Effect of trivalent manganese substitution in α-Al₂O₃ crystal on the absorption spectra based on first-principles calculations

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Abstract. The absorption spectra of α-Al₂O₃: Mn³⁺ at low-spin (LS) state have been estimated based on first-principles calculations without referring to any experimental parameter. The effect of lattice relaxation due to the Mn³⁺ substitution was considered under several computational procedures such as the Shannon’s crystal radii method and the geometry optimization using Cambridge Serial Total Energy Package (CASTEP) code. Two different sizes of model clusters consisting of 7 and 63 atoms were compared. Next, the molecular orbitals (MO) were estimated using the one-electron calculations discrete variational-Xα (DV-Xα) method while the absorption spectra were estimated using the many-electron calculations discrete variational multi-electron (DVME) method. The results show that the lattice-relaxation ratio is about ca. 104.05-106.43% depending on the computational conditions. Due to the Mn-O bond-length elongation, the crystal field splitting (10Dq) decreased ca. 0.24-0.41 eV. Thus, the peak position originating from ³T₁ → ³E transition energy shifted toward the lower energy ca. 0.10-0.26 eV. Both of the larger-cluster size and the lattice-relaxation effect decrease the peak energies.

1. Introduction
Transition metal (TM) ions doped compounds have attracted great interest due to a wide variety of applications such as phosphors used in various luminescence technologies. Their performance as luminescence materials mainly depends on their optical properties. The so-called Tanabe-Sugano diagrams have been widely recognized as the standard reference data to analyse the optical properties of TM 3d³ ions in crystals [1]. These diagrams generally express the multiplet energy levels which are depicted as function of energy (E) and crystal field splitting (Dq) for vertical and horizontal axes respectively. Both axes are normalized by the Racah parameter B which is generally determined from the experimental spectrum.
Previously we have successfully studied the absorption spectra of $\alpha$-Al$_2$O$_3$: 3$d^6$ ions i.e., V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$ based on the first-principles calculations using the discrete variational multielectron (DVME) method [2]. In the strong crystal field of TM 3$d^5$ configuration, there are several transitions which occur from $^4$A$_2$ ground state to $^2$E, $^2$T$_1$, $^4$T$_2$, $^2$T$_2$, $^4$T$_{1h}$, and $^4$T$_{2h}$ states. These transitions are generally called as R, R’, U, B, Y, and Y’ peaks, respectively. The R, R’, and B peaks appear as sharp lines originating from the emission spectra. On the other hand, the U, Y, and Y’ peaks appear as broad bands. In our studies, we found that the U- and Y-band increase in the order of V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$. However, similar study for $\alpha$-Al$_2$O$_3$: TM$^{3+}$ ions i.e., Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, Fe$^{3+}$, and Co$^{3+}$ need to be carried out to understand the complete picture of TM ions. Therefore, in 2017 we have reported a study on the optical properties of $\alpha$-Al$_2$O$_3$: V$^{3+}$ using similar method [3]. Since V$^{3+}$ belongs to 3$d^2$ configuration, there are several transitions which occur from $^3$T$_1a$ ground state to $^1$T$_2$, $^1$E, $^1$A$_1$,$^3$T$_2$, and $^3$T$_{1h}$ states. The transition energies from $^3$T$_{1a}$ to the singlet states are observed as weak and sharp lines, while the transition energies from $^3$T$_{1a}$ to the triplet states are observed as strong and broad bands. Our results point out the importance of lattice-relaxation consideration to produce the optical properties of $\alpha$-Al$_2$O$_3$: V$^{3+}$ accurately.

Based on what we have studied so far, in this work we want to investigate the $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ including the effect of lattice relaxation in detail. Since Mn$^{3+}$ belongs to 3$d^4$ configuration, there are two possible spin states i.e., high-spin (HS) and low-spin (LS) states. In the HS state, the spin-allowed transition is occurred from the $^3$E ground state to $^5$T$_2$ states ($^3$E $\rightarrow$ $^5$T$_2$). On the other hand, in the LS state, the spin-allowed transition was occurred from the $^3$T$_1$ ground state to $^5$E state ($^3$T$_1$ $\rightarrow$ $^5$E). Nevertheless, we limit our work in the LS state.

2. Method

2.1. Model clusters

In this work we used six different types of model clusters which were combinations of two different cluster sizes and three different lattice-relaxation estimations. The cluster sizes were constructed consisting of 7 atoms (MnO$_6$) and 63 atoms (MnAl$_{10}$O$_{48}$) under C$_3$ symmetry. On the other hand, the lattice-relaxation estimations were carried out based on Shannon’s crystal radii method [4,5] and Cambridge Serial Total Energy Package (CASTEP) method [6-8]. Table 1 shows the Mn-O bond length of $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ calculated using different computational methods.

| Computational Method | $d_1$ (Å) | $d_2$ (Å) | Ratio $d_1$ (%) | Ratio $d_2$ (%) |
|----------------------|-----------|-----------|----------------|----------------|
| No-relax [6]         | 1.855     | 1.971     | -              | -              |
| Shannon’s crystal radii | 1.959 | 2.084 | 104.05         | 104.05         |
| CASTEP               | 1.974     | 2.084     | 106.43         | 105.71         |

The model cluster considering lattice relaxation effect based on Shannon’s crystal radii method were estimated using the $\alpha$-Al$_2$O$_3$ crystal structure reported by Sawada et al. [9]. In this method, the Mn-O relaxed bond length were estimated by the ratio of Mn-O and Al-O Shannon’s crystal radii multiplies with the Al-O unrelaxed bond length. Since Cr$^{3+}$ has six coordination number, Al$^{3+}$ has six coordination number while O$^{2-}$ has four coordination number, their crystal radii are 0.7525, 0.675 and 1.24 Å, respectively. Therefore, the ratio of Mn-O and Al-O Shannon’s crystal radii was found to be 104.18%. We have used this method to estimate the lattice relaxation effect in several fluorides’ materials such as Al$_2$BF$_6$: Mn$^{3+}$ [10,11].

On the other hand, the model cluster considering lattice relaxation effect based on CASTEP method were estimated by performing the geometry optimization on $\alpha$-Al$_2$O$_3$: Mn$^{3+}$. The detailed procedure is similar with the optimized model cluster constructed in Ref. 10. We have used this method to estimate the lattice relaxation effect in oxide materials such as MgO, Mg$_2$TiO$_4$ doped with V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$ [12,13].
2.2. One-electron and many-electron approaches
We used the one–electron calculations DV-Xα method to calculate the molecular orbital (MO) energies of α-Al₂O₃: Mn³⁺. The detailed procedure is described in Ogasawara [14]. In this case, only one electron and nuclei are considered, while the other electrons are treated just as potentials on the other hand, the many-electron calculations DV-ME method was utilized to calculate the absorption spectra of α-Al₂O₃: Mn³⁺. The detailed procedure is described in McClure [15]. Here, four electrons occupying the impurity levels are treated explicitly. Both above mentioned methods are first-principles calculations which performed without referring to any experimental parameter. The calculations carried in this work were performed under LS state.

3. Results and discussion

![Figure 1. The molecular orbital (MO) energies of α-Al₂O₃: Mn³⁺ calculated using (a) 7-atom model cluster (MnO₆⁹⁻) and (b) 63-atom model cluster (MnAl₁₄O₄₈⁵¹⁻).](image)

Figure 1 shows the Mn-O bond length of α-Al₂O₃: Mn³⁺ calculated using different computational methods. The molecular orbital (MO) energies of α-Al₂O₃: Mn³⁺ calculated using (a) 7-atom model cluster (MnO₆⁹⁻) and (b) 63-atom model cluster (MnAl₁₄O₄₈⁵¹⁻). Two different types of lattice relaxation estimation i.e., Shannon’s crystal radii method and CASTEP method are compared. The conduction band and the valence band are indicated by dashed and solid lines, respectively. The impurity levels consist of $t_{2g}$ and $e_{g}$ which their difference energy is called as crystal field splitting (10$D_q$). In this case, the lowest impurity levels were set to zero. The results estimated based on 7-atom model cluster show that the crystal-field splitting was found to be 1.95, 1.71, 1.57 eV calculated using no-relax, Shannon’s crystal radii, and CASTEP methods, respectively. On the other hand, the results estimated based on 63-atom model cluster show that the 10$D_q$ were found to be 2.00, 1.74, 1.59 eV calculated using no-relax, Shannon’s crystal radii, and CASTEP methods, respectively. As we can see, by considering lattice relaxation effect in both 7-atom and 63-atom model clusters the calculated 10$D_q$ decreased. Further, compared to the other computational methods, the CASTEP method gives the lowest 10$D_q$.

Figure 2 shows the theoretical absorption spectra of α-Al₂O₃: Mn³⁺ calculated based on 7-atom model cluster (MnO₆⁹⁻) and 63-atom model clusters (MnAl₁₄O₄₈⁵¹⁻) model clusters. Several computational methods considering lattice relaxation-effect such as Shannon’s crystal radii and
CASTEP methods. The solid red line indicates the $\sigma$ spectrum, $E \perp c$. On the other hand, the dashed blue line indicates the $\pi$ spectrum, $E \parallel c$. The experimental absorption spectra of $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ at HS state obtained from Ref.16 are shown at the lowest panel. In the experimental spectra, a broad peak was observed either in the $\sigma$ or in the $\pi$ spectrum. It was assigned to the $5E \rightarrow 5T_2$ transition energy. Compared to the $\sigma$ spectra, the $5E \rightarrow 5T_2$ transition energy of $\pi$ spectrum has higher energy. However, they have similar relative intensity.

Figure 2. Theoretical absorption spectra of $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ under low-spin (LS) state were calculated based on (a) 7-atom model cluster (MnO69-) and (b) 63-atom model cluster (MnAl14O4851-). The experimental absorption spectra of $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ under high-spin (HS) state were obtained from Ref. 16.

Table 2. The peak position of $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ absorption spectra.

| Model cluster | Computational method     | Peak position in $\sigma$ spectrum (eV) | Peak position in $\pi$ spectrum (eV) |
|---------------|--------------------------|----------------------------------------|-------------------------------------|
| Experiment HS state [16] | 2.34                     | 2.53                                   |
| 7-atom        | No-relax                 | 2.55                                   | 2.62                                |
|               | Shannon’s crystal radii  | 2.43                                   | 2.52                                |
|               | CASTEP                   | 2.37                                   | 2.46                                |
| 63-atom       | No-relax                 | 2.49                                   | 2.57                                |
|               | Shannon’s crystal radii  | 2.24                                   | 2.33                                |
|               | CASTEP                   | 2.23                                   | 2.34                                |

On the other hand, the calculated absorption spectra, a broad peak observed either in the $\sigma$ or in the $\pi$ spectrum is assigned to the $^{3}T_1 \rightarrow ^{3}E$ transition energy. Similar to the experimental spectra, the $^{3}T_1 \rightarrow ^{3}E$ transition energy of $\pi$ spectrum has higher energy than those of $\sigma$ spectrum. This tendency has been reproduced by all computational conditions. These peaks shifted toward the lower energy by the consideration of lattice-relaxation effect. Table 2 shows the peak position of $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ absorption.
spectra in both $\sigma$ spectrum and $\pi$ spectrum. Nevertheless, the relative peak intensities are slightly different depending on the computational conditions.

4. Conclusion
Due to the Mn$^{3+}$ substitution in $\alpha$-Al$_2$O$_3$ crystal, the Mn-O bond lengths are longer than the original Al-O bond lengths. It results in the decreasing of crystal field splitting, $10Dq$, as has been estimated from DV-X$\alpha$ method. The $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ absorption spectra estimated from DVME method shows a broad peak which appears in both $\sigma$ and $\pi$ spectra. Their peaks were located at ca. 2.2-2.6 eV, depending on the computational conditions, which can be assigned to the $^3T_1 \rightarrow ^3E$ transition energy.

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