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Bonding and hardness of $LnMgAl_{11}O_{19}$(Ln = La; Pr; Nd; Sm; Eu; Gd)

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ABSTRACT

The chemical bond parameters of $LnMgAl_{11}O_{19}$ (Ln = La, Pr, Nd, Sm, Eu, Gd) were calculated using the chemical bond dielectric theory of complex structural crystals. The hardness of $LnMgAl_{11}O_{19}$ was predicted. The results indicated that the origin of the high hardness of $LnMgAl_{11}O_{19}$ results mainly from AlO units.

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1. Introduction

$LaMgAl_{11}O_{19}$ has a slightly distorted magnetoplumbite ($PbFe_{12}O_{19}$) structure, belonging to the hexagonal space group $P6_3/mmc$ [1]. La^{3+} can be substituted with a lanthanide ion Ln^{3+} (where Ln = Pr, Nd, Sm, Eu, Gd). Lanthanum-magnesium hexaaluminate $LaMgAl_{11}O_{19}$ is a remarkable good laser host for Nd^{3+} ions (LNA). $LnMgAl_{11}O_{19}$ can also be used as luminescence materials, saturable absorber Q-switches [2]. Oxides with magnetoplumbite structure of the general composition, $LnMAl_{11}O_{19}$ (Ln = La to Gd), have high melting point, high thermal expansion, and low thermal conductivity which make them suitable for applications as high-temperature thermal barrier coatings [3]. The first growth of $LaMgAl_{11}O_{19}$ crystal by using verneuil method (flame fusion method) and floating zone method was reported by Saber and Lejus [1]. For the various applications, $LnMgAl_{11}O_{19}$ crystals should also possess the excellent mechanical properties. The hardness of $LnMgAl_{11}O_{19}$ crystals are thus measured [1]. In this paper, we will employ the dielectric theory of complex structure crystals to calculate the chemical bond parameters of $LnMgAl_{11}O_{19}$, and apply the obtained chemical bond parameters to analyzed their hardness.

2. Theoretical method

A chemical bond theory of complex structure crystals is proposed by Zhang [4,5]. Its crucial step is decomposing the complex crystal into pseudobinary crystals each containing only one type of chemical bond. For the multibond crystal $A_aB_b\ldots$, the subformula for any kind of chemical bond A—B can be expressed as:

$$\left[\frac{N(B-A)a}{N_{CA}}\right]A\left[\frac{N(A-B)b}{N_{CB}}\right]B \quad (1)$$

where A, B, ... represent different elements or different sites of the same element in the crystal formula, and *a, b,* ... represent numbers of the corresponding element, N(B-A) represents the number of B ions in the coordination group of A ion, and N_{CA} represents the nearest coordination number of A ion. These binary crystals are related to each other, and every binary crystal includes only one type of chemical bond. However, the properties of these psuedo-binary crystals are different from those of real binary crystals, although their chemical bond parameters can be calculated in a similar way. According to Eq. (1), each type of bond has its corresponding subformula, and the sum of all subformula equals the crystal formula, which is called the bond-valence equation.

On the analogy of the work of Phillips [6], the average energy gap $E_g{}^{\mu}$ for every μbond in the psuedobinary crystals can be separated into homopolar $E_h{}^{\mu}$ and heteropolar C^{μ} parts. The homopolar gap $E_h{}^{\mu}$ can be interpreted as produced by the symmetric part of the total potential, while the ionic or charge-transfer gap C^{μ} results from the effect of the antisymmetric part. The average valence-conduction band gap is give by

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

The ionicity and covalency of any type of chemical bond is defined as follows

$$f_i^{\mu} = (C^{\mu})^2/(E_g^{\mu})^2 \quad (3)$$

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$$f_c^{\mu} = (E_h^{\mu})^2/(E_g^{\mu})^2 \quad (4)$$

and

$$E_h^{\mu} = 39.74/(d^{\mu})^{2.48}(eV) \quad (5)$$

where d^{μ} is the bond length. For any binary crystal, i.e. AB_n type compounds, the heteropolar C^{μ} part is defined as

$$(6)C^{\mu} = 14.4b^{\mu}[(Z_A^{\mu})^* + \Delta Z_A^{\mu} - n(Z_B^{\mu})^*]e^{-k_s^{\mu} r_0^{\mu}}/r_0^{\mu}\,(eV)$$

$$r_0^{\mu} = d^{\mu}/2$$

$$k_s^{\mu} = (4k_F^{\mu}/\pi a_B)^{1/2} = 1.551(k_F^{\mu})^{1/2} \quad (7)$$

$$(k_F^{\mu})^3 = 3\pi^2 N_e^{\mu} \quad (8)$$

$$N_e^{\mu} = (n_e^{\mu})^*/v_b^{\mu} \quad (9)$$

$$(n_e^{\mu})^* = [(Z_A^{\mu})^*/N_{CA}^{\mu} + (Z_B^{\mu})^*/N_{CB}^{\mu}] \quad (10)$$

$$v_b^{\mu} = (d^{\mu})^3/\sum_{\nu}[(d^{\nu})^3 N_b^{\nu}] \quad (11)$$

where $v_b{}^{\mu}$ is the bond volume, $(n_e{}^{\mu})^*$ is the number of effective valence electrons per μ bond, $N_e{}^{\mu}$ is the number of valence electrons of μ bond per cubic centimeter. $k_F{}^{\mu}$ and $k_s{}^{\mu}$ are Fermi wave number and Thomas-Fermi screening wave number of valence electron in binary crystal composed of only one type of bond μ, respectively. a_B is the Bohr radius and n is the ratio of element B to element A in the subformula. $(Z_A{}^{\mu})^*$ and $(Z_B{}^{\mu})^*$ are the number of effective valence electrons of the A and B ions, respectively, and $(Z_A{}^{\mu})^* = Q_{AB}^{\mu} \cdot N_{CA}^{\mu}$, $(Z_B{}^{\mu})^* = [(Q_{AB}^{\mu} \cdot N_{CB}^{\mu})/(8 - Z_B^{\mu})] \cdot Z_B^{\mu}$, Q_{AB}^{μ} is Pauling bond valence of A—B bonds, $Z_B{}^{\mu}$ is the number of valence electrons of the B atoms. $\Delta Z_A{}^{\mu}$ is correction factor from d electron effects such as the crystal field stable energy and Janh-Teller effect, etc [7,8]. b^{μ} is proportional to the square of the average coordination number $N_c{}^{\mu}$

$$b^{\mu} = \beta(N_c^{\mu})^2 \quad (12)$$

$$N_c^{\mu} = N_{CA}^{\mu}/(1+n) + nN_{CB}^{\mu}/(1+n) \quad (13)$$

The value of β can be deduced from the Kramers-Kronig relation of dielectric function at the long wave limit, which is written as

$$\chi^{\mu} = [(4\pi N_e^{\mu} e^2/m)D^{\mu}/(E_g^{\mu})^2](1 - E_g^{\mu}/4E_F^{\mu} + (E_g^{\mu})^2/48(E_F^{\mu})^2) \quad (14)$$

$$\varepsilon(\infty) = 1 + \chi = 1 + \sum_{\mu} F^{\mu}\chi^{\mu} \quad (15)$$

where χ is the macroscopic linear susceptibility, χ^{μ} is the total macroscopic susceptibility of a binary crystal composed of only one type of bond μ, E_F^{μ} is Fermi energy, F^{μ} is the fraction of the binary crystal composing the actual complex crystal. D^{μ} is periodic dependent constants.

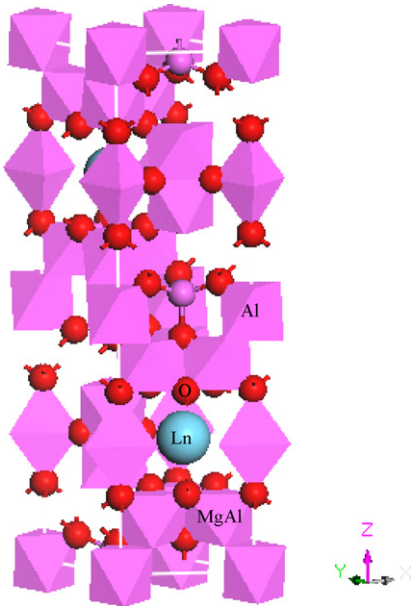

Fig. 1. Crystal structure of $LnMgAl_{11}O_{19}$.

3. Results and discussions

$LnMgAl_{11}O_{19}$ have a structural type close to the magnetoplumbite structure, $PbFe_{12}O_{19}$, in which Al^{3+} is substitutes for Fe^{3+} in the network, Ln^{3+} takes the place of Pb^{2+}, and Mg^{2+} takes the place of one Fe^{3+}. Al(3) and Mg inhabit the same site $4f_1$. The coordination number of Ln is 12, Al(1), Al(4), and Al(5) are all 6, Al(2) is 5, Al(3) and Mg is 4, O(1), O(2), and O(4) are 4, O(3) is 5. The crystal structure is shown in Fig. 1. According to Eq. (1), the bond-valence equation of $LnMgAl_{11}O_{19}$ is expressed as:

$$\begin{aligned} LnMgAl_{11}O_{19} = {} & LnAl(1)Al(2)MgAl(3)Al(4)_6Al(5)_2O(1)_2O(2)_2 \\ & O(3)_3O(4)_6O(5)_6 = 1/2LnO(3)_{12/5} + 1/2LnO(5)_3 + Al(1)O(4)_{3/2} \\ & + 2/5Al(2)O(1)_{5/4} + 3/5Al(2)O(3) + 1/2[Al(3)_{1/2}Mg_{1/2}]O(2) \\ & + 3/2[Al(3)_{1/2}Mg_{1/2}]O(4) + Al(4)O(1)_{3/2} + Al(4)O(2)_{3/2} \\ & + 2Al(4)O(4)_{3/2} + 2Al(4)O(5)_{3/2} + Al(5)O(3)_{6/5} + Al(5)O(5)_{3/2} \end{aligned} \quad (16)$$

The Pauling bond valences of the bonds in $LnMgAl_{11}O_{19}$ are shown in Fig. 2. Using the Pauling bond valences, $(Z_A{}^{\mu})^*$ and $(Z_B{}^{\mu})^*$ can be determined.

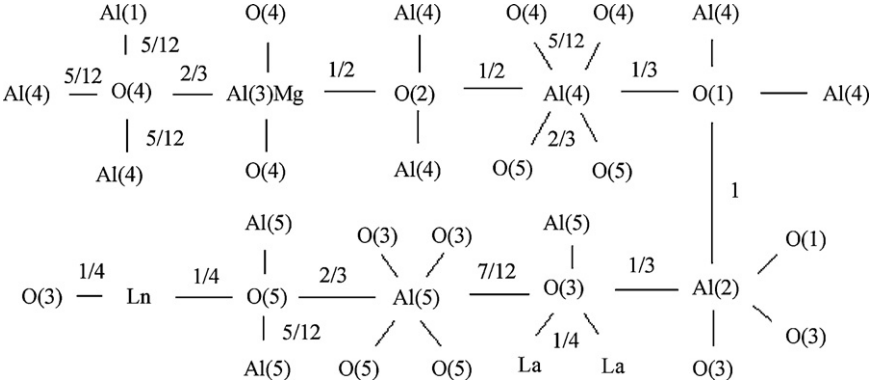

Fig. 2. Coordination and Pauling bond valences in $LnMgAl_{11}O_{19}$.

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