The energy barrier for the oxide-ion migration (E_b) of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ was estimated to be 0.46 eV using the BVE landscape. A majority of other compositions had higher E_b for the oxide-ion migration than that of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$. Therefore, we synthesized Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ by the solid-state reaction method, and investigated its electrical conductivity and crystal structure using high-angular-resolution synchrotron X-ray powder diffraction (SXRPD) data measured *in situ*
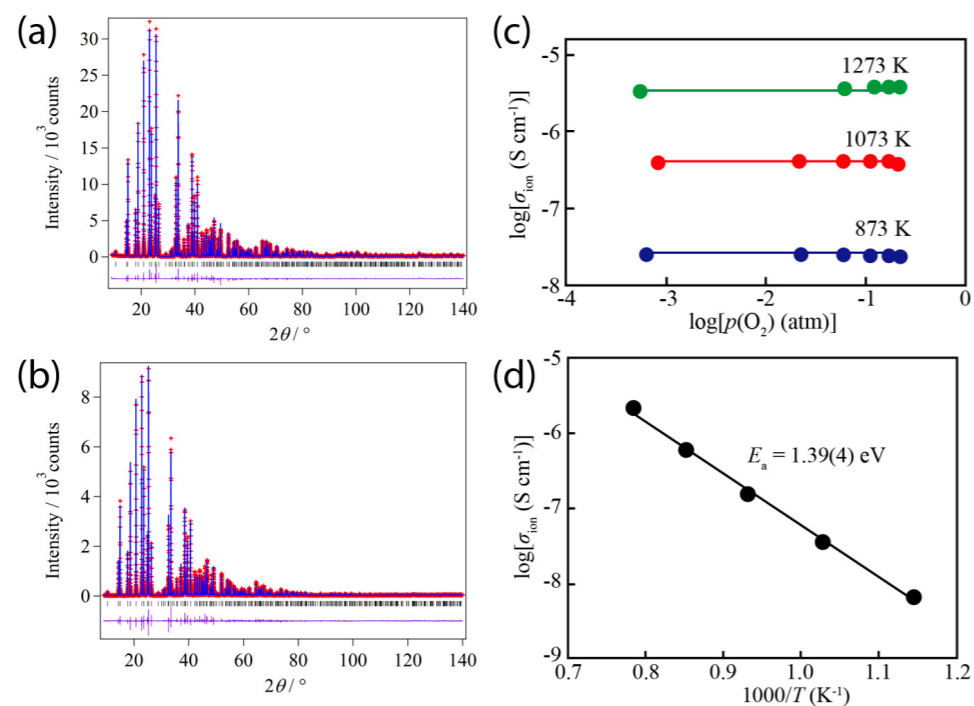

Figure 1: Rietveld patterns of the synchrotron X-ray powder diffraction data of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ taken in air at **(a)** 300 K, and **(b)** 1273 K. **(c)** Oxygen partial pressure (p(O$_2$)) dependence of the electrical conductivity of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ at 843 (blue), 1023 (red), and 1193 (green). **(d)** Arrhenius plot of the oxide-ion conductivity σ_{ion} of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ in air. © Royal Society of Chemistry [1].
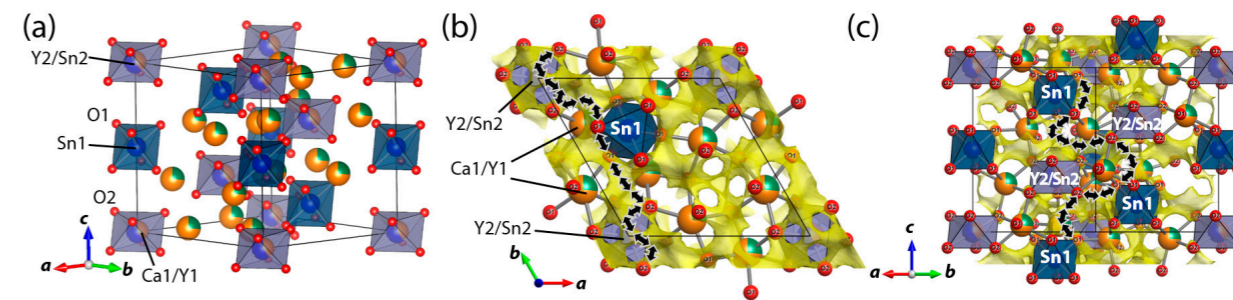

Figure 2: (a) Refined crystal structure of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ at 1273 K. **(b, c)** Bond valence-based energy (BVE) landscapes for an oxide ion with an isovalue at 0.6 eV in Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ at 1273 K, which are viewed along the [001] **(b)** and [110] directions. Arrows represent possible oxide-ion diffusion paths.

at 300 and 1273 K. SXRPD data of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ were measured using a multiple detector system at the BL-4B$_2$ beamline. The SXRPD data of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ taken at 300 K were analyzed by the Rietveld method. The results of Rietveld refinement gave a good fitting and reliable factors were R_{wp} = 7.29%, R_B = 3.40%, and GoF = 1.261 [**Fig. 1(a)**]. All the observed reflections of the SXRPD data were indexed by the trigonal cell, which indicates that the product was the single trigonal phase with the $R\bar{3}$ Mg$_3$TeO$_6$-type structure. The refined lattice parameters $a = b = 9.511049(11)$ Å, $c = 11.00686(3)$ Å and atomic coordinates of all atoms agreed well with those reported by Kaminaga *et al.* [4]. The oxygen partial pressure p(O$_2$) dependence of total electrical conductivity of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ measured at 843 K, 1023 K, and 1193 K showed constant conductivity against p(O$_2$) [**Fig. 1(c)**], indicating the dominant charge carrier in Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ is oxide ions at these temperatures. We also confirmed that Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ is an electric insulator from an optical band gap. The possibility of proton conduction was eliminated by conductivity measurements in wet air. From these experimental results, we concluded that Mg$_3$TeO$_6$-type Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ is a new structure family of oxide-ion conductors. SXRPD data of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ were also measured at 1273 K using a home-made furnace [5, 6]. The Rietveld analysis of the SXRPD data taken at 1273 K was successfully performed by the trigonal $R\bar{3}$ Mg$_3$TeO$_6$-type structure, which gave a good fitting and reliable factors were R_{wp} = 9.91%, R_B = 3.93%, and GoF = 0.90 [**Fig. 1(b)**]. The refined crystal structure is shown in **Fig. 2(a)**. The lattice parameters and volume V of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ at 1273 K ($a = b = 9.60204(3)$ Å, $c = 11.08009(6)$ Å, $V = 884.710(6)$ Å^3) were larger than those at 300 K ($a = b = 9.511049(11)$ Å, $c = 11.00686(3)$ Å, $V = 862.285(3)$ Å^3) due to thermal expansion. The BVE of an oxide ion was calculated using the refined

crystal structure of Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ at 1273 K, in order to investigate the oxide-ion migration pathway. **Figures 2(b)** and **2(c)** show the yellow isosurfaces of BVE for an oxide ion at +0.6 eV in Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$. In these BVE landscapes, the most stable position of an oxide ion was set to 0 eV. An oxide-ion migration path in Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ was found on the *ab* plane with the energy barrier of 0.53 eV. Arrows in **Fig. 2(b)** represent an example of the oxide-ion migration paths along the *b*-axis. The migration path follows the edges of the Y2/Sn2(O2)$_6$, Ca1/Y1(O1)$_3$(O2)$_3$, and Sn1(O1)$_6$ octahedra. An equivalent oxide-ion conduction path can be seen along the *a*-axis, because Ca$_{0.8}$Y$_{2.4}$Sn$_{0.8}$O$_6$ has a trigonal cell. In addition to these paths, there is a possible migration path of oxide ions along the *c*-axis with an energy barrier of 0.63 eV as shown by the arrows in **Fig. 2(c)**. Therefore, it is strongly suggested that the oxide ions diffuse three-dimensionally. The possible diffusion path along the *c*-axis follows the edges of the Ca1/Y1(O1)$_3$(O2)$_3$, and Sn1(O1)$_6$ octahedra.

REFERENCES

[1] R. Inoue, K. Fujii, M. Shiraiwa, E. Niwa and M. Yashima, *Dalton Trans.* **47**, 7515 (2018).
[2] S. Adams, *Solid State Ionics* **136–137**, 1351 (2000).
[3] M. Sale and M. Avdeev, *J. Appl. Cryst.* **45**, 1054 (2012).
[4] Y. Kaminaga, H. Yamane and T. Yamada, *Acta Crystallogr. C-Struct. Chem.* **62**, 57 (2006).
[5] M. Yashima, M. Tanaka, K. Oh-uchi and T. Ida, *J. Appl. Cryst.* **38**, 854 (2005).
[6] M. Yashima, K. Oh-uchi, M. Tanaka and T. Ida, *J. Am. Ceram. Soc.* **89**, 1395 (2006).

BEAMLINE

BL-4B2

K. Fujii, R. Inoue, M. Shiraiwa, E. Niwa and M. Yashima (Tokyo Tech.)