Chem. Mater. **1997,** *9,* 1649−1654

Trivalent Al^{3+} Ion Conduction in Aluminum Tungstate Solid

Yasuyuki Kobayashi, Takashi Egawa, Shinji Tamura, Nobuhito Imanaka, and Gin-ya Adachi*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan

Received January 4, 1997. Revised Manuscript Received April 16, 1997[⊗]

Ionic conduction of trivalent aluminum in solid aluminum tungstate, $Al_2(WO_4)_3$, has been directly and quantitatively demonstrated. Trivalent ions, especially for aluminum where the polarizability is considerably low, are strongly bonded in a crystal lattice and have been believed to be unlikely to exhibit migration in solids because of high electrostatic interaction with the surrounding skeleton structure. The material, $Al_2(WO_4)_3$, which has the $Sc_2(WO_4)_3$ structure, was selected in order to reduce the interaction between the framework and the mobile species, Al^{3+}, as much as possible. The ionic conduction characteristics of $Al_2(WO_4)_3$ were investigated by means of electrolysis and electromotive force measurement by constructing an aluminum concentration cell. The typical electrical conductivity of $Al_2(WO_4)_3$ was, approximately 2×10^{-5} S cm^{-1} at 800 °C. The dc electrolysis data strongly support the conclusion that ionic Al^{3+} is the mobile species in $Al_2(WO_4)_3$. By further electrochemical measurements, it was confirmed that the mobile species was aluminum ion in a trivalent state with no contribution due to electronic conduction. The ionic transference number was determined to be unity from the oxygen−air gas concentration cell and the aluminum concentration cell method.

Introduction

Solid electrolytes are ionic conducting solid materials with a conductivity comparable to that of molten salts and aqueous electrolytes. The ionic conducting species in a solid electrolyte is limited to only one species without any electron or hole conduction. Solid electrolytes have the important characteristic to transporting specific ions macroscopically with an accompanying electric charge. Some solid electrolytes have been already commercialized as the sensing element[1] in biomedical and industrial applications.

Many investigations have been undertaken on various kinds of solid electrolytes where the mobile species are monovalent ion such as Ag^+, Cu^+, H^+, Na^+, Li^+, and F^- or divalent ions such as Ca^{2+}, O^{2-}, etc. In general, the ionic mobility in solid electrolytes strongly depends on the valency and ionic size of the mobile ion. The mono- and divalent cationic conductors have the advantage of high ionic conductivity with an associated low activation energy. In contrast, trivalent cations have been considered as an extremely poor choice for ionic migration because of high electrostatic interaction of these highly charged species with the surrounding atomic framework structure. Only a few papers have reported some possibilities of trivalent ion conduction, e.g., Ln^{3+}-β''-alumina[2−9] and β-$LaNb_3O_9$.[10] However, these papers have indicated only a probability of trivalent cation conduction, and the full determination of conducting ion species has not been directly and quantitatively demonstrated.

Farrington et al.[2−5] and Urland et al.[6−9] have reported that Ln^{3+}-β''-alumina (Ln: rare earth), which was obtained by ionically exchanging the $3Na^+$ site of Na^+-β''-alumina single crystal for Ln^{3+} using molten salts such as nitrate or chloride, is a trivalent ion conductor, and the mechanism of the ionic conduction has been examined.[9] The ionic exchange ratio from Na^+ to Ln^{3+} in Na^+-β''-alumina has been described to be higher than 95%, while the total conductivity of the Ln^{3+}-β''-alumina decreased more than 3 orders of magnitude compared to that of pure Na^+-β''-alumina. Residual monovalent Na^+ ionic conduction might remain, since the ion-exchange step cannot be fully completed. George et al.[10] have reported the mixed ion−electronic conduction in β-$LaNb_3O_9$, which possesses an A site cation-deficient perovskite ABO_3 structure. At low temperatures, the niobate becomes mainly ionic, while at higher temperatures it shows mostly electronic conducting behavior. An electrolysis step was done at the lower temperature

---

[*] To whom all correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

(1) West, A. R. *Solid State Chemistry and its Applications*; John Wiley & Sons: Chichester, 1984; p 465.

(2) Dunn, B.; Farrington, G. C. *Solid State Ionics* **1983**, *9* and *10*, 223.

(3) Carrillo-Cabrera, W.; Thomas, J. O.; Farrington, G. C. *Solid State Ionics* **1983**, *9* and *10*, 245.

(4) Ghosal, B.; Mangle, E. A.; Topp, M. R.; Dunn, B.; Farrington, G. C. *Solid State Ionics* **1983**, *9* and *10*, 273.

(5) Farrington, G. C.; Dunn, B.; Thomas, J. O. *Appl. Phys.* **1983**, *A32*, 159.

(6) Dedecke, T.; Köhler, J.; Tietz, F.; Urland, W. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 185.

(7) Köhler, J.; Urland, W. *Solid State Ionics* **1996**, *86−88*, 93.

(8) Köhler, J.; Balzer-Jöllenbeck, G.; Urland, W. *J. Solid State Chem.* **1996**, *122*, 315.

(9) Köhler, J.; Urland, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 85.

(10) George, A. M.; Virkar, A. N. *J. Phys. Chem. Solids.* **1988**, *49*, 743.

S0897-4756(97)00004-5 CCC: $14.00

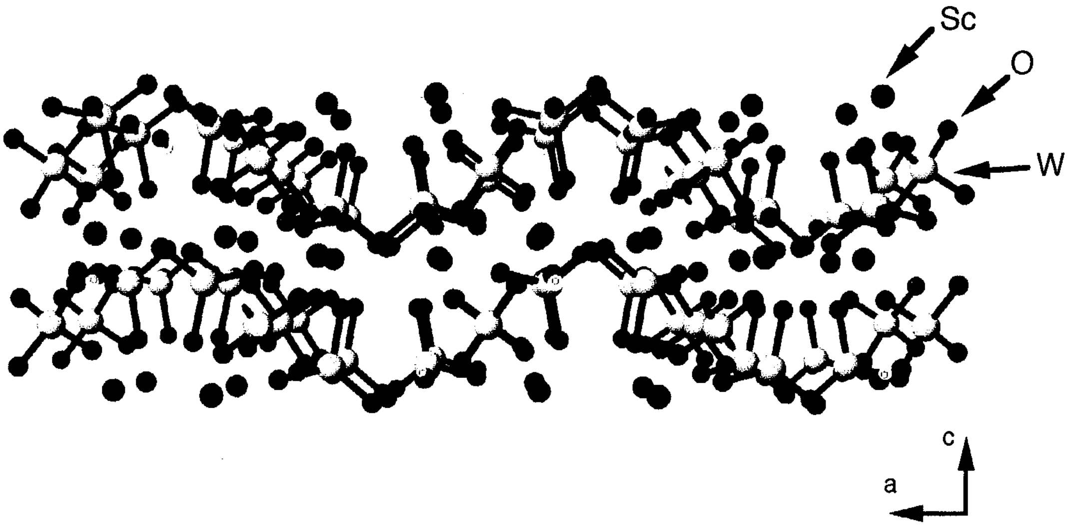

Figure 1. Structure of $Sc_2(WO_4)_3$ in ⟨001⟩ direction.

where ionic conduction is predominant, and an appreciable increase in La content was observed at the cathodic surface. This behavior indicates one such a possibility of La^{3+} migration. However, the phenomenon observed in the electrolysis is also supposed to occur by the decomposition of β-$LaNb_3O_9$ at the only cathodic surface without any La^{3+} ionic migration. Therefore, any trivalent ionic conduction in solids has not been directly and quantitatively demonstrated at all.

Recently, we have directly demonstrated a trivalent ion conduction such as Sc^{3+},[11] Y^{3+},[12] and Er^{3+}[12] in the tungstate with the $Sc_2(WO_4)_3$ type structure.[13] The crystal structure of $Sc_2(WO_4)_3$ is composed of a three-dimensional framework linked at the corner of ScO_6 octahedra and WO_4 tetrahedra (Figure 1).[14] Lithium scandium phosphate,[15] $Li_3Sc_2(PO_4)_3$, which has been reported to be a high lithium ionic conductor, also possesses the $Sc_2(WO_4)_3$ type structure. Lithium ions in $Li_3Sc_2(PO_4)_3$ lie in three crystallographic positions and conduct through the opening of a framework consisting of ScO_6 octahedra and PO_4 tetrahedra. The $Sc_2(WO_4)_3$ type structure possesses the unusual feature of a large tunnel size and the consequent characteristics of effectively reducing the electrostatic interaction between the mobile ions and the framework of the structure. Despite trivalent aluminum being very common in stable compounds, Al^{3+} has never been believed to migrate in solids because of its strong interaction with surrounding anions like O^{2-}, and its lower polarizability which results from its small ionic radius (0.0675 nm).[16] The challenge to demonstrate trivalent aluminum ion conduction in solids has not been carried out at all.

This paper presents the direct and quantitative demonstration of trivalent aluminum ion conduction in the aluminum tungstate, $Al_2(WO_4)_3$, with the $Sc_2(WO_4)_3$ type structure.

Experimental Section

Sample Preparation. $Al_2(WO_4)_3$ polycrystalline powder was prepared by mixing $Al[OCH(CH_3)_2]_3$ (purity 99.9%) and WO_3 (purity 99.9%) in a stoichiometric ratio which was kept initially at 150 °C in a water vapor saturated air atmosphere to decompose the alkoxide and then heated at 1000 °C for 12 h in dry air for several times until the reaction was complete. The resulting powder was made into pellets and heated first at 1000 °C for 12 h, and then the temperature was raised to 1220 °C at the rate of 50 °C/h. Immediately after reaching 1220 °C, the temperature was lowered to 1100 °C at the same rate in dry air to obtain well-sintered pellets. The samples were characterized by X-ray powder diffraction analysis.

Measurements. *Conducting Properties.* Electrical conductivity of the samples was measured by an ac and a dc method by sandwiching the sample between two platinum electrodes. The ac conductivity measurements were carried out by an ac complex impedance analysis in the frequency range from 20 Hz to 1 MHz by using Hewlett-Packard precision LCR meter (8284A). The measurements were carried out in oxygen, air (P_{O_2} 2×10^5 Pa), nitrogen (P_{O_2} 2×10 Pa), and $CO-CO_2$ mixture (P_{O_2} $10^{-9}-10^{-29}$ Pa) atmosphere for the temperature region between 400 and 800 °C. The oxygen pressures were monitored precisely by using an oxygen sensor with an yttria-stabilized-zirconia solid electrolyte. The dc voltage, V, was measured as a function of time, in oxygen, nitrogen (P_{O_2} 2×10 Pa), and helium (P_{O_2} 4 Pa) atmosphere at 700 °C at a constant current ($I = 0.1$ μA) through the sample by using platinum mesh electrodes. The dc conductivity was calculated from the following equation:

$$\sigma_{DC} = \frac{I}{V}\frac{d}{S} \qquad (1)$$

where d and S are the thickness of the sample and the area of the Pt-sputtered electrode, respectively. To determine the ionic transference number, the oxygen−air concentration cell measurement was carried out at temperatures between 700 and 800 °C. A constant current (0.1 μA) was passed through the sample, and the terminal voltage was monitored to clarify whether the oxide ion is the conducting species or not.

Electrolysis. The dc electrolysis was carried out for $Al_2(WO_4)_3$ with two platinum plates as the electrodes by applying a direct voltage of 10 V for 250 h at 850 °C in air. After electrolysis, scanning electron microscope (SEM) measurements and electron probe microanalysis (EMPA) were performed for the surface of both Pt electrodes.

---

[11] Imanaka, N.; Kobayashi, Y.; Adachi, G. *Chem. Lett.* **1995**, 433.

[12] Imanaka, N.; Adachi, G. *J. Alloys Compounds*, in press.

[13] Abrahams, S. C.; Bernstein, J. L. *J. Chem. Phys.* **1966**, *45*, 2745.

[14] Nassau, K.; Levinstein, H. J.; Loiacono, G. M. *J. Phys. Chem. Solids.* **1965**, *26*, 1805.

[15] Bykov, A. B.; Chipkin, A. P.; Demyanets, L. N.; Doromin, S. N.; Genkina, E. A.; Ivanov-Shits, A. K.; Kondratyuk, I. P.; Maksomov, B. A.; Melnikov, O. K.; Muradyan, L. N.; Simonov, V. I.; Timofeeva, V. A. *Solid State Ionics*, **1990**, *38*, 31.

[16] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Concentration Cell. Three types of Al–Pt alloys with the composition of 35, 42, and 55 Al at. % were prepared. The three alloys lie within two-phase regions between $AlPt_2$ and Al_3Pt_5, Al_3Pt_5 and AlPt, and AlPt and Al_3Pt_2, respectively.[17] The alloys were prepared by arc melting the appropriate mixture of aluminum wire (purity 99.99%) and platinum wire (purity 99.9%) under an argon atmosphere. The arc melted alloys were remelted at least four times to homogenize the composition. The alloys were annealed at 1000 °C for 50 h in a purified helium atmosphere (P_{O_2} 10^{-9} Pa) to complete the homogenization. The purification was conducted by passing helium gas through the liquid nitrogen trap. After the alloys were pulverized in a tungsten carbide mortar, the alloy powder smaller than 200 mesh was corrected by passing through a sieve, and the powder used as the electrode for the concentration cell measurements. The homogenized and size-controlled alloy powder was pelletized and sintered at 600 °C for 50 h in the same purified helium atmosphere. After annealing, the powder was identified to be composed of a mixture of the respective alloy from X-ray powder diffraction analysis.

To precisely determine the aluminum activity in the Al–Pt alloys, the electromotive force (emf) measurements were carried out with the CaF_2 solid electrolyte by constructing the following cell in a purified helium gas atmosphere:[18–20]

$$\text{Al, AlF}_3 \mid \text{CaF}_2 \mid \text{Al–Pt, AlF}_3 \qquad (2)$$

The electrodes were prepared by mixing aluminum powder (purity 99.9%) or Al–Pt alloy powder with AlF_3 powder (purity 99.9%). The mixing ratio was 80 to 20 in wt %. A single-crystal form of CaF_2 (purity >99.99%) grown by the FZ method was purchased from Oyo Koken Co. Ltd. and was used as the solid electrolyte. As the ambient atmosphere for the measurement, a purified helium atmosphere (P_{O_2} 10^{-9} Pa) was supplied in order to prevent the oxidation of aluminum metal and Al–Pt alloys during the measurements. The atmosphere in the cell was first evacuated, and then purified helium gas was introduced at room temperature. This procedure was done several times and then the cell was heated to 600 °C. After a steady emf value was obtained, it was monitored while changing the operating temperatures between 400 and 600 °C. The emf of the cell was measured using a digital electrometer (R8240, Advantest) with an input impedance of 10^{13} Ω.

Another electrochemical cell described below was also fabricated:

$$\text{Al}_{55}\text{Pt}_{45} \mid \text{Al}_2(\text{WO}_4)_3 \mid \text{Al–Pt} \qquad (3)$$

Al–Pt alloys represent $Al_{55}Pt_{45}$, $Al_{42}Pt_{58}$, and $Al_{35}Pt_{65}$. Experimental runs were carried out in a nitrogen atmosphere (P_{O_2} 2 × 10 Pa) at 400 °C. During the measurements, the oxygen partial pressure was monitored by the oxygen sensor.

Results and Discussion

Typical complex impedance (Cole–Cole plots) results for the $Al_2(WO_4)_3$ solid with Pt or Al electrode at 550 °C are shown in Figure 2. In the higher frequency region, one semicircle was observed irrespective of the electrode. In contrast, in the lower frequency region a different behavior was recognized. The difference is ascribed to the kind of metal used as the electrode. From these results, it is clear that the impedance value obtained by the intersection of semicircle with the abscissa is identified to the $Al_2(WO_4)_3$ solid resistance which includes both grain bulk and grain boundary components. The total conductivity of the $Al_2(WO_4)_3$ solid was calculated from the value of the intersection, the area of Pt electrode, and the thickness of the sample.

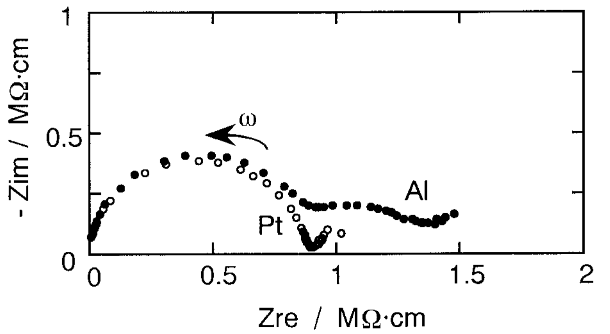

Figure 2. Complex impedance plots (Cole–Cole plot) for $Al_2(WO_4)_3$ with Pt or Al electrodes at 550 °C.

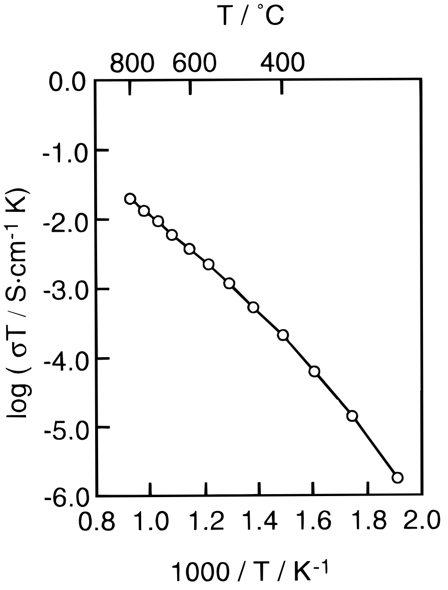

Figure 3. Temperature dependence of the electrical conductivity for $Al_2(WO_4)_3$ in air.

The temperature dependence of the typical conductivity for the $Al_2(WO_4)_3$ polycrystal is presented in Figure 3. The activation energy, E_a, is calculated from the following Arrhenius equation:

$$\sigma T = \sigma_0 \exp(-E_a/kT) \qquad (4)$$

where σ, T, σ_0, and k denote the conductivity, absolute temperature, preexponential factor, and Boltzmann constant, respectively. The E_a value for $Al_2(WO_4)_3$ was calculated to be 65.8 kJ/mol at the higher temperature region between 550 and 800 °C.

The time dependencies of the dc and ac conductivity ratios (σ_{DC}/σ_{AC}) for $Al_2(WO_4)_3$ are plotted in Figure 4a. A clear polarizing behavior was observed which was similar in the three types of atmosphere examined. The voltage between the two Pt electrodes approached to the same steady value after about 60 min and the conductivity value estimated from the voltage is 2 orders of magnitude lower than that calculated from the ac conductivity measurement. In contrast, in the case of the well-known O^{2-} ion conductor HfO_2 (20 mol% CaO) solid electrolyte[21] which shows a comparable ionic conductivity to $Al_2(WO_4)_3$, the dc conductivity was in agreement with the ac conductivity in oxygen atmo-

---

(17) Massalski, T. B. *Binary Alloy Phase Diagrams*; American Society of Metals: Metals Park, OH, 1986; p 153.

(18) Schaller, H.-J. *Thermochemistry of Alloys-Recent Devellopments of Experimental Methodes*; Brodowsky, H., Schaller, H.-J., Eds. Kluwer Academic Publishers: Dordrecht, 1989; p 329.

(19) Schaller, H.-J. *Ber. Bunsen-Ges. Phys. Chem.* **1978**, *82*, 365.

(20) Schaller, H.-J. *Z. Phys. Chem. N. F.* **1978**, *112*, 85.

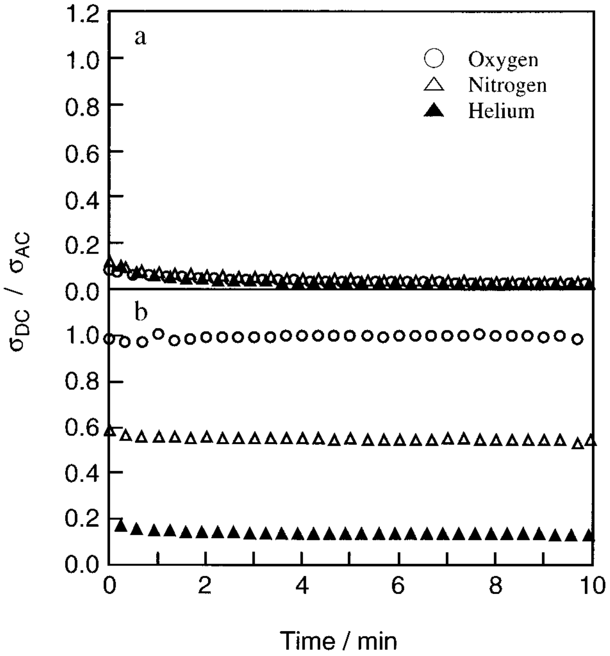

Figure 4. Time dependencies of the ratio, σ_{DC}/σ_{AC} in atmosphere of oxygen (○), nitrogen (△), and helium (▲) for (a) $Al_2(WO_4)_3$ and (b) HfO_2 (20 mol % CaO) at 700 °C.

sphere, while the polarization behavior increased with the decrease of oxygen pressure from nitrogen to helium atmosphere (Figure 4b). Therefore, the same clear polarization phenomenon observed in oxygen, nitrogen, and helium atmospheres in the $Al_2(WO_4)_3$ solid suggests that oxide ion is eliminated as the mobile ion candidate in the tungstate solid and that the mobile species is neither electron nor hole but only ion.

The ionic transference number, t_i, was calculated from oxygen–air gas concentration cell measurements. The measured and theoretical emf values coincided well 700 (32.7 mV) to 800 °C (36.1 mV) and the t_i was estimated to be unity. By drawing the current, the terminal voltage between the sample appreciably decreased and a steady current could not be drawn out from the concentration cell. In the case of the oxide ion conductor, it is possible to draw a constant current. Therefore, it can be also easily elucidated that the oxide ion is not a conducting species in $Al_2(WO_4)_3$.

The $Al_2(WO_4)_3$ conductivity dependence on the oxygen partial pressure (P_{O_2}) was studied in the temperature range 400–800 °C. In all cases the conductivities were obtained by the ac method. In general, the component of ionic conductivity in solids is independent of the oxygen partial pressure, while that of electronic conductivity strongly depends on the pressure.[22] Therefore, the total conductivity is described by[23]

$$\sigma = \sigma_i + \sigma_e°P_{O_2}^{\ -1/n} + \sigma_h°P_{O_2}^{\ 1/n} \qquad (5)$$

At low and high P_{O_2} ranges, n-type and p-type electronic components appear, respectively. In the middle P_{O_2} range, the total conductivity is steady and is equal to the ionic conductivity. The relation between the conductivity and the oxygen partial pressure at 400, 600, and 800 °C is presented in Figure 5. Two P_{O_2} regions, namely, 10–10^5 Pa and 10^{-9}–10^{-29} Pa, were obtained by using N_2–O_2 mixtures and CO–CO_2 mixtures, respectively. The total conductivity was independent of the P_{O_2} variation at 400 and 600 °C. At 800 °C and below the P_{O_2} of 10^{-11} Pa, the conductivity increased slightly with the P_{O_2} decrease and n-type electronic conduction appears, although the proportion of the electronic conduction to the total conductivity is appreciably small. From these results, the conducting species is predominally ionic in the whole P_{O_2} variation range (P_{O_2} 10^5–10^{-20} Pa) for temperatures lower than 600 °C.

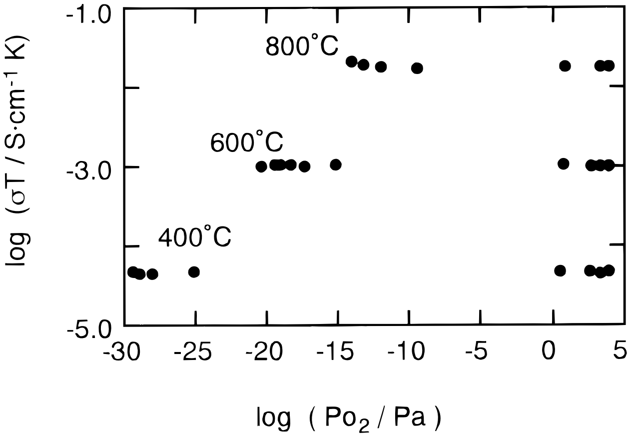

Figure 5. Oxygen pressure dependence of the electrical conductivity for $Al_2(WO_4)_3$ at 400, 600, and 800 °C.

To determine the candidate species for mobile ion in $Al_2(WO_4)_3$, an electrolysis was carried out by sandwiching the tungstate between two platinum electrodes. The electrode surface in contact with the sample was analyzed by a scanning electron microscope (SEM) and an electron probe microanalysis (EPMA). After the electrolysis, some white spotlike deposits were observed on the platinum electrode surface of the cathode from the SEM analysis (Figure 6a). From the EPMA analysis, the spot deposits were found to contain element aluminum with platinum which is the component of the electrode (Figure 6b). No peak ascribed to the tungsten component was observed. On the other hand, the color of the anodic surface of the sample changed from white before electrolysis to green after electrolysis. These phenomena indicate that aluminum ions migrate from anode to cathode, and as a result, aluminum appears on the cathode surface, and the green color of tungsten oxide appears on the opposite anode surface. This behavior strongly suggests that Al^{3+} ion is one of potential candidates for the mobile species in $Al_2(WO_4)_3$.

To identify the Al^{3+} ion conduction quantitatively, the Al concentration cell was constructed by using three types of aluminum–platinum alloys, namely, $Al_{55}Pt_{45}$, $Al_{42}Pt_{58}$, and $Al_{35}Pt_{65}$. To determine the aluminum activity in the Al–Pt alloys precisely, emf measurements were performed for the electrochemical cell with single-crystal calcium fluoride as the solid electrolyte for the temperature region between 400 and 600 °C in a purified helium atmosphere(P_{O_2} 10^{-9} Pa).

The emf appears when a solid electrolyte is fixed between two electrodes with a different chemical po-

---

(21) Johansen, H, A; Cleary, J. G. *J. Electrochem. Soc.* **1964**, *111*, 100.

(22) Rickert, H. *Electrochemistry of solids, An Introduction*; Springer-Verlag: Berlin, 1982; p 6.

(23) Schmalzried, H. *Z. Phys. Chem. N. F.* **1963**, *38*, 87.

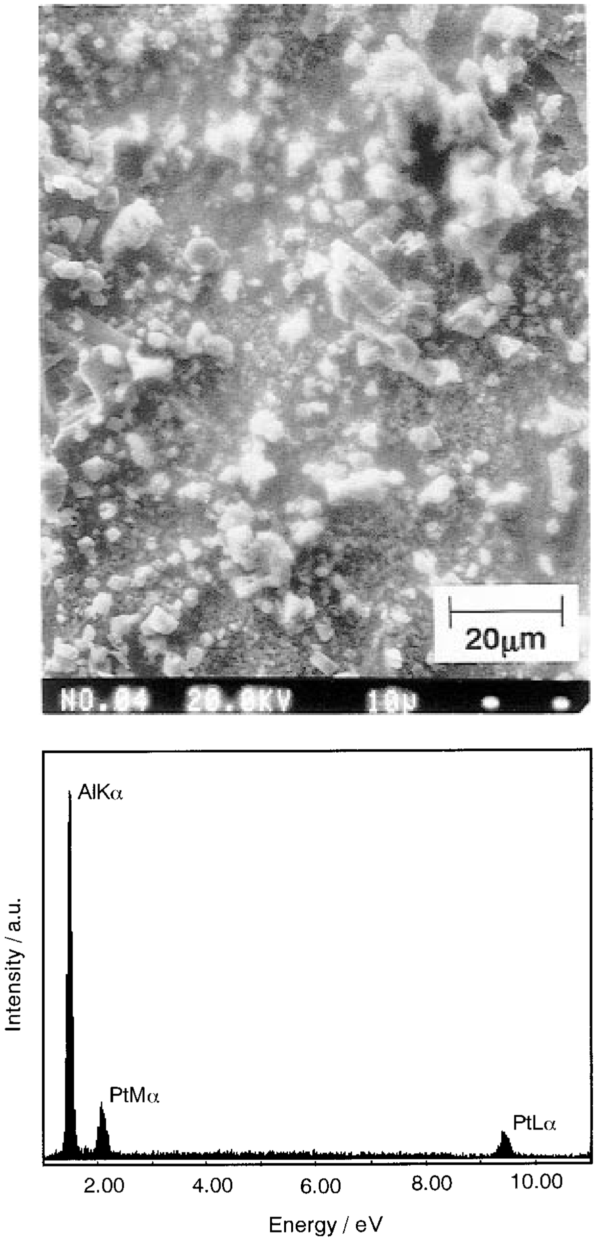

Figure 6. (a, top) SEM photograph of the cathodic platinum electrode surface. (b, bottom) EPMA results obtained for the deposition spots shown in (a).

tential. In the case where the calcium fluoride was applied as a solid electrolyte, the emf corresponds to a difference in the partial pressure of fluorine gas is measured as described in the following Nernst equation:

$$E = -\frac{RT}{2F}\ln\frac{P_{F_2(II)}}{P_{F_2(I)}} \quad (6)$$

where R, T, F, $P_{F_2(I)}$ and $P_{F_2(II)}$ denote gas constant, absolute temperature, Faraday constant, and the partial fluorine pressure in Al + AlF_3 and in Al−Pt + AlF_3, respectively. In the individual electrode, there is a chemical equilibrium as shown below:

$$Al + {}^{3}/_{2}F_2 \rightleftarrows AlF_3 \quad (7)$$

$$Al(Al{-}Pt) + {}^{3}/_{2}F_2 \rightleftarrows AlF_3 \quad (8)$$

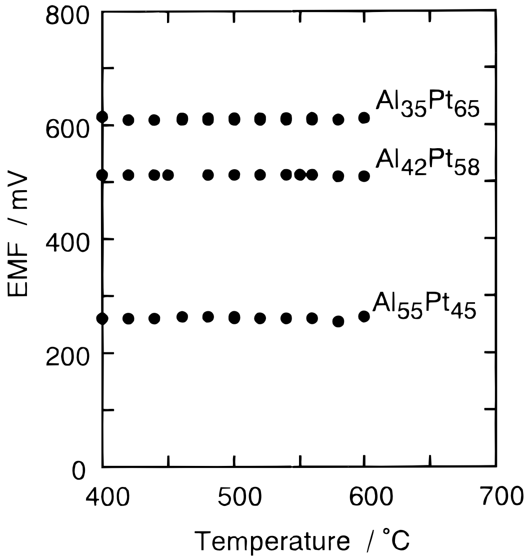

Figure 7. Temperature dependence of the emf obtained in the concentration cell with Al metal and with various Al−Pt alloys. The cells are $Al_{35}Pt_{65}$, $AlF_3|CaF_2|Al$, AlF_3, $Al_{42}Pt_{58}$, $AlF_3|CaF_2|Al$, AlF_3, and $Al_{55}Pt_{45}$, $AlF_3|CaF_2|Al$, AlF_3.

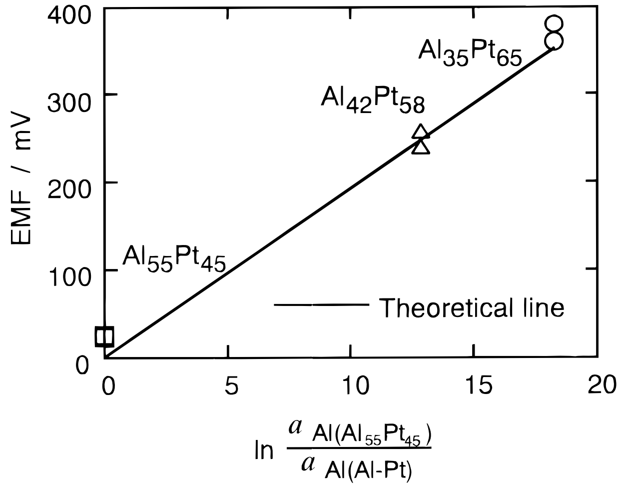

Figure 8. Relationship between the emf and the logarithm of the Al activity ratio in the alloy (Al 55 at. %) to the various alloys at 400 °C. The solid line indicates the theoretical relationship of the emf as calculated from the Nernst equation (12). Open circles, triangles and squares are the measured emf for the cells $Al_{55}Pt_{45}|Al_2(WO_4)_3|Al_{35}Pt_{65}$, $Al_{55}Pt_{45}|Al_2(WO_4)_3|Al_{42}Pt_{58}$, and $Al_{55}Pt_{45}|Al_2(WO_4)_3|Al_{55}Pt_{45}$, respectively.

Therefore, the equilibrium constant, K, is written as follows:

$$K = \frac{a_{AlF_3}}{a_{Al}(P_{F_2(I)})^{3/2}} = \frac{a_{AlF_3}}{a_{Al(Al-Pt)}(P_{F_2(II)})^{3/2}} \quad (9)$$

From relation 9, the next relation is derived:

$$P_{F_2(II)}/P_{F_2(I)} = (a_{Al}/a_{Al(Al-Pt)})^{2/3} \quad (10)$$

Because the aluminum activity in Al metal is unity, the Al activity in Al−Pt alloy was calculated by substituting the emf value obtained from the cell (2) into

$$E = -\frac{RT}{3F}\ln a_{Al(Al-Pt)} \quad (11)$$

The temperature dependencies of the emf obtained by the concentration cell (2) are plotted in Figure 7. Approximately 10 h is necessary to obtain a stable emf. The emf measurements were carried out in such a manner to monitor both increasing and decreasing temperatures, and the reproducible emf value was assessed. The relationship between emf and temperature in Figure 7 was linear between 400 and 600 °C, and the emf value was higher those electrodes consisting of alloys with lower aluminum content. The aluminum activity in $Al_{55}Pt_{45}$, $Al_{42}Pt_{58}$, and $Al_{35}Pt_{65}$ at 400 °C were calculated to be 1.3×10^{-6}, 3.4×10^{-12}, and 1.3×10^{-14}, respectively, from eq 11.

For the Al concentration cell (3) with the $Al_2(WO_4)_3$ between two Al–Pt alloy electrodes, the emf was stable within ±1 mV at the same temperature during the cooling and heating process in the temperature range from 380 to 420 °C in nitrogen atmosphere (P_{O_2} 2×10 Pa), where $Al_2(WO_4)_3$ shows predominally ionic conducting characteristics from the result obtained in Figure 5. Figure 8 presents the relation between the emf obtained by the three types of Al concentration cell with respect to the logarithm of the Al activity ratio in the alloy (Al 55 at. %) to the three alloys at 400 °C. The solid line in Figure 8 indicates the theoretical emf value calculated from the following Nernst equation:

$$E = -\frac{RT}{3F} \ln \frac{a_{Al}}{a_{Al}'} \qquad (12)$$

where a_{Al} and a_{Al}' designate the Al activity in $Al_{55}Pt_{45}$ and that in various Al–Pt alloys. The emf values obtained by the concentration cell (3) are in a good agreement with the theoretical emf solid line. This means that the mobile species is only ionic alone and that the ionic transference number as estimated from the aluminum concentration cell is unity. The overall interpretation of these results is that aluminum ion in the trivalent state is the mobile species in polycrystalline $Al_2(WO_4)_3$. This is the first precise and quantitative evidence to prove the ionic migration in solids of trivalent ion.

Acknowledgment. We thank Prof. I. Katayama and Dr. M. Post for helpful discussions and Dr. K. Yamada for the EPMA measurements. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 08229235 on Priority Areas (No. 260), Nos. 06241106, 06241107, and 083065 from The Ministry of Education, Science, Sports and Culture. Y.K. is the Fellowship member of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

CM970004B