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Journal of Alloys and Compounds 323–324 (2001) 540–544

Journal of ALLOYS AND COMPOUNDS

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Trivalent cation conduction in $R_{1/3}Zr_2(PO_4)_3$ (R: rare earths) with the NASICON-type structure

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Abstract

New trivalent cationic conductors with NASICON-type structure, $R_{1/3}Zr_2(PO_4)_3$ (R: rare earths), were prepared by a sol–gel method and the trivalent ionic conducting properties were investigated. As increasing the R^{3+} radius, the lattice expanded and the conductivity decreased. The $Sc_{1/3}Zr_2(PO_4)_3$ which contained the smallest trivalent cation in the rare earth series, Sc^{3+}, showed the highest conductivity among the $R_{1/3}Zr_2(PO_4)_3$ as expected from relationship between the migrating cation size and the lattice volume. The trivalent Sc^{3+} ion conduction in the $Sc_{1/3}Zr_2(PO_4)_3$ solid electrolyte was directly demonstrated by a dc electrolysis.

Keywords: Rare earths; Ionic conduction; Solid electrolyte; NASICON-type

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1. Introduction

Solid electrolytes are functional materials in which only ion migrates with charge carrying in solids and some of them are applied for various electrical applications, e.g. lithium batteries for heart pacemakers, sensing devices etc. Although many kind of ions are well known to migrate in solids, those ions were limited to monovalent and divalent state because of the strong electrostatic interaction between conducting ion species and surrounding constituents of the lattice. The conductivity of monovalent ion is, in general, higher than that of divalent ion. Among the monovalent cationic conductors, alkali metal ions such as Na^+ and Li^+ were especially well known for their high ionic conduction in solid electrolytes such as NASICON-type and β-/β″-alumina-type so far, and some of them are called super ionic conductors. All solid electrolytes mentioned above have the structure which holds comparatively large conducting pathway in those structure. For trivalent cation species, the migration in solids had been believed to be greatly difficult because of strong electrostatic interaction with surrounding anions. Ln^{3+}-β″-alumina [1–7], β-$LaNbO_3$ [8] and $LaA_{11}O_{18}$ [9] had been claimed to be trivalent ion conductors. However, any trivalent ion migration in these materials has not been directly and quantitatively demonstrated yet at all.

Recently, $R_2(WO_4)_3$ (R: Al, Sc, Y, Lu–Er) solid electrolytes with the $Sc_2(WO_4)_3$ type structure have been reported as pure trivalent cationic conductors [10–16]. The structure is the quasi-layered and contains hexavalent tungsten ion, W^{6+}, which is strongly bonded to surrounding oxide anions resulting in reducing the electrostatic interaction between trivalent R^{3+} cation and oxide anions. Furthermore, since the valence states of all cations in the structure are higher than three, no monovalent or divalent cation conduction appears and the R^{3+} conduction in the $R_2(WO_4)_3$ was directly demonstrated by a dc electrolysis. However, the $R_2(WO_4)_3$ has a disadvantage that W^{6+} cation which contributes for the trivalent cation migration in solids might be reduced to lower valence state in a reducing atmosphere.

The NASICON is the solid electrolyte which contains cations with high valence cations such as Zr^{4+} and P^{5+} and possesses the three dimensional network structure suitable for ionic conduction, and the high Na^+ conductivity is also well known. Recently, $Ln_{1/3}Zr_2(PO_4)_3$ (Ln: lanthanoids) with the NASICON-type structure were reported as new phosphates by Talbi et al. [17] and the thermal stability of them was studied. However, the Ln^{3+} cations contained in these materials are limited to some lanthanoid atoms and ionic conducting characteristics of them were not investigated at all. We selected the

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0925-8388/01/$ – see front matter
PII: S0925-8388(01)01139-2

NASICON-type structure as the candidate, and selected the trivalent rare earth ions as the migrating cation species.

In this paper, the $R_{1/3}Zr_2(PO_4)_3$ (R: Sc, Eu, Gd, Er, Lu) phosphates were prepared by a sol–gel method and trivalent cation conducting properties in these solid electrolytes were studied.

2. Experimental

$R_{1/3}Zr_2(PO_4)_3$ (R: Sc, Eu, Gd, Er, Lu) was prepared by a sol–gel method from high purity of R_2O_3 (99.9%), $ZrO(NO_3)_2 \cdot 2H_2O$ (99.95%) and $(NH_4)_2HPO_4$ (>99.99%) as the starting materials. R_2O_3 and $ZrO(NO_3)_2 \cdot 2H_2O$ were separately dissolved in nitric acid solution (3 N), then mixed together. The 3% $(NH_4)_2HPO_4$ solution was dropped into the mixed nitric acid solution afterwards. After precipitations (the color was white except for the Er system (light pink)) were obtained, the solution was heated at 75°C for 24 h, then water in the solution was vaporized by heating at 130°C for 6 h. The dried precipitant was heated at 300°C for 6 h and the powder obtained was pelletized and sintered at 850°C for 24 h. Pt electrodes were sputtered on both center surfaces of the sample pellet. The ac conductivity of the sample was measured by a complex impedance method using the Precision LCR meter (8284A, Hewlett Packard) in the frequency range from 20 Hz to 1 MHz at the temperature range between 350 and 600°C in air atmosphere. The dc conductivity measurement of the sample was carried out by monitoring the voltage generated by passing the constant current of 0.1 μA in the sample, and the polarization behavior was investigated as the time dependence of the σ_{dc}/σ_{ac} ratio. Here, σ_{dc} and σ_{ac} denotes dc conductivity and ac conductivity, respectively. The oxygen partial pressure dependencies of the electrical conductivity were measured in the oxygen pressure range between 10^{-12} and 10^5 Pa. The oxygen–air gas concentration cell was fabricated with $Sc_{1/3}Zr_2(PO_4)_3$, and the electromotive force (EMF) was measured at the temperature from 650 to 850°C. The dc electrolysis of the $Sc_{1/3}Zr_2(PO_4)_3$ pellet was performed by applying a dc voltage of 3 V at 700°C for 400 h for the purpose of identifying the conducting species, and the investigation of the cathodic surface of the sample after electrolysis was carried out by SEM (SEM, S-800, Hitachi) and EPMA (EPMA-1500, Shimadzu).

3. Results and discussion

All the $R_{1/3}Zr_2(PO_4)_3$ (R: Sc, Eu, Gd, Er, Lu) prepared were found to possess the NASICON-type structure with hexagonal symmetry from the XRD measurements. Fig. 1 shows the R^{3+} radius dependencies of *a*- and *c*-axes, and lattice volume calculated for the prepared $R_{1/3}Zr_2(PO_4)_3$. As R^{3+} cation radius increases, *a*-axis decreases and *c*-axis increases monotonously, and the lattice volume was found to increase.

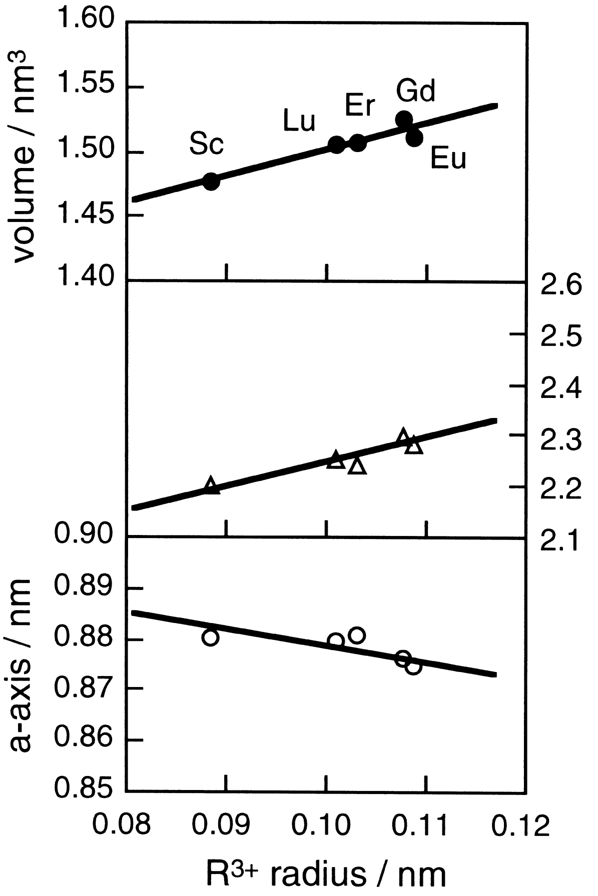

Fig. 1. The R^{3+} radius dependencies of the lattice parameters (*a*-, *c*-axis) and the lattice volume for $R_{1/3}Zr_2(PO_4)_3$.

For monovalent Li^+ ion conductor with the NASICON-type structure, the existence of the most appropriate lattice size for Li^+ ion conduction has been clarified by Aono et al. [18] and they reported the detail of the relationship between the Li^+ ion size and the lattice volume of LISICON (Li^+ super ionic conductor) with the NASICON-type structure. Among $LiM_2(PO_4)_3$ (M=Ge, Ti, Hf) with the NASICON-type structure, the $LiTi_2(PO_4)_3$ solid electrolyte is verified to be the suitable lattice size for Li^+ ion conduction. An optimum ratio of the conducting ion size to the lattice volume in the NASICON-type structure is calculated to be ca. 2.33×10^{-3} for $LiTi_2(PO_4)_3$.

Fig. 2 shows the (R^{3+} volume/lattice volume) ratio (W ratio) of the $R_{1/3}Zr_2(PO_4)_3$ with the corresponding datum of $LiTi_2(PO_4)_3$ solid electrolyte. In the case of trivalent cationic conduction, the electrostatic interaction between R^{3+} and surrounding oxide anions would be stronger than for the case of monovalent Li^+ ion conduction.

Therefore, the suitable lattice size for R^{3+} migration should be obtained for the solid electrolyte with the smaller W ratio compared with that ratio of the monovalent Li^+ conductor. Since only the $Sc_{1/3}Zr_2(PO_4)_3$ has the

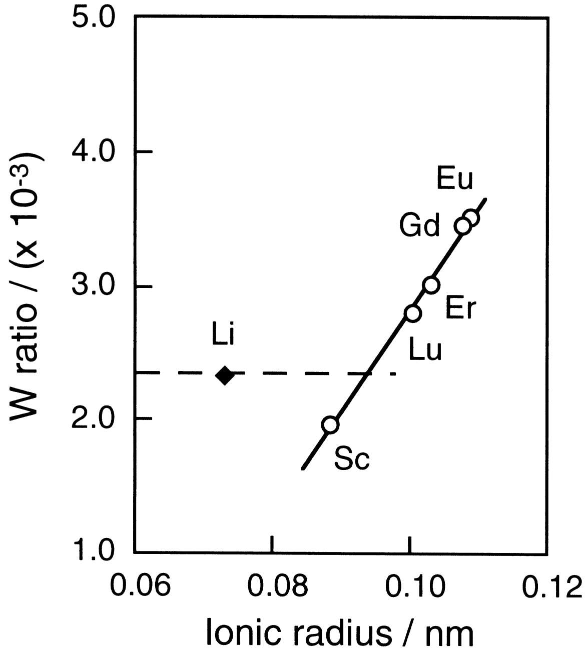

Fig. 2. The W ratio variation of $R_{1/3}Zr_2(PO_4)_3$ with the corresponding datum of $LiTi_2(PO_4)_3$. The W ratio represents the trivalent cation size to lattice volume ratio.

smaller W ratio of 1.97×10^{-3} than that of Li^+ (2.33×10^{-3}) which is lined as a broken line in Fig. 2, among $R_{1/3}Zr_2(PO_4)_3$, the highest conductivity is expected for Sc^{3+}.

The trivalent R^{3+} radius dependencies of the electrical conductivity for the $R_{1/3}Zr_2(PO_4)_3$ at 600°C is shown in Fig. 3. As expected from the W ratio variation of $R_{1/3}Zr_2(PO_4)_3$, the conductivity monotonously increased with reducing the R^{3+} ion size, and the $Sc_{1/3}Zr_2(PO_4)_3$ showed the highest conductivity of 1.06×10^{-5} $S\cdot cm^{-1}$. The conductivity is comparable to that of $Sc_2(WO_4)_3$-type solid electrolyte series described in a previous communication [19]. Although we tried to prepare the $Al_{1/3}Zr_2(PO_4)_3$ which is expected to have smaller W ratio than the $Sc_{1/3}Zr_2(PO_4)_3$, the sample obtained was a two phase mixture of $AlPO_4$ and ZrP_2O_7 because the Al^{3+} radius is too small to hold the NASICON-type structure, so that the $Sc_{1/3}Zr_2(PO_4)_3$ was found to possess the highest conductivity among the $R_{1/3}Zr_2(PO_4)_3$ with NASICON-type structure.

Fig. 4 depicts the oxygen partial pressure dependence of the ac conductivity for the $Sc_{1/3}Zr_2(PO_4)_3$ at 700°C. No meaningful deviation of the conductivity was observed for the whole oxygen pressure region measured, which indicates that the predominant charge carrier is only ion and

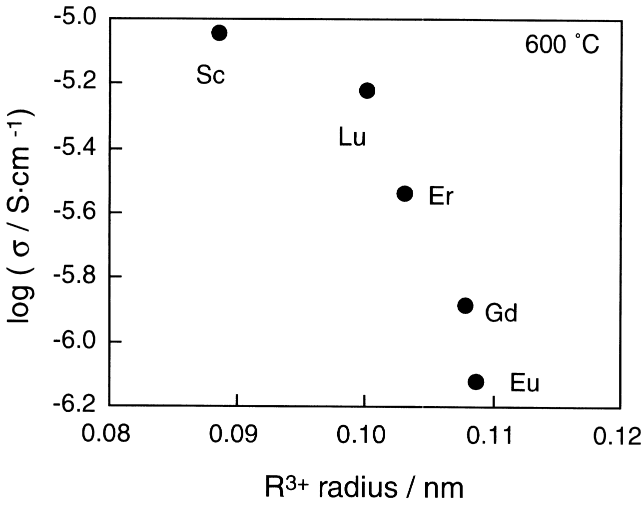

Fig. 3. The R^{3+} radius dependencies of the electrical conductivities for $R_{1/3}Zr_2(PO_4)_3$ at 600°C.

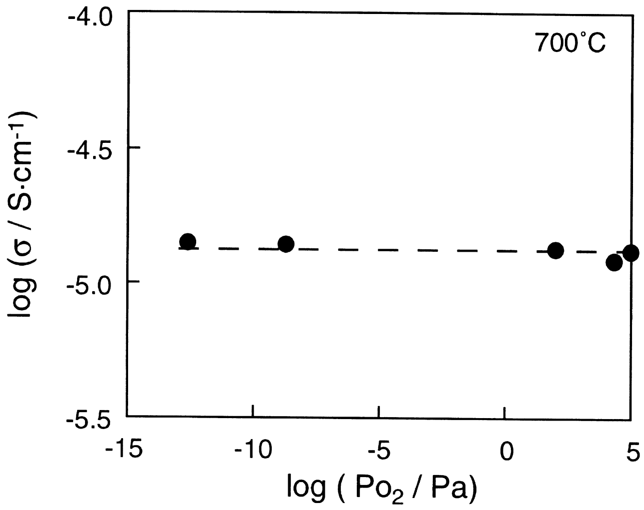

Fig. 4. Oxygen partial pressure dependencies of the ac conductivity for $Sc_{1/3}Zr_2(PO_4)_3$ at 700°C.

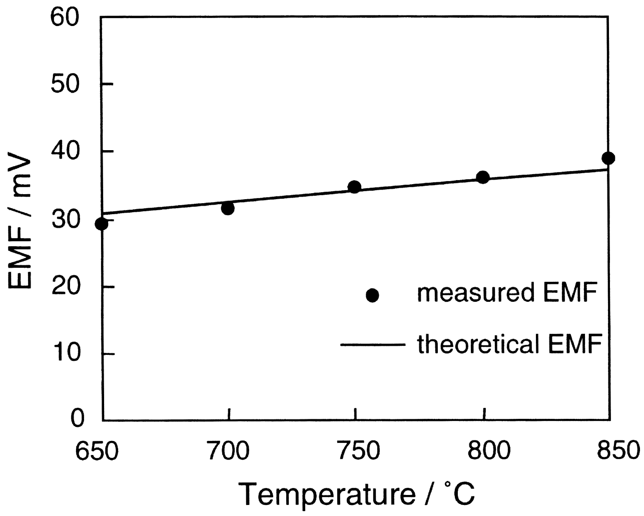

Fig. 5. The EMF value obtained for the oxygen–air gas concentration cell fabricated with the $Sc_{1/3}Zr_2(PO_4)_3$ solid electrolyte at the temperature between 650 and 850°C. The solid line indicates the theoretical EMF calculated from the Nernst equation.

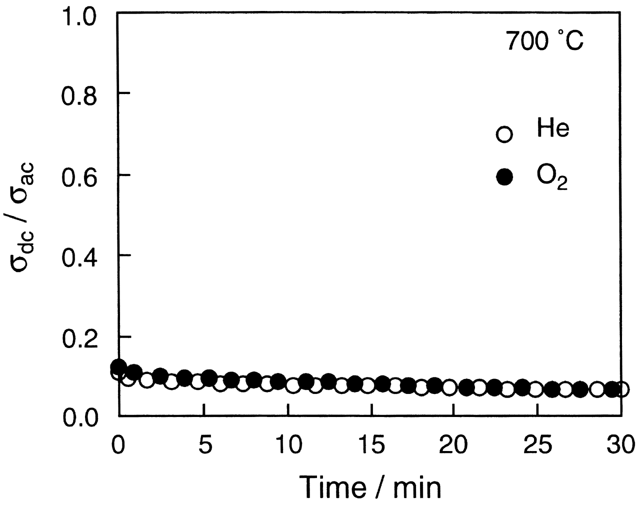

Fig. 6. The dc to ac conductivity ratio (σ_{dc}/σ_{ac}) plotted as the function of time.

neither electron nor hole. Furthermore, oxygen–air concentration cell (1) as described below was fabricated and the EMF generated was measured at the temperature range between 650 and 850°C. Fig. 5 plots the EMF measured and the theoretical value calculated from the following Nernst Eq. (2):

$$\mathrm{Pt}, O_2|Sc_{1/3}Zr_2(PO_4)_3|\mathrm{Air}, \mathrm{Pt} \quad (1)$$

$$E = -(RT)/(4F)\ln(p''_{O_2}/p'_{O_2}) \quad (2)$$

The measured EMF was in excellent accordance with the theoretical value of Nernst Eq. (2). This result also supports the predominant cationic conduction in $Sc_{1/3}Zr_2(PO_4)_3$.

In the case of O^{2-} ion conductor, the dc conductivity is the same as the ac one in O_2 atmosphere since the conducting O^{2-} ion can be provided from the O_2 gas atmosphere, and the σ_{dc}/σ_{ac} ratio holds the value of one constantly. In contrast, the σ_{dc}/σ_{ac} ratio decreases in low O_2 pressure such as He where O^{2-} ion can not be supplied enough into the solid electrolyte and a clear polarizing behavior would be observed. Fig. 6 shows the dc to ac conductivity ratio as a function of time in O_2 ($p_{O_2}=10^5$ Pa) and He ($p_{O_2}=4$ Pa) atmosphere at 700°C for $Sc_{1/3}Zr_2(PO_4)_3$ solid electrolyte. It shows an abrupt decrease in the σ_{dc}/σ_{ac} ratio for both O_2 and He atmospheres, and this result is definitely different from that of oxide anion conductors, indicating no O^{2-} ion migration in the $Sc_{1/3}Zr_2(PO_4)_3$ solid electrolyte.

For the purpose of identifying the migrating cation species in $Sc_{1/3}Zr_2(PO_4)_3$, a dc electrolysis which can directly determine the conducting species in solid electrolytes was performed using two Pt bulk as blocking electrodes at 700°C (The decomposition voltage of the $Sc_{1/3}Zr_2(PO_4)_3$ solid electrolyte had been preliminary measured at 700°C and is determined to be ca. 2 V.). By applying a dc voltage of 3 V which is higher than the decomposition voltage at 700°C, the conducting cation species should migrate successively from the anode to the cathode direction and deposits on the cathodic surface which is in contact with the Pt blocking electrode. After the electrolysis, deposits were recognized at only cathodic surface. From the EPMA spot analysis, the Sc/(Sc+Zr+P) ratio in the deposit increased approximately 7.6 times as high as that in the bulk before electrolysis as shown in Fig. 7. These results explicitly indicate that the Sc^{3+} ions macroscopically migrate from anode to cathode direction by applying a dc voltage and deposit on the cathodic surface, thus, the mobile cationic species in $Sc_{1/3}Zr_2(PO_4)_3$ is directly identified to be Sc^{3+} ion.

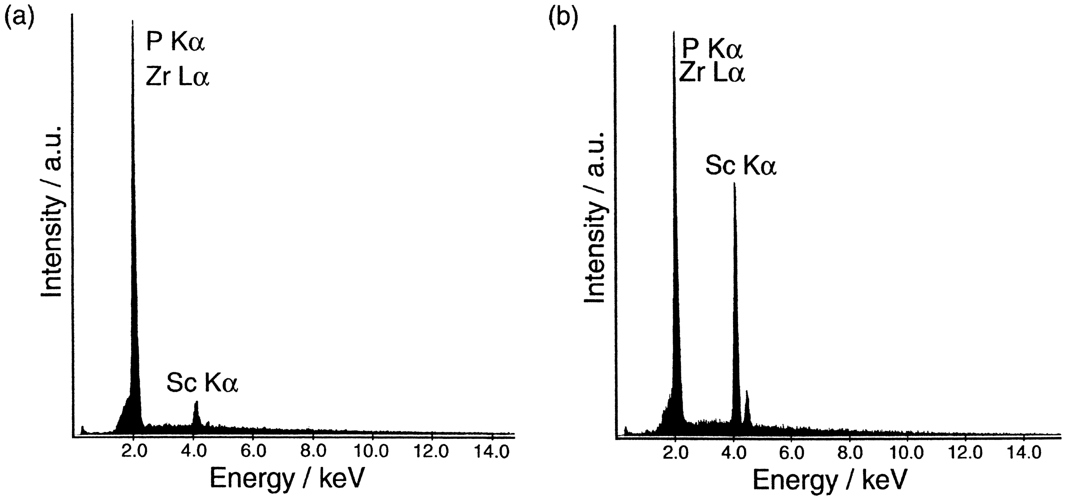

Fig. 7. The result of EPMA spot analysis for (a) the bulk before the electrolysis and (b) the deposit at the cathodic surface after the electrolysis.

4. Conclusions

The suitable lattice size for trivalent R^{3+} ion conduction in $R_{1/3}Zr_2(PO_4)_3$ with NASICON-type structure was obtained for $Sc_{1/3}Zr_2(PO_4)_3$ which is composed of the smallest trivalent cation of Sc^{3+} among the rare earth series. With decreasing the R^{3+} size in the $R_{1/3}Zr_2(PO_4)_3$, the trivalent ion conductivity monotonously increased.

Since the $R_{1/3}Zr_2(PO_4)_3$ solid electrolyte is chemically stable enough in addition to holding the high ion conductivity comparable to that of the $Sc_2(WO_4)_3$-type trivalent cationic conductors, the utilization for various electrical devices applicable from in oxidizing to reducing atmosphere is greatly expected.

Acknowledgements

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 09215223 on Priority Areas (No. 260), Nos. 06241106, 06241107, and 093065 from The Ministry of Education, Science, Sports and Culture. This work was also supported by the ‘Research for the Future, Preparation and Application of Newly Designed Solid Electrolytes (JSPS-RFTF96P00102)’ Program from the Japan Society for the Promotion of Science.

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