A non-empirical lattice-relaxation estimation of TM$^{3+}$ doped $\alpha$-Al$_2$O$_3$

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Abstract. We investigated the effect of lattice relaxation in the trivalent transition metal ions doped $\alpha$-Al$_2$O$_3$ crystal ($\alpha$-Al$_2$O$_3$: TM$^{3+}$). The transition metal ions are Sc$^{3+}$, Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, Fe$^{3+}$, and Co$^{3+}$. The lattice relaxation effect was considered by comparing two different methods such as Shannon’s crystal radii methods and Cambridge Serial Total Energy Package (CASTEP) methods. In the Shannon’s crystal radii methods, the lattice relaxation effect was estimated as the ratio of the crystal radii of the substituted ion and the replaced ion. On the other hand, in the CASTEP method, the lattice relaxation effect was estimated by geometry optimization. The detail results show that in the case of Shannon’s crystal radii method, the lattice relaxation ratio was ca. 111.0 - 100.5%. Whereas in the case of CASTEP method, the lattice relaxation ratio was ca. 107.8 - 102.1%. However, the lattice relaxation ratio of $\alpha$-Al$_2$O$_3$: Sc$^{3+}$, Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, Fe$^{3+}$, and Co$^{3+}$ is unique depends on the ion type.

1. Introduction
Transition metal (TM) ions doped compounds are one of important materials in the luminescence technologies such as light emitting diodes (LEDs). LEDs are made of semiconductors, but the conductivity of the semiconductors in LEDs has been specially enhanced to allow for the unique properties of LEDs. The conductivity of semiconductors can be increased by adding small, controlled amounts of "impurities". This process is known as doping. However, when an impurity ion (in this case TM ion) substitutes for a metal (M) ion, the transition metal-ligand (TM-L) bond lengths change due to the nature of lattice relaxation. It can be shorter or longer than the original metal-ligand (M-L) bond lengths. For example, in the case of ruby or $\alpha$-Al$_2$O$_3$: Cr$^{3+}$. The trivalent chromium (Cr$^{3+}$) is one of TM ion which has 3 electrons in the 3d orbital (3d$^3$). When a Cr$^{3+}$ ion is substituted into $\alpha$-Al$_2$O$_3$ crystal, the Cr-O bond lengths are longer than the Al-O bond length. Previously, we have studied the bond length of $\alpha$-Al$_2$O$_3$: 3d$^3$ ions such as V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$ using a combination method of Shannon’s crystal radii and Extended X-ray absorption fine structure (EXAFS) methods [1]. The results show that the TM-L bond
lengths increase when the atomic number increases. In the other study, we have also shown that in order to theoretically reproduce the optical properties that agree to the experimental values, creating model close to the real material cannot be neglected [1-4]. Since the consideration of lattice relaxation effect is especially important to mimic the real material, in this work we want to perform a study on the lattice relaxation estimation of α-Al2O3: TM3+ ions such as Sc3+, Ti3+, V3+, Cr3+, Mn3+, Fe3+, and Co3+. Several approaches are compared. The lattice relaxation effects were estimated using a non-empirical approach i.e., Shannon’s crystal radii and the geometry optimization using Cambridge Serial Total Energy Package (CASTEP) methods.

2. Methods
We constructed three types of model namely no-relax model, Shannon’s model and CASTEP model. The no-relax models are obtained from the experimental crystallographic information file (CIF) of pure α-Al2O3 crystal [5]. The Shannon’s models are obtained by modifying the no-relax model according to the Shannon’s crystal radii. On the other hand, the CASTEP models are obtained from the geometry optimization process using CASTEP code.

2.1. Shannon’s crystal radii method
Shannon’s crystal radii method is one of the simplest approach to estimate the lattice relaxation effect. We have reported some studies employing this method for oxide and fluoride materials [1-4]. Table 1 shows the lattice relaxation ratio of α-Al2O3: TM3+ estimated using Shannon’s crystal radii method. The values of crystal radii were obtained from Refs. 9 and 10. It is defined by the ratio between the crystal radii of the system after substituting the dopant (TM3+-O2-) and the crystal radii of system before substituting the dopant ion (Al3+-O2-). Therefore, the estimated bond length with considering lattice relaxation effect can be easily calculated by multiplying the lattice relaxation ratio with the original bond length as shown in the equation (1). S indicates the Shannon’s crystal radii value, while d indicates the bond length.

\[
d(\text{TM} – \text{O})_{\text{relaxed}} = \frac{S(\text{TM}^{3+}) + S(\text{O}^{2-})}{S(\text{Al}^{3+}) + S(\text{O}^{2-})} \times d(\text{Al} – \text{O})_{\text{unrelaxed}}
\]

Table 1. Lattice relaxation ratio of α-Al2O3: TM3+ estimated using Shannon’s crystal radii method [6,7].

| Atom | Atomic number | Ionic charge | Coordination number (CN) | Crystal radii | Relaxation ratio (%) |
|------|---------------|--------------|--------------------------|---------------|----------------------|
| Al   | 18            | +3           | 6                        | 0.675         | -                    |
| O    | 8             | -2           | 4                        | 1.240         | -                    |
| Sc   | 21            | +3           | 6                        | 0.885         | 110.97               |
| Ti   | 22            | +3           | 6                        | 0.810         | 107.05               |
| V    | 23            | +3           | 6                        | 0.780         | 105.48               |
| Cr   | 24            | +3           | 6                        | 0.755         | 104.18               |
| Mn   | 25            | +3           | 6                        | 0.785         | 105.74               |
| Fe   | 26            | +3           | 6                        | 0.785         | 105.74               |
| Co   | 27            | +3           | 6                        | 0.685         | 100.52               |

2.2. Geometry optimizations
The first-principles band-structure calculations were carried out using CASTEP code [8-10] in Material Studio 6.0. The Vanderbilt [11] ultrasoft pseudopotentials were used. Here we consider the Generalized Gradient Approximation (GGA) exchange-correlation potential proposed by Perdew, Burke, and Ernzerhof (PBE) [12]. It has been known for its general applicability and gives rather accurate results for a wide range of systems. In the first step, the structural optimizations on the pure α-Al2O3 crystal were carried out. We have reported some studies employing this method for oxide and fluoride materials [13-15]. The procedure employed here is similar with those used in [16]. Next, one TM3+ such as Sc3+,
Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, Mn$^{3+}$, Fe$^{3+}$, or Co$^{3+}$ ion was substituted in the Al$^{3+}$ site and then followed by the geometry optimization step.

3. Results and discussion

Figure 1 shows the estimated bond length of $\alpha$-Al$_2$O$_3$: TM$^{3+}$ based on (a) no-relax model, (b) Shannon’s model and (c) CASTEP model. In the case of pure $\alpha$-Al$_2$O$_3$ crystal, there are two different bond lengths called d1 and d2 for the shorter and longer bond length respectively. Here we calculated the d1, d2 and the average of d1-d2. Figure 1a shows that the TM-O bond lengths are the same for all kind of ions. The d1 was 1.855 Å, d2 was 1.971 Å and the average of d1-d2 was 1.913 Å. Figure 1b shows that the TM-O bond lengths are decreased in the order of Sc$^{3+}$, Ti$^{3+}$, V$^{3+}$, Cr$^{3+}$, and then increased for Mn$^{3+}$, Fe$^{3+}$ and decreased again for Co$^{3+}$. On the other hand, Figure 1c shows that the TM-O bond lengths depend on ion type. However, if we see carefully, the average of TM-O bond length estimated from Shannon’s model was found to be from ca. 2.12–1.92 Å for Sc$^{3+}$ to Co$^{3+}$. On the other hand, the average of TM-O bond length estimated from CASTEP model was found to be from ca. 2.06–1.96 Å for Sc$^{3+}$ to Co$^{3+}$. Therefore, the ranges of the average TM-O bond length were ca. 0.2 and 0.1 Å for Shannon’s and CASTEP models respectively.

![Figure 1](image.png)

Figure 1. The TM-O bond length of $\alpha$-Al$_2$O$_3$: TM$^{3+}$ estimated using no-relax, Shannon, CASTEP models. The shorter TM-O bond length (d1) are indicated by circles (●). The longer TM-O bond length (d2) are indicated by squares (■). The averages of d1-d2 are indicated by triangle (▲).

Figure 2 shows the lattice relaxation ratio of $\alpha$-Al$_2$O$_3$: TM$^{3+}$ estimated using Shannon’s and CASTEP models. Although it depends on the ion type, they were relatively decreased. In the case of Sc$^{3+}$, Ti$^{3+}$, and Mn$^{3+}$, the lattice relaxation ratios estimated from Shannon’s model were overestimated. On the other hand, in the case of V$^{3+}$ and Co$^{3+}$, the lattice relaxation ratios estimated from Shannon’s model were underestimated. Whereas in the case of Cr$^{3+}$ and Fe$^{3+}$, lattice relaxation ratios estimated from Shannon’s model were almost the same by those estimated from CASTEP model.
Figure 2. Lattice relaxation ratio of $\alpha$-Al$_2$O$_3$: TM$^{3+}$ estimated using Shannon’s crystal radii and CASTEP method are indicated by circles (●) and squares (■) respectively.

In both cases, $\alpha$-Al$_2$O$_3$: Sc$^{3+}$ has the highest lattice relaxation ratio compared to the other TM$^{3+}$ ions. They are 111.0 and 107.8% estimated from Shannon’s and CASTEP model respectively. On the other hand, the lowest lattice relaxation ratios are different. the lowest lattice relaxation obtained from Shannon’s model is $\alpha$-Al$_2$O$_3$: Co$^{3+}$ 100.5%. Whereas the lowest lattice relaxation obtained from CASTEP model is $\alpha$-Al$_2$O$_3$: Mn$^{3+}$ ca. 102.1%.

4. Conclusion

In this work, 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 results show that the lattice relaxation estimated from Shannon’s crystal radii method and those estimated from CASTEP method strongly depends on the ion type. This results should be investigated further such as compare the calculated lattice parameter with the observed Extended X-Ray Absorption Fine Structure (EXAFS) data.

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