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Trivalent rare earth ion conduction in the scandium tungstate type structure

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Abstract

From the consideration of the mobile trivalent ions and the structure which reduces the electrostatic interaction between the framework and the mobile trivalent ionic species as much as possible, a trivalent-ion conduction in solids was successfully realized with the $Sc_2(WO_4)_3$-type structure. Among the molybdates and the tungstates with the $Sc_2(WO_4)_3$-type structure, $Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$ were found to be of the most suitable size for the trivalent-ion conduction in the tungstate and the molybdate series, respectively. By a dc electrolysis, the mobile species was clearly demonstrated to be a trivalent ion in the $Sc_2(WO_4)_3$-type structure.

Keywords: Rare earths; Trivalent; Ion conduction; Solid electrolyte; Tungstate; Molybdate

1. Introduction

In general, the ionic migration in solid electrolytes directly depends on the valency and ionic radius of the mobile ion. Trivalent cations have been regarded as being extremely poor migrant species in solids because of the high electrostatic interaction of the highly charged cations with the constituents of the surrounding framework such as O^{2-}, while mono and divalent ion conducting solid electrolytes have the advantage of high ionic conductivity with an associated low activation energy.

To achieve trivalent-ion conduction in solid electrolytes, the mobile ion species should be stable enough to hold the trivalent state and to possess a relatively small ionic radius. Furthermore, the framework of the electrolytes should have a large tunnel size, which reduces the electrostatic interaction between the mobile ions and the framework as much as possible. As a suitable structure for trivalent-ion migration, we choose the $Sc_2(WO_4)_3$-type structure [1–5] with a mobile ion species such as aluminum and rare earths. In this structure, the hexavalent tungsten ion W^{6+} bonds strongly to constituent oxide anions and as a result, the interaction between a mobile trivalent ion and the oxide ions is greatly reduced. Recently, we have directly demonstrated trivalent-ion conduction in the $Sc_2(WO_4)_3$-type structure [6–14] for trivalent ions such as Al^{3+}, Sc^{3+}, Y^{3+}, and Er^{3+}. Molybdenum also has a hexavalent state and the molybdates with aluminum and rare earths also possess the same $Sc_2(WO_4)_3$-type structure. Since the ionic radius of Mo^{6+}(0.055 nm) [15] is smaller than that of W^{6+}(0.056 nm) [15], the trivalent-ion conductivity in the molybdate family is expected to become higher between tungstate and molybdate series because of higher Mo–O bonding compared with W–O bonding.

In this paper, the trivalent-ion conducting characteristics were investigated in detail for the molybdate family and the results were compared with the tungstate family reported previously [6–14].

2. Experimental

Molybdates and tungstates, $M_2(M'O_4)_3$ (M=Al, In, Sc, Er, Tm, Yb, and Lu, M′=Mo, W), were prepared by a conventional solid-state reaction. Stoichiometric amounts of R_2O_3(purity: 99.9%) and MoO_3 (purity: 99.9%) were mixed in a mortar and calcined in a platinum boat at 700–1000°C for 5–17 h in air. The calcined powder was ground and reheated at 800–1100°C for 12 h in air. The resulting powder was pressed into pellets (10 mm in diameter) and sintered at 800–1100°C for 12 h in air. In the case of the molybdates of heavy rare earths, Er–Lu, the sample powders were dried in vacuum at 150°C before sintering due to their hygroscopic nature. The procedure of

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$Al_2(MoO_4)_3$ pellet preparation was the same as mentioned above, except for using $Al(OH)_3$ as one of the starting materials. For the preparation of rare earth tungstates, a stoichiometric amount of R_2O_3(purity: 99.9%) and WO_3(purity: 99.9%) was mixed and calcined on a platinum boat at 1000°C for 12 h in air and reheated at 1200°C for 12 h in air. The resulting powder was pelletized (10 mm in diameter) and sintered at 1300–1400°C for 12 h in air. In the case of the tungstates of Y and heavy rare earths, Er–Lu, the sample powder was also dried before reaction in a similar manner as mentioned above. The $Al_2(WO_4)_3$ preparation method was mentioned previously [8]. The sample characterization and the details of the measurements were described in our previous papers [8–14].

3. Results and discussion

Rare earth tungstates and molybdates with the $Sc_2(WO_4)_3$-type structure are orthorhombic with the space group *Pbcn*. The structure is composed of a three-dimensional skeleton framework with corner-linked ScO_6 octahedra and $M'O_4(M'=Mo, W)$ tetrahedra as shown in Fig. 1. Each ScO_6 octahedron is bonded to six WO_4 tetrahedra and each WO_4 tetrahedron is connected to four ScO_6 octahedra. All molybdates and tungstates were single phase with the $Sc_2(WO_4)_3$-type structure and the X-ray powder diffraction peak angles of the sample were shifted towards a lower degree with increasing trivalent ionic radius.

Fig. 2 shows the trivalent ionic radius dependencies on the unit cell volume for the molybdate and the tungstate systems. The lattice parameters and the cell volumes increase monotonously with increasing trivalent ionic size. The expansion ratio of each lattice parameter toward the trivalent ionic radius was similar and an isotropic expansion was observed.

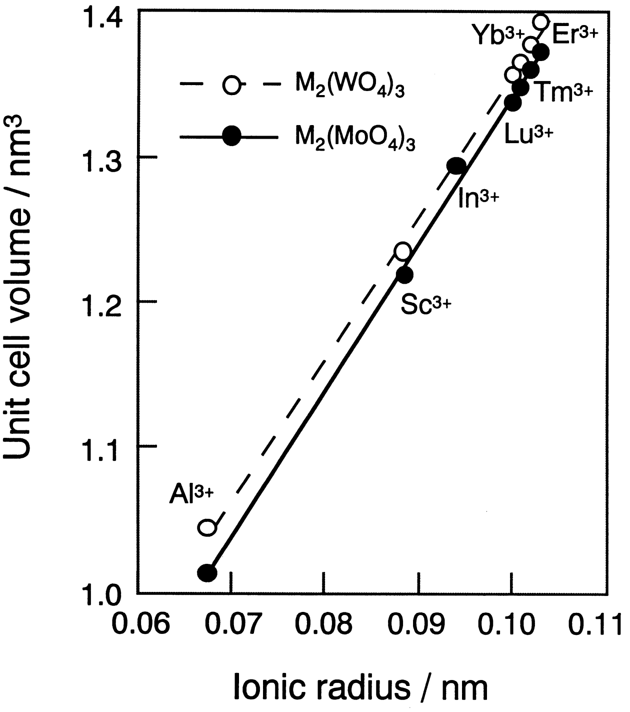

Fig. 2. Trivalent ionic radius dependencies on the unit cell volume for the molybdate and the tungstate system.

The electrical conductivity at 600°C and the activation energy (E_a) variation for both the tungstates and the molybdates as a function of the trivalent ionic radius is presented in Fig. 3. The tungstate and the molybdate with Sc^{3+} shows the highest conductivity and the lowest activation energy in the $Sc_2(WO_4)_3$-type structure. In the case of the larger trivalent ions compared with Sc^{3+}, the electrical conductivity decreases, while the activation energy increases with the ionic radius. This behavior is mainly attributed to the fact that the ratio of the ionic volume is higher than that of the lattice volume. In contrast to this, the conductivity was the lowest and the activation energy was the highest for the smallest ion (Al^{3+}) in both

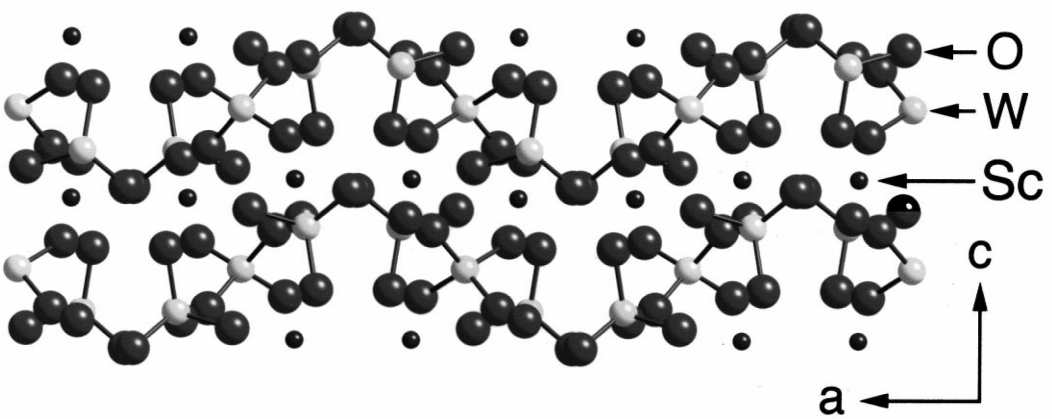

Fig. 1. The $Sc_2(WO_4)_3$-type structure viewed from the *b*-axis.

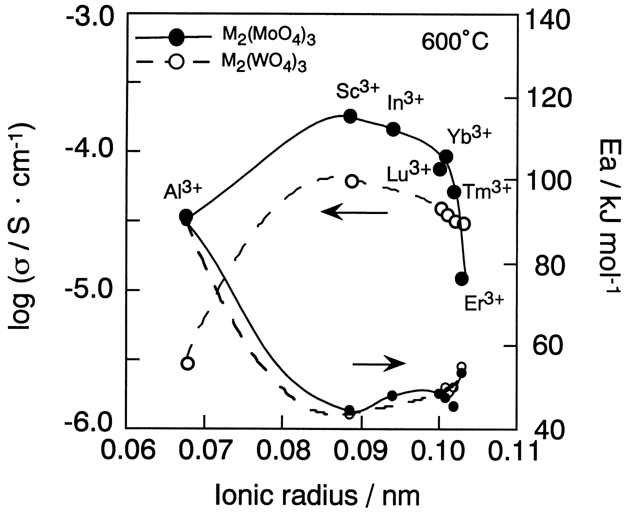

Fig. 3. Electrical conductivity at 600°C and activation energy (E_a) variation for both the tungstates [$M_2(WO_4)_3$] and the molybdates [$M_2(MoO_4)_3$] as a function of the trivalent ionic radius.

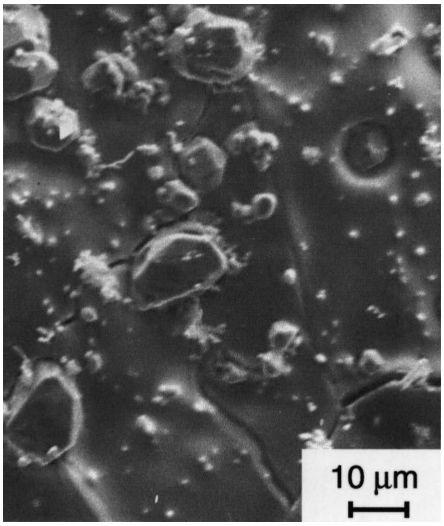

Fig. 4. SEM photograph of the cathodic bulk surface of $Sc_2(MoO_4)_3$ after the electrolysis.

series. The extremely poor Al^{3+} migration in the $Sc_2(WO_4)_3$-type structure is ascribed to the high electrostatic interaction caused by Al^{3+} low polarizability toward the surrounding anions in the skeleton structure because of the considerable small ionic size of Al^{3+}.

The dc conductivity was measured as a function of time and compared with the ac conductivity in both helium (P_{O_2}: 4 Pa) and oxygen (P_{O_2}: 10^5 Pa) atmosphere so as to investigate the electrical conducting properties. In both atmospheres, the dc conductivities decreased abruptly compared to the ac conductivities and approached to steady current. The dc conductivities were more than two orders of magnitudes lower than the ac conductivities. The similar polarization behaviors and the large ionic transference number, which is more than 0.99 for both $Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$, indicate that the predominant migrating species are neither holes nor electrons but ions.

An electrolysis was carried out by sandwiching the pellet between two platinum electrodes to directly determine the mobile ionic species. The SEM photograph of the cathodic bulk surface of $Sc_2(MoO_4)_3$ after the electrolysis is presented in Fig. 4. Many plate-shape deposits were observed on the cathodic surface. In contrast, the color of the anodic surface of the pellet changed from white before the electrolysis to yellow after the electrolysis. From electron probe microanalysis (EPMA) measurements, Sc was the only element identified by EPMA and the Sc element was found to segregate on the cathodic surface after the electrolysis. The results observed above clearly indicate that trivalent Sc^{3+} ions migrate in the $Sc_2(WO_4)_3$-type structure from anode to cathode direction and precipitate as Sc metal. Since the electrolysis was carried out in air, Sc metal deposits were immediately oxidized to Sc_2O_3 on the cathodic surface.

The temperature dependencies of trivalent-ion conductivity for $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$ [10] with the $Sc_2(WO_4)_3$-type structure are depicted in Fig. 5 with the data obtained for $Al_2(WO_4)_3$ [8]. Among the trivalent-ion-conducting solid electrolytes with the $Sc_2(WO_4)_3$-type structure, $Sc_2(MoO_4)_3$ was found to show the highest

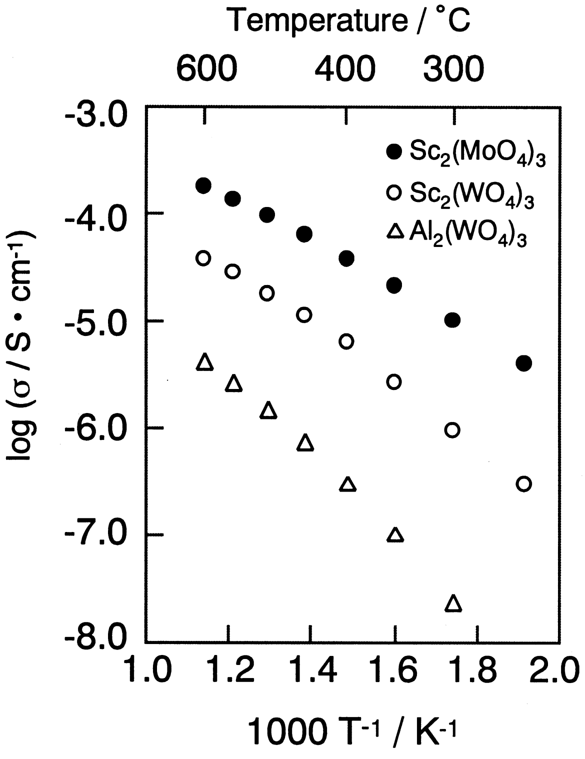

Fig. 5. Temperature dependencies of trivalent-ion conductivity for $Sc_2(MoO_4)_3$ and $Sc_2(WO_4)_3$ [10] with the $Sc_2(WO_4)_3$-type structure. The data obtained for $Al_2(WO_4)_3$ [8] are also presented.

trivalent-ion conductivity($\sigma = 1.93 \times 10^{-4}$ S·cm^{-1} at 600°C) in the structure.

4. Conclusion

Molybdates and tungstates with trivalent aluminum and rare earth ions in the $Sc_2(WO_4)_3$-type structure were demonstrated to be suitable for trivalent-ion conduction. With the increase of the trivalent ionic radius, the ratio of the trivalent-ion volume/the lattice volume increases monotonically. In contrast, Al^{3+} ion, whose ionic size is the smallest among the trivalent ions presented in this paper, has a low polarizability toward the surrounding anions in the skeleton structure because of the considerable small ionic size. As a result, within the structure family, $Sc_2(WO_4)_3$ and $Sc_2(MoO_4)_3$ were found to be an optimum size for trivalent ion conduction in the tungstate and molybdate series. DC electrolysis demonstrated that the mobile ion species in the $Sc_2(WO_4)_3$-type structure was directly the trivalent rare earths and aluminum ions.

Acknowledgements

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References

[1] S.C. Abrahams, J.L. Bernstein, J. Chem. Phys. 45 (1966) 2745.
[2] K. Nassau, H.J. Levinstein, G.M. Loiacono, J. Phys. Chem. Solids 26 (1965) 1805.
[3] H.J. Borchardt, J. Chem. Phys. 39 (1963) 504.
[4] K. Nassau, J.W. Shiever, E.T. Keve, J. Solid State Chem. 3 (1971) 411.
[5] E.Y. Rode, G.V. Lysanova, V.G. Kuznetsov, L.Z. Gokhman, Russ. J. Inorg. Chem. 13 (1968) 678.
[6] N. Imanaka, Y. Kobayashi, G. Adachi, Chem. Lett. (1995) 433.
[7] N. Imanaka, G. Adachi, J. Alloys Comp. 250 (1997) 492.
[8] Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, G. Adachi, Chem. Mater. 9 (1997) 1649.
[9] S. Tamura, T. Egawa, Y. Okazaki, Y. Kobayashi, N. Imanaka, G. Adachi, Chem. Mater. 10 (1998) 1958.
[10] N. Imanaka, Y. Kobayashi, K. Fujiwara, T. Asano, Y. Okazaki, G. Adachi, Chem. Mater. 10 (1998) 2006.
[11] N. Imanaka, M. Hiraiwa, S. Tamura, G. Adachi, H. Dabkowska, A. Dabkowski, J.E. Greedan, Chem. Mater. 10 (1998) 2542.
[12] Y. Kobayashi, T. Egawa, Y. Okazaki, S. Tamura, N. Imanaka, G. Adachi, Solid State Ionics 111 (1998) 59.
[13] N. Imanaka, Y. Kobayashi, S. Tamura, G. Adachi, Electrochem. Solid-State Lett. 1 (1998) 271.
[14] Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, G. Adachi, Solid State Ionics 118 (1999) 325.
[15] R.D. Shannon, Acta Cryst. A32 (1976) 751.