

Relationship Between Thermal Expansion Coefficient and Ionic Conduction in Perovskite-Type Oxides

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(Received November 12, 2009; accepted December 28, 2009)

The thermal expansion coefficient of complex perovskite-type oxides 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. The ionicity f_i^μ of the individual bond μ , A-O and B-O bonds, and the thermal expansion coefficient of $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ were estimated theoretically. It is found that the oxygen ionic conductivity and the thermal expansion coefficient decrease with the increase in the difference of ionicity Δf_i .

KEYWORDS: thermal expansion coefficient, oxygen ionic conductivity, ionicity, perovskite oxides, chemical bonding

1. Introduction

Perovskite-type oxides are attracting much interest due to their manifold applications as functional materials. For instance, they are used as electrodes for solid oxide fuel cells, electromagnetic materials, oxide catalysts, etc.¹⁻⁴⁾ Oxides with the perovskite structure allow the synthesis of solid solutions containing various ions. The properties of perovskite oxides 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 the mechanism of ionic conduction is required. Many investigations have been performed till date to improve the properties of the materials. Regarding fundamental properties, Ranlov *et al.* have studied the correlation between structural and thermodynamic parameters and discussed the criteria for high oxide ionic conductivity.⁵⁾ According to their report, the oxide ion conductivity increases with the cation radius of the central octahedron. Ullmann *et al.* have shown that the thermal expansion coefficient in perovskite-type oxides increases with the increase in the oxygen ionic conductivity.⁶⁾ 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 studies concerning the effects of temperature, constituent atoms, structure (or tolerance factor), pressure and deficiency on ionic conduction and thermal expansion have been done.⁷⁻⁹⁾ However, the theoretical background of the relationship between the thermal expansion coefficient and the ionic conduction is not clear.

The aim of this work is to explain the correlation between ionic conduction and thermal expansion from a chemical bond point of view. The ionicity f_i^μ of the individual bond μ , A-O and B-O bonds, and the thermal expansion coefficient of $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ were estimated by using semiempirical methods.^{10,11)} It is found that the oxygen ionic conductivity and the thermal expansion coefficient decrease with the difference in ionicity Δf_i between A-O and B-O bonds, $|f_i^{AO} - f_i^{BO}|$. The present result suggests that the ionic conduction mechanism could be understood from the point of view of materials chemical bonding.¹²⁾

2. Approach

2.1 Structure

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 $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ (A, A' = rare earth, alkaline earth, B, B' = Al, Mn, Fe, Co, Ni, Ga, Mg, etc.), the oxygen defects δ are introduced by partial substitution of metal atom A and/or B, or by adjusting the oxidation state.

2.2 Theoretical expressions

The concepts of ionicity f_i and covalency f_c have been used successfully to understand systematically the properties of many kinds of materials.^{10,13)}

The chemical bonding of a multicomponent material can be decomposed into binary components. This method has been commonly used in the literature.^{14,15)} 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.

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

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

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

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

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

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 $m \geq n$. 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.*¹¹⁾ 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 .

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

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

$$U_{mnc}^\mu = 2100 \beta_{mn}^\mu \frac{(\zeta_+^\mu)^{1.64}}{(d^\mu)^{0.75}} f_c^\mu, \quad (8)$$

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

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

The thermal expansion coefficient for a binary crystal is written as

$$\alpha_{mn}^\mu = -3.1685 + 0.8376 \gamma_{mn}^\mu, \quad (10)$$

$$\gamma_{mn}^\mu = \frac{k_B Z_A^\mu N_{CA}^\mu}{U_{mn}^\mu \Delta_A^\mu} \beta_{mn}^\mu, \quad (11)$$

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 the experimental values.¹¹⁾

The thermal expansion coefficient of a complex crystal is written as

$$\alpha = \sum_\mu F_{mn}^\mu \alpha_{mn}^\mu \quad (10^{-6} \text{ K}^{-1}), \quad (12)$$

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.¹¹⁾

3. Results

The relationship between the thermal expansion coefficient and the ionicity in complex perovskite-type oxides $\text{La}_{1-x}\text{Sr}_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-\delta}$ ($\text{B}, \text{B}' = \text{Fe}, \text{Co}$) are shown in Figs. 1-3. The solid circles are calculated values and the lines are guides to the eyes. Concerning the effective ionic radii, we have used the values reported by Ullmann, which

take into account the effect of the defect concentration and the cell volume.¹⁶⁾ Therefore, the estimated values of the ionicities for A-O and B-O bonds include the effect of oxygen defects. According to the calculation, the TEC exhibits different trend for A-O bond and B-O bond. As shown in Fig. 1, the thermal expansion coefficient (TEC) of the system decreases with the increase in the ionicity of A-O bond. On the other hand, for the B-O bond, the TEC increases with the ionicity as shown in Fig. 2.

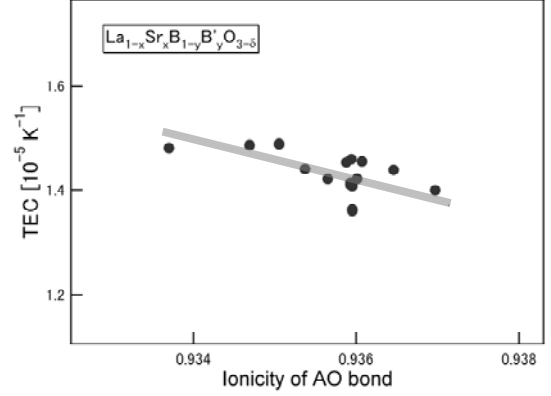


Fig. 1. Thermal expansion coefficient and the ionicity of AO bond.

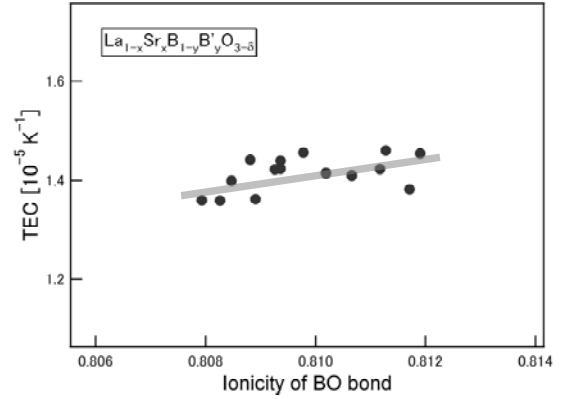


Fig. 2. Thermal expansion coefficient and the ionicity of BO bond.

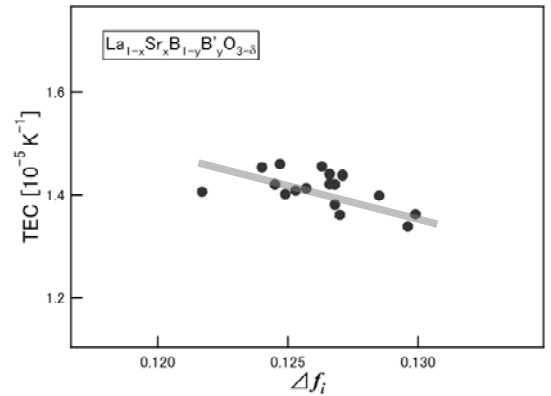


Fig. 3. Thermal expansion coefficient as a function of the difference in the ionicity between AO and BO bonds.

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, $|f_i^{AO} - f_i^{BO}|$. It is seen that the thermal expansion coefficient decreases with the increase in Δf_i . In Fig. 4, the experimental values of the thermal expansion coefficient (300-1000°C)⁶⁾ and the oxygen ionic conductivity σ_o (800°C, air)⁶⁾ are shown as a function of the difference in ionicity. The values of the TEC measured are consistent with those found in our calculation. From Fig. 4, we can note that the oxygen ionic conductivity decreases with Δf_i .

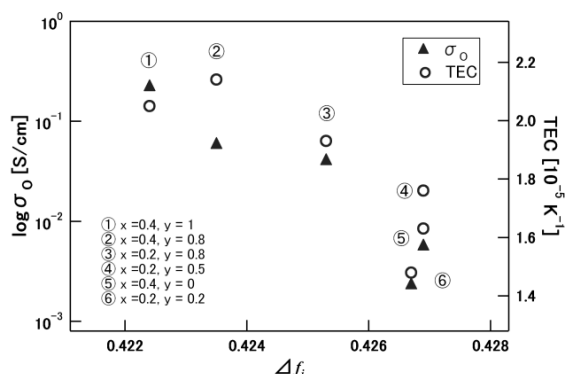


Fig. 4. Measured ionic conductivity⁶⁾ and thermal expansion coefficient⁶⁾ as a function of Δf_i in $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$.

4. Discussion

The ionicity of A-O bond is larger than that of B-O bond. In other words, the B-O bond has large covalency caused by the overlap of orbitals. This observation is consistent with the short bond length of B-O than that of A-O. It is also consistent with the results of Raman and IR measurements, where the frequency of vibrational mode related to B-O bond is larger than that related to the mode of A-O bond.^{17,18)} That is, the binding of B-O is stronger compared to that of A-O bond.

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 of its strong bond. In contrast, when the difference in ionicity is small, 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. The close correlation between thermal expansion coefficient and ionic conductivity shown in Fig. 4 can be explained in this way.

5. Conclusion

The thermal expansion and the ionic conduction in complex perovskite oxides have been discussed from a chemical bond point of view. It is found that the oxygen ionic conductivity and the thermal expansion coefficient decrease with the increase in the difference of ionicity between A-O and B-O bonds. The relationship found suggests that the oxygen ion conduction mechanism in perovskite type oxides could be understood from the point of view of materials chemical bonding.

Acknowledgments

S.T. thanks the GCOE program (Pulsed Power) of Kumamoto University for the financial support. This work was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19560014).

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