Mixed Electronic-Oxide Ionic Conductivity and Oxygen Permeating Property in Ni Doped $LaGaO_3$ Perovskite Oxide

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It was found that $LaGaO_3$ perovskite oxide doped with Ni for Ga site exhibits a high mixed electronic-oxide ionic conduction. Oxygen permeation rate was increased with increasing Ni content and it attained to a maximum value of 2.15 $cm^3/min\ cm^2$ at 1273 K when 25 mol% Ni was doped.

Mixed electronic-ionic conductor is a conductor in which both electron and ion carry an electric charge. Mixed electronic-ionic conductor has various application fields such as an oxygen separating membrane, electrode, and gas sensor. In particular, a stable mixed electronic-oxide ionic conductor against reduction and oxidation is strongly demanded for the oxygen separating film in CH_4 partial oxidation process ($CH_4+1/2O_2= CO+2H_2$).[1] Perovskite oxides of Co or Fe based oxide have been mainly investigated as the mixed electronic-oxide ionic conductor.[1,2] However, it is reported that these oxides are easily reduced in a reducing atmosphere resulting in the formation of crack.[3] Recently, we found that $LaGaO_3$ based perovskite oxide doped with Sr and Mg exhibits high oxide ion conductivity.[4] In addition, it was found that doping small amount of a transition metal cation to Ga site is effective for increasing the oxide ion conductivity.[5] However, hole conduction appeared and $LaGaO_3$ based oxide became a mixed electronic-oxide ionic conductor. Among the examined cations, Ni was the most effective for increasing the oxide ion conductivity in $LaGaO_3$ based oxide.[5] In the present study, the mixed electronic-oxide ionic conduction in Ni doped $La_{0.8}Sr_{0.2}GaO_3$ (denoted as LSGN in this paper) was investigated.

All the specimens were prepared by the conventional powder mixing method. Commercial oxides of La_2O_3 (Kishida, 99.99%), $SrCO_3$(Wako, 99.9%), MgO(Wako,99.9%), NiO(Rare metal, 99.9%) and Ga_2O_3(Kishida, 99.99%) at stoichiometric ratios were mixed in Al_2O_3 pestle and mortar. The mixture was precalcined at 1273 K for 6h in air and after isostatic pressing at 275 MPa the disk was sintered at 1773 K for 6 h in air. Conductivity was measured with the conventional dc four probe method in flowing N_2. The oxygen permeation rate was measured by using air-N_2 gas concentration cell. The disk shaped specimens (17 mm in diameter, 0.5 mm in thickness) were sealed to a mullite tube with a molten Pyrex glass. Perovskite oxide of $La_{0.6}Sr_{0.4}CoO_3$ was applied for both faces of the specimens (ϕ 10mm) to improve the surface activity to the oxygen dissociation and association. Oxygen permeating from air to N_2 flow was analyzed by TCD gas chromatography.

Figure1 shows the XRD patterns of Ni doped $LaGaO_3$ based oxide. It is clear that the diffraction pattern mainly consisted of the pattern of $LaGaO_3$. Therefore, main phase in all specimens was assigned to $LaGaO_3$ perovskite phase. However, diffraction peaks shifted to a higher diffraction angle with increasing Ni content since the ionic size of six coordinated Ni^{3+} was smaller than that of Ga^{3+}. On the other hand, the diffraction peak from a secondary phase of SrO was observed next to the main peak. This diffraction peak became significant with increasing Ni content and another diffraction peak from an secondary phase which may be assigned to $LaSrGaO_4$, was observed in XRD pattern of LSGN at X=0.4. However, formation of an impurity phase containing Ni or NiO

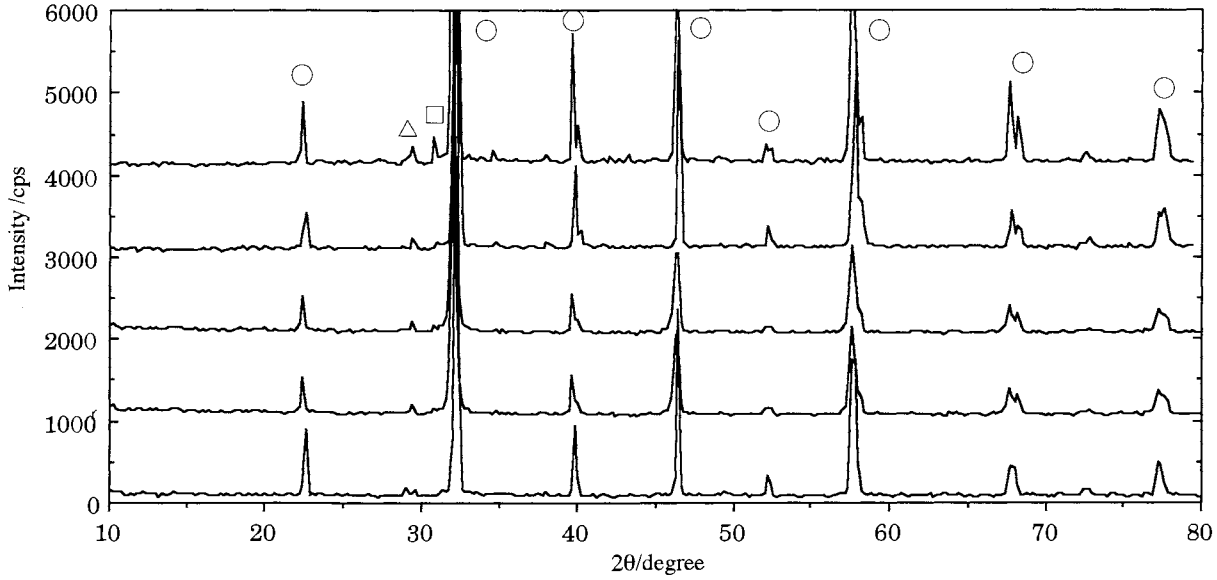

Figure 1. XRD pattern of $La_{0.8}Sr_{0.2}Ga_{1-X}Ni_XO_3$. (○)$LaGaO_3$ (△)SrO (□)$LaSrGaO_4$.

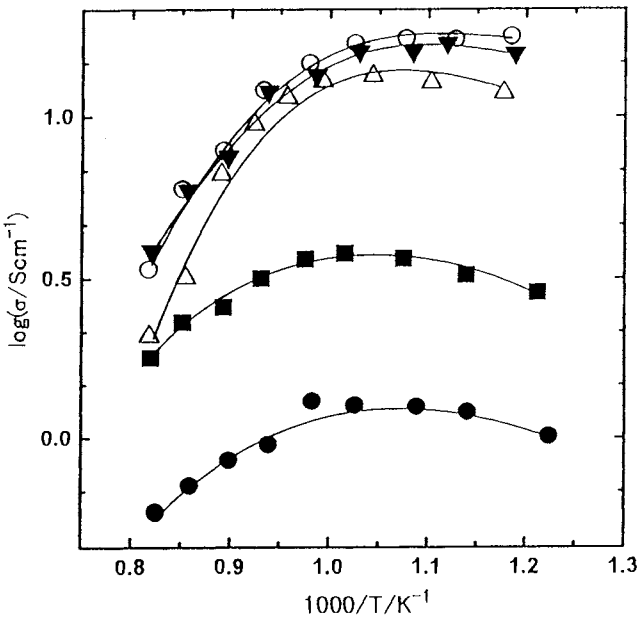

Figure 2. Arrhenius plots of conductivity of $La_{0.8}Sr_{0.2}Ga_{1-X}Ni_XO_3$ (●) X=0.2, (■) X=0.25, (△) X=0.3, (○) X=0.4, (▼) X=0.5.

was not recognized. Therefore, it seems that Ni^{3+} was substituted for Ga^{3+} in $LaGaO_3$ lattice.

Figure 2 shows the Arrhenius plots of the electrical conductivity of Ni doped $LaGaO_3$ in N_2 atmosphere (Po_2= 10^{-5}atm). It is clear that electrical conductivity increased with increasing temperature at low temperature and it became a metallic like temperature dependence at high temperature. Since no significant change in XRD pattern was observed at elevating temperature, change in temperature dependence of conductivity may result from a decrease in mobility by increasing the electron density. This also suggests that the electronic conduction is dominant in LSGN. The electrical conductivity increased with increasing Ni amount and it attained to a maximum value at X=0.4 in $La_{0.8}Sr_{0.2}Ga_{1-X}Ni_XO_3$. Since the electrical conductivity monotonously decreased with decreasing oxygen partial pressure in the range from P_{O2}=1 to 10^{-21} atm, electronic hole seems to be a main charge carrier in LSGN. For example, conductivity of $La_{0.8}Sr_{0.2}Ga_{0.75}Ni_{0.25}O_3$ were $\log(\sigma/Scm^{-1})$ = 0.5 and −1.0 at P_{O2}=1 and 10^{-21} atm respectively. The total electrical conductivity in Ni doped $La_{0.8}Sr_{0.2}GaO_3$ was lower than those in the conventional mixed electronic-oxide ionic conductors such as Co or Fe based perovskite oxide by an order of magnitude. However, Ni doped $La_{0.8}Sr_{0.2}GaO_3$ exhibited the electromotive forces (emf) which was ranged from 40 % to 60% against the Nernst emf in H_2-O_2 gas concentration cell. Therefore, transport number of oxide ion in Ni doped $LaGaO_3$ based oxide seems to be much higher than that in the conventional mixed electronic-oxide ionic conductor.

Oxygen permeating property was further studied to confirm the superior mixed electronic-oxide ionic conduction in LSGN. Figure 3 shows the oxygen permeation rate from air to N_2 in LSGN as a function of Ni content. At all temperatures, oxygen permeation rate increased with increasing Ni content. Although the highest conductivity was attained at X=0.4, the maximum oxygen permeation rate was attained at X=0.25. This

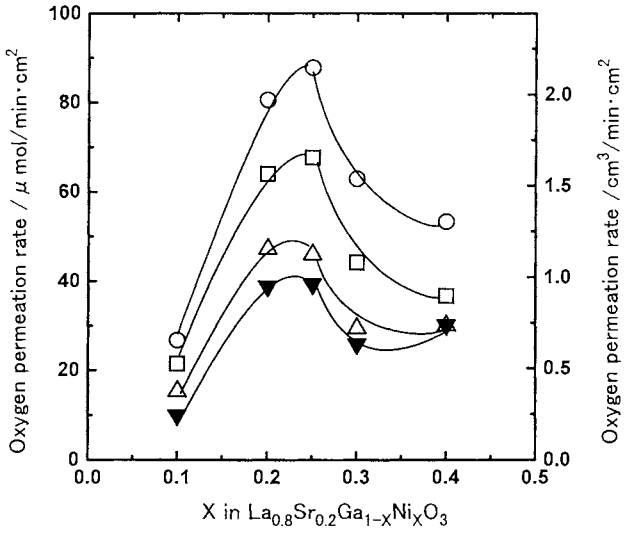

Figure 3. Oxygen permeation rate as a function of X value in $La_{0.8}Sr_{0.2}Ga_{1-X}Ni_XO_3$ (▼) 973 K, (△) 1073 K, (□) 1173 K, (○) 1273 K .

difference may be attributed to the decreasing transport number with increasing Ni content. Oxygen permeation rate was attained to values of 2.2 and 1.0 cm^3/min cm^2 at 1273 and 1073 K respectively on the specimen at X=0.25. Since the oxygen permeation rate of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$, which is considered as a one of the promising mixed ion conductor for oxygen separation[3], was 1.5 and 0.3 cm^3/min cm^2 at 1273 and 1073 K, respectively under the same condition, it can be concluded that perovskite oxide of $La_{0.8}Sr_{0.2}Ga_{0.75}Ni_{0.25}O_3$ exhibits the large oxygen permeation. Consequently, this study reveals that $LaGaO_3$ based perovskite oxide doped with Ni is a promising mixed electronic-oxide ionic conductor which may be applied for the oxygen separating membrane in CH_4 partial oxidation process. This is because a stable conductivity was exhibited and no change in XRD pattern was observed in H_2 atmosphere. Further detail study on the stability of LSGN against reduction is under way.

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