Optical properties of Co$^{3+}$ doped in $\alpha$-Al$_2$O$_3$ with Considering Lattice Relaxation Effect

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Abstract. Search of new luminescence materials to improve the current white-light emitting diode (LED) is still ongoing. Several investigations such as the ion dependence, the host crystal dependence has been done previously. Since we want to get a complete picture of ion-host combination dependence, we investigated $\alpha$-Al$_2$O$_3$: TM$^{3+}$. In this work we estimated the optical properties of $\alpha$-Al$_2$O$_3$ doped with Co$^{3+}$. We constructed model clusters consisting of 7 atoms. The lattice relaxation effects due to the Co$^{3+}$ substitution were calculated using Shannon’s crystal radii method and geometry optimizations in the Cambridge Serial Total Energy Package (CASTEP) method. The one-electron Discrete Variational-X$\alpha$ (DV-X$\alpha$) method was used to estimate the molecular orbital energies, while the many-electron Discrete Variational Multielectron (DVME) method was used to estimate the d-d absorption spectra. Since Co$^{3+}$ belongs to 3$d^6$ configuration, there are two possible spin states i.e., high-spin (HS) and low-spin (LS) states.

1. Introduction

Up to recently, transition metal (TM) ions doped compounds have attracted great interest due to a wide variety of applications such as phosphors used in white light emitting diode (LED). However, search of new luminescence materials to improve the current white-LED is still ongoing. In our previous studies, we performed several investigations such as the ion dependence and the host crystal dependence. In the case of ion dependence, we found out that the U- and Y-band increase in the order of V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$ [1-3]. On the other hand, in the case of host crystal dependence, we found out that when the Mn-F bond length decreased, the U- and Y-band energies increased whereas the R-line energy decreased [4,5]. Nevertheless, 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 conducted to understand the complete picture of TM ions in the octahedral system. Therefore, we have reported a study on the optical properties of $\alpha$-Al$_2$O$_3$: V$^{3+}$ and Mn$^{3+}$ using similar method [6,7]. In the case of $\alpha$-Al$_2$O$_3$: V$^{3+}$, since V$^{3+}$ belongs to 3$d^2$ configuration, there are
several transitions which occur from $^3T_{1a}$ ground state to $^1T_2$, $^1E$, $^1A_1$, $^3T_2$, and $^3T_{1b}$ states. The transition energies from $^3T_{1a}$ to the singlet states are observed as weak and sharp lines, while the transition energies from $^3T_{1a}$ 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 α-Al$_2$O$_3$: V$^{3+}$ accurately. On the other hand, in the case of α-Al$_2$O$_3$: Mn$^{3+}$, 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 $^5E$ ground state to $^5T_2$ states ($^5E \rightarrow ^5T_2$). On the other hand, in the LS state, the spin-allowed transition was occurred from the $^3T_1$ ground state to $^3E$ state ($^3T_1 \rightarrow ^3E$). Nevertheless, we limit our work in the LS state.

In this work, we want to do similar investigation for α-Al$_2$O$_3$: Co$^{3+}$. The lattice relaxation effects due to the Co$^{3+}$ substitution were calculated using Shannon’s crystal radii method and geometry optimizations in the Cambridge Serial Total Energy Package (CASTEP) method. The one-electron Discrete Variational-Xα (DV-Xα) method was used to estimate the molecular orbital energies, while the many-electron Discrete Variational Multielectron (DVME) method was used to estimate the d-d absorption spectra.

### Table 1. The Co-O bond length of α-Al$_2$O$_3$: Co$^{3+}$ calculated using different computational methods.

| Computational Method         | $d_1$ (Å) | $d_2$ (Å) | Ratio $d_1$ (%) | Ratio $d_2$ (%) |
|------------------------------|-----------|-----------|----------------|----------------|
| No-relax [1]                 | 1.855     | 1.971     | -              | -              |
| Shannon’s crystal radii      | 1.864     | 1.981     | 100.5          | 100.5          |
| CASTEP                       | 1.952     | 1.965     | 105.2          | 99.7           |

#### 2. Methods

In this work, we used 7- atoms model clusters constructed from α-Al$_2$O$_3$ crystal structure [8], CoO$_6$. The lattice relaxation effect was estimated by Shannon’s crystal radii [9,10] and geometry optimization using CASTEP code [11-13]. The detailed procedures were explained in Ref. 14. Table 1 shows the Co-O bond length of α-Al$_2$O$_3$: Co$^{3+}$ calculated using different computational methods. There are two different bond lengths; the shorter bonds indicated by ($d_1$) and the longer bonds indicated by ($d_2$). The lattice relaxation ratios described as the ratio between the bond length after relaxation process and the original bonds were shown in the right columns. It shows that $d_1$ increases when model clusters with considering lattice relaxation effect calculated by both Shannon’s crystal radii and the geometry optimization using CASTEP code were used. On the other hand, $d_2$ increased when we used the model clusters with considering lattice relaxation effect calculated by Shannon’s crystal radii, and then decreased when we used the model clusters with considering lattice relaxation effect calculated by the geometry optimization using CASTEP code.

In order to calculate the molecular orbital (MO) energies of α-Al$_2$O$_3$: Co$^{3+}$, We used the one–electron calculations DV-Xα method. The detailed procedure is described in Ref. 15. 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 DVME method was utilized to calculate the absorption spectra of α-Al$_2$O$_3$: Co$^{3+}$. The detailed procedure is described in Ref. 16. 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 low spin (LS) state.
3. Results and discussion

Figure 1. The molecular orbital (MO) energies of α-Al₂O₃: Co³⁺ estimated without and with lattice relaxation effect.

Figure 1 shows the molecular orbital of α-Al₂O₃: Mn³⁺ calculated using different computational methods. The 7-atom model cluster (CoO₆⁹⁻) were used in the calculations. 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 ($10Dq$). In this case, the lowest impurity levels were set to zero. The results show that the $10Dq$ were found to be 1.78, 1.75, and 1.92 eV calculated using no-relax, Shannon’s crystal radii, and CASTEP methods, respectively. As we can see, the crystal field splitting calculated based on the model cluster with considering lattice relaxation effect using CASTEP code has the highest $10Dq$. It might be understood since the $t_{2g}$ and $e_{g}$ levels split largely.

Figure 2. The absorption spectra of α-Al₂O₃: Co³⁺ estimated without and with considering lattice relaxation effect. The observed spectra were obtained from Ref. 17.

Figure 2 shows the theoretical absorption spectra of α-Al₂O₃: Co³⁺. 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 $\alpha$-$\text{Al}_2\text{O}_3$: $\text{Co}^{3+}$ at HS state obtained from Ref. 17 are shown at the lowest panel. In the experimental spectra, two broad peaks were observed either in the $\sigma$ or in the $\pi$ spectrum. The first peak appears at ca. 2 eV, while the second peak appears at ca. 2.8 eV.

![Figure 3](image-url)

**Figure 3.** The absorption spectra of $\alpha$-$\text{Al}_2\text{O}_3$: $\text{Co}^{3+}$ estimated without and with lattice relaxation effect. The observed spectra were obtained from Ref. 17.

Our results show that the calculated absorption spectra obtained using the model clusters without considering lattice relaxation effect and with considering lattice relaxation effect estimated based on Shannon’s crystal radii were identical. The tendency of the absorption spectra was changed significantly when we used the model cluster with considering lattice relaxation effect estimated based on the geometry optimization using CASTEP code. Figure 3 magnifies the absorption spectra of $\alpha$-$\text{Al}_2\text{O}_3$: $\text{Co}^{3+}$ estimated with considering lattice relaxation effect calculated by the geometry optimization using CASTEP code. The peaks positions agree with the observed absorption spectra reported from Ref. 17.

4. Conclusion

In this work, the optical properties of $\alpha$-$\text{Al}_2\text{O}_3$: $\text{Co}^{3+}$ have been successfully estimated by first-principles calculations DV-X$\alpha$ and DVME method. The lattice relaxation effect was investigated thoroughly by comparing two different methods using Shannon’s crystal radii method and first-principles band structure calculations CASTEP. The estimated absorption spectra shows that the results based on 7-atom model cluster with considering lattice relaxation effect using CASTEP improves the agreement with the experimental data.

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