

Water vapor absorption and proton conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$

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Received: 4 August 2004 / Accepted: 13 July 2005 / Published online: 21 September 2006
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Abstract The proton conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system has been investigated as a function of the La content, temperature and amount of absorbed water. The proton conductivity increased with La content up to $x = 0.10$, to reach a maximum of 1.12×10^{-5} (S/cm) at 400 °C. From that point on, it decreased. From the results of thermogravimetry and mass spectra, we confirmed that the water was absorbed in the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system, in a maximum quantity of 0.14 mol/mol (sample). The proton conductivity increased monotonically with the quantity of water uptake, suggesting that this variable is one of the dominant parameter of proton conductivity in this system.

Introduction

The $\text{Ba}_2\text{In}_2\text{O}_5$ system, one of those with a Brownmillerite structure, was discovered by Goodenough in 1990 [1]. The system has ordered oxygen vacancies with a low oxide-ion conductivity at low temperatures [1, 2]; however, above 930 °C, the oxygen vacancies

transform into a disordered state and a higher oxide-ion conductivity, which exceeds that of yttria-stabilized zirconia, appears. Although investigators have doped several elements into the In-site in order to increase the low-temperature oxide-ion conductivity, it did not surpass that of yttria-stabilized zirconia [3–5]. In previous papers, we reported that the oxide-ion conductivity of the $\text{Ba}_2\text{In}_2\text{O}_5$ system, in which La^{3+} and Sr^{2+} were co-doped, was higher than that of yttria-stabilized zirconia [6–8]. Another author also discussed an increase in oxide-ion conductivity due to a doping with La^{3+} [9]. Furthermore, we have suggested that the dominant factors relevant to oxide-ion conductivity in this system are the unit cell free volume, oxygen content and crystal symmetry [10, 11]. Both TEM and EXAFS studies have confirmed that the oxygen vacancies arrangement of the La-doped system was in a disordered state [12–14].

On the other hand, proton conductivity in the $\text{Ba}_2\text{In}_2\text{O}_5$ system has been confirmed by ac-impedance and EMF methods [15]. The proton transference number was reported to be 0.45 at 650 °C at a low oxygen partial pressure. A high proton conductivity was found also in Sn-doped $\text{Ba}_2\text{In}_2\text{O}_5$ [16]. The water content of the $\text{Ba}_2\text{In}_2\text{O}_5$ was dependent on the temperature and humidity [17]. On the basis of a Rietveld analysis of X-ray diffraction data, it has been speculated that absorbed water in $\text{Ba}_2\text{In}_2\text{O}_5$ was located in the oxygen vacancies [18]. This suggestion was supported by a computer simulation technique [19].

In this paper, we present our measurements of the proton conductivity and thermogravimetry of the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system, whose mother substrate was $\text{Ba}_2\text{In}_2\text{O}_5$, as a function of La content, temperature and water vapor pressure. Our analysis of these data

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includes a discussion of proton conductivity as a key parameter in this system.

Experimental

The starting materials, BaCO₃ (99.9%, Wako Chemical Co.), La₂O₃ (99.9%, Kojundo Chemical Co.) and In₂O₃ (99.95%, Kojundo Chemical Co.) were mixed with a ball mill for 24 h with ethanol as a medium. The mixture was dried at 100 °C for several hours, and then calcined at 1000 °C for 10 h. The powder, which was sieved to under 54 μm, was pressed at 49 MPa into a rectangular shape (30 mm × 5 mm × 5 mm) and pellet (10 mm^φ × 2 mm^t). Then, these samples were isostatically pressed again at 196 MPa and sintered at 1400 °C for 10 h in air.

From their dimensions and weight, we estimated the relative density of all the sintered specimens to be higher than 90%. The single phase nature of the samples was confirmed by X-ray diffractometry using CuK_α radiation at room temperature. The electrical conductivity was measured by the four probe method from 600 °C to 900 °C and by the AC impedance method from 350 °C to 600 °C.

Platinum electrodes were connected to the samples by sintering at 950 °C for 1 h in air. The water vapor pressure was controlled by a humidified apparatus and was measured by a humidity sensor (General Eastern Co. Model D-2). The water partial pressure of the humid and dry Ar atmosphere was found to be $\log[P_{\text{H}_2\text{O}}(\text{Pa})] = 3.69$ and 1.16. Thermogravimetry (TG) was measured by a RIGAKU TG/DTA-8140 equipped with an atmosphere controller. These samples for the TG were annealed at 1400 °C in conditioned air ($\log[P_{\text{H}_2\text{O}}(\text{Pa})] = 3.20$) and cooled to room temperature at the rate of 10 °C/min. in the same atmosphere. The TG measurement was conducted from room temperature to 800 °C at a heating rate of 10 °C/min. in a dry He atmosphere ($\log[P_{\text{H}_2\text{O}}(\text{Pa})] = 1.10$), which flowed through at a rate of 200 ml/min. At the same time, mass spectra of the atmosphere were measured by a quadrupole mass spectrometer (ANELVA M-2000A) to confirm the identity of the substances vaporized from the samples. Dry He gas was used as a carrier gas.

Results and discussion

In Fig. 1, we show the electrical conductivity of (Ba_{1-x}La_x)₂In₂O_{5+x} ($x = 0.10, 0.20$ and 0.30) at 400 °C and 800 °C as a function of oxygen partial pressure. Each

of these results was measured with the sample in a dried condition. We have reported the conductivity of $x = 0.20$ and 0.30 at 800 °C in a previous paper [20]. At each temperature, in the region of $\log[P_{\text{O}_2}(\text{Pa})] \geq 3.0$, the electrical conductivity of this system was due to a hole and an oxide ion. The hole conductivity rose with the increase in oxygen partial pressure. In the Ba₂In₂O₅, a similar oxygen partial pressure dependency had been reported elsewhere [15]. Here, we have also measured the electrical conductivity in an Ar atmosphere ($\log[P_{\text{O}_2}(\text{Pa})] = 1.5$) to estimate the proton conductivity of this system in a low oxygen partial pressure region, because the proton transference number in such a region would be larger than that in a high oxygen partial pressure region.

Figure 2 contains the Cole-Cole plots of the impedance spectra for (Ba_{0.90}La_{0.10})₂In₂O_{5.10} at 400 °C. We carried out the conductance measurement in both dry Ar ($\log[P_{\text{H}_2\text{O}}(\text{Pa})] = 1.15$) and humid Ar ($\log[P_{\text{H}_2\text{O}}(\text{Pa})] = 3.68$) atmospheres. The bulk resistivity in the humid Ar atmosphere was lower than that in the dry Ar one. The reduction of resistivity by the increasing water partial pressure suggested the appearance of proton conductivity in this system.

Measurements of the total electrical conductivity for (Ba_{1-x}La_x)₂In₂O_{5+x} in the Ar humid or dry Ar atmosphere are shown as an Arrhenius plots in Fig. 3(a–c). Each set of electrical conductivities measured in an Ar atmosphere were reproducible. The discontinuous jump, appearing for values of $x \leq 0.10$, corresponds to an order-disorder transition in the oxygen vacancies

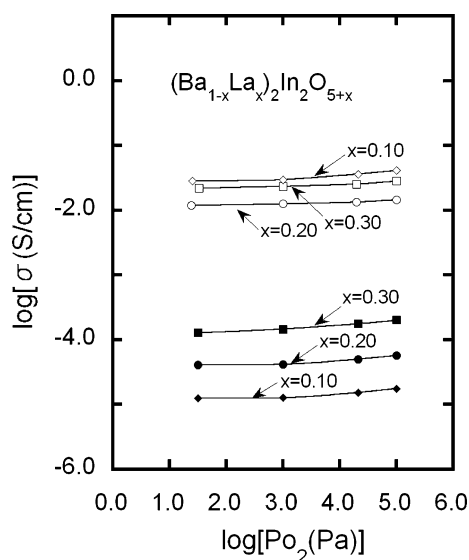


Fig. 1 Electrical conductivity of (Ba_{1-x}La_x)₂In₂O_{5+x} as a function of oxygen partial pressure at 400 °C and 800 °C. Solid symbols denote results at 400 °C; Open symbols represent results at 800 °C

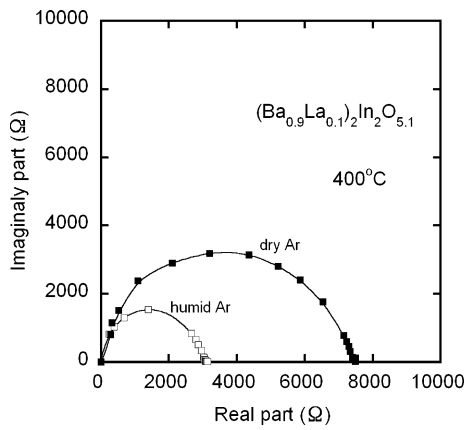
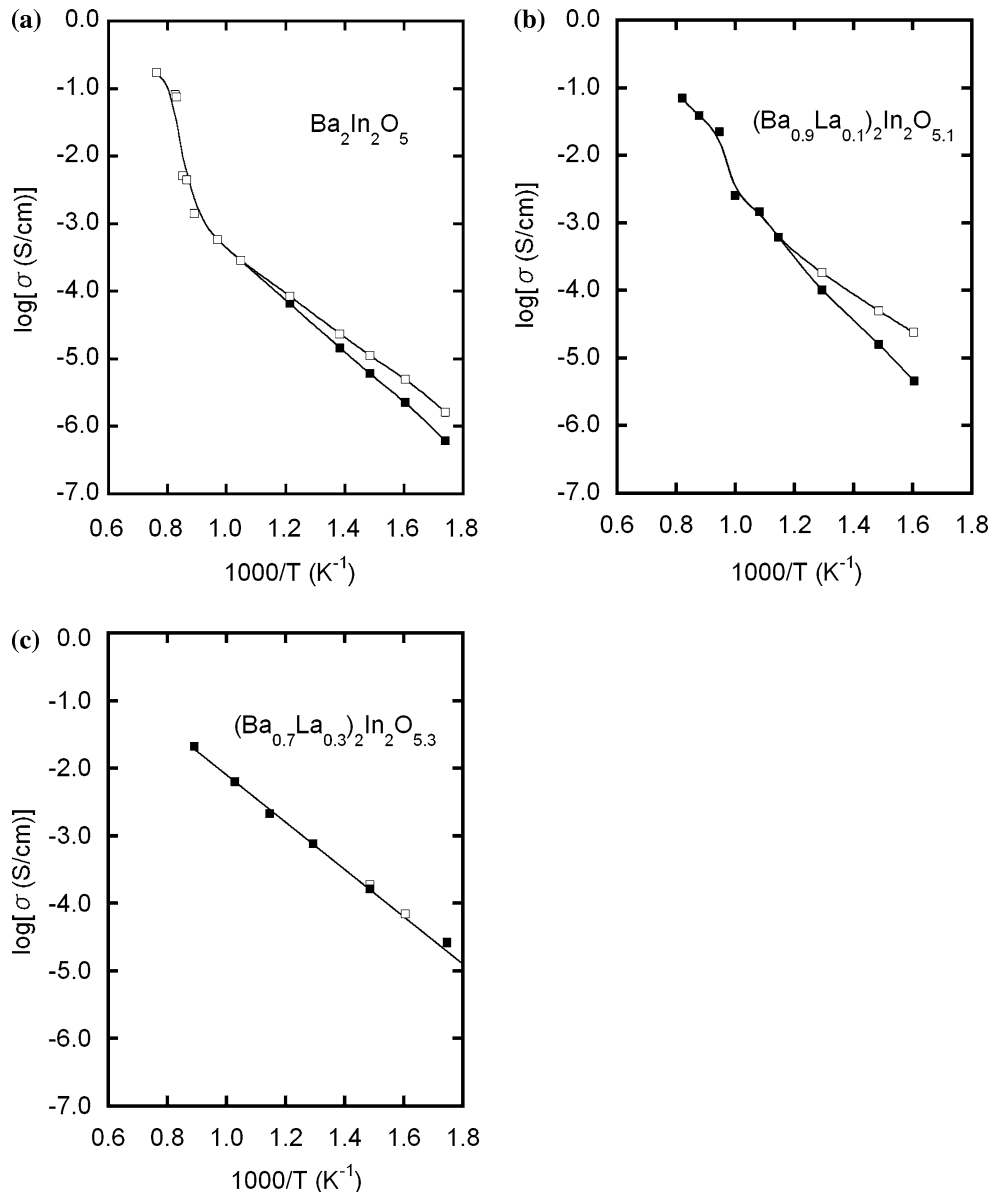


Fig. 2 Cole–Cole plots of electrical conductivity of $(\text{Ba}_{0.9}\text{La}_{0.1})_2\text{In}_2\text{O}_{5.1}$ at 400°C

arrangement [1, 6, 7]. In systems with the same La content, the total electrical conductivities in different water partial pressures were equal to each other above 600°C . These results suggested that the proton conductivity would not appear above this high temperature. Under 600°C , the electrical conductivity of samples in a humid Ar atmosphere was higher than those in a dry Ar in the compositional region where $x < 0.30$.

As illustrated in Fig. 4, the activation energy of the system in the humid Ar atmosphere was of the same magnitude as that of other proton conductors [21, 22]. The proton conductivity (σ_{H}) at 400°C was estimated by formula 1 [15],

Fig. 3 Arrhenius plots of electrical conductivity for $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$:
(a) $\text{Ba}_{2.0}\text{In}_{2.0}\text{O}_{5.0}$,
(b) $(\text{Ba}_{0.9}\text{La}_{0.1})_2\text{In}_2\text{O}_{5.1}$,
(c) $(\text{Ba}_{0.7}\text{La}_{0.3})_2\text{In}_2\text{O}_{5.3}$ Solid symbols are results in a dry Ar atmosphere; open symbols are results in a humid Ar atmosphere



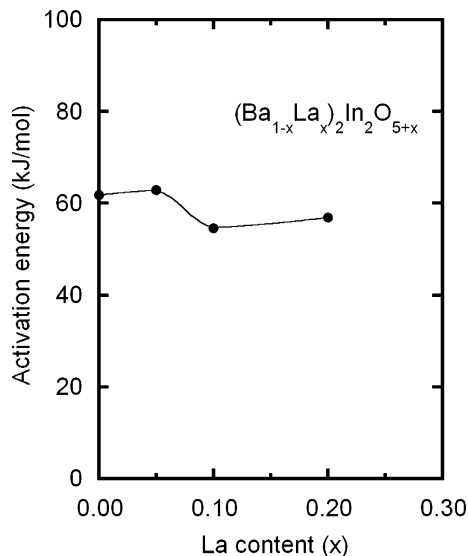


Fig. 4 Activation energy of proton conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system as a function of La content

$$\sigma_H = \sigma_{\text{humid}} - \sigma_{\text{dry}} \quad (1)$$

where σ_{humid} and σ_{dry} represent the electrical conductivity in humid and dry Ar atmosphere. The compositional dependency of the proton conductivity appears in Fig. 5. The σ_H increased with La content and reached a maximum value at $x = 0.10$. Then, around $x = 0.30$, the σ_H decreased to zero. In principle, the proton conductivity depends on the magnitude of the proton mobility and the number of mobile protons. A mobile proton would bind to the oxide ion and behave as a hydroxyl ion [18, 24]. In the perovskite-related oxides, other researchers propose that the tilting of oxygen octahedra would affect proton migration, and, as that tilt angle increased, the heightened mobility of the proton would elevate the proton conductivity [23]. In the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system ($x = 0.0$ and 0.10), the crystal symmetry remains orthorhombic. Nevertheless, the proton conductivity increased with La content in the compositional region from $x = 0.0$ to 0.10 . Evidently, the dependency of the proton conductivity on composition is related to the amount of water uptake.

In general, gaseous water is absorbed in the perovskite oxides and is the source of the proton conducting carrier. In order to estimate the quantity of absorbed water in the system, we performed thermogravimetry analysis of the samples in a dried Ar atmosphere, and show the results in Fig. 6(a). At first, the weight increased with the increasing temperature, but from 250°C to 400°C , it fell. We characterized the He carrier gas, in situ by mass spectroscopy, and present the mass spectra, as a function of temperature, in

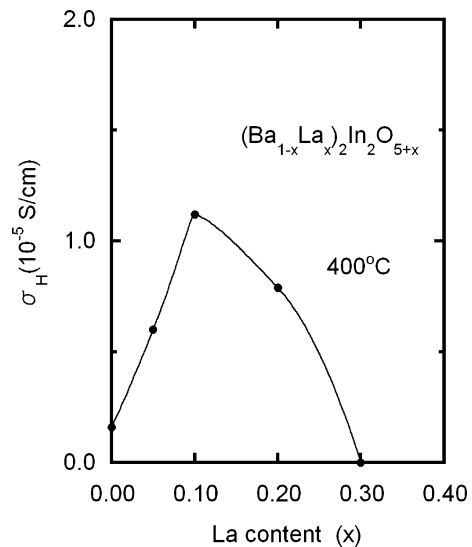


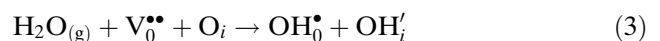
Fig. 5 Proton conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system at 400°C as a function of La content

Fig. 6(b). Only signals at $m/z = 18$ and 17 were detected that corresponded to the thermogravimetry changes. From the ratio of the peak height and the mass number, we conclude that the spectra at $m/z = 18$ and 17 correspond to the water and its fragment peak, respectively. A similar result has been reported for $\text{Ba}_2\text{In}_2\text{O}_5$ [24]. Evidently, the decrease of weight, as shown in Fig. 6(a), results from the emission of absorbed water from the system. Other researchers report that the crystal phase of $\text{Ba}_2\text{In}_2\text{O}_5$ changes from a water rich phase (β phase) to a water poor one (α phase) at a given temperature [17]. A phase transition in the crystal symmetry might also occur in the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system, and might be one of the reasons for the decrease in water uptake.

Zhang et al. proposed that the proton generation mechanism responsible for the electrical conductivity in $\text{Ba}_2\text{In}_2\text{O}_5$ is as follows [15]:



Another author suggested that the same reaction as that of formula (2) might have absorbed the water in the $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ system [22]. Fisher et al. also proposed that the $\text{Ba}_2\text{In}_2\text{O}_5$ system has a high oxygen content and a Frenkel defects, and that the mobile proton of $\text{Ba}_2\text{In}_2\text{O}_5$ also might be generated by the following;



which incorporates the interstitial site of the oxide ion [19]. In both cases, speculation exists that the quantity

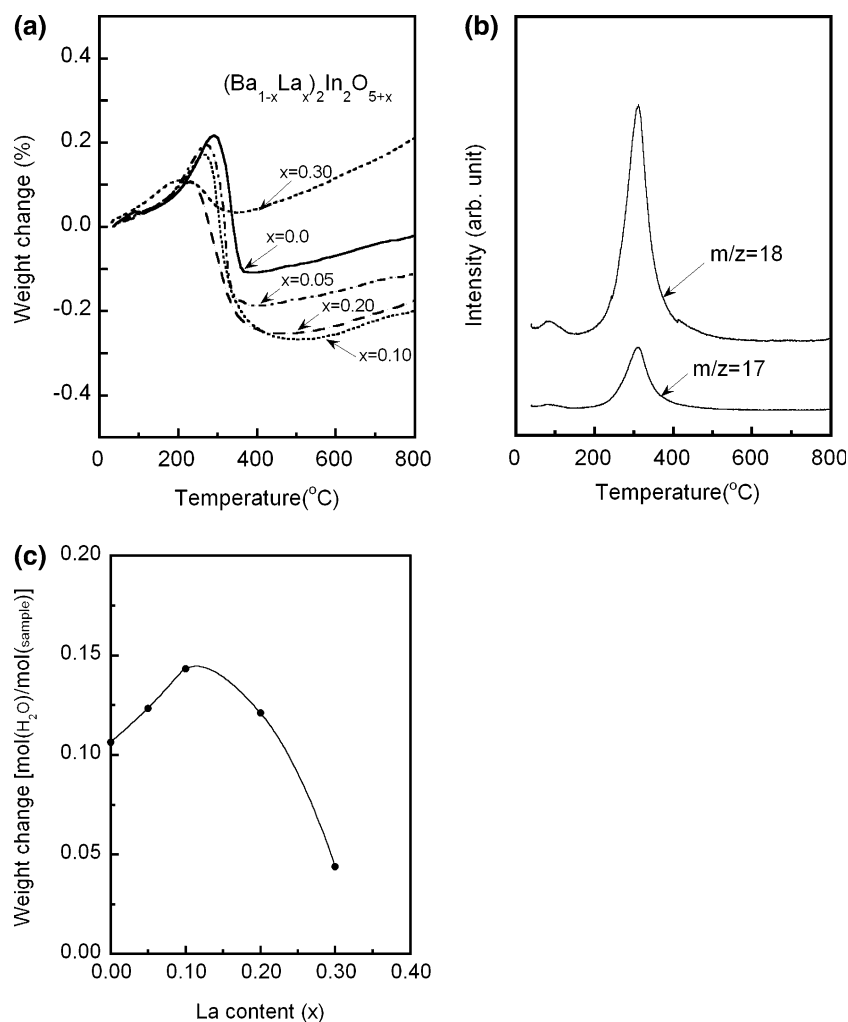


Fig. 6 (a) Thermogravimetric results of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system as a function of temperature. (b) Mass spectra of $m/z = 17$ and 18. (c) Quantity of water uptake as a function of La content

of mobile protons would increase monotonically with water vapor pressure and the number of oxygen vacancies. In Fig. 6(c), we show the weight change of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ between 200 °C and 400 °C as a function of the La content. In the measurement of proton conductivity, we kept the water vapor pressure constant, and controlled the number of oxygen vacancies by doping with La^{3+} . The amount of absorbed water rose with increasing La content and reached a maximum value at $x = 0.10$. The maximum water solubility of $(\text{Ba}_{0.9}\text{La}_{0.1})_2\text{In}_2\text{O}_{5.1}$ was 0.14 mol/(mol system), a value equal to 0.07 mol/(mol system) in a primitive lattice with a perovskite structure. The water uptake in $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$, which is one of the better proton conductors, is reported to be up to 0.036 mol/(mol system) at 500 °C [22]. One of the reasons why $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ includes a larger amount of absorbed water than $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ might be the difference in the number of oxygen. In the

compositional region between $x = 0.10$ and 0.30, the amount of absorbed water decreased against the La content, as shown in Fig. 6(c). This result might also be related to the decreased numbers of oxygen vacancies in this system.

Furthermore, other investigators have reported that the A-site cation or the vacancies in the ABO_3 would also affect the water solubility [25, 26]. With La^{3+} doping in the A-site the unit cell free volume increased in this system [7, 8]. This property might be cause a preferential absorption of the water vapor, and thus, the increased water uptake in the region between $x = 0.0$ and 0.10.

In order to elucidate the relationship between proton conductivity and the quantity of water uptake, we plotted σ_{H} against the amount of water uptake per one mol of sample ($=\Delta W$) in Fig. 7. The σ_{H} increased linearly with ΔW , a result very similar to those reported for $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ [27], $\text{BaTb}_{0.6}\text{In}_{0.4}\text{O}_{2.8}$

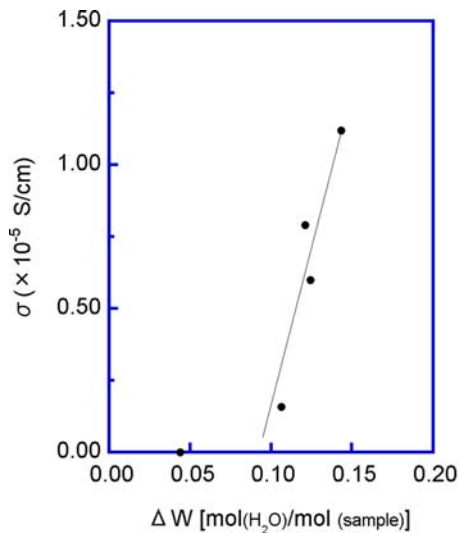


Fig. 7 Proton conductivity of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system at 400 °C as a function of amount of water uptake

[28] and $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$ [22]. It appears that one of the dominant parameters for proton conductivity is the amount of absorbed water, and the decrease in σ_{H} is related to the degree of water solubility in the system.

Conclusion

The proton conductivity and water uptake of $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system has been investigated as a function of the La content, temperature and amount of absorbed water. The proton conductivity increased with La content and reached a maximum value of 1.12×10^{-5} (S/cm) at $x = 0.10$. After that point, the conductivity fell against the La content and vanished at $x = 0.30$. Our thermogravimetric results indicated that the quantity of water taken up affected the proton conductivity in a manner similar to the La content. One of the dominant parameters determining the proton conductivity appears to be the quantity of water uptake in the $(\text{Ba}_{1-x}\text{La}_x)_2\text{In}_2\text{O}_{5+x}$ system.

Acknowledgement This study was supported by the High Technology Research Project at KANAGAWA University

from the Ministry of Education, Science, Sports and Culture and by a Grant-in-Aid for Scientific Research from the same Ministry.

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