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Ab-initio study on the absorption spectrum of color change sapphire based on first-principles calculations with considering lattice relaxation-effect

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Abstract. In this study, we performed an investigation on α-Al₂O₃: V³⁺ material, or the so-called color change sapphire, based on first-principles calculations without referring to any experimental parameter. The molecular orbital (MO) structure was estimated by the one-electron MO calculations using the discrete variational-Xα (DV-Xα) method. Next, the absorption spectra were estimated by the many-electron calculations using the discrete variational multi-electron (DVME) method. The effect of lattice relaxation on the crystal structures was estimated based on the first-principles band structure calculations. We performed geometry optimizations on the pure α-Al₂O₃ and with the impurity V³⁺ ion using Cambridge Serial Total Energy Package (CASTEP) code. The effect of energy corrections such as configuration dependence correction and correlation correction was also investigated in detail. The results revealed that the structural change on the α-Al₂O₃: V³⁺ resulted from the geometry optimization improved the calculated absorption spectra. By a combination of both the lattice relaxation-effect and the energy correction-effect improve the agreement to the experiment fact.

1. Introduction

Various crystals containing transition metal ions as impurities are used as optical materials. Corundum, or α-Al₂O₃ is an important rock-forming mineral, which is transparent, if it does not contain any impurities. If, however, it contains a small amount of chromium (α-Al₂O₃: Cr³⁺), the color is changed to red and the material is called ruby. If, on the contrary, there is vanadium impurity instead of chromium (α-Al₂O₃: V³⁺), it shows unique ability to change color when viewed under different light, thus the material is called color change sapphire. However, their applications are not limited to jewelry only, those materials can be utilized in the laser technology. Their performances mostly depend on the optical properties such as the absorption spectrum and the multiplet energies.

The prediction of the optical properties of the transition metal ions in various crystals has been feasible using the discrete variational multi-electron (DVME) method [1]. This method has been proved to be useful for the theoretical design of new optical spectra and new artificial jewelry. In the early development of DVME method, α-Al₂O₃: V³⁺ material has been investigated [1]. Ogasawara’s group used VAl₁₄O₄₈ model cluster which consists of 63 atoms and the energy correction namely configuration dependent correction and correlation correction (CDC-CC) was considered in the...
calculations [1]. Although the calculated absorption spectra have been successfully reproduced, the peak energies were overestimated. In our previous studies on the $3d^1$ ions such as $V^{2+}$, $Cr^{3+}$ and $Mn^{4+}$ doped in crystals based on DVME method [2-6], we figured that the consideration of lattice relaxation-effect in the calculations is important to improve the agreement with the experiment. Therefore, here we performed a similar calculation with some improvement in the $\alpha$-Al$_2$O$_3$: $V^{3+}$ structure by considering lattice relaxation effect.

In this work, we investigated the absorption spectra of $V^{3+}$-doped $\alpha$-Al$_2$O$_3$ crystal based on the first-principles DVME method. The effect of lattice relaxation on the crystal structures was considered by performing geometry optimization using Cambridge Serial Total Energy Package (CASTEP) code [7-9]. Here, the CDC-CC energy correction was also considered to improve the accuracy.

2. Computational procedure

2.1. Model cluster

Two types of model clusters, non-optimized and optimized clusters consisting of 7 and 63 atoms were used in the calculations. The 7-atom model cluster consists of one trivalent vanadium atom surrounded by six oxygen atoms, VO$_6^{3+}$. The 63-atom model cluster consists of one trivalent vanadium atom surrounded by 14 Aluminum atoms and 48 oxygen atoms, VA1$_{14}$O$_{48}^{5+}$. The non-optimized cluster was simply constructed from the experimental crystal structure of $\alpha$-Al$_2$O$_3$ which has a rhombohedral $A_2X_3$ structure (space group $R\bar{3}c$) reported by H. Sawada, et al., [10]. On the other hand, the optimized cluster including the lattice relaxation effect was constructed by the geometry optimization using CAMbridge Serial Total Energy Package (CASTEP) code [7-9] (CASTEP module in Materials Studio 6.0). This code is a first-principles band structure calculations program which is based on density functional theory (DFT) [11] combined with plane-wave basis sets and pseudopotentials [12]. The Vanderbilt [13] ultrasoft pseudopotentials were used. The orbitals explicitly treated as the valence state were 3s,3p, calculated with the $3s^23p^1$ configuration and a core radius of 2.00 a.u. for Al; 2s,2p calculated with the $2s^22p^4$ configuration and a core radius of 1.30 a.u. for O; and 3s,3p,3d,4s calculated with the $3s^23p^63d^{5.75}4s^2$ configuration and a core radius of 1.80 a.u. for V. The exchange-correlation potential was considered within the Generalized Gradient Approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [14].

In order to construct the optimized cluster, we begin with performing a structural optimization of pure $\alpha$-Al$_2$O$_3$ crystal. The cutoff energy of the plane wave was 500 eV and the Brillouin zone was sampled on the rhombohedral $3\times3\times3$ Monkhorst-pack grids. Second, the external pressure from 0 to 110 GPa was applied and the Al-O bond lengths in the $\alpha$-Al$_2$O$_3$ host crystal were estimated. Next, the optimized structure surrounding dopant- $V^{5+}$ ion in $\alpha$-Al$_2$O$_3$ crystal was estimated using the same method. The $2\times2\times1$ supercell consisting of 120 atoms was constructed based on the optimized hexagonal structure. $Cr^{3+}$ ion was then substituted into one Al$^{3+}$ site. The cutoff energy of the plane wave was 500 eV and the Brillouin zone was sampled on $3\times3\times2$ Monkhorst-pack grids. The numerical error was estimated to be less than $5\times10^{-6}$ eV/atom by cutoff and $k$-point convergence tests. In this case, the effect of spin polarization was also taken into account. Under the calculations including the impurity ion, the local symmetry of Al site in pure $\alpha$-Al$_2$O$_3$ crystal ($C_3$ symmetry) was kept to minimize the computational error.

2.2. One-electron calculations

In this work, the molecular orbital (MO) structure was estimated by the one-electron MO calculations using the discrete variational-Xo (DV-Xo) method which was developed by Adachi and co-worker [15]. In this case, the numerical atomic orbitals (AO) such as 1s-4p for Cr, 1s-3d for Al and 1s-2p for O were used as basis functions in the MO calculations. The Madelung potential was considered by locating 13,000-16,000 point charges at external atomic sites, i.e., +3 for Al and V sites and -2 for O site. In order to preserve the charge neutrality, these point charges were selected in such a way that the
total charge of the cluster and the point charges equals zero. For the numerical integration, 160,000 and 216,000 sample points were used for 7- and 63-atom model clusters, respectively.

2.3. MANY-ELECTRON CALCULATIONS

After one electron approximation calculations, the many-electron calculations using the configuration interaction (CI) methods were performed. In this case, the electron-electron interactions are directly calculated. \( \gamma_0 C_2 = 45 \) Slater determinants were constructed with MOs mainly consisting of V 3d orbitals were used as the basis functions. The many-electron wave functions and the electronic states were obtained by diagonalizing the many-electron Hamiltonian. The matrix element of the effective many-electron Hamiltonian \( H \) between two Slater determinants, \( \Phi_p \) and \( \Phi_q \), can be generally expressed as

\[
H_{pq} = \langle \Phi_p | H | \Phi_q \rangle = \sum_{i=1}^{L} \sum_{j=1}^{L} A_{ij}^{pq} \langle i | h | j \rangle + \sum_{i=1}^{L} \sum_{j=1}^{L} \sum_{k=1}^{L} \sum_{l=1}^{L} B_{ijkl}^{pq} \langle ij | g | kl \rangle, \tag{2.1}
\]

where \( L \) is the number of impurity-state orbitals and \( A_{ij}^{pq} \) and \( B_{ijkl}^{pq} \) are coefficients obtained by the expansion of the Slater determinants.

Since multiplet energies according to CI calculations are generally overestimated [16], several corrections, known as configuration-dependent correction (CDC) and correlation correction (CC) in this case, were used. These corrections were introduced based on the consistency between the spin-restricted and the spin-unrestricted calculations, respectively. In this approach, the Hamiltonian including CDC and CC is expressed as

\[
H_{pq}^{\text{CDC-CC}} = \sum_{i=1}^{L} \sum_{j=1}^{L} A_{ij}^{pq} \langle i | h | j \rangle + \sum_{i=1}^{L} \sum_{j=1}^{L} \sum_{k=1}^{L} \sum_{l=1}^{L} c B_{ijkl}^{pq} \langle ij | g | kl \rangle + D_{\text{CDC}}(m, n) \delta_{pq} \tag{2.2}
\]

where \( c \) is the CC factor estimated based on the consistency of the transition energy of the spin-flip transition from \( (t_2g)^7 \) to \( (t_2g)^5(t_2g)^2 \) between the many-electron CI calculations and the spin-polarized one-electron MO calculations. On the other hand, \( D_{\text{CDC}}(m, n) \) is the correction of the barycenter of the \( (t_2g)^3, (t_2g)^5(e_g)^2, (t_2g)^7(e_g)^2 \), and \( (e_g)^3 \) configurations based on the one-electron MO calculation.

Using the eigenvector obtained by the diagonalization of the many-electron Hamiltonian, the many-electron wave functions corresponding to each multiplet state can be obtained explicitly as a linear combination of the Slater determinants. Therefore, the oscillator strength for the electric-dipole transition (transition probability) between multiplets can be calculated directly using [17]

\[
I_{if} = 2(E_f - E_i) \left| \langle \Psi_f | \sum_{k=1}^{n} r_k | \Psi_i \rangle \right|^2. \tag{2.3}
\]

where \( \Psi_i \) and \( \Psi_f \) are the many-electron wave functions of the initial and final states, while \( E_i \) and \( E_f \) are the energy eigenvalues of these states. \( e \) denotes the unit vector parallel to the direction of the electric field of the incident light. The detailed procedure of DVME method is available in Ref. 1.
3. Results and Discussions

3.1. Geometry optimization
In the structural optimization, the lattice parameters of the unit cell of pure \( \alpha \)-Al\(_2\)O\(_3\) host crystal with 0 pressure was optimized and compared to the experimental values. The theoretical lattice constants on \( a \), \( b \) and \( c \) axes were found to be 4.806, 4.806, and 13.119 Å while the experimental values [10] are 4.759, 4.759, 12.992 Å for \( a \), \( b \), and \( c \) axes, respectively. Since the difference between the experimental and theoretical values is about 1%, the optimized structures of the host crystals are considered to be in good agreement with the experiment. In the geometry optimization, we obtained the estimated V-O bond lengths of \( \alpha \)-Al\(_2\)O\(_3\): \( V^{3+} \) are \( d_1 = 1.956 \) and \( d_2 = 2.079 \) Å. The V-O bond lengths were elongated for about ca. 0.09 Å. Since the experimental data of Al-O bond lengths in the pure \( \alpha \)-Al\(_2\)O\(_3\) crystal are \( d_1 = 1.855 \) and \( d_2 = 1.971 \) Å, therefore the relaxation ratio is about 105.48%.

![Figure 1](image.png)

Figure 1. The molecular orbital (MO) energy of \( \alpha \)-Al\(_2\)O\(_3\): \( V^{3+} \) calculated based on (a) 7-atom model cluster (VO\(_6^{9-}\)) and (b) 63-atom model clusters (VAl\(_{14}\)O\(_{48}^{\text{51+}}\)) model clusters. Models without and with considering lattice relaxation-effect are indicated by non-optimized and optimized models.

3.2. Molecular orbital (MO) structure
The MO energy levels of \( \alpha \)-Al\(_2\)O\(_3\): \( V^{3+} \) calculated based on 7- and 63-atom model clusters using non-optimized and optimized clusters are shown in Fig. 1. The solid black lines indicate the valence band which are mainly consisting of O 2p orbital. The dashed black lines indicate the conduction band which are mainly consisting of Al 3s, 3p, and 3d orbitals. Moreover, the impurity levels split into \( t_{2g} \) and \( e_g \) set are indicated by solid blue lines and dashed red lines, respectively. The energy difference between them is denoted as 10\( D_q \), crystal field splitting. Although the \( t_{2g} \) level splits further into \( a \) and \( e \) levels due to the trigonal crystal field, however these splittings are negligibly small. Therefore, the
notations of $O_h$ symmetry were borrowed for simplicity. The calculated 10$Dq$ obtained from the calculations based on 7-atom model clusters are 2.26 and 1.88 eV, for the non-optimized and the optimized models, respectively. On the other hand, the calculated 10$Dq$ obtained from the calculations based on 63-atom model clusters are 2.32 and 1.93 eV, for the non-optimized and the optimized models, respectively. As we can see, when we use the larger size of model cluster, the energy difference between $t_{2g}$ and $e_g$ state becomes larger. Nevertheless, the consideration of lattice-relaxation effect decreases the crystal field splitting.

3.3. Absorption Spectra

Figure 2 shows the theoretical absorption spectra of $\alpha$-Al$_2$O$_3$: $V^{3+}$ calculated using the first-principles DVME method without referring to any experimental data. The theoretical absorption spectra estimated by several computational conditions involving lattice-relaxation effect and energy-correction effect are compared. The spectra obtained from the calculations based on 7-atom model clusters are shown on the left panel, Fig. 2a. On the other hand, the spectra obtained from the calculations based on 63-atom model clusters are shown on the right panel, Fig. 2b. Here, we used the Gaussian function with 0.2 eV FWHM (full width at half maximum) for broadening. The observed absorption spectra at 77 K obtained from the work reported by D.S. McClure [18] are shown at the bottom of each panel. The dashed red line indicates the $\sigma$ spectrum, $E \perp c$. On the other hand, the solid blue line indicates the $\pi$ spectrum, $E \parallel c$.

In the observed spectra, the first peak was assigned to the transition energy from the $3T_{1a}$ ground state to the $3T_{2}$ state, while the second peak was assigned to the transition energy from the $3T_{1a}$ ground state to the $3T_{1b}$ state. It was shown that the intensity of the observed $3T_{1b}$ state is much stronger in the $\pi$ spectrum compared to the $\sigma$ spectrum. This tendency has been successfully reproduced in this work. The calculated spectra obtained based on either 7-atom or 63-atom model clusters. On the other hand, in the case of $3T_{2}$ state, the observed intensity of $\sigma$ spectrum is slightly stronger than the $\pi$ spectrum. Unfortunately, this tendency could only be reproduced by the calculations based on 7-atom model cluster. Next, in the case of observed $\pi$ spectrum, it was also shown that the relative intensity of $3T_{1b}$ state is stronger than in those of $3T_{2}$ state. Oppositely, in the case of $\sigma$ spectrum, the relative intensity of $3T_{1b}$ state is weaker than in those of $3T_{2}$ state. In this work, we have successfully reproduced the tendency of $\pi$ spectrum by various computational conditions. On the other hand, the calculated $\sigma$ spectra of $3T_{2}$ and $3T_{1b}$ states are comparable.

Detailed investigation shows that although the lattice relaxation ratio was estimated to be about ca. 105.48% or elongated from the original structure of pure $\alpha$-Al$_2$O$_3$, the calculated absorption spectra shift towards the lower energy region. On the other hand, the effect of energy correction, CDC-CC, plays an important role to also shift the peak position toward the lower energy side. Therefore, when the lattice relaxation-effect and the CDC-CC effect were combined, the agreement between the calculated and the observed absorption spectra was improved excellently.
3.4. Multiplet Energy Levels

Since V$^{3+}$ belongs to 3$d^2$ configuration, the ground state $^3T_{1b}$ has triply degenerate spatial functions. It splits into the $^3T_{1a}(A)$ and $^3T_{1a}(E)$ states due to the trigonal field, the energy of the $^3T_{1a}(A)$ state is set at zero. The transition from the $^3T_{1a}$ ground state to the triplets such as $^3T_2$, $^3T_1$, $^3T_1 b$, and $^3T_1 a$ are observed as strong broad bands, while the transition to the singlets such as $^1T_2$, $^1E$ and $^1A_1$ are observed as weak and sharp lines. The calculated multiplet energies both singlets and triplets are presented in Table 1 together with the experimental data obtained from Refs. 18-20. The calculations were based on 7-atom model cluster (VO$^6_9$) and 63-atom model clusters (VA$^{14}_{14}O_{48}^{51}$) with various computational conditions such as...
lattice relaxation effect and CDC-CC energy correction effect. Table 1 shows that the consideration of CDC-CC energy correction reduces the multiplet energies of both singlets and triplets. Similarly, the consideration of lattice relaxation reduces the multiplet energies especially for the triplets. When we used the combination of both the lattice relaxation and the CDC-CC energy correction, the calculated $^3T_2$ states were underestimated and the other states were slightly overestimated. However, those energies reasonably agree with the experimental data. Compared to the calculations based on the 7-atom model cluster, the calculations based on the 63-atom model cluster reproduce the experimental data more suitably.

**Table 1.** The multiplet energy levels (eV) estimated based on 7-atom model cluster ($\text{VO}_6^{3-}$) and 63-atom model clusters ($\text{VAI}_6\text{O}_{48}^{31-}$) with various computational conditions involving lattice relaxation-effect and CDC-CC energy correction. The estimated values were averaged within each state in the $O_h$ notation. The experimental multiplet energies obtained from several reports are listed on the top.

| Multiplet state | $^1T_2$ | $^1E$ | $^1A_1$ | $^3T_2$ | $^3T_{1h}$ |
|-----------------|---------|-------|---------|---------|---------|
| **Experiment**  | 1.09 [19] | 1.21 [20] | 2.61 [19] | 2.17 ($\sigma$) [18] | 3.09 ($\pi$) [18] |
| **7-atom model cluster** | | | | | |
| Non-optimized    | 1.80     | 1.87   | 3.83    | 2.46    | 4.01    |
| With CDC-CC     | 1.45     | 1.51   | 3.10    | 2.27    | 3.51    |
| Optimized        | 1.78     | 1.85   | 3.73    | 2.16    | 3.70    |
| With CDC-CC     | 1.43     | 1.51   | 3.01    | 1.91    | 3.13    |
| **63-atom model cluster** | | | | | |
| Non-optimized    | 1.56     | 1.63   | 3.41    | 2.79    | 4.07    |
| With CDC-CC     | 1.26     | 1.36   | 2.75    | 2.40    | 3.41    |
| Optimized        | 1.57     | 1.68   | 3.37    | 2.27    | 3.62    |
| With CDC-CC     | 1.31     | 1.43   | 2.80    | 1.98    | 3.11    |

**4. Conclusion**

The improved calculations for the absorption spectra of $\alpha$-$\text{Al}_2\text{O}_3$; $V^{3+}$ have been performed by DVME method without referring to any experimental parameter. Our results show that the lattice relaxation ratio was estimated to be ca. 105.48%. Due to the fact that the crystal radius of $V^{3+}$ ion with 6 coordination number (0.78 Å) is larger than those of $\text{Al}^{3+}$ ion (0.675 Å), the V-O bond lengths of $\alpha$-$\text{Al}_2\text{O}_3$; $V^{3+}$ were elongated about ca. 5.48% of $\text{Al}_2\text{O}_3$ crystal. Improvement on the $\alpha$-$\text{Al}_2\text{O}_3$; $V^{3+}$ structure through the geometry optimization evidently enhanced the accuracy of the calculated absorption spectra. Overall calculations show that the combination of the lattice relaxation and CDC-CC energy correction is especially important to correct the overestimation in the absorption spectra of $\alpha$-$\text{Al}_2\text{O}_3$; $V^{3+}$. 


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