Evaluation of Bond Covalency and Bond Valence in Sr-Doped Perovskite-Type Compounds

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Formulas for decomposing of complex crystals to a sum of binary crystals are described and applied to the study of bond covalency in $La_{1-x}Sr_xFeO_3$ ($0.0 \leq x \leq 0.9$) and $Ca_{1-x}Sr_xMnO_3$ ($0.0 \leq x \leq 0.5$). The bond valence is treated by bond-valence sums scheme. The results indicate that, for both compounds, with the increasing doping level, the bond covalency and bond valence show the same trend, namely, larger bond covalency corresponds to higher bond valence. For $La_{1-x}Sr_xFeO_3$, with the increase of doping level, the bond covalency of La–O, Ca–O decreases in the orthorhombic ($0.0 \leq x \leq 0.2$) and rhombohedral ($0.4 \leq x \leq 0.7$) systems, then increases slightly for the cubic ($0.8 \leq x \leq 0.9$) system, but that of Fe–O increases for all crystal systems. A sharp decrease in bond covalency was observed where the crystal changes from orthorhombic to rhombohedral, while a smooth trend was seen for the rhombohedral-to-cubic transition. On the other hand, for orthorhombic $Ca_{1-x}Sr_xMnO_3$, the bond covalency of Ca–O, Sr–O, and Mn–O (4-coordinate site) decreases with the increasing doping level, that of Mn–O (2-coordinate site) increases.

1. Introduction. – The study of chemical bond properties has long been considered very important toward explaining and classifying many basic properties in diverse areas including chemistry and condensed-matter physics [1–7]. Reviews concerning bond covalency and its application have been published by *Phillips* [1][2], *Van Vechten* [3], *Levine* [4][5], and *Tanaka* [6]. It is known that *PV* (*Phillips-Van Vechten*) [1–3] theory can only be applied to the binary crystals, especially $A^N B^{8-N}$ type. On the other hand, although theory which can deal with complex crystals has been developed by *Levine* [4][5] and *Tanaka* [6], an explicit expression for decomposition of complex multiple-bond crystals into binary crystals was not given. Recently, we [8–12] extended the *Phillips-Van Vechten-Levine-Tanaka* (*PVLT*) theory for application to multiple-bond systems. Combining this method with the previous theory, the chemical-bond parameters of any complex crystals can be treated. In this paper, the bond covalency of the Sr-doped perovskite-type compounds $La_{1-x}Sr_xFeO_3$ ($0.0 \leq x \leq 0.9$) and $Ca_{1-x}Sr_xMnO_3$ ($0.0 \leq x \leq 0.5$) has been studied. In $La_{1-x}Sr_xFeO_3$, with increasing doping level, the crystal system changes from orthorhombic for $0.0 \leq x \leq 0.2$, to rhombohedral for $0.4 \leq x \leq 0.7$ to cubic for $0.8 \leq x \leq 0.9$. On the other hand, for all doping levels considered, $Ca_{1-x}Sr_xMnO_3$ ($0.0 \leq x \leq 0.5$) remains orthorhombic.

2. Theoretical Method. – Denoting cations with A and anions with B, any multibond complex crystal can be written as $A^1_{a1}A^2_{a2}\cdots A^i_{ai}\cdot B^1_{b1}B^2_{b2}\cdots B^j_{bj}$, where A^i and B^j represent different elements or different sites of a given element of cations and anions, respectively, and ai, bj represent the number of the corresponding elements. Aided by crystallographic data, the formula can be decomposed into a sum of binary crystals according to the following equations.

$$A^1_{a1}A^2_{a2}\cdots A^i_{ai}\cdots B^1_{b1}B^2_{b2}\cdots B^j_{bj}=\sum_{i,j} A^i_{mi}B^j_{nj} \tag{1}$$

$$mi=N(B^j-A^i)ai/N_{CAi} \quad \text{and} \quad nj=N(A^i-B^j)\,bj/N_{CBj} \tag{2}$$

Where N_{CAi} and N_{CBj} represent the nearest total coordination numbers of A^i and B^j ions in the crystal, $N(B^j-A^i)$ represents the nearest coordination number contributed by the A^i ion, and $N(A^i-B^j)$ represents the nearest coordination number contributed by the B^j ion. After decomposing the complex crystal into the sum of different kinds of isotropic binary crystals, which are isotropic system, *PVLT* [1–6] theory can be applied to estimate chemical bond parameters in complex crystals.

According to *Philips-Van Vechten-Levine* (*PVL*) [1–5] theory, the macroscopic linear susceptibility χ (long-wavelength index of refraction) can be resolved into contributions χ^μ from the various types of bonds or from the various binary crystals, and can be obtained by the following equation

$$\chi=\sum_\mu F^\mu\chi^\mu=\sum_\mu N^\mu_b\chi^\mu_b \tag{3}$$

where χ^μ is the total macroscopic susceptibility of bond type μ, F^μ is the fraction of bonds of type μ composing the actual complex crystal, χ^μ_b is the susceptibility of a single bond of type μ, and N^μ_b is the number of bonds per cubic centimeter. According to *PVL* theory, χ^μ_b can be written as

$$\chi^\mu_b=(4\pi)^{-1}\,[(h\Omega^\mu_p)^2/(2\pi E^\mu_g)^2] \tag{4}$$

where E^μ_g is the average energy gap for the type-μ bond. Ω^μ_p is the plasma frequency obtained from the number of valence electrons of type μ per cubic centimeter N^μ_e, using

$$(h\Omega^\mu_p)^2=(4\pi N^\mu_e\, e^2/m)\,D^\mu\,A^\mu \tag{5}$$

where D^μ and A^μ are the correction factors of order unity defined in [3]. The average energy gap E^μ_g appearing in *Eqn. 4* for every type of μ bond can be separated into homopolar E^μ_h and heteropolar C^μ parts as follows

$$(E^\mu_g)^2=(E^\mu_h)^2+(C^\mu)^2 \tag{6}$$

The bond ionicity f^μ_i and bond covalency f^μ_c of any type of μ bond are defined as follows

$$f^\mu_i=(C^\mu)^2/(E^\mu_g)^2$$

$$f^\mu_c=(E^\mu_h)^2/(E^\mu_g)^2 \tag{7}$$

where

$$E^\mu_h=39.74/(d^\mu)^{2.48} \tag{8}$$

For any binary crystal with $A^i_{mi}B^j_{nj}$ type, the heteropolar C^μ part is given as

$$C^\mu=14.4b^\mu\exp(-\kappa^\mu_s\,r^\mu_0)[(Z^\mu_\alpha/r^\mu_0)-(nj/mi)\,(Z^\mu_\beta/r^\mu_0)],\ \text{if } nj>mi \tag{9a}$$

$$C^\mu=14.4b^\mu\exp(-\kappa^\mu_s\,r^\mu_0)[(mi/nj)(Z^\mu_\alpha/r^\mu_0)-(Z^\mu_\beta/r^\mu_0)],\ \text{if } mi>nj \tag{9b}$$

where

$$\kappa_s^\mu = (4\kappa_F^\mu/\pi a_B)^{1/2}$$
$$\kappa_F^\mu = (3\pi^2\, N_e^\mu)^{1/3} \tag{10}$$
$$r_0^\mu = d^\mu/2$$

a_B is the *Bohr* radius and d^μ is the bond distance. Correction factor b^μ is proportional to the square of the average coordination number N_c^μ:

$$\begin{gathered} b^\mu = \beta \langle N_c^\mu \rangle^2 \\ \langle N_c^\mu \rangle = [mi/(mi+nj)]N_{\mathrm{CA}i} + [nj/(mi+nj)]N_{\mathrm{CB}j} \end{gathered} \tag{11}$$

β is 0.089 [4]. N_e^μ is expressed as follows

$$N_e^\mu = n_e^\mu / v_b^\mu \tag{12}$$

$$n_e^\mu = Z_A^\mu / N_{\mathrm{CA}i}^\mu + Z_B^\mu / N_{\mathrm{CB}j}^\mu \tag{13}$$

where n_e^μ is the number of valence electrons per μ bond, v_b^μ is the bond volume, and Z_A^μ, Z_B^μ are the numbers of valence electrons of A and B atoms, respectively. When atoms, usually cations, have d and f electrons, the number of valence electrons Z_A^μ should be replaced by an effective value $(Z_A^\mu)^*$, which is usually the sum of s, p, d, and f electrons as suggested by *Tanaka* [6]. Since the nearest-neighbor bond distance d^μ is expected to be proportional to the bond volume $[v_b^\mu \propto (d^\mu)^3]$, we can write

$$v_b^\mu = (d^\mu)^3 / \sum_\nu \,[(d^\nu)^3\, N_b^\nu] \tag{14}$$

For complex crystals which are usually anisotropic systems, the coordination number $N_{\mathrm{CA}i}^\mu$ in *Eqn. 13* should be written as

$$N_{\mathrm{CA}i}^\mu = V_i / s_i^\mu \tag{15}$$

V_i is the oxidation state of atom A_i, and s_i^μ is the bond valence of μ bond associated with atom *i*.

In light of bond-valence sums (*BVS*) [13–15], V_i and s_i^μ can be written as

$$V_i = \sum_\mu s_i^\mu \tag{16}$$

$$s_i^\mu = \exp[(R_i^\mu - d_i^\mu)/b] \tag{17}$$

where R_i^μ is the bond valence parameter, d_i^μ is the bond distance, and b is equal to 0.37.

3. Results and Discussion. – According to crystallographic data [16][17] and the presented theoretical method, $La_{1-x}Sr_xFeO_3$ $(0.0 \leq x \leq 0.9)$ [16] and $Ca_{1-x}Sr_xMnO_3$ $(0.0 \leq x \leq 0.5)$ [17], having the general formula $A_{1-x}Sr_xBO_3$, can be decomposed into the following sum of binary crystals (*Eqn. 18*):

$$\begin{aligned}A_{1-x}Sr_xBO_3 = A_{1-x}(1)Sr_x(1)B(1)O(1)O_2(2)\\ = A_{(1-x)/3}O(1)_{2(1-x)/3} + A_{2(1-x)/3}O(2)_{4(1-x)/3}\\ + Sr_{x/3}O(1)_{2x/3} + Sr_{2x/3}O(2)_{4x/3}\\ + B_{1/3}O(1)_{1/3} + B_{2/3}O(2)_{2/3}\end{aligned} \qquad (18)$$

Table 1. *Bond Covalencies* (B.C. [%]), *Bond Valences* (B.V. [valence units]), *and Oxidation States* (O.S.) *of Elements in* $La_{1-x}Sr_xFeO_3$. Note the three different crystal systems: orthorhombic for $0.0 \le x \le 0.2$, rhombohedral for $0.4 \le x \le 0.7$, and cubic for $0.8 \le x \le 0.9$.

x	0.0	0.1	0.2	0.4	0.5	0.6	0.7	0.8	0.9
B.C.									
La–O(1)	2.47	2.43	2.41	2.27	2.27	2.23	2.20	2.20	2.22
La–O(2)	2.43	2.38	2.31						
Sr–O(1)	–	5.37	5.33	5.09	5.09	5.02	4.98	4.98	5.01
Sr–O(2)	–	5.26	5.16						
Fe–O(1)	14.10	13.97	13.90	14.35	14.37	14.43	14.46	14.49	14.51
Fe–O(2)	14.22	14.35	14.45						
B.V.									
La–O(1)	0.2508	0.2436	0.2401	0.2245	0.2220	0.2204	0.2187	0.2195	0.2231
La–O(2)	0.2448	0.2385	0.2315						
Sr–O(1)	–	0.2106	0.2075	0.1940	0.1919	0.1905	0.1890	0.1897	0.1928
Sr–O(2)	–	0.2062	0.2001						
Fe–O(1)	0.5088	0.5157	0.5299	0.5762	0.5762	0.6033	0.6181	0.6265	0.6333
Fe–O(2)	0.5130	0.5327	0.5553						
O.S.									
La	2.96	2.88	2.81	2.69	2.66	2.65	2.62	2.63	2.68
Sr	–	2.49	2.43	2.33	2.30	2.29	2.27	2.28	2.31
Fe	3.07	3.16	3.28	3.46	3.46	3.62	3.71	3.76	3.80
O(1)	2.02	1.99	1.99	2.00	1.98	2.01	2.03	2.04	2.05
O(2)	2.01	2.01	2.01						

The calculated bond covalencies, bond valences, and oxidation states of elements are listed in *Table 1* for $La_{1-x}Sr_xFeO_3$ and in *Table 2* for $Ca_{1-x}Sr_xMnO_3$. The bond-valence parameters (R_i^μ in *Eqn. 17*) in the present study are taken from [13].

$La_{1-x}Sr_xFeO_3$. For this compound, three different crystallographic systems were found: orthorhombic for $0.0 \le x \le 0.2$, rhombohedral for $0.4 \le x \le 0.7$, and cubic for $0.8 \le x \le 1.0$ (the corresponding parameters are not calculted for $x = 1.0$ because of the lack of crystallographic data). In our calculation, with increasing doping level, in the orthorhombic system the bond covalency of La–O (including O(1) and O(2), similarly hereinafter), Sr–O, and Fe–O(1) decreases, but that of Fe–O(2) increases. In rhombohedral system, the same trend has been observed for La–O and Sr–O as in the orthorhombic system, but the bond covalency of Fe–O increases. When the crystal system changes from rhombohedral to cubic, the bond covalency of all considered types

Table 2. *Bond Covalencies* (B.C. [%]), *Bond Valences* (B.V. [valence unit]), *and Oxidation* States (O.S.) *of Elements in Orthorhombic* $Ca_{1-x}Sr_xMnO_3$

x	0.0	0.2	0.4	0.5
B.C.				
Ca–O(1)	5.55	5.04	4.77	4.71
Ca–O(2)	5.07	5.07	4.92	4.86
Sr–O(1)	–	4.92	4.67	4.61
Sr–O(2)	–	4.96	4.82	4.75
Mn–O(1)	15.36	15.62	16.03	16.07
Mn–O(2)	16.05	15.88	15.80	15.81
B.V.				
Ca–O(1)	0.2237	0.1885	0.1671	0.1606
Ca–O(2)	0.1963	0.1925	0.1740	0.1637
Sr–O(1)	–	0.1790	0.1587	0.1526
Sr–O(2)	–	0.1829	0.1653	0.1589
Mn–O(1)	0.6414	0.6578	0.6811	0.6811
Mn–O(2)	0.6713	0.6747	0.6702	0.6688
O.S.				
Ca	2.46	2.29	2.06	1.98
Sr	–	2.17	1.96	1.88
Mn	3.97	4.01	4.04	4.04
O(1)	2.18	2.06	2.02	1.99
O(2)	2.13	2.11	2.02	1.99

of bonds slightly increases. From *Table 1*, it can also be seen that when the structure changes from orthorhombic to rhombohedral, the change in bond covalency for all considered types of bonds is quite sharp, while there is a smoother transition in bond covalency for the rhombohedral-to-cubic transition. The trend in the calculated bond valences is similar to that of the bond covalencies. The oxidation state of O is apparently insensitive to the change of doping level, while that of La and Ca decreases, and that of Fe increases with the increasing doping level. The oxidation states of Fe obtained in this paper are slightly different from those of *Dann et al.* [16], because a slightly different bond-valence parameter for the Fe–O bond was used. It is known that the BVS scheme proposed by *Brown* [14][15] can be used to examine the internal stress and lattice distortions around each atom. That the bond-valence sum around La^{3+} is smaller than its apparent oxidation state +3.0, and that Sr^{2+} is larger than its apparent state +2.0, indicate that the La ion is under tension and the Sr ion is under compression. The stress can be partially relieved by twisting of the cubic cage FeO_3.

$Ca_{1-x}Sr_xMnO_3$. From *Table 2*, it is seen that, with increasing doping level, the bond covalency of Ca–O, Sr–O and Mn–O(2) decreases, while that of Mn–O(1) increases. The trend in calculated bond valences parallels in regularity that of the bond covalencies with the exception of the Mn–O(2) bond at $x = 0.2$. The oxidation states of Ca, Sr, O(1), and O(2) decrease with the increasing doping level, those of Ca and Sr more dramatically than those of O(1) and O(2). The oxidation state of Mn remains relatively unchanged. According to BVS, for $x = 0.0$, 0.2, the Ca and Sr ions are under compression; for $x = 0.5$, both are under tension; while for $x = 0.4$, Ca is under compression but Sr is under tension.

In summary, both compounds show that, with the increasing doping level, the bond valence and bond covalency follow the same trend. This supports the viewpoint that bond valence measures not only the number of electrons associated with a bond, but also the degree of covalency [14]. Where the crystal-system transition occurs, a change is seen in the bond covalency, most notably the sharp decrease upon transition from the orthorhombic to the rhombohedral system.

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