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Structure and electrical characteristics of Ce^{4+}-doped $Ba_2In_2O_5$

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The *In-site* of $Ba_2In_2O_5$ with Brownmillerite structure was partially substituted for Ce^{4+} ions in order to examine the doping effect on the order-disorder transition. $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 0.3, 0.5, 1.0, and 1.5) were prepared by solid state reaction. X-Ray diffraction analyses of these powder samples demonstrated that $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$ and 0.2) possesses Brownmillerite structure. With increasing content of Ce^{4+} ion the crystal system of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.3$, 0.5, and 1.0) changed to cubic perovskite structure above the order-disorder transition temperature of $Ba_2In_2O_5$. Arrhenius plots of the electrical conductivities of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.2$, 0.3, and 1.0) exhibited no discontinuity. These compounds had high transference numbers of oxide ion above 973 k. © *2003 Kluwer Academic Publishers*

1. Introduction

Solid electrolytes with oxide-ion conductivity have been widely studied for use as materials for oxygen sensors, oxygen pumps, and electrolytes of solid oxide fuel cells. In particular, electrolytes for solid oxide fuel cells (SOFCs) have been intensively investigated due to its generation of powers with high efficiency and low environmental pollution. At present, zirconia stabilized by 8 mol% yttria $(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$ (YSZ) is used as the electrolyte for SOFCs. However, high operation temperatures are essential for SOFCs composed of YSZ which shows the ionic conductivity of 0.1 Scm^{-1} at ca.1270 K. Because of the high temperatures required to achieve useful oxide ion conductivities in current materials, there is a great interest in developing new materials that exhibit high oxide ion conductivities (10^{-2} to 10^{-1} Scm^{-1}) at lower temperatures (670–1070 K) [1]. Ishihara *et al.* [2] have reported that $LaGaO_3$ with perovskite structure doped with Sr for the La site and Mg for the Ga site ($la_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{2.9}$) exhibits higher oxide ionic conductivities at lower temperatures than YSZ. Thus, compounds with perovskite and perovskite-related structures, which are candidate electrolytes that exhibit high oxide ion conductivity, have recently been investigated [1–5]. Goodenough *et al.* [6] have reported that $Ba_2In_2O_5$ with orthorhombic Brownmillerite structure exhibits high oxide ionic conductivity at temperatures higher than 1223 K. Oxygen vacancies in a Brownmillerite compound distribute randomly above a characteristic order-disorder temperature T_d. Since the random distribution results in high oxide ionic conductivity of the compound, it should be necessary to stabilize the disordered phase to low temperatures in order to accept the compound as an useful oxide ionic conductor in the low temperature range [1]. The substitution of cations of the A-site or of the B-site in $Ba_2In_2O_5$ for other ones led to the stabilization of the disordered form (reduction of T_d) and the improvement of oxide ionic conduction [6–11]. Goodenough *et al.* [6] found that by doping Ce^{4+} into the In site (B site) the discontinuity in the conductivity data disappeared at a doping level of 12.5% ($Ba_2In_{1.75}Ce_{0.25}O_{5.125}$) at $P_{O_2} = 10^{-4}$ atm. Below the transition temperature the conductivity of the Ce^{4+}-doped system was higher than that of the parent compound. These findings suggest that the substitution of larger cations with larger valence like Ce^{4+} for indium (III) ions would result in the stabilization of the disordered phase and the improvement of the oxide ionic conductivity. However, they examined only the doped system of the above composition.

Thus, in the present work, In^{3+} ions (radius for six-coordination = 0.80 Å [12]) in $Ba_2In_2O_5$ were systematically substituted for larger Ce^{4+} ions (radius for six-coordination = 0.87 Å [12]) in order to examine the reduction of T_d's and the improvement of oxide ionic conductivities of the substituted compounds in a low temperature range. Since the valence of Ce^{4+} ion is higher than that of In^{3+} ion in addition to the fact that the former is larger than the latter, it is expected that the substitution will decrease oxygen vacancies, which should result in the reduction of T_d and the improvement of the oxide ionic conductivity.

2. Experimental

Samples of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ (X = 0.1, 0.2, 0.3, 0.5, 1.0, and 1.5) were prepared according to solid state reaction by using barium carbonate, indium oxide, and cerium oxide of reagent grade as starting materials. The reagents in stoichiometric proportion were mixed for

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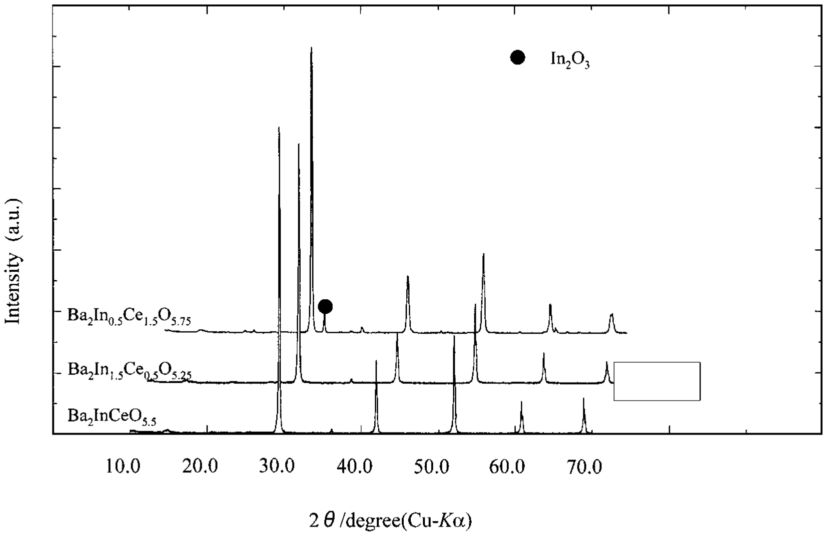

Figure 1 XRD patterns of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 0.3, and 1.0) at room temperature.

6 h by means of an electric mortar with methanol as a dispersing agent. The dried samples were calcined twice at 1373 K for 6 h in air. Powders prepared by crashing were passed through a 75-mesh sieve and pressed into disks of 13 mm in diameter and 1 mm in thickness. After a rubber press at 3.14 tons/cm^2, the disks were sintered at 1723–1923 K for 6 h in air.

The powdered samples were analyzed by X-ray diffraction (XRD) using a Rigaku RINT 2000 with Cu K_α in order to determine phases and lattice constants. The total electrical conductivities of the sintered disks of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1, 0.2, 0.3,$ and 1.0) with platinum electrodes were measured by using an impedance analyzer (Solatoron FRA 1255) over a frequency range from 0.2 Hz to 2 MHz in a temperature range of 673–1273 K in air, N_2, and O_2. Flow rates of N_2 and O_2 were kept at 80 ml/min. The bulk resistances were derived from complex-impedance plane diagrams. Measuring temperatures were determined by a P-R thermocouple placed near a sample. The oxide ionic transference number at high oxygen partial pressure of 1 atm was estimated from the electromotive force (EMF) of the oxygen concentration cell of oxygen-air and the number at low oxygen partial pressures from the EMF value of the cell of (96% nitrogen + 4% hydrogen) saturated with water vapor at 303 K-air. In the estimation the EMF value of 8YSZ measured under the same conditions as above was considered to correspond to the transference number of unity.

3. Results and discussion

3.1. Crystal structure of $Ba_2In_{2-x}Ce_xO_{5+x/2}$

Fig. 1 shows XRD patterns of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.5$, 1.0, and 1.5) measured at room temperature. It is apparent from the positions and shapes of the peaks that the samples of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.5$ and 1.0) retain a cubic lattice of perovskite. A peak at $2\theta =$ ca. 31 deg. indicated by a filled circle in the XRD pattern of $Ba_2In_{0.5}Ce_{1.5}O_{5.75}$, which was not observed in the patterns for $x = 0.5$ and 1.0, was attributed to indium oxide. The XRD patterns of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 0.3, and also 1.0 for comparison) measured at room temperature are diagrammed in Fig. 2. Indexing all the peaks in a JCPDS card of $Ba_2In_2O_5$ suggested that $Ba_2In_{1.9}Ce_{0.1}O_{5.05}$ and $Ba_2In_{1.8}Ce_{0.2}O_{5.10}$ have orthorhombic lattices of

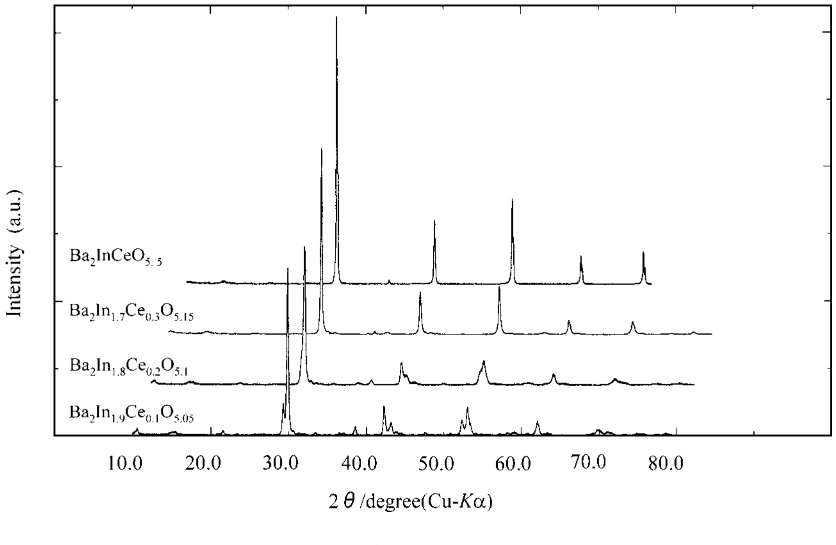

Figure 2 XRD patterns of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.5$, 1.0, and 1.5) at room temperature.

TABLE I Crystal structural data of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 0.3, 0.5, and 1.0)

Compounds	Crystal systems	Lattice parameters (Å)				Cell volumes (Å^3)
		a	*a**	*b*	*c*	
$Ba_2In_{1.9}Ce_{0.1}O_{5.05}$	Orthorhombic	6.10	4.23	16.73	5.95	607.2
$Ba_2In_{1.8}Ce_{0.2}O_{5.10}$	Orthorhombic	6.09	4.25	16.86	5.97	613.0
$Ba_2In_{1.7}Ce_{0.3}O_{5.15}$	Cubic	4.26				
$Ba_2In_{1.5}Ce_{0.5}O_{5.25}$	Cubic	4.26				
$Ba_2InCeO_{5.5}$	Cubic	4.31				

*Pseudo cubic lattice parameters.

Brownmillerite structure. On the other hand, the XRD pattern of $Ba_2In_{1.7}Ce_{0.3}O_{5.15}$ was indexed to a cubic lattice. It is appropriate to consider that as the oxygen vacancies decrease due to the successive substitution of In^{3+}-sites for Ce^{4+} ions with higher valence, the remaining oxygen vacancies become disordered and the crystal system changed to cubic perovskite structure through orthorhombic Brownmillerite structure, while in an early substitution step where the vacancies are abundant and oriented in an ordered pattern the structure is dominat. The crystal systems and lattice parameters of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 0.3, 0.5, and 1.0) are summarized in Table I. The pseudo-cubic lattice parameters of $Ba_2In_{1.9}Ce_{0.1}O_{5.05}$ and $Ba_2In_{1.8}Ce_{0.2}O_{5.10}$ with Brownmillerite structure were calculated by taking the cube root of the unit cell volumes multiplied by 1/8. There is a tendency that the lattice parameters increase with increasing Ce^{4+}-ion content. This is probably because the radius of Ce^{4+} ion is larger than that of In^{3+} ion.

3.2. Characteristics of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ in electrical conduction

The Arrhenius plots of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0$, 0.1, 0.2, 0.3, and 1.0) measured in N_2 are depicted in Fig. 3. A sample of $x = 0.5$ suitable for the measurements could not be prepared. $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0$ and 0.1) showed a rapid rise in conductivity at about 1200 K and 1027 K, respectively. The large increase is attributed to the order-disorder transition of the oxygen vacancies at high temperatures [1]. The temperature dependence of the conductivities of the parent compound was similar to those reported previously [6, 8, 10]. On the other hand, $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.2$, 0.3, and 1.0) exhibited no discontinuity in conductivity in the measured temperature range. These results indicate that the disordered phase of $Ba_2In_2O_5$ is stabilized to lower temperatures to about 770 K by doping Ce^{4+} ions with the content higher than $x = 0.2$. $Ba_2In_{1.8}Ce_{0.2}O_{5.10}$ showed higher electrical conductivities in a low temperature range than $Ba_2In_{1.9}Ce_{0.1}O_{5.05}$, while both compounds exhibited similar conductivities above the transition temperature for the compound of $x = 0.1$. With increasing doped Ce^{4+}-ion content the slopes of the Arrhenius plots became more gentle, and the conductivities rose in a low temperature range and lowered in a high temperature range. The conductivity of the parent compound above the transition temperature was higher than those of the Ce^{4+}-doped compounds. Fig. 4 shows the Arrhenius plots of the same compounds as in Fig. 3, which were measured in O_2. It is apparent from the comparison of the conductivities in Figs. 3 and 4 that the conductivities of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0$

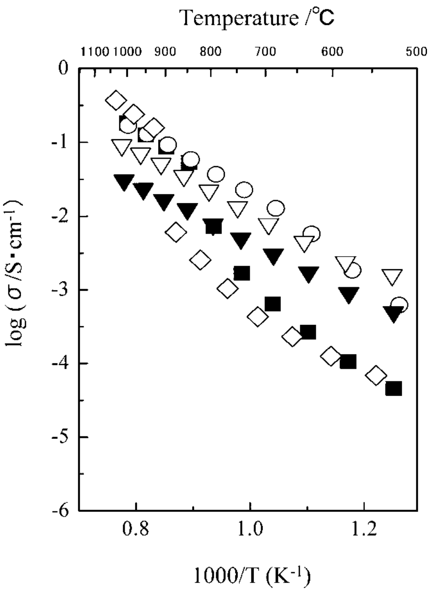

Figure 3 Total electrical conductivities of $Ba_2In_2O_5$ and $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 0.3 and 1.0) measured in N_2. ◇: $Ba_2In_2O_5$, ■: $Ba_2In_{1.9}Ce_{0.1}O_{5.05}$, ○: $Ba_2In_{1.8}Ce_{0.2}O_{5.10}$, ▽: $Ba_2In_{1.7}Ce_{0.3}O_{5.15}$, and ▲: $Ba_2InCeO_{5.5}$.

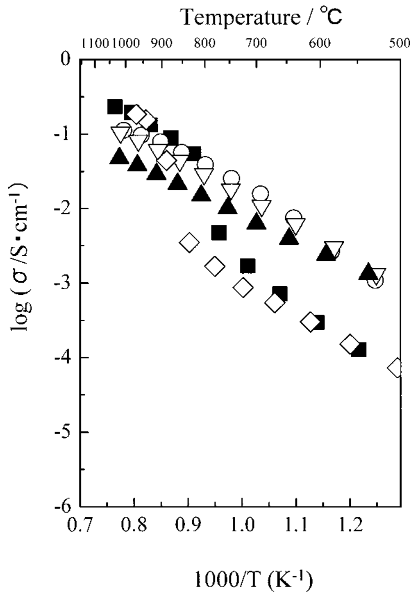

Figure 4 Total electrical conductivities of $Ba_2In_2O_5$ and $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 0.3, and 1.0) measured in O_2. ◇: $Ba_2In_2O_5$, ■: $Ba_2In_{1.9}Ce_{0.1}O_{5.05}$, ○: $Ba_2In_{1.8}Ce_{0.2}O_{5.10}$, ▽: $Ba_2In_{1.7}Ce_{0.3}O_{5.15}$, and ▲: $Ba_2InCeO_{5.5}$.

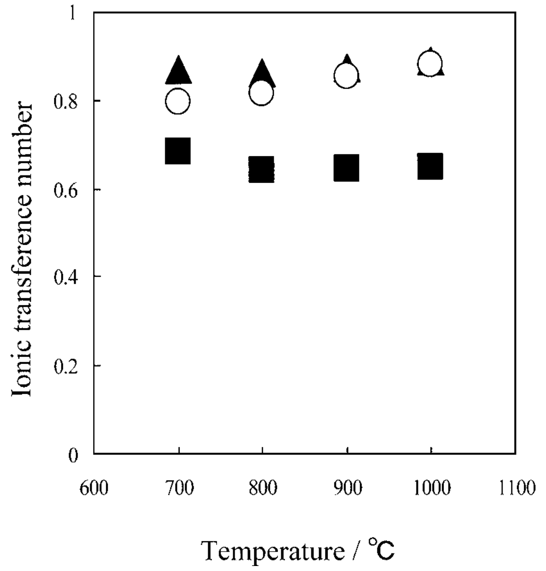

Figure 5 Ionic transference numbers of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, and 1.0) at oxygen partial pressure of 1 atm. ○: $x = 0.1$, ▲: $x = 0.2$, and ■: $x = 1.0$.

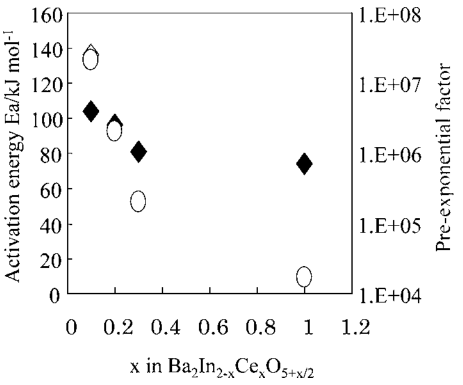

Figure 6 Activation energies and pre-exponential factors of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, 1, and 1.5) in N_2. ♦: activation energy (◇ before jump of $x = 0.1$) and ○: pre-exponential factor.

and 0.1) above the transition temperatures and those of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.2$ and 0.3) measured in N_2 show almost the same values as the corresponding ones measured in O_2. Almost the same values of conductivity both in N_2 and O_2 imply that the charge carrier is the oxide ion. On the other hand, $Ba_2InCeO_{5.5}$ exhibited lower conductivities in N_2 compared with those in O_2. This suggests that with increasing doped Ce^{4+}-ion content the *p*-type electronic conduction probably due to defect equilibrium between vacancy and oxygen in the compound occurs at the high oxygen partial pressure. For the confirmation of this conclusion the transference numbers of $Ba_2In_{2-x}Ce_xO_{5+x/2}$ ($x = 0.1$, 0.2, and 1.0) measured at the high oxygen partial pressure of 1 atm are plotted in Fig. 5. The samples of $x = 0.1$ and 0.2 and $x = 1.0$ showed the transference numbers higher than 0.8 and ca. 0.6–0.7, respectively. The three samples measured at the low oxygen partial pressure exhibited the transference numbers of approximately unity of oxide ion. The high transference number higher than 0.8 at the high oxygen partial pressure suggests that the conductivity is primarily ionic and the charge carrier is an oxide ion at temperatures higher than 970 K as far as the data in Fig. 5 are concerned and at temperatures higher than 770 K according to the data in Figs. 3 and 4. Samples of $x = 0.3$ and 0.5 suitable for the measurements could not be prepared. A change in activation energy in the compounds of $x = 0.3$ and 1.0 disappeared, while it is still slightly present in $x = 0.2$. The reason for the presence is not clear at the present state of investigation. Activation energies and pre-exponential factors for the electrical conduction of the samples estimated from the data in Fig. 3 are shown in Fig. 5. As for $x = 0.2$ the data above 970 K were employed. It is apparent that the increase of doped Ce^{4+}-ion content causes the decrease in both activation energy and pre-exponential factor. The decrease in pre-exponential factor is attributed probably to the reduction of the content of the mobile oxygen vacancy due to the doping of Ce^{4+} ions. The doping of Ce^{4+} ions resulted in the change of the original orthorhombic crystal system to the cubic one in which the oxygen vacancies were disordered, and as such the crystal symmetry increased. It is appropriate to consider that the disorder and the increase in crystal symmetry led to the decrease in activation energy.

4. Summary

1. Compounds prepared by doping 5 and 10 mol% of Ce^{4+} ions in parent compound $Ba_2In_2O_5$ retained the orthorhombic Brownmillerite structure as that of the parent. Doping more than 15 mol% of Ce^{4+} ions provided compounds with the cubic structure, in which oxygen vacancies were disordered and the number of the oxygen vacancies was reduced. With decreasing number of the oxygen vacancies, the remaining oxygen vacancies became disordered even at room temperature.

2. The electrical conductivity raised at lower temperatures with increasing content of the doped Ce^{4+} ions. As a result, the conductivity jump in the Arrhenius plots observed in the parent compound shifted toward the lower temperature region, accompanied by the decrease in jump height. Compounds in which Ce^{4+} ions of 10–50 mol% were doped showed no conductivity jump. The further doping of Ce^{4+} ions caused the decrease in conductivity in the higher temperature region, probably due to the decrease in number of oxygen vacancies, where oxide ions are mobile.

3. All the compounds yielded transference numbers close to unity under low oxygen partial pressures. Under high oxygen partial pressures, the compound with 5 mol% of Ce^{4+} ions being doped showed high transference numbers in the high temperature region after the occurrence of the conductivity jump, whereas the compound in which 50 mol% of Ce^{4+} ions were doped exhibited the low values of 0.6–0.7.

References

1. K. R. KENDALL, C. NAVAS, J. K. THOMAS and H.-C. LOYE, *Solid State Ionics* **82** (1995) 215 and references therein.
2. T. ISHIHARA, H. MATSUDA and Y. TAKITA, *J. Amer. Chem. Soc.* **116** (1994) 3801.

3. J. A. KILNER and R. J. BROOK, *Solid State Ionics* **6** (1982) 237.
4. R. L. COOK and A. F. SAMMELS, *ibid.* **45** (1991) 311.
5. A. F. SAMMELS, R. L. COOK, J. W. WHITE, J. J. OSBORNE and R. C. MACDUFF, *ibid.* **52** (1992) 111.
6. J. B. GOODNOUGH, J. E. RUIZ-DAIZ and Y. S. ZHEN, *ibid.* **44** (1990) 21.
7. G. B. ZHANG and D. M. SMYTH, *ibid.* **82** (1995) 161.
8. H. KURAMOCHI, T. MORI, H. YAMAMURA, H. KOBAYASHI and T. MITAMURA, *J. Ceram. Sos. Jpn.* **102** (1994) 1159.
9. H. YAMAMURA, Y. YAMADA, T. MORI and T. ATAKE, *Solid State Ionics* **108** (1998) 337.
10. T. YAO, Y. UCHIMOTO, K. KINUHATA, T. INAGAKI and H. YOSHIDA, *ibid.* **132** (2000) 189.
11. K. KAKINUMA, H. YAMAMURA, H. HANEDA and T. ATAKE, *ibid.* **140** (2001) 301.
12. R. D. SHANNON, *Acta Crystallogr.* A **32** (1976) 751.

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