

## A Direct Evidence for Trivalent Ion Conduction in Solids

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In order to realize a higher valency ion conduction in solids, the  $\text{Sc}_2(\text{WO}_4)_3$  material which possesses a larger tunnel size for ion migration was selected to reduce the electrostatic interaction and the single crystals of  $\text{Sc}_2(\text{WO}_4)_3$  were grown to eliminate grain boundary effects found in polycrystalline state. By both the alternative and direct current measurements, a direct evidence of  $\text{Sc}^{3+}$  trivalent ion migration in single crystal  $\text{Sc}_2(\text{WO}_4)_3$  has been successfully demonstrated.

Trivalent cation conduction in a solid, for the first time, has been demonstrated directly and quantitatively, and the existence of a trivalent ion conducting solid electrolyte has been clarified.

Ion migration in liquid electrolytes or molten salts is very common. In some solids, a migrating species is only ionic, and the solid is called as "solid electrolyte". In the solid electrolytes developed, mono or divalent ion conduction is often found. Monovalent fluoride or divalent oxide conducting solid electrolytes have been already commercialized as a fluoride ion and oxygen gas sensing element in the biomedical and industrial fields, respectively.<sup>1</sup>

The greatest advantage of developing a higher valency ion conducting solid electrolyte is that as many electrons as the ratio of the valency per ion can be transported by a single ion. The success in obtaining a higher valency ion conducting solid electrolyte contributes greatly toward developing more valuable and functional materials. Here, a direct evidence of trivalent ion conduction in a solid was successfully demonstrated.

A trivalent cationic conduction has been claimed for  $\text{Ln}^{3+}$  in  $\text{Ln}^{3+}$ - $\beta$ (beta)-alumina ( $\text{Ln}$ : rare earths)<sup>2-4</sup> and  $\text{La}^{3+}$  in  $\beta$ - $\text{LaNb}_3\text{O}_9$ .<sup>5</sup> The  $\text{Ln}^{3+}$ - $\beta$ -alumina was prepared by an ion exchange method. However, there still remains some doubts concerning the residual hydrogen or sodium monovalent ionic conduction, since perfect ion substitution for  $\text{Ln}^{3+}$  can not be completed. For  $\beta$ - $\text{LaNb}_3\text{O}_9$ , an electrolysis was carried out and a meaningful increase of the La amount was observed at the anodic surface. This finding, however, does not necessarily mean  $\text{La}^{3+}$  migration because decomposition of the material at the anode may have happened.

To demonstrate clearly a higher valency ion conduction in solids, we selected the structure which possesses a larger tunnel size for ion migration to reduce the electrostatic interaction. The structure chosen was the  $\text{Sc}_2(\text{WO}_4)_3$  type,<sup>6</sup> a tunnel size of which is around 0.22 nm. In the series of rare earths, we selected  $\text{Sc}^{3+}$  as the most probable ion to migrate through the tunnel because  $\text{Sc}^{3+}$  is the smallest ion (0.18 nm)<sup>7</sup> among the relatively large rare earth ions. In order to investigate the ion conducting characteristics in crystals precisely, single crystals of  $\text{Sc}_2(\text{WO}_4)_3$  were grown to eliminate grain boundary effects found in polycrystalline materials.

Prior to single crystal growth, a polycrystalline powder of

$\text{Sc}_2(\text{WO}_4)_3$  was prepared by a conventional solid state reaction of  $\text{Sc}_2\text{O}_3$  (99.99% purity) and  $\text{WO}_3$  (99.5% purity).  $\text{Sc}_2\text{O}_3$  and  $\text{WO}_3$  was mixed in a molar ratio of 1:3 and heated at 1000°C for 12 h in air. Polycrystalline  $\text{Sc}_2(\text{WO}_4)_3$  powder was mixed with a flux in a molar ratio of 0.14 to 1. The flux used was a  $\text{Bi}_2\text{O}_3$ - $\text{WO}_3$  eutectic mixture (1:3 in molar ratio). The powder with the flux was first heated at 1200°C for 5 h and then cooled down to 1100°C at 2°C/h. The size of the single crystals obtained was approximately 3 x 3 x 0.3 mm. The quality of the single crystals was confirmed to be a satisfactory one from a Laue photograph.<sup>8</sup> Scandium or platinum metal was evaporated as an electrode on both surfaces toward the (001) direction of the single crystals by a conventional resistance heating or sputtering method, respectively. Here, the scandium metal was evaporated to steadily supply  $\text{Sc}^{3+}$  ions and the platinum metal was sputtered to block  $\text{Sc}^{3+}$  ion migration.

A single  $\text{Sc}_2(\text{WO}_4)_3$  crystal with either the scandium or platinum metal film was placed between two Pt or Sc metal electrodes for a polarization analysis, respectively. A direct voltage of 3 V was applied between the electrodes at 550 °C in a vacuum condition ( $<1.3 \times 10^{-4}$  Pa) and the current passing through the single crystal was measured. Conductivity measurements were carried out with Precision LCR Meter (HP4284A) from 20 to 1MHz and a personal computer (HP Vectra ES/12).

Figure 1 presents the polarization results for the cells with Pt metal electrode (a) and Sc metal electrode (b). In the case of cell (a), the ratio ( $I/I_0$ ) of the transient current to the current calculated from alternative current measurement decreased abruptly and approached a constant value. This clear polarization behavior

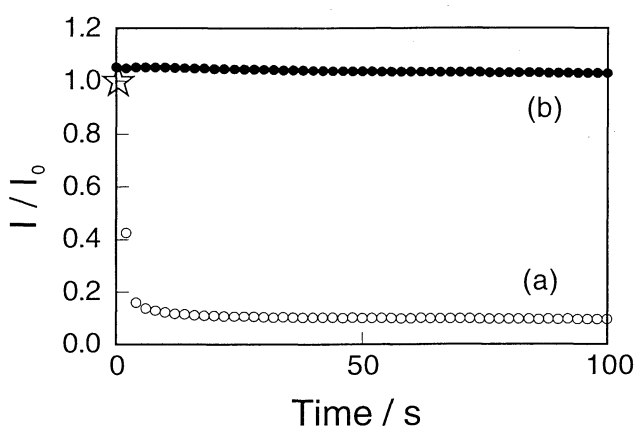
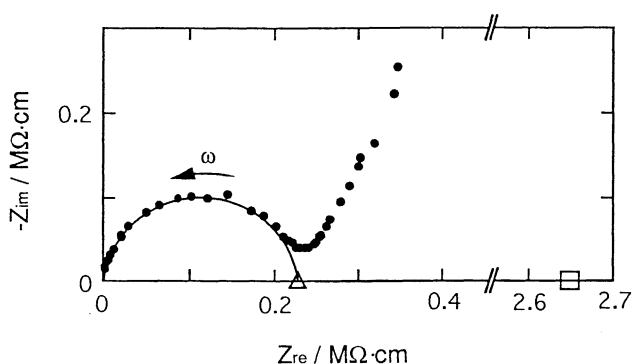


Figure 1. Polarization results for the cells with Pt metal irreversible electrode (a) and Sc metal reversible electrode (b). ☆ indicates the current value ( $I_0$ ) calculated from alternative current measurement.

indicated that ions in the tungstate single crystal had polarized in the crystal bulk. This phenomenon suggests a possibility of some ionic polarization. The Pt metal used for the cell (a) works as an irreversible (ion-blocking) electrode. In contrast to cell (a), the  $I/I_0$  ratio for the cell (b) was constant and no polarization was observed. Here, the suspicion of the reduction of W in the tungstate by the Sc metal is excluded because no difference in the resistivity of the tungstate is observed between the cell (a) and (b). Two possible explanations are expected for the phenomenon (b). One is that  $\text{Sc}^{3+}$  ions supplied from the Sc metal anode migrate in the  $\text{Sc}_2(\text{WO}_4)_3$  single crystal and reach the Sc metal cathode. In this case, all the electricity passed are transported by  $\text{Sc}^{3+}$  ions and the Sc metal functions as a reversible electrode. The second case is that mobile species are not ions but only electrons.

One appropriate way to distinguish the mobile species is to compare the resistivity measured by alternative current (ac) with that by direct current (dc) methods.<sup>9</sup> When ac is applied, both electrons and ions migrate in a solid. However, in the dc case, ions polarize at an irreversible electrode<sup>10</sup> and can not migrate in a solid any longer, while electrons are able to conduct similarly to the case for the ac method. In order to clarify the migrating species, the ac measurements were carried out for the cell (a) at 550 °C in the same vacuum condition. The impedance vector obtained by the measurements was divided into two parts, namely a real part and an imaginary part. By plotting the points at every measuring frequency, one semi-arc was obtained as shown in Figure 2. The intersection of the semi-arc at the lower frequency range ( $\Delta$ ) corresponds to the bulk conductivity of the single crystal.<sup>11</sup> The square ( $\square$ ) in the figure shows the resistivity value after the polarization for the dc case for  $\text{Sc}_2(\text{WO}_4)_3$  with the Pt metal electrode (a). If an electron is a main conducting species in  $\text{Sc}_2(\text{WO}_4)_3$ , the resistivity value after a dc polarization with an irreversible electrode should be equal to that from an ac method. The resistivity from the ac measurement ( $\Delta$ ) is considerably lower



**Figure 2.** The ac (Cole-Cole plots) ( $\Delta$ ) and dc resistivity ( $\square$ ) results for the cell (a). The applied frequencies for the ac method were varied from 20 Hz to 1 MHz.

than that from the dc one ( $\square$ ) and the electrical conductivity is estimated to be  $4.35 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$  and  $3.78 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ , respectively. This definitely indicates that main conducting species is ionic and that the ion is  $\text{Sc}^{3+}$ . An electrolysis investigation was also performed for the single  $\text{Sc}_2(\text{WO}_4)_3$  crystal with two Pt electrodes. After the electrolysis, some deposits were observed on the cathodic surface. From the electron probe microanalysis, the Sc/W ratio of the deposits was found to be 11 times higher than that of the surface before the electrolysis. This phenomenon supports the first explanation that the main conducting species is  $\text{Sc}^{3+}$  in the  $\text{Sc}_2(\text{WO}_4)_3$  single crystal. The ionic transference number, which is calculated from the ac and the dc resistivity values, is approximately 0.92. This means that 92 % of the electrical conducting species is ionic and, hence, that the ion migration in  $\text{Sc}_2(\text{WO}_4)_3$  is quantitatively demonstrated. From the two possible mechanisms for the phenomenon of the cell (b), the results shown above explicitly identify that  $\text{Sc}^{3+}$  ions conduct in single crystal  $\text{Sc}_2(\text{WO}_4)_3$ . The mechanism occurring during electrolysis with the Sc reversible electrode is that scandium in the anode conducts in the single crystal bulk in the trivalent  $\text{Sc}^{3+}$  state, and reaches the cathode.

The  $\text{Sc}_2(\text{WO}_4)_3$  single crystal was selected as a candidate for trivalent ion conducting solid electrolyte which is free from grain boundaries and possesses a larger tunnel size. From both ac and dc measurements, most of the mobile species in the single crystal were demonstrated to be  $\text{Sc}^{3+}$ . This is the first direct evidence for trivalent cation conduction in solids.

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