Conducting Properties of SrCeO$_3$ System Doped with Various Rare Earth Metals

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Relationship between electrical conductivities and local structure was studied for SrCeO$_3$-based perovskite-type oxides doped with various rare earth metals, $M$ (M = Sc$^{3+}$, Yb$^{3+}$, Y$^{3+}$, Gd$^{3+}$, Sm$^{3+}$ and La$^{3+}$). The conducting behavior was considered to be protonic below 973 K. The local distortion around dopant ions in perovskite-type oxide was evaluated by examining relative area of the Raman band at around 345 cm$^{-1}$ which is connected with stretching vibrational modes of CeO$_6$ octahedra. The maximal band area was obtained for Yb-doped SrCeO$_3$. The electrical conductivity increased with increasing the relative area of this Raman band, and the maximal conductivity was observed for Yb$^{3+}$ doped SrCeO$_3$. [Received August 7, 2003; Accepted December 10, 2003]

Key-words: SrCeO$_3$-based oxide, High temperature protonic conductor, Ionic radius, Raman spectroscopy (RS), Local distortion, Proton, Oxide ions, Hole

1. Introduction

Perovskite-type oxides of SrCeO$_3$, BaCeO$_3$ and SrZrO$_3$ doped with various rare earth metals such as Yb$^{3+}$, Y$^{3+}$ and Sc$^{3+}$ are known as protonic conductive oxides under hydrogen-containing atmosphere at elevated temperatures.1-3) In these system, lattice defects such as oxygen vacancies, introduced due to as charge compensation for replacement of Ce$^{4+}$ site with trivalent metal ions, and interstitial protons, taken from water vapor or hydrogen in ambient gas, play an important role in electrical conduction. A typical example is SrCeO$_3$ replaced 5 mol% of Ce$^{4+}$ with Yb$^{3+}$, SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\alpha}$, where $\alpha$ is oxygen vacancy concentration. It is mentioned that its proton conductivity is the highest in SrCeO$_3$-based oxide, because the dopant cation, Yb$^{3+}$ (0.868 Å; 6CN)4] has closer ionic radius against the host cation, Ce$^{4+}$ (0.87 Å; 6CN).5] Recently, it was reported that CeO$_2$-based fluoride-type oxides also incorporate interstitial protons by dissolution of water vapor into oxygen vacancies, and the proton concentration is the highest in case of Yb$^{3+}$ doped CeO$_2$6]. Hence, combination of Ce$^{4+}$ and Yb$^{3+}$ may be suitable for proton dissolution. However, the highest proton conductivity is observed in the case of replacement of Ce$^{4+}$ partially with Sm$^{3+}$ in BaCeO$_3$-based perovskite-type oxide,7] and in SrZrO$_3$, it is effective to replace Zr$^{4+}$ (0.72 Å; 6CN)8] with Yb$^{3+}$,9] It has not been clear how the dopant ionic radius relates to the proton conductivity.

In the present work, local distortions around dopant ions induced by various trivalent dopant ions was studied for SrCeO$_3$-based oxide and dependencies of the local distortion and electrical conductivity on the dopant ionic radius was discussed.

2. Experimental

The specimens SrCe$_{0.95}$M$_{0.05}$O$_{3-\alpha}$ were prepared by normal solid state reaction. Powders of SrCeO$_3$ (>99.9% purity), CeO$_2$ (>99.9% purity) and M$_2$O$_3$ (M = Sc$^{3+}$, Yb$^{3+}$, Y$^{3+}$, Gd$^{3+}$, Sm$^{3+}$ and La$^{3+}$, >99.9% purity) were mixed, pressed into pellets and fired. Each of them had a relative density over 94%. An XRD analysis (RIGAKU, RINT-2200) was used for phase characterization of specimens. Raman spectroscopy (Jobin-Yvon, T64000) was employed to obtain short-range order structural information. Raman spectra were excited by using a 514.5 nm line (50 mW) of an argon ion laser (Showa Optronics, GLSG2165).

Conductivity of each specimen was measured by DC four probe method in wet Ar atmosphere from 873 to 1273 K. The wet gas was prepared by moistening Ar (>99.999% purity) at 20°C using a water vapor saturator. For SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\alpha}$, D$_2$O (>99% purity) was also used for moistening. The water vapor pressure was monitored by a chilled mirror hygrometer (General Eastern, M4–DP/D2–SR).

3. Results and discussion

3.1 XRD analysis and Raman spectroscopy

In each of specimens, a single phase of solid solution SrCe$_{0.95}$M$_{0.05}$O$_{3-\alpha}$ with orthorhombic symmetry was obtained according to the XRD analysis. In case of doping with La$^{3+}$ (1.032 Å; 6CN),4] well-sintered pellet could not be obtained. Hence, it was impossible to measure electrical-sintered SrCe$_{0.95}$La$_{0.05}$O$_{3-\alpha}$.

Figure 1 indicates Raman spectra of as-sintered SrCe$_{0.95}$M$_{0.05}$O$_{3-\alpha}$ specimens. They were normalized by the main band intensity at 345 cm$^{-1}$. Similar spectra were previously reported by Kosacki et al.6] for SrCe$_1$Yb$_{0.05}$O$_{3-\alpha}$ (0 ≤ x ≤ 0.20) system. The bands around 315, 345, and 375 cm$^{-1}$ were attributed to the stretching vibrational modes of CeO$_6$ octahedra, while the bands bellow 275 cm$^{-1}$ were connected with the lattice vibration involving strontium ions.1] In addition, doped SrCeO$_3$ had the defect-induced Raman bands, which indicate existence of oxygen vacancies2] created by substitution of trivalent metals (denoted by arrows in Fig. 1). For SrCe$_{0.95}$Yb$_{0.05}$O$_{3-\alpha}$, they were observed at 520 and 630 cm$^{-1}$.

The relative band area at 345 cm$^{-1}$ of SrCe$_{0.95}$M$_{0.05}$O$_{3-\alpha}$ was...
plotted as a function of dopant ionic radius in Fig. 2. Here, the relative band area was defined as peak area of the band, after the spectrum is normalized by the main band as shown in Fig. 1. This value increased with 5 mol% doping from the value of 13.8 for undoped SrCeO$_3$ to above 15. With increasing dopant concentration, this relative band area lineally increases for SrCe$_{1-x}$Yb$_x$O$_{1-x/2}$ in addition, there was a clear relationship between this value and the dopant ionic radius. It increased with increasing ionic radius when $r < 0.868$ Å, while it decreased when $r > 0.868$ Å. For the sample doped with Yb$^{3+}$, that has closer ionic radius against host cation, the maximal value was obtained. The broadening of the band at 345 cm$^{-1}$ was probably induced by local distortion around dopant ions. From Fig. 2, it is found that the local distortion around dopant ions is the most remarkable for the specimen doped with Yb$^{3+}$, though a difference in ionic radii between the dopant and host ions was minimal.

3.2 Electrical conductivity

Figures 3(a) and (b) indicate electrical conductivity of specimens in wet Ar as a function of reciprocal temperature and dopant ionic radius, respectively. It should be noted that this is the total (proton, oxide ion and p-type electron) conductivity. The slopes of their Arrhenius plots of conductivities exhibited curvature at around 1173 K in all specimens. This indicated that conductivities of p-type electrons and oxygen ions became remarkable at elevated temperatures. From conductivity measurement for SrCe$_{0.05}$Yb$_{0.05}$O$_{1.52}$ under D$_2$O-Ar as shown in Fig. 4, a distinct isotope effect was observed below 973 K, and the conducting behavior was considered to be protonic in this temperature range. Fukatsu evaluated the temperature dependence of conductivities of SrCe$_{0.95}$Yb$_{0.05}$O$_{1.52}$ in wet (H$_2$O/D$_2$O) air. In his study, isotope effect of conductivities could be observed in the low temperature region (573-1073 K). While each contribution of charge carriers, protons, oxygen ions, electrons and holes, is dependent on $P$(O$_2$) and $P$(H$_2$O) as well as temperature, the predominant charge carrier might be proton especially below 1073 K.

Over the whole temperature range, SrCe$_{0.95}$Yb$_{0.05}$O$_{1.52}$ exhibited the maximum conductivity [Fig. 3(a)]. In addition, conductivity decreased either with increasing or decreasing ionic radius from $r = 0.868$ Å [Fig. 3(b)]. Comparing Fig. 3 (b) with Fig. 2, it is evident that the dependency of electrical conductivity on dopant ionic radius was quite similar to that of the relative band area at 345 cm$^{-1}$. Hence, it is concluded that the dependency of proton conductivity on the dopant ionic radius is closely connected with the local structure evaluated by Raman spectroscopy. It was probably due to enhancement of proton concentration and/or mobility resulted from a local distortion around dopant ions.

4. Conclusion

The relation between the local distortions in SrCeO$_3$-based oxide doped with various rare earth metals and the proton conductivity was investigated. As shown in Fig. 2, Raman...
s spectroscopy suggested that the local distortion around dopant ions in perovskite tended to increase with increasing ionic radius when \( r < 0.868 \, \text{Å} \), or decreasing it when \( r > 0.868 \, \text{Å} \), and was the most remarkable for the specimen doped with \( \text{Yb}^{3+} \). Over the whole temperature range tested, \( \text{SrCe}_{0.95} \text{Yb}_{0.05}\text{O}_{2-x} \) exhibited the maximum conductivity and conductivity decreased gradually with deviating dopant ionic radius from that of \( \text{Yb}^{3+} \). Hence, the proton conductivity is closely connected with the local distortions around dopant ions.

Acknowledgment  This work has been supported by CREST of JST (Japan Science and Technology Corporation).

References