Modification of Local Electronic Structures Due to Phase Transition in Perovskite-Type Oxides, SrBO_3 (B=Zr, Ru, Hf)

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The local electronic structures are simulated for a perovskite-type oxide with four polymorphous phases, SrZrO_3 , using the DV- $X\alpha$ molecular orbital method. It is found that a series of phase transitions occurs at certain temperatures so as to retain not only the Zr-O bond strength, but also the Sr-O bond strength, by the tilting of ZrO_6 octahedra and the attendant accommodation to the Zr-O and the Sr-O interionic distances. The occurrence of such smart phase transitions is observed in other perovskite-type oxides, SrRuO_3 and SrHfO_3 . Another type of phase transition occurs by the cooperative ionic displacements along the [100] direction in BaTiO_3 . The differences in the local chemical bond are discussed between the two types of phase transitions.

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1. Introduction

The perovskite-type oxides possess a wide variety of chemical and physical properties such as superconductivity, ferroelectricity, pyroelectricity and proton conductivity.¹⁾ In most perovskite-type oxides phase transition takes place at a certain temperature. For example, four polymorphous phases appear in SrZrO_3 , depending on temperatures.^{2,3)} The sequence of the phase transitions is expressed as,

Here, space groups and transition temperatures are given in parentheses.

It is known that these phase transitions occur mainly by the successive tilting or rotation of ZrO_6 octahedra around the three O-Zr-O crystal axes,^{4,5)} as shown in Fig. 1(a). Such tilting-type phase transitions have been observed in many oxides, and extensive experiments have been performed for the crystal structure determination. However, despite great efforts, as yet any consistent explanation has not given for the appearance of the tilting-type phase transitions in the perovskite oxides.

On the other hand, in BaTiO_3 , as shown in Fig. 1(b), there is another type of phase transition characteristic mainly of the

cooperative displacements of both Ti and O ions along the [100] direction, being very different from the tilting-type phase transition. The structural stability was treated following the total energy calculations.^{6,7)} Also, the transition temperature was calculated using the molecular dynamics and the Monte-Carlo simulations.^{8,9)}

In this study, the electronic structures of SrZrO_3 , SrRuO_3 and SrHfO_3 are simulated by the DV- $X\alpha$ molecular orbital method in order to account for the characteristic features for the tilting-type phase transition in view of the nature of the chemical bond between ions. Further, the electronic structure of BaTiO_3 is simulated together with that of CaTiO_3 and SrTiO_3 , in order to compare between the displacement-type and tilting-type phase transitions on the same ground of electron theory.

2. Calculation

2.1 DV- $X\alpha$ cluster method

The DV- $X\alpha$ cluster method is a molecular orbital method, assuming a Hartree-Fock-Slater (HFS) approximation. In this method, the exchange-correlation between electrons is given by the Slater's $X\alpha$ potential, and the self-consistent charge approximation is used in this calculation. The matrix elements of Hamiltonian and the overlap integrals are calculated by a random sampling method. Further detailed explanation of the calculation method is given elsewhere.^{10,11)}

For a characterization of chemical bonding between ions, the ionicity of each element and the bond order between ions in the cluster are estimated following the Mulliken population analysis. Here, the ionicity is a measure of the ionic interaction and the bond order is a measure of the covalent interaction between ions.

2.2 Cluster models

The cluster models used in the calculation of SrZrO_3 are constructed on the basis of the crystal structures at room temperature (R.T.), 1033 K, 1173 K, 1473 K and 2273 K.^{4,5)} For example, the cluster models for the cubic phase at 1473 K

Fig. 1 Schematic illustration of (a) tilting-type and (b) displacement-type phase transitions.

Fig. 2 Cluster models used in the calculation for (a) the cubic phase of SrZrO_3 at 1473 K, (b) the orthorhombic phase of SrZrO_3 at R.T. and (c) the tetragonal phase of BaTiO_3 at 350 K.

Fig. 3 Distribution of the interionic distances in polymorphous phases of SrZrO_3 .

and for the orthorhombic phase at R.T. are shown in Figs. 2(a) and (b), respectively. For comparison, another calculation is performed using a hypothetical cubic cluster with a shorter Zr-O interionic distance than the experimental value in the cubic phase. In order to take account of the Madelung potential between ions, the space with the size of about $8 \times 8 \times 8 \text{ nm}^3$ is set around the cluster and point charges are arranged at the position of each ion inside this space.

Similar cluster models are employed in the calculations for SrRuO_3 ¹²⁻¹⁴⁾ and SrHfO_3 ,¹⁵⁾ while changing only the crystal data and ionic species. This is also the case for CaTiO_3 ¹⁶⁾ and SrTiO_3 .¹⁷⁾ For BaTiO_3 , the electronic structures of the cubic phase at 474 K and the tetragonal phase at 350 K are simulated using the lattice parameter measured at each temperature.^{18,19)} The cluster model for the cubic phase is similar to the one shown in Fig. 2(a), but the model used for the tetragonal phase is constructed as shown in Fig. 2(c).

3. Interionic Distances in Polymorphous Phases in SrZrO_3

Before showing the calculated results, some characteristics of the interionic distances in polymorphous phases are described briefly using the crystal data of SrZrO_3 .^{4,5)}

Both the Sr-O and the Zr-O interionic distances in SrZrO_3 are distributed in each polymorphous phase as shown in

Fig. 3. There is a remarkably wide distribution in the Sr-O interionic distances especially at lower temperatures. However, their average distances do not change significantly with crystal structures. On the other hand, there is a very narrow distribution in the Zr-O interionic distances, irrespective of temperatures. As shown in Fig. 4, the average Sr-O interionic distances tend to increase with increasing temperature, but the average Zr-O interionic distances show a minimum at about 1443 K. The minimum distance is about 0.2074 nm, which is comparable to the shortest Zr-O distance, 0.2054 nm, in pure ZrO_2 . Below 1443 K, the average Zr-O interionic distance increases with decreasing temperature, while accompanying phase transitions by the tilting of ZrO_6 octahedra. This is an unusual temperature dependence of interionic distances.

It is stressed here that these modifications of the interionic distances with phase transitions are not peculiar to SrZrO_3 , but common to other tilting-type perovskite oxides, SrRuO_3 and SrHfO_3 .

4. Results

4.1 SrZrO_3

The effective ionicity of elements and the average bond order between ions in four polymorphous phases are shown in Figs. 5(a) and (b), respectively. As shown in (a), the

Fig. 4 Change in the average interionic distances in SrZrO_3 with temperature.

Fig. 5 (a) Ionicities and (b) bond orders between ions in four polymorphous phases of SrZrO_3 .

effective ionicity of each element is nearly constant despite the occurrence of the phase transitions in the range of R.T. to 1473 K. Also, the average bond orders between ions do not show any large dependence on the crystal structure, as shown in (b). Needless to say, the Zr-4d - O-2p hybridization is most important in the components of the bond order. From these results, it is evident that the average chemical interactions between ions are scarcely modified by the phase transition.

For the cubic phase existing stably at high temperatures, both the ionicity and the bond order between ions are calculated as a function of the lattice parameter and the results are shown in Figs. 6(a) and (b). Here, a hypothetical cubic phase is assumed to exist at room temperature, R.T. (cubic), while having a lattice parameter which is extrapo-

Fig. 6 Changes in (a) the ionicities and (b) the bond orders between ions with the lattice parameter of the cubic phase.

lated simply from high temperature to room temperature. As shown in Fig. 6(a), the ionicity of each element is almost constant. Also, as shown in Fig. 6(b), both the Zr-Sr and the Sr-O bond orders exhibit the less dependence on the lattice parameter. On the contrary, only the Zr-O bond order decreases significantly with decreasing lattice parameter, and hence with decreasing Zr-O interionic distance. Thus, it is apparent that the decreasing Zr-O interionic distance leads to the weakening of the covalent bond strength between Zr and O ions in the cubic phase. Also, as explained in Fig. 4, the minimum Zr-O distance in the cubic phase at 1443 K is close to the shortest Zr-O distance in pure ZrO_2 , so that the phase transition (*i.e.*, the tilting of the ZrO_6 octahedra) seems to occur around 1443 K so as to increase the Zr-O interionic distance and to retain the covalent bond strength between Zr and O ions. In fact, as shown in Fig. 7, the Zr-O bond orders are recovered by tilting (or rotation) at each transition temperature. Unless such a tilting does take place, the Zr-O chemical bond will become very weak as shown in Fig. 6(b).

On the other hand, from both the results of the ionicity and the bond order shown in Fig. 5, it is expected that the Sr-O chemical interaction is weaker than the Zr-O chemical interaction. So, the Sr-O bond probably acts as a buffer when the ZrO_6 octahedra are tilted, and the Sr-O interionic distances change variously as shown in Fig. 3(a). However, as shown in Fig. 8, it is noted that the Sr-O bond orders do not decrease rapidly, but decrease linearly with their distances. Recalling that the average Sr-O interionic distance does not show any large dependence on the crystal structure, we may say that the average Sr-O bond order is approximately same

Fig. 7 Modifications of the Zr-O interionic distances due to the phase transitions at certain temperatures in SrZrO_3 . Each number placed near solid circle is the value of the Zr-O bond order.

Fig. 8 Relationship between the Sr-O interionic distance and the bond order in polymorphous phase.

among the four polymorphous phases, as shown in Fig. 5(b). In addition, judging from the ionicity of Sr shown in Fig. 5(a), the Sr-O chemical interaction may be rather ionic in this oxide. But even the ionic interaction seems to be nearly same among the four polymorphous phases according to our estimation of the Coulomb interaction between them. Thus, the phase transitions occur in a smart way so as to retain not only the Zr-O bond strength but also the Sr-O bond strength in SrZrO_3 .

4.2 SrRuO_3

In SrRuO_3 the phase transition occurs at about 950 K from cubic to tetragonal phases, and at about 820 K from tetragonal to orthorhombic phases.¹²⁾ The minimum Ru-O interionic distance, 0.1975 nm, in cubic SrRuO_3 is comparable to the shortest Ru-O interionic distance, 0.1943 nm in RuO_2 .

Similar results are obtained in SrRuO_3 , as shown in Fig. 9(a) for the ionicity and (b) for the bond order. As is evident from Fig. 9(a), the average ionicities of elements in this oxide are nearly independent of the crystal structures. Also, as shown in Fig. 9(b), both the average Ru-O bond order and the average Sr-O bond order scarcely change with the successive phase transition, even though there is the small scattering in

Fig. 9 (a) Ionicities and (b) bond orders between ions in four polymorphous phases of SrRuO_3 .

the average Ru-O bond order. Such a scattering is also seen in SrZrO_3 shown in Fig. 5. The convergences of the electronic structure calculations are, however, good even in the most scattered one. So, the reason for the small scattering may not be attributable to the poor calculation, but to the high sensitivity of the bond order value to the bond lengths between ions which are determined from diffraction experiments in the wide temperature range and used for the present calculation. Also, as shown in Fig. 10, there is a recovery of the Ru-O bond order by the tilting of RuO_6 octahedra in SrRuO_3 , as is found similarly in SrZrO_3 . The magnitude of each bond order is, however, larger in SrRuO_3 than in SrZrO_3 .

4.3 SrHfO_3

The successive phase transitions take place in SrHfO_3 as follows.¹⁵⁾

The transition temperatures shown in parentheses still remain uncertain.

The minimum Hf-O interionic distance, 0.2057 nm, at about 1400 K in cubic SrHfO_3 is comparable to the shortest Hf-O interionic distance, 0.2036 nm in HfO_2 .

Similarly to SrZrO_3 and SrRuO_3 , the average bond order and the average ionicity scarcely change with the phase transitions in SrHfO_3 . As shown in Fig. 11, the tilting of HfO_6 octahedra occurs at each transition temperature so as to retain the average Hf-O bond order as possible, although the

Fig. 10 Modifications of the Ru-O interionic distances due to the phase transitions at certain temperatures in SrRuO_3 . Each number placed near solid circle is the value of the Ru-O bond order.

magnitude of the bond order is weaker in SrHfO_3 than in SrZrO_3 and SrRuO_3 .

Thus, there are common characteristics of the nature of the chemical bond between ions in the perovskite oxides, SrBO_3 ($\text{B}=\text{Zr}, \text{Ru}, \text{Hf}$), all of which transform by the tilting of BO_6 octahedra.

5. Discussion

In BaTiO_3 the displacement-type transition occurs at about 403 K. Discussed here is the problem of what is a chemical bonding factor to distinguish between the tilting-type and displacement-type phase transitions in the perovskite-type oxides, ABO_3 . For this purpose, electronic structures are simulated for ATiO_3 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$), where the tilting-type transition occurs in CaTiO_3 and SrTiO_3 , as is contrasted to the displacement-type transition in BaTiO_3 .

5.1 Interionic distances in ATiO_3 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$)

First, the average ionic distances, A-O and Ti-O, in ATiO_3 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$), are compared with the respective ones in pure oxides, AO and TiO_2 . Because, it is supposed here that the chemical bond nature in ATiO_3 inherits more or less from the chemical bonding in AO and TiO_2 .

As shown in Fig. 12, the average Ca-O interionic distance in CaTiO_3 is much longer than that in CaO, but the average Ti-O interionic distance in CaTiO_3 is very slightly shorter than that in TiO_2 . This is also the case in SrTiO_3 . Such a trend is seen not only in these oxides, but also in other tilting-type oxides, SrZrO_3 , SrRuO_3 and SrHfO_3 .

On the other hand, in case of BaTiO_3 , the average Ba-O interionic distance is longer than that in BaO, but the increment is much smaller in the Ba-O compared to the Ca-O or the Sr-O. More important is the average Ti-O interionic distance in BaTiO_3 , which is significantly longer than that in TiO_2 . In this respect BaTiO_3 is in great contrast to the other tilting-type oxides. Such an increment in the average Ti-O interionic distance may allow a TiO_6 octahedron to keep a large space in BaTiO_3 . In other words, the tilting so as to increase the Ti-O interionic distance may not necessitate in BaTiO_3 .

Fig. 11 Modifications of the Hf-O interionic distances due to the phase transitions at certain temperatures in SrHfO_3 . Each number placed near solid circle is the value of the Hf-O bond order.

5.2 Chemical bond strength

Such differences in the interionic distances influence the ionicities and the bond orders as shown in Figs. 13(a) and (b). They are calculated for cubic ATiO_3 ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$), by using the experimentally determined lattice parameters for each oxide in the cubic state.¹⁶⁻¹⁸⁾ For comparison, the calculated results of tetragonal BaTiO_3 at 350 K are included in Fig. 13.

As shown in Fig. 13(b), the A-O bond order is smallest and the Ti-O bond order is largest in BaTiO_3 among three cubic oxides. Also, as shown in Fig. 13(a), the ionicity of each element in BaTiO_3 is comparable to or even smaller than that in CaTiO_3 and SrTiO_3 . Judging from such an ionic character and also longer interionic distances shown in Fig. 12, the Ba-O bond may be weaker than the Sr-O or the Ca-O bond. Thus, the presence of the stronger Ti-O bond and weaker Ba-O bond is characteristic of BaTiO_3 . In particular, the Ti-3d - O-2p covalent bond is strong in BaTiO_3 , in agreement with the previous calculation.^{6,7)}

In case of tetragonal BaTiO_3 the Ti-O bond order is strengthened for a longer pair and weakened for a shorter pair. But still the average Ti-O bond order scarcely changes with

Fig. 12 Comparison of the average interionic distances between AO, TiO_2 and ATiO_3 ($\text{A}=\text{Ca}, \text{Sr}$ and Ba).

Fig. 13 (a) Ionicity of elements and (b) the bond order for cubic ATiO_3 ($\text{A}=\text{Ca}$, Sr and Ba). The results for tetragonal BaTiO_3 are also indicated by small symbols to show an average value and also by error bars to show a distribution range of respective values.

the phase transition, as shown in Fig. 13(b). The average ionicity of each element also remains nearly unchanged as shown in Fig. 13(a). It is supposed that the Ba-O bond may not play a significant role in this phase transition, because its bond strength may be too weak to modify the Ti-O bond character, as explained before. Therefore, the cooperative displacements of Ti and O ions along the $[100]$ direction in the tetragonal phase may be attributable to the presence of strong Ti-O chemical bond in the oxide. In some oxides, for example, in ZrO_2 , the transition from cubic to tetragonal phases occurs by the cooperative displacements of oxygen ions along the $[100]$ direction.^{20–22} This phase transition is very similar to the one observed in BaTiO_3 , although both oxygen and titanium ions moves in the $[100]$ direction in BaTiO_3 .

6. Conclusion

Some characteristics of the phase transition in the perovskite-type oxides are investigated using the DV- $X\alpha$ molecular orbital method.

It is shown that the phase transition occurs in SrZrO_3 by the successive tilting of the ZrO_6 octahedra so as to retain the Zr-O bond strength as possible. The weak Sr-O bond acts as a buffer for the adjustment in both the chemical bond and crystal geometry. As the result, the Sr-O bond lengths are inevitably distributed over a wide range, but still the average

Sr-O bond strength appears to remain unchanged with the phase transitions. This trend is also seen in SrRuO_3 and SrHfO_3 .

On the other hand, in BaTiO_3 , the cubic to tetragonal phase transition is characteristic of the cooperative ionic displacements along the $[100]$ direction. This transition is probably attributable to the presence of strong Ti-O covalent bond owing to a relatively long Ti-O interionic distance. Thus, either phase transition can be understood qualitatively in the light of the nature of the chemical bond in perovskite-type oxides.

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