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Chemical bond properties of rare earth ions in crystals

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Abstract

By using the dielectric description theory of ionicity of solids, chemical bond properties of rare earth ions with various ligands are studied. Calculated results show that chemical bond properties of the same rare earth ion and the same ligand in different crystals depend on the crystal structures. In a series of compounds, chemical bond properties of crystals containing different rare earth ions are similar. The magnitude of covalency of chemical bonds of trivalent rare earth ions and various ligands has an order like F<Cl<Br<As<Sb. © 1998 Elsevier Science S.A.

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1. Introduction

Chemical bond properties between rare earth ions and ligands in crystals have been paid great attention for a long time. Researches were carried out extensively from various angles but, up to now, the clear concept of quantity on chemical bond of rare earth ions cannot given. In solid physics, the dielectric description of ionicity developed by Phillips and Van Vechten (PV) has been successfully employed in various fields [1,2], this theory provides us a simple and clear scale for chemical bond in crystals, but it has been limited only to the simple $A^N B^{8-N}$ compounds. Levine generalized PV theory to $A_n B_m$-type compounds [3]. In recent years, we have systematically given a theoretical method for the chemical bonding of crystals with complex structures [4]; researches on chemical bonding of rare earth ions and their ligands in crystals therefore become realizable. In this paper, using the above methods, chemical bond behaviors of rare earth ions in rare earth oxysulfides, rare earth oxyhalides and other crystals, are studied and discussed.

2. Theoretical method

In order to solve the problems of chemical bonding of complex crystals, we must separate a multibond crystal into single-bond structure crystals, and thus the problem is converted into separating the crystal formula into bond subformulae. The relation between the crystal formula and all of its constituent bond subformulae can be expressed as the subformula equation (bond-valence equation) [4], which shows that the crystal formula is a linear combination of all types of constituent bond subformula. The subformula of any kind of chemical bond A–B in a multibond crystal $A_a B_b D_d G_g \ldots$ can be acquired by the following formula

$$[N(B-A)\cdot a/N_{CA}]A[N(A-B)\cdot b/N_{CB}]B = [N(B-A)\cdot a/N_{CA}][AB_n] \qquad (1)$$

$$n = [N(A-B)\cdot b/N_{CB}]/[N(B-A)\cdot a/N_{CA}] \qquad (2)$$

In the formula, A, B, D, G, etc., represent different elements or different sites of the same element in the crystal formula, and $a, b, d, g, \ldots$ represent the numbers of the corresponding element, $N(I-J)$ represents the number of I ions in the coordination group of a J ion, and $N_{CA}, N_{CB}, \ldots$ represent the nearest coordination numbers of elements A and B in the crystal. After listing the subfomula equation of the complex crystal, we can calculate each type of subformula by using the PV theory, but the parameters in the calculation do not have the same meanings as the original ones, these parameters need to be modified according to the present charge of ions in the chemical bond. In a complex crystal, the number of valence electrons associated with a particular bond μ between A and B ions are Z_A^μ and Z_B^μ, respectively, the

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Table 1
The covalency of chemical bonds in rare earth oxyhalide and rare earth oxysulfide

Crystals	Bond type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
LnOCl	Ln–O	0.139	0.138	0.139	0.135	0.141	0.141	0.141	0.142	0.142	0.142	0.142				0.142
	Ln–Cl	0.049	0.048	0.048	0.047	0.049	0.049	0.049	0.049	0.049	0.049	0.049				0.049
LnOBr	Ln–O	0.142	0.139	0.143	0.144	0.145	0.146	0.147	0.147	0.148	0.148	0.149	0.149	0.150	0.150	0.148
	Ln–Br	0.052	0.051	0.052	0.054	0.056	0.056	0.057	0.058	0.058	0.059	0.059	0.059	0.059	0.061	0.059
LnOI	Ln–O	0.154				0.161	0.161						0.168	0.168		
	Ln–I	0.075				0.079	0.079						0.090	0.090		
Ln_2O_2S	Ln–O	0.154	0.154	0.154	0.155	0.155	0.155	0.155	0.162	0.156	0.156	0.156	0.156	0.156	0.157	0.156
	Ln–S	0.095	0.095	0.095	0.095	0.095	0.095	0.095	0.100	0.095	0.095	0.095	0.095	0.096	0.096	0.095

nearest coordination numbers are N_{CA}^{μ} and N_{CB}^{μ}, respectively, and the effective charges of each valence electron of A and B ions are q_A^{μ} and q_B^{μ} (whose values can be determined by using the presented approach [4]), respectively. Here we can obtain the number of effective valence electrons of A and B ions

$$(Z_A^{\mu})^* = Z_A^{\mu} \cdot q_A^{\mu} \tag{3}$$

$$(Z_B^{\mu})^* = Z_B^{\mu} \cdot q_B^{\mu} \tag{4}$$

We suppose E_g^{μ} to be the average gap between bonding and antibonding states for a μ bond, which can be separated into homopolar E_h^{μ} and hetropolar C^{μ} parts

$$(E_g^{\mu})^2 = (E_h^{\mu})^2 + (C^{\mu})^2 \tag{5}$$

The ionicity f_i^{μ} and covalency f_c^{μ} are defined as

$$f_i^{\mu} = (C^{\mu})^2/(E_g^{\mu})^2, \; f_c^{\mu} = (E_h^{\mu})^2/(E_g^{\mu})^2 \tag{6}$$

The susceptibility of the μ bond is written as

$$\chi^{\mu} = (4\pi)^{-1}(\hbar\Omega_p^{\mu}/E_g^{\mu})^2 \tag{7}$$

where the Ω_p^{μ} is plasma frequency. If the crystal is composed of different type of bonds, then the total χ can be resolved into contribution χ^{μ} from the various type of bonds

$$\chi = \sum_{\mu} F^{\mu}\chi^{\mu} \tag{8}$$

The detailed calculation method of the above parameters can be found in our previous publications [4,5].

3. Chemical bonds of rare earth oxyhalides and oxysulfides

Rare earth oxyhalides LnOX (Ln = La–Lu, Y, X = Cl, Br, I) belong to a tetragonal structure, each unit cell containing two molecules, their constituent atoms are in the positions of P4/nmm [6]. According to their crystal structures, the bond subformula equation of this type of crystals can be written as

$$LnOX = Ln_{4/9}O + Ln_{5/9}X \tag{9}$$

Rare earth oxysulfides Ln_2O_2S (Ln = La–Lu, Y) are hexagonal crystals with the space group C3m [6], there is one molecule in each unit cell. The bond subformula equation can be written as

$$Ln_2O_2S = Ln_{6/7}S + Ln_{8/7}O_2 \tag{10}$$

By using the above theories, chemical bond parameters of each bond subformula can be calculated; briefly and to the point, we show the covalency between rare earth ions and ligands in crystals in Table 1. From the results in Table 1, we can see that the covalency of different rare earth ions with the same ligand are approximately equal, the order in magnitude of covalency between rare earth ion and various ligands is Cl < Br < S.

4. Covalency Y–O bond in various crystals

To study the regularity of chemical bond behaviors of rare earth ion and its ligand, we calculate the covalency of some crystals containing Y–O bonds (see Table 2), their bond subformula equations are given in Eq. (9) and Eq. (10). The bond subformula equation of $Y_3Al_5O_{12}$, $YAlO_3$, YVO_4, YPO_4 and Y_2O_3 crystals are written as

$$Y_3Al_5O_{12} = 3[YO_2] + 2[Al(1)O_{3/2}] + 3[Al(2)O] \tag{11}$$

$$YAlO_3 = YO_{9/5} + AlO_{6/5} \tag{12}$$

$$YVO_4 = YO_{8/3} + VO_{4/3} \tag{13}$$

Table 2
The covalency of Y–O bond in various crystals

	$Y_3Al_5O_{12}$	$YAlO_3$	Y_2O_3	YVO_4	YPO_4	YOCl	Y_2O_2S
Symmetry	D_2	C_s	C_2	D_{2d}	D_{2d}	C_{4v}	C_{3v}
Coordination of Y ion	8	9	6	8	8	9	7
f_c	0.066	0.077	0.157	0.130	0.039	0.142	0.156

Table 3
The covalency of rare earth ions—halide bonds in various crystals

	LaF_3	$LaCl_3$	$LaBr_3$	KY_3F_{10}	$LiYF_4$	YOCl	YOBr
Symmetry	C_2	C_{3h}	C_{3h}	C_{4v}	S_4	C_{4v}	C_{4v}
Coordination of rare earth ions	9	9	9	8	8	9	9
f_c	0.044	0.055	0.056	0.044	0.023	0.049	0.059

Table 4
The covalency of LnM (M=N, P, As, Sb) crystals

Crystals	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Y
LnN	0.241	0.248	0.245	0.245	0.248	0.248	0.249	0.251	0.252	0.252	0.253	0.255	0.255	0.252
LnP	0.320	0.324	0.325	0.326	0.328			0.330		0.332				
LnAs	0.333	0.334	0.336	0.337	0.338		0.340	0.341	0.343	0.343	0.344	0.345	0.346	0.343
LnSb	0.377	0.379	0.381	0.382	0.383		0.385	0.386	0.387	0.388	0.389	0.390	0.395	

$$YPO_4 = YO_{8/3} + PO_{4/3} \tag{14}$$

$$Y_2O_3 = 1/2[Y(1)O_{3/2}] + 1/2[Y(2)O_{3/2}] \tag{15}$$

We can calculate the covalency of Y–O bonds in various crystals, using the above theories. From Table 2, we find these covalency values are different, which show us that the chemical bond characteristic not only reflects the behavior of two bonded ions, but reflects the effect on structure and composition of this crystal. Therefore, the physical and chemical properties of a crystal can be measured by its constituent chemical bond properties. For example, in luminescent materials, Y_2O_3, YVO_4 and Y_2O_2S are all better luminescent materials, and all of their covalency values are also larger. Thus, the chemical bond property can become a scale on physical characteristic of crystals.

5. Covalency on rare earth and halide

We have studied the covalency of rare earth ions and halide in LaX_3 (X=F, Cl, Br), KY_3F_{10} and $LiYF_4$ crystals, their bond subformula equation are given in the followings

$$KY_3F_{10} = 3/4[KF(1)_4] + 1/4[KF(2)_4] + 3/2[YF(1)_2] + 3/2[YF(2)_2] \tag{16}$$

$$LiYF_4 = LiF_{4/3} + YF_{8/3} \tag{17}$$

the calculated results are shown in Table 3. We can see that their covalency values are smaller, but there is an order in the magnitude of covalency, F<Cl<Br, in agreement with chemical experiments.

6. Covalency of LnM (M=N, P, As, Sb) crystals

LnM crystals belong to a cubic structure with four molecules in one unit cell, each constituent ion has six atoms as the nearest neighbors [6]. The covalency values of chemical bonds of LnM were previously obtained [7], and are shown in Table 4. From calculated covalency values, we can see that these covalency values increase with the increasing order from N, P, As, to Sb.

7. Conclusion

In this paper, we use the chemical bond theory of complex crystals to study chemical bond properties of some rare earth crystals, and obtain a number of regularities of chemical bonding between rare earth ions and various ligands. We find that the order of covalency of chemical bonds between trivalent rare earth ions and various ligands is F<Cl<Br<As<Sb, and the covalency values of chemical bonds between rare earth ions and the same ligand are approximately equal in isologous crystals.

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