

Relationship between Thermal Expansion, Ionic Conduction and Ionicity in Perovskite-Type Oxides

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Abstract

In complex perovskite-type oxides, which have been studied as cathode materials, the thermal expansion coefficient (TEC) increases with the increase in the oxygen ionic conductivity. The aim of the present study is to explain such a behavior from a chemical bond point of view. For the perovskite oxides expressed as $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ and ABO_3 , the ionicity of A-O and B-O bonds and the thermal expansion coefficient were evaluated theoretically by using semiempirical methods. It is found 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.

Keywords: ionicity, thermal expansion coefficient, oxygen ion conductivity, perovskite oxides, chemical bonding

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1. Introduction

The search of alternative cathode materials of the complex perovskite-type oxides is attracting much interest in the field of functional ceramics. Oxides with the perovskite structure allow the synthesis of solid solutions containing various ions. Their properties can be modified in a wide range with defect formations generated by substitutions. They are also promising materials which can combine the properties of electronics and solid electrolytes. For the development of a variety of power generation applications, a better understanding of physical properties is required. Many studies concerning the effects of temperature, chemical composition, structure and tolerance factor, pressure, defect related properties, ionic conduction and thermal expansion have been done on these oxides [1-4]. Ullmann *et al.* have shown that the thermal expansion coefficient in perovskite-type oxides increases with the increase in the oxygen ionic conductivity [5]. They have focused on the oxygen deficiencies created by substitution and showed that the oxygen vacancy concentration is the dominating factor for both quantities. Many investigations have been performed till date to improve the properties of the materials. However, the theoretical background of the relationship between the thermal expansion coefficient and the ionic conduction is not clear. Recently, we have explained the correlation between ionic conduction and thermal expansion in $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ from a chemical bond point of view [6]. In the present paper, the analysis has been extended to other perovskite oxides. For perovskite oxides with chemical formula $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-\delta}$ and ABO_3 , the ionicity f_i^μ of the individual bond μ , A-O and B-O, and the thermal expansion coefficient were evaluated by using semiempirical methods [7,8]. It is found that the thermal expansion coefficient decreases as a function of the difference of the ionicity Δf_i between A-O and B-O bonds, $|f_i^{\text{AO}} - f_i^{\text{BO}}|$. The values of TEC calculated are consistent with those found experimentally. It is also found that the measured oxygen ionic conductivity

decreases with Δf_i . The result suggests that the ionic conduction mechanism could be understood from the point of view of materials chemical bonding.

2. 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 δ are introduced by partial substitution of metal atom A and/or B, or by adjusting the oxidation state.

The concepts of ionicity f_i and covalency f_c have been used successfully to understand systematically the properties of many kinds of materials [7,9]. The chemical bonding of a multicomponent material can be decomposed into binary components. This method has been commonly used in the literature [10,11]. The fractions of the ionicity f_i^μ and covalency f_c^μ of any individual bond μ 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^μ is the average band gap energy that consists of homopolar E_h^μ and heteropolar C^μ parts.

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

where

$$E_h^\mu = \frac{39.74}{(d^\mu)^{2.48}} \text{ (eV)}, \quad (3)$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu) \left[Z_A^\mu - \frac{n}{m} Z_B^\mu \right] \frac{1}{r_0^\mu} \quad (n \geq m), \quad (4a)$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_0^\mu) \left[\frac{m}{n} Z_A^\mu - Z_B^\mu \right] \frac{1}{r_0^\mu} \quad (m \geq n), \quad (4b)$$

$$b^\mu = b(N_c^\mu)^2, \quad (5)$$

where r_0^μ is the average radius, which is a half of the bond length d^μ , $\exp(-k_s^\mu r_0^\mu)$ is the Thomas-Fermi screening factor, Z_A^μ and Z_B^μ are the effective number of valence electrons of A and B ions, respectively, b^μ is a correction factor that is proportional to the square of the average coordination number N_c^μ . Eq. (4a) should be used when $n \geq m$ and eq. (4b) when $n \leq m$. In the above equations, d^μ and r_0^μ are expressed in Å and energy is in eV.

A semiempirical method for the evaluation of linear thermal expansion coefficient from the lattice energy has been presented by Zhang *et al* [8]. For a pseudo binary crystal A_mB_n , the lattice energy U_{mn}^μ of bond type μ consists of two parts, ionic U_{mni}^μ and covalent U_{mnc}^μ .

$$U_{mn}^\mu = U_{mnc}^\mu + U_{mni}^\mu, \quad (6)$$

$$U_{mni}^\mu = \frac{2540(\zeta_+^\mu)^2}{d^\mu} \beta_{mn}^\mu \left(1 - \frac{0.4}{d^\mu} \right) f_i^\mu, \quad (7)$$

$$U_{mnc}^\mu = 200 \beta_{mn}^\mu \frac{(\zeta_+^\mu)^{1.64}}{(d^\mu)^{0.75}} f_c^\mu, \quad (8)$$

$$\beta_{mn}^\mu = \frac{m(m+n)}{2n}, \quad (9)$$

where ζ_+^μ is the valence of the cation.

The thermal expansion coefficient of a complex crystal is written as

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

where F_{mn}^μ is the fraction of the chemical bonding of type μ . The thermal expansion coefficient for a complex crystal is written as a linear combination of the thermal expansion

coefficients of binary systems. This is a simple approximation. However, previous studies have revealed that this approximation works quite well in the prediction of materials properties [8]. The thermal expansion coefficient for a binary crystal is written as

$$\alpha_{mn}^{\mu} = -3.1685 + 0.8376\gamma_{mn}^{\mu}, \quad (11)$$

$$\gamma_{mn}^{\mu} = \frac{k_B Z_A^{\mu} N_{CA}^{\mu}}{U_{mn}^{\mu} \Delta_A^{\mu}} \beta_{mn}^{\mu}, \quad (12)$$

where γ_{mn}^{μ} is a parameter connecting the lattice energy and the thermal expansion, k_B is the Boltzmann constant, N_{CA}^{μ} is the coordination number of cation A in the bond μ , Δ_A^{μ} 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 are determined by fitting to experimental values.

3. Results and Discussion

In Fig. 1-3, the thermal expansion coefficient (TEC) of $A_{1-x}A'_x B_{1-y}B'_y O_{3-\delta}$ ($A, A' = \text{La, Pr, Sr} / B, B' = \text{Fe, Co, Mn}$) and ABO_3 ($A = \text{La, B} = \text{Al, Cr, Fe, Ga, Rh, Ti, V}$) are expressed as a function of the ionicity. The data points are calculated values and the lines are guides to the eyes. The Greek number in the figures indicates the valence of the cation, i.e. II-III means $A^{2+}-B^{3+}$. Concerning the effective ionic radii, we have used the values reported by Ullmann and Ubig, which took into account the effects of defect concentration and cell volume of complex perovskite oxides [12]. Therefore, the estimated values of the ionicities for A-O and B-O bonds include the effect of oxygen defects. Compounds with the form ABO_3 have been regarded as the structure with no defects [13]. Fig. 1 shows the relationship between the thermal expansion coefficient and the ionicity of A-O bond. Regarding the III-III group, the

thermal expansion coefficient of the system decreases with the increase in the ionicity of A-O bond. On the other hand, as shown in Fig. 2, the TEC increases slightly with the ionicity of the B-O bond. It is noted from Figs. 1-3 that the TEC of II-III group shows large values. According to the model, this observation can be understood as follows. The valence ζ_+^μ of A atom in II-III group is small compared with the III-III group. The lattice energy U_{mn}^μ is proportional to ζ_+^μ as shown in Eqs. (7) and (8). Since the thermal expansion is inversely proportional to the lattice energy as given in Eq (12), the TEC of II-III group is larger than that of III-III group.

In Fig. 3, the calculated thermal expansion coefficient is shown as a function of the difference of ionicity Δf_i between A-O and B-O bonds, $|f_i^{AO} - f_i^{BO}|$. Recently, we have explained the correlation between ionic conduction and thermal expansion in some oxides with the composition $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ from a chemical bond point of view [6]. There it has been shown that the values of the thermal expansion coefficient and the oxygen ionic conductivity decrease with the difference in ionicity Δf_i . As shown in Fig. 3, in $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-\delta}$ and ABO_3 the calculated values of the thermal expansion coefficient decrease with the increase of Δf_i . In Fig. 4, the experimental values [5] of the thermal expansion coefficient (300-1000°C) and the oxygen ionic conductivity σ_o (800°C, air) are shown as a function of the difference of ionicity. We can note that both, the TEC and the oxygen ionic conductivity decreases with Δf_i , as found previously [6].

The ionicity of A-O bond is larger than that of B-O bond. In other words, the covalency which is caused by the overlap of orbitals is larger in the B-O bond than in the A-O bond. This observation is consistent with the short bond length of B-O than that of A-O. This implies that the binding of B-O is strong compared to that of A-O bond. The results of Raman and IR measurements support these conjectures [14,15]. When there is a large difference in

ionicity between A-O and B-O bonds, the oxygen ion will be located near the B site, because the bonding is strong. This situation is illustrated schematically in Fig. 5(a). In contrast, when the difference in ionicity is small as shown in Fig. 5(b), their nature of the chemical bonding become closer, and the oxygen ion might bind to B-site or to A-site ions. 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 thermal expansion.

4. Conclusions

The thermal expansion and the ionic conduction in perovskite-type oxides have been discussed from a chemical bond point of view. For oxides of the type $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ and ABO_3 , it is found that the thermal expansion coefficient and the oxygen ionic conductivity decrease with the increase of Δf_i . The result suggests that the oxygen ion conduction mechanism in perovskite-type oxides could be understood from the point of view of materials chemical bonding.

Acknowledgments

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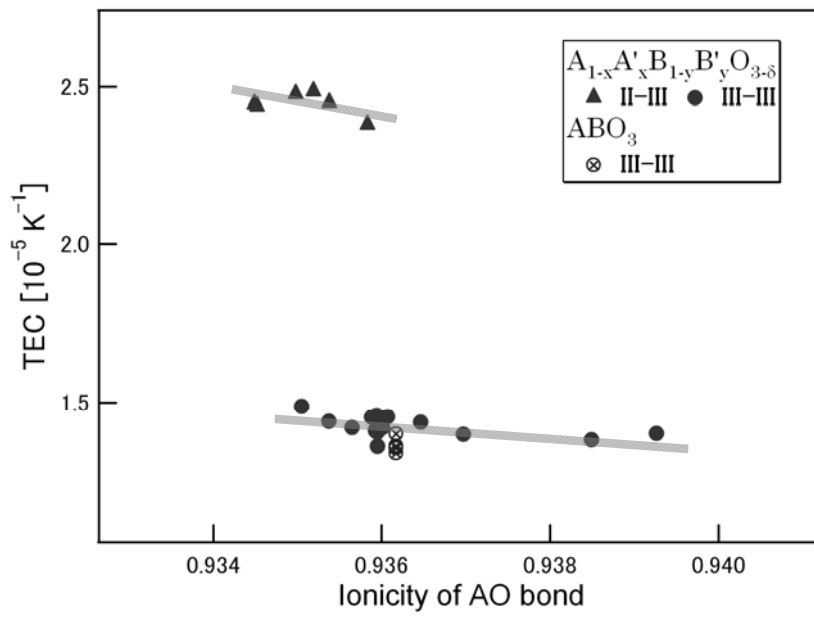


Fig.1. Thermal expansion coefficient and the ionicity of A-O bond.

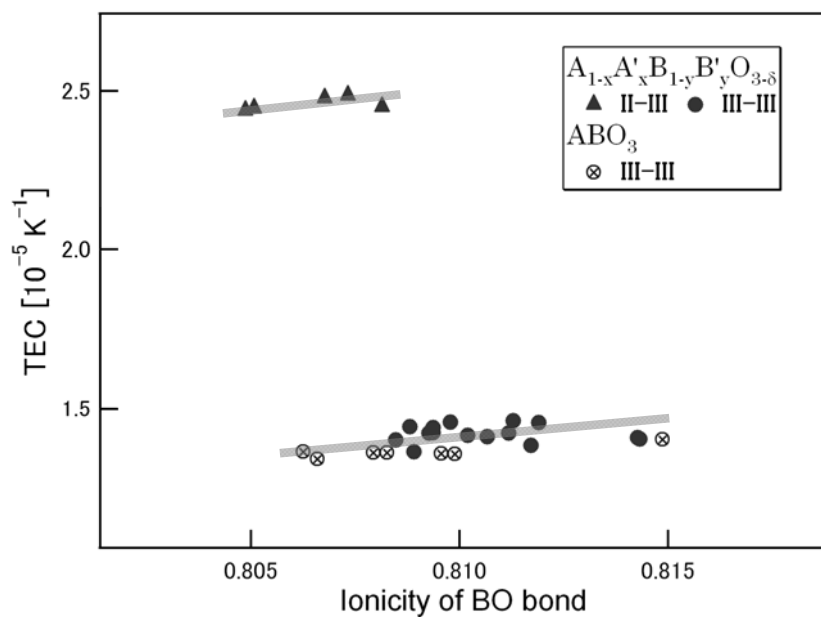


Fig.2. Thermal expansion coefficient and the ionicity of B-O bond.

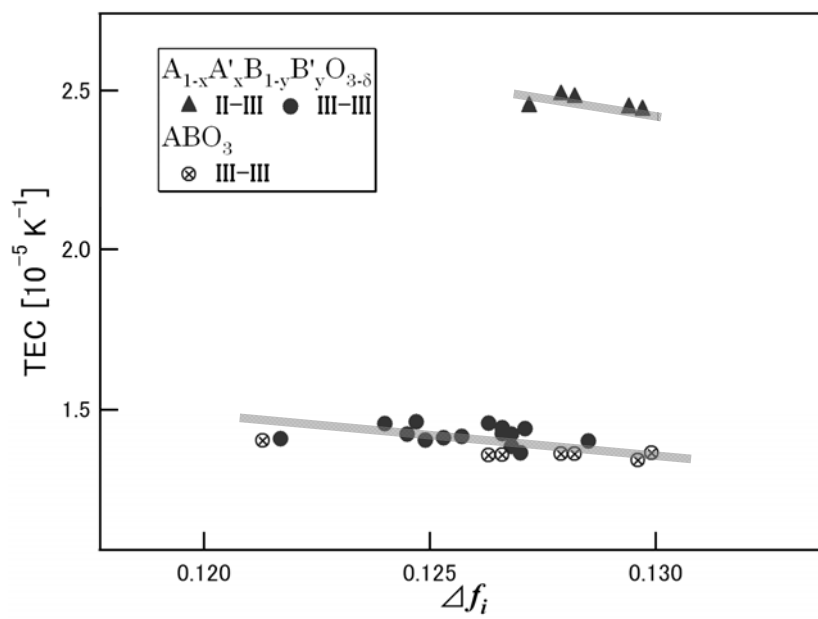


Fig. 3. Thermal expansion coefficient as a function of the difference of ionicity between A-O and B-O bonds.

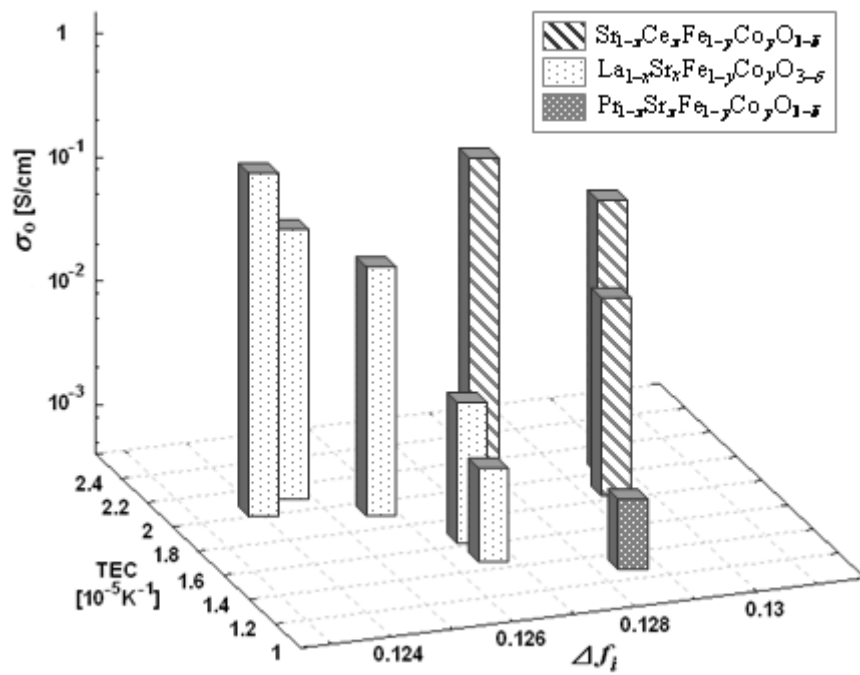


Fig. 4 Ionic conductivity and thermal expansion coefficient as a function of Δf_i in $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-\delta}$.

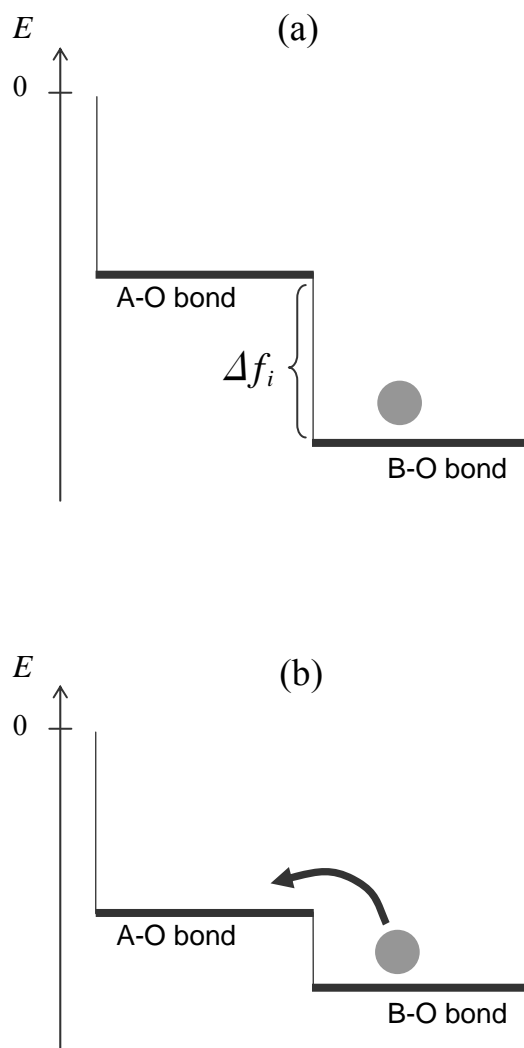


Fig. 5. Schematic views of the bonding when the difference of ionicity between A-O and B-O is (a) large and (b) small.