Band Structures of Molecules and Solids
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1. Introduction

A crystal of metal oxide can be considered to be formed as a result of polycondensation of the corresponding aquo complex of the metal. A variety of crystal structures are formed through various types of polycondensation. These metal oxide crystals have been used for functional materials, such as insulating material (Al_2O_3), photocatalyst (TiO_2), transparent electrode (SnO_2, In_2O_3), electrochromic display material (WO_3), photoconductor (ZnO), oxygen ion conductor (ZrO_2), using their variety of electronic property based on their crystal structures.

In this research, the relation between metal elements and the crystal and electronic structures of their oxides was studied using tight binding method.

2. Crystal structures for metal oxides

Crystal structures of metal oxides are classified using the oxidation numbers z and coordination numbers n of the metal ions, as shown in Table 1.

Because oxygen ions in metal oxides are usually much larger in size than metal ions, they by themselves tend to form a close-packed structure such as cubic or hexagonal close-packed structure. The close-packed structures possess octa- and tetrahedral interstices, whereas simple cubic structure possesses hexahedral interstices.

Table 1. Classification of metal oxides

z	n	crystal st.	metal ion
1	2	cuprite	I B (noble m.)
	4	antifluorite	I A (alkaline m.)
2	4	wurtzite	II B (Zn)
	6	rocksalt	II A (alkaline earth m.), [trans. m.]
3	6	corundum	III B(Al, Ga), [trans. m.]
	6	rare earth	III A (rare earth m.), III B (In, Tl)
4	6	rutile	IV B (Ge, Sn) , [trans. m.]
	8	fluorite	IV A (Zr, Hf)
6	6	ReO$_3$	(Re, W)

Metal ion having a coordination number of 4 is to enter into tetrahedral interstice, that with a number of 6 into octahedral one and that with 8 into hexahedral one. These metal ions, as well as the oxygen ions, compose a lattice structure because they enter into interstices of the oxygen lattice regularly. Table 2 shows the crystal structures of metal oxides classified according to the lattice structure of oxygen ions and that of metal ions.

Table 2. Oxygen lattice and metal lattice

oxygen lattice	crystal structure	n	element	metal lattice
bcc	cuprite	2	I B	ccp
hcp	wurtzite	4	II B	hcp
	corundum	6	III B	honeycomb layers
	rutile	6	IV B	bc tetragonal
ccp	antifluorite	4	I A	cubic
	ReO$_3$	6		cubic
	rocksalt	6	II A	ccp
cubic	rare earth	6	III A	ccp
	fluorite	8	IV A	ccp

3. Band structure of metal oxides

Rock salt and rhenium oxide structures have a symmetry for x, y and z directions, where each metal ion has a coordination number of 6. Both of them have linear chains along each direction composed of alternative bonds with oxygen and metal ions. Each metal ion in the crystals makes six bonds with its nearest neighbor oxygen ions. We suppose here the bond between metal ion and oxygen ion is formed only by the interaction between $|s>$ (s-type orbital of metal ion) and $|p_j^i>$ (p_j^i denotes p_j type orbital of the oxygen located at the neighbor site in i-direction).

The Hamiltonian for the crystal structure is expressed as a matrix in Eq. (1) with the Bloch functions $|k, s>$, $|k, p_x^x>$, $|k, p_y^y>$, $|k, p_z^z>$, which are linear combinations of each atomic orbitals, $|l, s>$, $|l, p_x^x>$, $|l, p_y^y>$, $|l, p_z^z>$, respectively,

$$\hat{H} \sim \begin{array}{l} \langle s, k| \\ \langle p_x^x, k| \\ \langle p_y^y, k| \\ \langle p_z^z, k| \end{array} \begin{pmatrix} \varepsilon_s^M & H_{sx} & H_{sy} & H_{sz} \\ H_{sx}^* & \varepsilon_p^O & & \\ H_{sy}^* & & \varepsilon_p^O & \\ H_{sz}^* & & & \varepsilon_p^O \end{pmatrix} \quad (1)$$

Along k_x axis ($k_y = k_z = 0$), the matrix element H_{sx} can be reduced to

$$H_{sx} = 2i\beta \sin(k_x a/2) \quad (2)$$

and the other non-diagonal elements become zero. Here, we define μ and γ as

$$\mu \equiv (\varepsilon_s^M + \varepsilon_p^O)/2, \quad \gamma \equiv (\varepsilon_s^M - \varepsilon_p^O)/2, \quad (3)$$

then, the eigenvalue $\varepsilon(k_x)$ for matrix (1) is easily obtained as follows:

$$\varepsilon(k_x) = \mu \pm \sqrt{\gamma^2 + \left(2\beta\sin\left(k_x a / 2\right)\right)^2} . \qquad (4)$$

The energy band along k_y and k_z axis is the same in shape as that along k_x axis. The positive branch of Eq. (4) corresponds to the conduction band and the negative to the valence band. The closest point for both bands locates at Γ point ($k = 0$), where the energy difference ε_g between these two bands becomes

$$\varepsilon_g = 2\gamma, \qquad (5)$$

as obtained from Eq. (4). The calculated (ε_g) and experimental (E_g) values for each metal oxide were tablated in Table 3.

Elements in II A and II B column of the periodic table form the rocksalt type metal oxides. For II A elements, the calculated values ε_g were found in good agreement with the experimental values E_g reported in references. For II B elements, the agreement were not good, probably due to their d-orbital effect.

The electronic structure for A-group metal cation (I-IV A) is the rare gas configuration $((n-1)s)^2 ((n-1)p)^6$, having ns orbital as the lowest unoccupied atomic orbital (LUAO) which composes the conduction band in metal oxide crystal. The valence band of metal oxide is mainly composed of 2p orbital of oxygen. Therefore, the band gap can be expressed as $\varepsilon_g = \varepsilon_s^M - \varepsilon_p^O$, as shown in Eq. (5).

The electronic structure for B-group metal cation (I-IV B) is the pseudo-rare gas configuration $((n-1)s)^2 ((n-1)p)^6 ((n-1)d)^{10}$. In this case, the LUAO of the cation is ns orbital and the highest occupied atomic orbital (HOAO) is $(n-1)d$ orbital of the metal, not 2p orbital of oxygen. Therefore, the approximation in Eq. (1) was inadequate for B group metals, resulting the disagreement with experiment values in Table 3.

Elements in V-VII A and VIII are transition metal. Both LUAO and HOAO of these cations are $(n-1)d$ orbitals and the approximation in Eq. (1) is not adequate for these metal oxides.

4. Conclusion

It was found that A-group metal oxides have a oxygen lattice of ccp or cubic structure and B-group metal oxides have that of bcc or hcp structure. The band gap for metal oxides having rocksalt and ReO$_3$ structures was found to be expressed as $\varepsilon_g = \varepsilon_s^M - \varepsilon_p^O$.

Table 3 Band gap of metal oxides

0	I A	II A	III A	IV A	V A	VI A	VII A	VIII			I B	II B	III B	IV B	V B	VI B	VII B
-9.1	8.7	6.0	ε_g /eV = 2γ/eV (E_g /eV (experimental values))								1.6	-3.4	-8.9	0	-21		
-29	9.0	7.3 (7.7)									4.0 (8.4)	-0.6	-3.0	-6.7	-10		
-28	10	8.7 (7)	4.8	3.0	1.6	0.2	-1.1	-2.4	-3.6	-4.8 (4)	-6.0 (1.5)	5.7 (3.4)	2.8 (4.6)	-0.2	-3.2	-6.2	-9.2
-12	10	9.0	7.3	5.7	4.0	2.6	1.1	-0.4	-2.0	-3.5	-5.1	6.4 (2.1)	4.0 (2.5)	1.6 (3.6)	-0.7	-3.0	-5.3
-7.7	10	9.7	7.5	6.0	.6	/////	/////	0.4	-1.0	-2.4	-2.8	6.5	4.2	2.0 (2.8)	0 (2.8)	-2.1	-4.1
-18	10	9.9	9.5														

Reference

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2. Bodie E. Douglas, Darl H. McDaniel, John J. Alexander, *Concepts and Models of Inorganic Chemistry*, 3rd edition, John Wiley & Sons, Inc., 1995