

Title	Ba <sub>2</sub> In <sub>2</sub> O <sub>5</sub> 基化合物の電氣的、熱的性質
Author(s)	謝, 国俊
Citation	
Issue Date	2005-09
Type	Thesis or Dissertation
Text version	none
URL	<a href="http://hdl.handle.net/10119/2194">http://hdl.handle.net/10119/2194</a>
Rights	
Description	Supervisor:辻 利秀, 材料科学研究科, 博士

# Thermal and Electrical Properties of Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>-based Compounds.

辻研究室・240203・TUAN QUOC TA

## 1. Introduction

Oxide ion conductor is an exciting class of materials and is involved in an increasing number of application domains, e.g. oxygen sensors and fuel cell. An oxygen sensor is essential for combustion control, and a fuel cell is expected to be a new and clean electric power supply, in particular, for electric vehicles. The oxide ionic conductivity in solids was considered for a long time as typically a high temperature phenomenon. Significant oxide mobility was only observed at temperatures between 800 and 1000°C with conductivity values ranging from  $10^{-2}$  to  $10^{-1}$  Scm<sup>-1</sup>. A lot of research work has been conducted to tailor advanced materials that would allow operation at lower temperature, typically in the range 500-700°C. New high performance materials which can satisfactorily operate at medium temperature in oxidizing atmosphere have been proposed, but no fully satisfactory solutions have been proposed up to now in reducing atmosphere like in Solid Oxide Fuel Cell (SOFC) applications.

In last decade, the perovskite-related system has been considered intensively as a potential solid oxide ion conductor due to its great geometrical and chemical flexibility. Recently, a chemical compound Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>, which has a brownmillerite structure related to perovskite structure, has been discovered as a potential material for oxide ion conductor. Its conductivity after a phase transition at around 930°C is higher than that of widely-used commercial material yttria-stabilized zirconia [1]. The brownmillerite structure is considered as a perovskite structure where one-sixth of oxygen sites are empty. At room temperature, the oxygen vacancies are ordered along alternate [101] direction on alternate (010) planes (Fig. 1). The high oxide ion conductivity after transition is considered as a result of mobile and disordered oxygen vacancies.

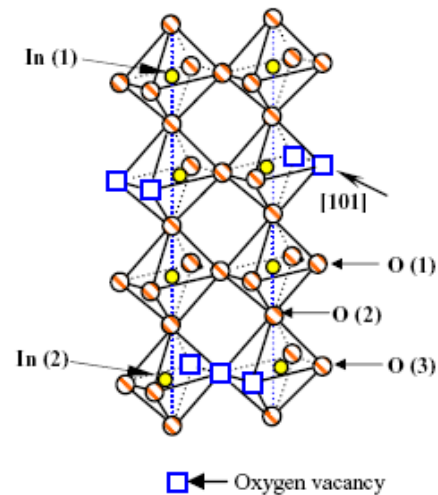


Fig. 1. Ideal brownmillerite structure of Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>.

The high oxide ion conductivity after transition is considered as a result of mobile and disordered oxygen vacancies.

This phenomenon suggests that if the transition temperature can be reduced to lower temperature, we can get the high oxide ion conductivity at low temperature. The strategy to lower this transition temperature is substitution of component elements by other chemical elements. In this dissertation, the first purpose is of understanding the effect of the substitution of In<sup>3+</sup> ions by other chemical elements on the order-disorder transition of oxygen vacancies in brownmillerite structure compound Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>. The second is find out the most suitable element which can bring down the order-disorder transition temperature of oxygen vacancies and improve the oxide ion conductivity at low temperature to useful level.

## 2. Result and discussion

To understand mechanism of the order-disorder transition of oxygen vacancies in brownmillerite structure, the In<sup>3+</sup> ions were substituted partially by other iso-valence ions such as Y<sup>3+</sup>, Ga<sup>3+</sup>, Sc<sup>3+</sup>, Al<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Yb<sup>3+</sup>, Lu<sup>3+</sup>. Dependence on the size, the substituting

ions will be settled in the energetic favor sites. The ions larger than  $\text{In}^{3+}$  are favor to be settled in octahedral site In(1) (see Fig. 1), whereas the smaller ions favor to be settled in tetrahedral site In(2). Each site has different effect on order-disorder transition of oxygen vacancies. The ions larger than  $\text{In}^{3+}$  push up the order-disorder transition temperature of oxygen vacancies become higher than mother compound's one, but the smaller ions bring down the transition temperature as shown in Fig. 3. The bigger ion substitutes, the higher transition temperature occurs, but bigger than  $\text{Y}^{3+}$  the trend becomes opposed. In accordingly, the slop of the dependence of unit cell volume on ionic radius also changes around the ionic radius of  $\text{Y}^{3+}$  as shown in Fig 2.

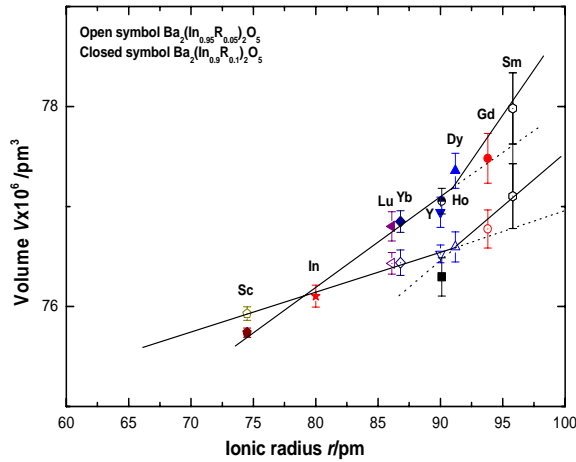


Fig. 2. Unit cell volume of  $\text{Ba}_2(\text{In}_{1-x}\text{R}_x)_2\text{O}_5$

To improve the oxide ion conductivity and investigate dependence on the oxygen vacancy concentration of transition temperature, the substitution of alio-valence ions such as  $\text{Zn}^{2+}$ ,  $\text{Sn}^{4+}$  had been carried out.

At first, substitution of lower valence ion  $\text{Zn}^{2+}$  creates more oxygen vacancies. The transition temperature decreases when increasing the oxygen vacancies, resulting of increasing the substituting contents. The conductivity at low temperature is increased a little bit but the conductivity at high temperature is decreased significantly (Fig. 4). This phenomenon probably causes by association of mobile oxygen ions with substituting ions  $\text{Zn}^{2+}$ .

The compounds  $\text{Ba}_2(\text{In}_{1-x}\text{Sn}_x)_2\text{O}_{5+x}$  ( $x = 0.0 \sim 0.2$ ) was prepared by a solid state reaction method. The substitution of higher valence  $\text{Sn}^{4+}$  ion bring more oxygen into material, and fill up the oxygen vacancies. The result shows the conductivity and transition temperature had been changed significantly. The higher valency ion  $\text{Sn}^{4+}$  improves the low temperature conductivity and stabilizes the high temperature phase at lower temperature but the thermal stability is decrease due to water absorption around  $300^\circ\text{C}$  as shown in Fig 5. The compound with substituting content  $x = 0.2$ ,  $\text{Ba}_2(\text{In}_{0.8}\text{Sn}_{0.2})_2\text{O}_{5.2}$  has the highest oxide ion conductivity in In-site substituted  $\text{Ba}_2\text{In}_2\text{O}_5$  based compounds (Fig 6).

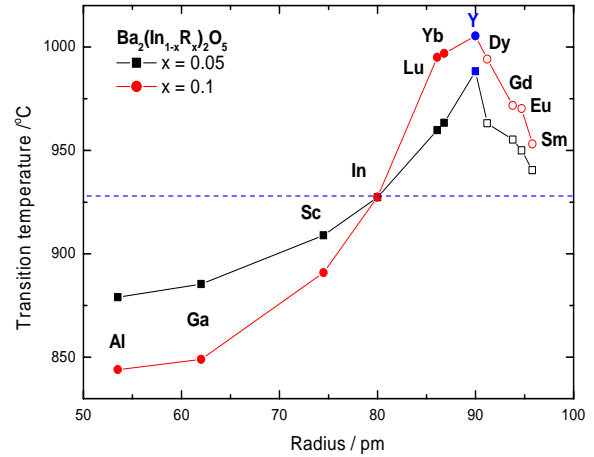


Fig. 3. Transition temperature vs. ionic radius

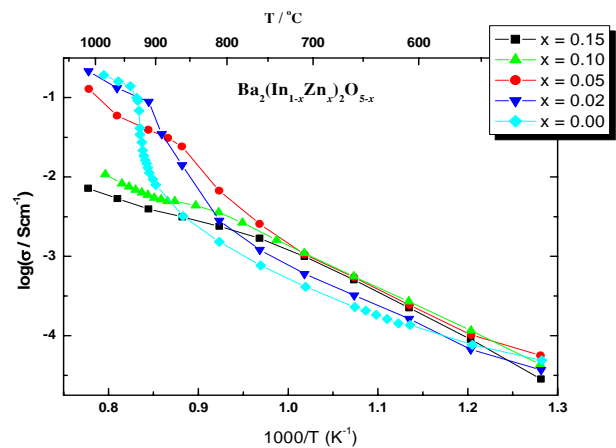


Fig. 4. Electrical conductivity of  $\text{Ba}_2(\text{In}_{1-x}\text{Zn}_x)_2\text{O}_{5-x}$ .

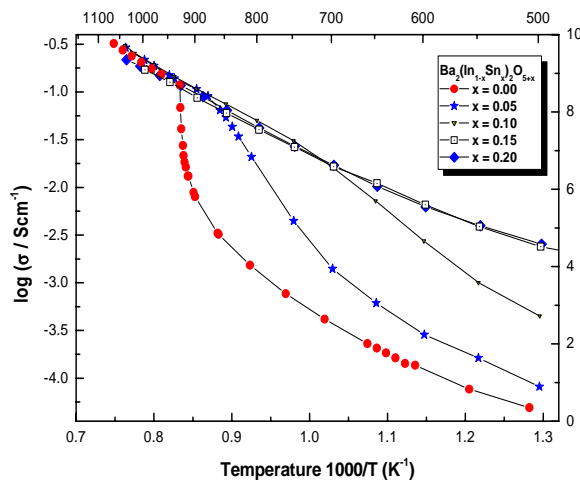


Fig 5. Arrhenius plots of conductivity of  $\text{Ba}_2(\text{In}_{1-x}\text{Sn}_x)_2\text{O}_{5+x}$ .

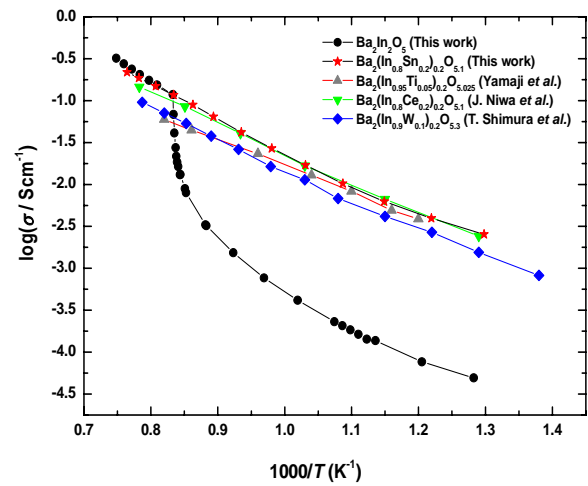


Fig 6. Arrhenius plots of conductivity of  $\text{Ba}_2(\text{In}_{1-x}\text{M}_x)_2\text{O}_{5+\delta}$ .

### 3. Conclusion

The  $\text{Ba}_2\text{In}_2\text{O}_5$  based brownmillerite structure compounds were prepared and investigated systematically in view of controlling the order-disorder transition temperature of oxygen vacancies and improving the oxide ion conductivity. Found out that the order-disorder transition increases with increasing the ionic radii of substituents up to radii of  $\text{Y}^{3+}$ , and then decreases with further increase, this phenomenon are explained by the substituted favored sites of  $\text{In}^{3+}$ , which are dependent on the size of the substituents. Found out that when increasing the oxygen vacancies, the mobile oxygen concentration decreases, in opposite when fill up the oxygen vacancies with additional oxygen ions, the concentration of mobile oxygen ions are increased. Found out that compound  $\text{Ba}_2(\text{In}_{0.8}\text{Sn}_{0.2})_2\text{O}_{5.2}$  has the highest oxide ion conductivity in In-site substituted  $\text{Ba}_2\text{In}_2\text{O}_5$  based compounds. Finally, in order to get high performance oxide ion materials the substitution of donors for both Ba and In sites are necessary to get an optimum oxygen vacancy concentration for high oxide ion conductivity, at which all oxygen vacancies are free to move.

### References

- [1] J. B. Goodenough, et al. Solid State Ionics, 44 (1990) 21.

## Contents of doctoral dissertation

Chapter 1 Oxide ion conductor.....	1
Chapter 2 Divalency substitution for In site of $Ba_2In_2O_5$ .....	32
Chapter 3 Trivalency substitution for In site of $Ba_2In_2O_5$ .....	51
Chapter 4 Tetravalency substitution for In site and double substitution of $Ba_2In_2O_5$ .....	
Conclusion .....	

## List of publications

### *Journal*

1. T.Q. Ta, T. Tsuji, Y. Yamamura, Thermal and electrical properties of  $Ba_2In_2O_5$  substituted for In site by rare earth elements. Journal of Alloys and Compounds, in print.
2. T.Q. Ta, T. Tsuji, Y. Yamamura, Electrical properties of  $Ba_2(In_{1-x}Sn_x)_2O_{5+x}$ . International Conference on Solid State Ionics, July 17th - 22nd, 2005, Baden-Baden, Germany/Europe, submitted.

### *Conferences*

1. T.Q. Ta, T. Tsuji, Y. Yamamura, Electrical properties of  $Ba_2In_2O_5$  substituted for In site. Fall Meeting of Kinki branch of The Chemical Society of Japan. 8 November 2003, Kanazawa.
2. T.Q. Ta, T. Tsuji, Y. Yamamura, Electrical properties of  $Ba_2In_2O_5$  substituted for In-site by rare earth elements. 84th Spring Meeting of The Chemical Society of Japan, 26-29 March 2004, Kansai University.
3. T.Q. Ta, T. Tsuji, Y. Yamamura, Thermal and electrical properties of  $Ba_2In_2O_5$  substituted for In site by rare earth elements. The International Conference on Rare Earths in Nara, Japan. November 2004.
4. T.Q. Ta, T. Tsuji, Y. Yamamura, Electrical properties of  $Ba_2(In_{1-x}Sn_x)_2O_{5+x}$ . International Conference on Solid State Ionics, July 17th - 22nd, 2005, Baden-Baden, Germany/Europe, submitted.