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Journal of Solid State Chemistry 171 (2003) 387–390

JOURNAL OF
SOLID STATE
CHEMISTRY

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# Cerium ion conducting solid electrolyte

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Received 29 April 2002; received in revised form 15 August 2002; accepted 28 August 2002

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## Abstract

A cerium ion conducting solid electrolyte, $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$, was successfully realized with the NASICON-type structure which possesses a three-dimensional network, especially suitable for bulky ion migration. The cerium ion conductivity exceeds approximately one order of magnitude in comparison to that of the rare-earth ion conducting $R_2(WO_4)_3$ and $R_{1/3}Zr_2(PO_4)_3$ ($R$ = Sc, Y, Eu–Lu) series and the value is in the range between typical oxide anion conductors of yttria stabilized zirconia (YSZ) and calcia stabilized zirconia (CSZ). Since cerium ion has been demonstrated to be another migrating ion species in solid electrolyte field, a promising application for various functional materials is greatly expected.

*Keywords:* Cerium; Solid electrolyte; Ion conductivity; NASICON; Phosphates

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## 1. Introduction

Solid electrolytes are one of functional materials where only ion species conducts in solids as an electric charge carrier, and they are greatly expected to be applied in various fields such as rechargeable batteries and specific gas sensing unique tools, etc. In the solid electrolyte field, a number of monovalent and divalent ions have been extensively known to conduct in solids [1,2]. In contrast, in the case for trivalent ions, electrical conductivity measurements (for example [3–5]) were mainly studied with $\beta''$-alumina where monovalent $Na^+$ ions are ionically exchanged by trivalent cation species. However, in their cases, the residual $Na^+$ ion conduction also occurs with the trivalent ion conduction and the ion-exchanged $\beta''$-alumina series is not categorized as pure trivalent ion conducting solid electrolytes. Therefore, up to 1995, the macroscopic conducting ion species have been limited only to the low valent (mono- or divalent) ions and it has been believed to be only these two groups that show pure ion conducting characteristics with single ion species from the view point of electrostatic interaction between the conducting ion and the surrounding counter ions [2].

In order to realize a higher valent trivalent ion migration in solids, the surroundings which reduce the above-mentioned strong electrostatic interaction in addition to realize the suitable lattice structure for the trivalent ion migration, are strongly requested. For the purpose of overcoming above-described two key points, a light was shed on the trivalent ion species that stably hold the trivalent state and also on two- or three-dimensional framework suitable for bulky trivalent ion conduction. Among various trivalent ions, the rare-earth ions including Sc and Y are selected as the candidates due to their high stability in the valency state. Since 1995, the $M_2(WO_4)_3$ ($M$ = Al, Sc, Y, Er-Lu) tungstate series with $Sc_2(WO_4)_3$-type structure has been developed and their trivalent $M^{3+}$ ion conducting properties were extensively investigated (for example [6–8]). The $M_2(WO_4)_3$ series has a quasi-two-dimensional open layered structure and $M^{3+}$ ions migrate between the layers. After the discovery of the $M_2(WO_4)_3$ ($M$ = Al, Sc, Y, Er–Lu) tungstate series, another series of $R_{1/3}Zr_2(PO_4)_3$ ($R$ = Sc, Y, Eu-Lu) with the NASICON-type structure (NASICON is the $Na^+$ super ionic conductor, which is a tailored solid electrolyte series and has a three-dimensional network structure suitable for ion migration) has also been demonstrated to be suitable $R^{3+}$ ion conductors [9–11]. Among rare-earth elements including Sc and Y, many rare-earth ion species have been clarified to ionically migrate in

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doi:10.1016/S0022-4596(02)00218-9

solids. However, cerium ion conductors have not been realized yet.

In this paper, for the purpose of obtaining the cerium ion conducting solid electrolyte, the solid was strictly selected from a view point of attaining an open three-dimensional network structure of the NASICON-type structure. Furthermore, as the constituent high valent ions, $Nb^{5+}$ was also chosen in addition to tetravalent $Zr^{4+}$ and pentavalent $P^{5+}$ ions in $R_{1/3}Zr_2(PO_4)_3$ to further reduce the electrostatic interaction between the migrating cerium ion and the counter oxide anions and to realize appropriate surroundings for high valent cerium ion conduction in the NASICON-type structure.

## 2. Experimental

The stoichiometric amount of $Ce_2(SO_4)_3 \cdot 8H_2O$ (99.999%), $ZrO_2$ (99.99%), $Nb_2O_5$ (99.99%), and $(NH_4)_2HPO_4$ (99.99%) was mixed in an agent pot at a rotation speed of 300 rpm for 6 h by a ball milling method (Pulverisette 7, FRITSCH GmbH). After pelletizing the mixed powder, the sample was heated at 1000°C for 12 h, 1200°C for 12 h, and then 1300°C for 12 h in air atmosphere. The resulting sample was pulverized and then the X-ray powder diffraction (M18XHF, Mac Science) analysis was carried out to identify the formation of the NASICON-type $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ phase. The sample powder was made into pellets again and then sintered at 1300°C for 12 h in air atmosphere. The platinum-sputtered layer was formed on both center surfaces of the sintered pellet in order to obtain a good contact with the platinum electrode. The ac conductivity of the $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ pellet was measured by sandwiching the sample between two Pt electrodes at the temperatures between 300°C and 800°C in a frequency range from 5 Hz to 13 MHz by using LCR meter (4192A, Hewlett-Packard). The dc conductivity was measured by passing the dc current of 1 μA between two Pt electrodes. The dc electrolysis of the sintered sample pellet was performed by applying a dc voltage of 3 V for 100 h at 700°C, and the conducting ion species was directly identified by scanning electron microscope (SEM) observation and electron-probe microanalysis (EPMA-1500, Shimadzu) at the surface of the electrolyzed pellet. The magnetic susceptibility measurement was carried out by the SQUID method with Quantum Design (PPMS Model 6000).

## 3. Results and discussion

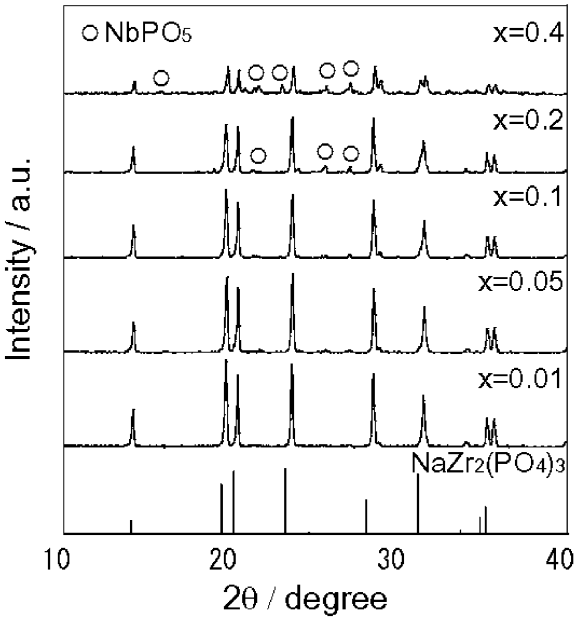

Fig. 1. XRD patterns of the $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ series with a typical compound ($NaZr_2(PO_4)_3$) holding the NASICON-type structure (Rhombohedral, JCPDS No.33-1312).

The XRD patterns of the $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ series are shown in Fig. 1 with the pattern of a typical compound ($NaZr_2(PO_4)_3$) holding the NASICON-type structure. The $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ series were found to hold the single phase of the NASICON-type structure with hexagonal symmetry in the range $0 < x \leqslant 0.1$. The samples with the $x$ content higher than 0.1, were in two-phase mixture of the NASICON phase with $NbPO_5$. From these results, it becomes clear that the solid solution limit in $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ is identified to be around $x = 0.1$. In addition, from the measurement of effective magnetic moment of the sample by the SQUID method, 90% of the cerium was found to exist in the trivalent $Ce^{3+}$ state in it.

Fig. 2 presents the composition dependence of the electrical conductivity for $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ ($x = 0-0.4$) at 600°C. The conductivity significantly increased with the cerium content up to $x = 0.1$ and the $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ ($x = 0.1$) solid exhibited the highest conductivity among the phosphate series obtained. The conductivity enhancement from $x = 0$ to 0.01 is attributed to the migrating ion species change from tetravalent $Zr^{4+}$ ion in $ZrNb(PO_4)_3$ which has been already demonstrated to be a $Zr^{4+}$ ion conductor [12] to cerium ions. (The cerium ion conduction in $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ was demonstrated as shown below.) For the samples with two-phase mixture ($x > 0.1$), the conductivity reduces monotonously with the cerium content since the amount of the secondary $NbPO_5$ phase whose conductivity is appreciably lower than that of the NASICON-type $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (see Fig. 3) increases (also see Fig. 1). The ac conductivity of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ was constant for the oxygen pressure range between 4 and $10^5$ Pa, indicating that the predominant conducting

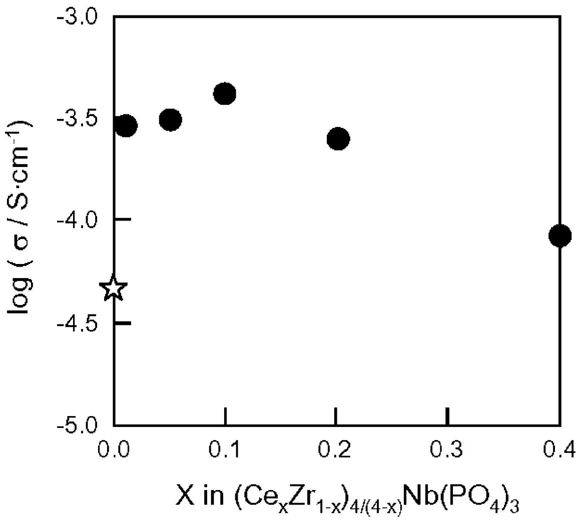

Fig. 2. Composition dependence of the electrical conductivity for $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ ($0 \leqslant x \leqslant 0.4$) at 600°C. (☆) presents the conductivity for $ZrNb(PO_4)_3$ which has been reported to be a tetravalent $Zr^{4+}$ ion conductor [12].

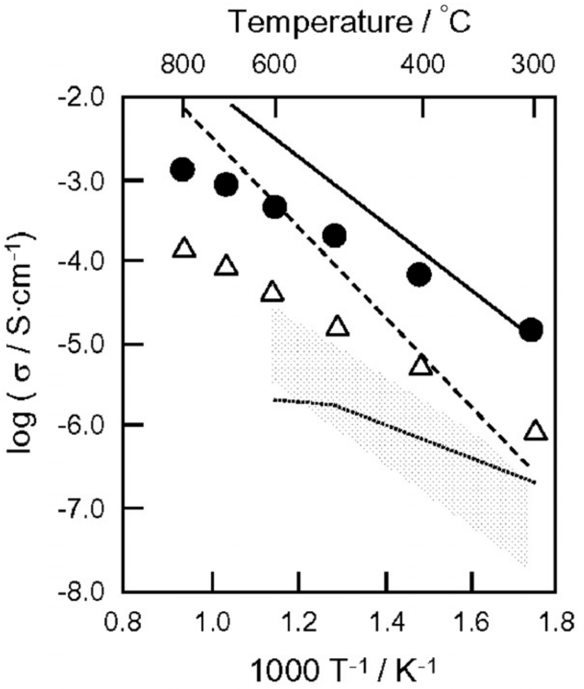

Fig. 3. Temperature dependence of the ion conductivity for $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (●), $ZrNb(PO_4)_3$ (△), $R_{1/3}Zr_2(PO_4)_3$ series (shaded area), $NbPO_5$ (⋯⋯), YSZ (—), and CSZ (- -).

species in $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ is only ion species in the above oxygen pressure region as described in Ref. [7].

Fig. 3 depicts the temperature dependence of the ion conductivity for $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (•), $ZrNb(PO_4)_3$ (△), $R_{1/3}Zr_2(PO_4)_3$ series (shaded area), $NbPO_5$ (⋯⋯), YSZ (—), and CSZ (- -). The ion conductivity of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ exceeds approximately one order of magnitude in comparison with that of $ZrNb(PO_4)_3$. $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ also shows an appreciable high conductivity compared with those of the $R_{1/3}Zr_2(PO_4)_3$-type series which has the NASICON structure and the ion conductivity of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ below 600°C is in the region between the typical oxide anion conductors of YSZ and CSZ.

The dc to ac conductivity ratio ($\sigma_{dc}/\sigma_{ac}$) was also measured as a function of time in both $O_2$ ($P_{O_2} = 10^5$ Pa) and $N_2$ ($P_{O_2} = 20$ Pa) atmosphere at 800°C to clarify its polarizing behavior. From the polarization measurements, it is clarified that the $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid electrolyte shows an abrupt decrease in the $\sigma_{dc}/\sigma_{ac}$ ratio for both atmosphere, and the ratio reached below 0.01 after 10 min. This result definitely indicates that the ion transference number ($t_i$) is estimated to be higher than 0.99. The same polarizing behavior in both atmosphere suggests that the oxide anion ($O^{2-}$) is not a migrating ion species in $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ as demonstrated in Ref. [7]. From the results described above, the electric charge carrier in the $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid is identified to be predominantly cation species of the constituent ions in $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$.

For the purpose of exactly identifying the conducting cation species among cerium, zirconium, niobium, phosphorous in the $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid electrolyte, a dc electrolysis (3 V at 700°C for 100 h in air) was carried out to enforce the target migrating ion species to conduct inside the solid and deposit on the phosphate solid surface where the phosphate solid electrolyte is in contact with the cathodic Pt electrode. Before the electrolysis, the decomposition voltage of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ was determined to be ca. 1.2 V from the current–voltage measurement and the applied voltage was set intentionally higher than that of the decomposition voltage of 1.2 V to supply the conducting cation species from the anodic to the cathodic side (details of the experiment are reported in Refs. [7,8]).

Fig. 4 shows the SEM photograph of the representative deposit appeared at the cathodic surface of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ after dc electrolysis. The deposit was clearly observed, while any deposition was not recognized on the counter anodic surface. The EPMA spot measurements were conducted for representative three spots of the deposit on the cathodic surface and the results are tabulated in Table 1. Among four elements in the $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid electrolyte, an outstanding increase was observed only for cerium. This result clearly indicates the fact that cerium cation species formed at the interface between the anodic solid surface and the anodic Pt electrode migrates inside the $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid electrolyte and deposits at the interface between the cathodic solid surface and the cathodic Pt electrode.

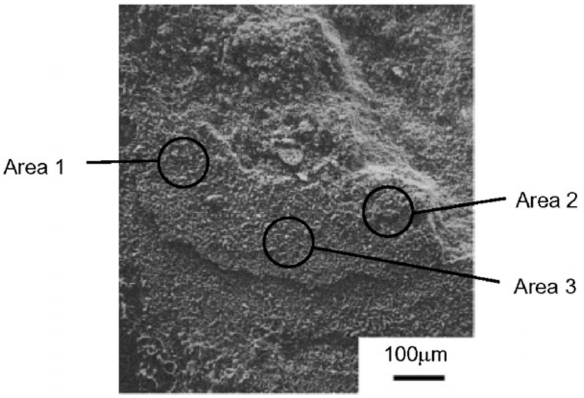

Fig. 4. SEM photograph of the representative deposit appeared at the cathodic surface of $(Ce_xZr_{1-x})_{4/4-x}Nb(PO_4)_3$ $(x = 0.1)$ after dc electrolysis.

Table 1
The atomic ratio in $(Ce_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ $(x = 0.1)$ before and after dc electrolysis

| Element | Atomic ratio (%) | | | | |
|---|---|---|---|---|---|
| | Bulk before electrolysis | Anodic surface after electrolysis | The deposits at the cathodic surface after electrolysis | | |
| | | | Area 1 | Area 2 | Area 3 |
| Ce | 1.4 | 1.8 | 28.0 | 29.1 | 35.7 |
| Zr | 17.2 | 18.0 | 7.0 | 4.9 | 1.9 |
| Nb | 17.5 | 16.8 | 5.0 | 8.1 | 3.4 |
| P | 63.9 | 63.4 | 60.0 | 57.9 | 59.0 |

Since no electronic conduction was observed by both ac conductivity measurements in various $P_{O_2}$ atmosphere and the polarization behavior, the lower valent $Ce^{3+}$ was thought to be the only conducting ion species while the $Ce^{4+}$ ion seemed to function as the constituent of the framework by the strong electrostatic interaction with oxide anions.

## 4. Conclusions

A new cerium ion conductor, $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$, was successfully realized for the first time by strictly selecting the constituent elements and the crystal structure of NASICON which possesses the three-dimensional network suitable for bulky ion macroscopic migration. The cerium ion conductivity is the highest and the value is approximately one order of magnitude higher than those of the rare-earth ion conducting solid electrolytes reported. Since the $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ electrolyte has as high ion conductivity as the representative oxide anion conducting solid electrolytes of YSZ and CSZ, cerium ion would be one of promising migrating ion candidates in Solid State Ionics among the rare-earth ions.

## Acknowledgments

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 13555241 from The Ministry of Education, Science, Sports and Culture. This work was also supported by Iketani Science and Technology Foundation.

## References

[1] T. Kudo, K. Fueki, Solid State Ionics, VCH, Berlin, 1990.
[2] G. Adachi, N. Imanaka, S. Tamura, Chem. Rev. 102 (2002) 2405–2430.
[3] B. Dunn, G.C. Farrington, Solid State Ionics 9/10 (1983) 223–226.
[4] G.C. Farrington, B. Dunn, J.O. Thomas, Appl. Phys. A 32 (1983) 159–161.
[5] S. Sattar, B. Ghosal, M.L. Underwood, H. Mertwoy, M.A. Saltzberg, W.S. Frydrych, G.S. Rohrer, G.C. Farrington, J. Solid State Chem. 65 (1986) 231–240.
[6] N. Imanaka, Y. Kobayashi, G. Adachi, Chem. Lett. (1995) 433–434.
[7] Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, G. Adachi, Chem. Mater. 9 (1997) 1649–1654.
[8] N. Imanaka, Y. Kobayashi, K. Fujiwara, T. Asano, Y. Okazaki, G. Adachi, Chem. Mater. 10 (1998) 2006–2012.
[9] S. Tamura, N. Imanaka, G. Adachi, Adv. Mater. 11 (1999) 1521–1523.
[10] S. Tamura, N. Imanaka, G. Adachi, Solid State Ionics 136–137 (2000) 423–426.
[11] S. Tamura, N. Imanaka, G. Adachi, J. Alloys and Compounds 323–324 (2001) 540–544.
[12] N. Imanaka, T. Ueda, G. Adachi, Chem. Lett. (2001) 446–447.