

# A Chemical Bonding Approach to Ionic Conduction and Thermal Expansion in Oxide Ion Conductors

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**Abstract.** In complex perovskite-type oxides which have been studied as cathode materials, the thermal expansion coefficient increases with the increase in the oxygen ionic conductivity. In the present study, with the aim to explain such a behavior, a research has been carried out from a chemical bond point of view. For oxides  $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$  with perovskite structure, the ionicity of the individual bond, A-O and B-O, and the thermal expansion coefficient of mixed compounds were estimated by using semiempirical methods. It has been shown that the thermal expansion coefficient and the oxygen ionic conductivity decrease with the increase in the difference of the ionicity between A-O and B-O bonds. It is also found that the tolerance factor and the specific free volume are linearly correlated with the difference of ionicity.

## Introduction

Mixed oxides with the perovskite structure allow the synthesis of solid solutions containing various ions. They are also promising materials which can combine the properties of electronics and solid electrolytes. Therefore, the search of alternative cathode materials of the complex perovskite-type oxides is attracting much interest in the field of functional ceramics and other fields of applications. For the development of functional materials, many investigations concerning the effects of temperature, chemical composition, structure and pressure have been performed to clarify the oxygen conduction mechanism and the structural stability [1-4]. However, its understanding from the fundamental point of view remains still unclear. For instance, it is known that the thermal expansion coefficient in perovskite-type oxides increases with the increase in the oxygen ionic conductivity [5], but its theoretical background is not clear.

Recently, we have explained the correlation between the ionic conduction and the thermal expansion in  $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$  from a chemical bond point of view [6]. In the present work, we extend the previous study. For perovskite oxides with chemical formula  $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ , the ionicity  $f_i^\mu$  of the individual bond  $\mu$ , A-O and B-O, was evaluated theoretically and examined the relation with the thermal expansion coefficient (TEC). Additionally, the relation between the bond ionicity and the Goldschmidt's tolerance factor used in the criterion for the symmetry of perovskite structure, and the specific free volume are discussed.

## Theoretical Approach

The ideal perovskite structure with stoichiometric composition  $ABO_3$  is cubic. The A-site is coordinated to twelve oxygen ions. The B-site is coordinated to six oxygen ions, forming an octahedron. In complex perovskite-type oxides, the oxygen defects  $\delta$  are introduced by partial substitution of metal atom A and/or B, or by adjusting the oxidation state. In the calculation, the estimated values include the effect of oxygen defects.

The concepts of ionicity  $f_i$  and covalency  $f_c$  have been used successfully to understand systematically the properties of many kinds of materials [7,8]. As used commonly in the literature [9,10], the chemical bonding of a multicomponent material can be decomposed into binary components. The fractions of ionicity  $f_i^\mu$  and covalency  $f_c^\mu$  of any individual bond  $\mu$  in a multibond crystal are defined as follows,

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2}, \quad f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2}, \quad (1)$$

where  $E_g^\mu$  is the average band gap energy that consists of homopolar  $E_h^\mu$  and heteropolar  $C^\mu$  parts.

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2. \quad (2)$$

A semiempirical method for the evaluation of linear thermal expansion coefficient from the lattice energy has been presented by Zhang *et al* [11]. For a pseudo binary crystal  $A_mB_n$ , the lattice energy  $U_{mn}^\mu$  of bond type  $\mu$  consists of two parts, ionic  $U_{mni}^\mu$  and covalent  $U_{mnc}^\mu$ .

$$U_{mn}^\mu = U_{mnc}^\mu + U_{mni}^\mu, \quad (3)$$

$$U_{mni}^\mu = \frac{2540(\zeta_+^\mu)^2}{d^\mu} \beta_{mn}^\mu \left(1 - \frac{0.4}{d^\mu}\right) f_i^\mu, \quad (4)$$

$$U_{mnc}^\mu = 2100 \beta_{mn}^\mu \frac{(\zeta_+^\mu)^{1.64}}{(d^\mu)^{0.75}} f_c^\mu, \quad (5)$$

The thermal expansion coefficient for a binary crystal is written as

$$\alpha_{mn}^\mu = -3.1685 + 0.8376 \gamma_{mn}^\mu, \quad (6)$$

$$\gamma_{mn}^\mu = \frac{k_B Z_A^\mu N_{CA}^\mu}{U_{mn}^\mu \Delta_A^\mu} \beta_{mn}^\mu, \quad (7)$$

$$\beta_{mn}^\mu = \frac{m(m+n)}{2n}, \quad (8)$$

where  $\gamma_{mn}^\mu$  is a parameter connecting the lattice energy and the thermal expansion,  $k_B$  is the Boltzmann constant,  $N_{CA}^\mu$  is the coordination number of cation A in the bond  $\mu$ ,  $\Delta_A^\mu$  is a correction factor which depends on the position of the cation in the periodic table of the elements. The numerical factors appearing in the above expressions were determined by fitting to the experimental values.

The thermal expansion coefficient of a complex crystal is written as

$$\alpha = \sum_\mu F_{mn}^\mu \alpha_{mn}^\mu \quad (10^{-6} \text{K}^{-1}), \quad (9)$$

where  $F_{mn}^\mu$  is the fraction of the chemical bonding of type  $\mu$ . The thermal expansion coefficient for a complex crystal is written as a linear combination of thermal expansion coefficients of binary systems. This is a simple approximation.

## Results & Discussion

**Ionicity, Thermal Expansion and Ionic Conduction.** In Fig. 1, the experimental values [5] of the thermal expansion coefficient (300-1000°C) and the oxygen ionic conductivity  $\sigma_o$  (800°C, air) of complex perovskite type oxides  $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$  (A, A' = La, Sr, Ce, B, B' = Fe, Co) are shown as a function of the difference in ionicity  $\Delta f_i$ . The Greek number in the figures indicates the valence of the cation, i.e. II-III means  $A^{2+}-B^{3+}$ . The values of the TEC measured are consistent with those found in our calculation. From Fig. 1, we can note that the oxygen ionic conductivity decreases with  $\Delta f_i$ .

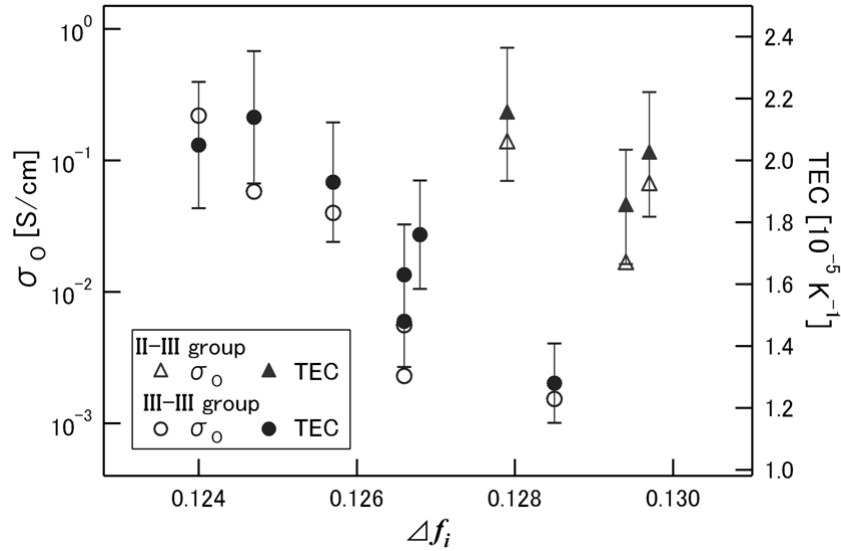


Fig. 1 Ionic conductivity and thermal expansion coefficient as a function of the difference in the ionicity between AO and BO bonds  $\Delta f_i$ .

The result shown in Fig. 1 can be explained as follows. When there is a large difference in ionicity  $\Delta f_i$  between A-O and B-O bonds, the oxygen ion will be located near the B site, because its bonding is strong. In this case, the oxygen ions are localized. In contrast, when the difference in ionicity is small, the nature of the chemical bonding between A-O and B-O become closer, and the oxygen ion might bind to B-site or to A-site ions. The idea is illustrated schematically in Fig. 2. That is, the site where the oxygen ion is located becomes unstable. This effect will result in the increase of the oxygen ion mobility and the thermal expansion.

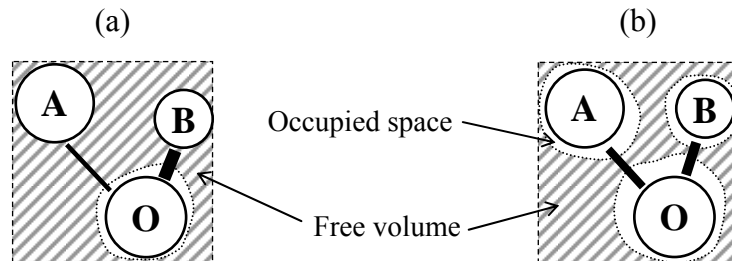


Fig. 2 Schematic representation of the bonding when the difference of ionicity between A-O and B-O is large (a) and small (b), respectively.

**Ionicity and  $t$ -Factors.** Fig. 3 shows the relationship between the difference of ionicity and the tolerance factor in  $La_{1-x}Sr_xB_{1-y}B'_yO_{3-\delta}$  (B, B' = Fe, Co). We can see that the points of II-III and III-III group are located in the same straight line. Concerning the effective ionic radii, we have used the values reported by Ullmann, which take into account the effect of defect concentration and the cell

volume [12]. Therefore, the estimated values of the ionicities for A-O and B-O bonds include the effect of oxygen defects. As shown in Fig. 3, the  $t$ -factor is close to 1 when the difference in ionicity is small. The  $t$ -factor departs from  $t = 1$ , the value for ideal perovskite structure, when  $\Delta f_i$  becomes large.

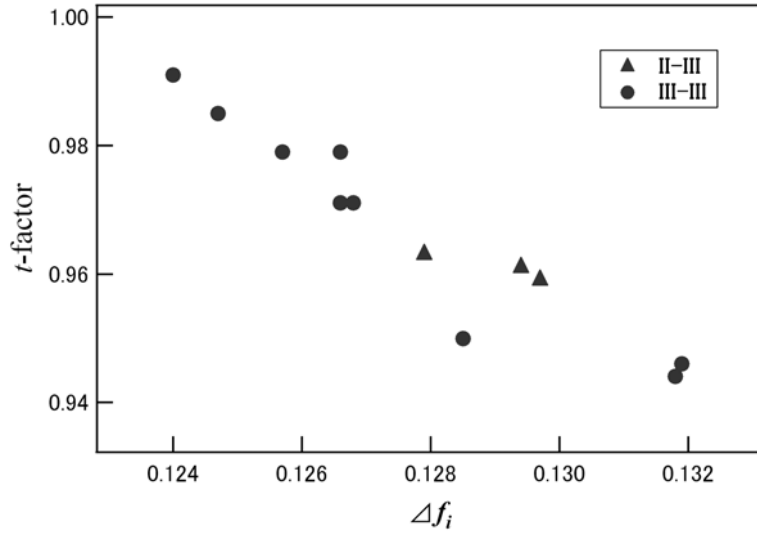


Fig. 3 Relationship between the difference of ionicity  $\Delta f_i$  and the tolerance factor in  $\text{La}_{1-x}\text{Sr}_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-\delta}$ .

**Ionicity and Free Volume of the Unit Cell.** The specific free volume as a function of the difference of ionicity is shown in Fig. 4. The specific free volume is defined as  $V_{f,s} = (\text{unit cell volume} - \text{occupied space}) / \text{unit cell volume}$ . Oxides of II-III group have many defects compared with III-III group. In these kinds of compounds with high concentration of defects, the free volume is large. It indicates that the specific free volume is influenced by the concentration of defects. As can be seen from Fig. 4, the free volume increases with the difference of ionicity  $\Delta f_i$ .

Fig. 4 could be explained as follows. As mentioned above, when the difference of ionicity  $\Delta f_i$  is large, the oxygen ions tend to localize. This results in the decrease of the space occupied by the oxygen and the increase of the specific free volume. On the other hand, when  $\Delta f_i$  is small, the amplitude of oxygen vibration increases, resulting in the increase of the space effectively occupied by the oxygen and the decrease of the specific free volume.

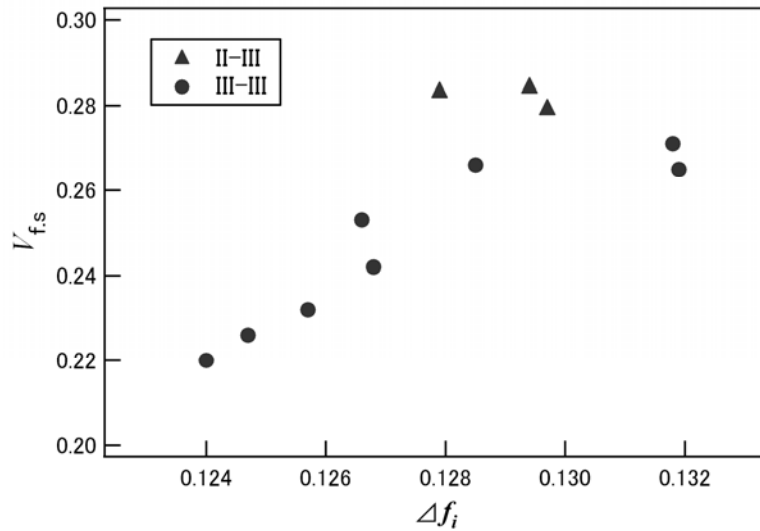


Fig. 4. Specific free volume of the unit cell as a function of the difference of ionicity  $\Delta f_i$ .

## Summary

The thermal expansion, the ionic conduction and the structural parameter in perovskite-type oxides have been discussed from a chemical bond point of view. For oxides  $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ , it is found that the thermal expansion coefficient and the oxygen ionic conductivity decrease with the increase of the difference of the ionicity between A-O and B-O bonds. It has been also shown that the t-factor and the specific free volume exhibit a linear relationship with the difference of ionicity.

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