Prediction on the multiplet energy diagram of $\alpha$-Al$_2$O$_3$: Mn$^{4+}$ under pressure

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Abstract. To review the recommendations for the production of novel red phosphor materials, in this work we established the multiplet energy diagram of Mn$^{4+}$ in $\alpha$-Al$_2$O$_3$ under pressure. By the discrete variational multi-electron (DVME), the calculations were conducted based on many-electron approaches. Since the experimental data of Mn$^{4+}$ in $\alpha$-Al$_2$O$_3$ at zero pressure was the only data reported so far, the results in this work are our predictions. The effect of increasing pressure is naturally similar with the effect of decreasing bond length. This work indicates that the multiplet energies responsible for the absorption process increase as the pressure increase. Whereas, those responsible for the emission process decrease. These tendencies are the same as our previous calculations on $\alpha$-Al$_2$O$_3$: Cr$^{3+}$.

1. Introduction

Previously we have calculated the optical properties of transition metal (TM) 3d$^3$ ions doped in materials. They are V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$ doped oxides such as MgO, MgTiO$_4$, $\alpha$-Al$_2$O$_3$. The investigations were about the ionic dependence on the lattice relaxation, energy correction, cluster size on the bond length, optical properties and the multiplet energies. In all cases, we found out that the absorption bands, i.e., the transition energies from ground state $^4$A$_2$ to $^4$T$_2$ to $^4$T$_{1u}$, namely U and Y bands, rise in the order of V$^{2+}$, Cr$^{3+}$ and Mn$^{4+}$ [1–3]. It indicates that Mn$^{4+}$ exhibits highest absorption energy among these ions. Many studies reported that Mn$^{4+}$ doped compounds deep red emission under visible-light excitation. The emitted light originates from the transition energy from $^2$E state to the ground state $^4$A$_2$ (R-line). In the host crystal dependency analysis such as Mn$^{4+}$-doped hexafluoro family (A$_2$BF$_6$) crystals reveals that the energies of the absorption bands increased when the Mn-F bond length decreased, while the energy of the emission line decreased [4,5].

Mn$^{4+}$ has a high potential to be commercially used in lighting industry replacing the rare earth-doped phosphors. For example, europium (Eu) activated in nitrides and oxynitrides [6,7], because their
excellent riches, they are the most commercialized. The non-rare earth Mn$^{4+}$ ion activated red phosphor is an alternative with desirable properties and not as expensive as those including rare earth ion. Especially, Mn$^{4+}$ activated in fluorides and oxides have gained great interest. Based on the observed spectra, the red emission of Mn$^{4+}$ activated in phosphors is peaking at ~630 nm [8–15]. Regretfully, as far as high temperatures and high humidity are concerned, they are unstable. A more stable host material such as oxide is required, as described above. However, their emission wavelength shorter than those in fluoride host, the shortest emission wavelength is about 650 nm [16]. Thus, it is important to establish guidelines to control the emission wavelength by the multiple energy levels. Basically, there are unlimited number of combination of substituting ion and the host crystal, the trial and error experiments are rather ineffective. Therefore, here we try to establish guidelines based on Mn$^{4+}$ doped compounds. Here, the applied pressures were naturally similar with the decreasing bond length. A practical energy diagram was constructed. Rather recently, we have published a non-empirical analysis focused on first-principles calculations on ruby, Cr$^{3+}$ doped in $\alpha$-Al$_2$O$_3$. The pressure dependency on its molecular orbital and multiplet energies was investigated [17–21]. Here, similar investigation was performed in $\alpha$-Al$_2$O$_3$: Mn$^{4+}$. Since the observed data reported so far was only for zero pressure, the results reported here are our prediction.

2. Methods

Two types of clusters were generated, i.e., no relax and CASTEP clusters, consisting of 15 aluminiums and 48 oxygens (Al$_{15}$O$_{48}^{3+}$). Based on crystal structure data of $\alpha$-Al$_2$O$_3$ with different pressures from 0-113 GPa, no-relax cluster was generated. The Mn$^{4+}$ was substituted in the centre of the clusters. On the other hand, the CASTEP clusters were generated by performing first-principles band-structure calculations on $\alpha$-Al$_2$O$_3$ at 0 pressure. First, we performed a structural optimization on the initial unit cell obtained from with ICSD #75560. Second, the pressure was applied from 0-120 GPa. Third, one Mn$^{4+}$ ion was substituted into one Al$^{3+}$ site. The detailed procedures to obtained the CASTEP clusters were similar with those used in Refs. [22,23]. After the MnAl$_{15}$O$_{48}^{3+}$ clusters were developed, the first-principle calculations were performed using the discrete variational multi electron (DVME) method. There are two steps i.e., (1) the one-electron approach-based molecular orbital (MO) calculations using the discrete variational Xα (DV-Xα) method and (2) the many-electron approach-based multiplet energy calculations using the configuration interaction (CI) method. In order to increase the accuracy, the energy correction called configuration dependence correction and correlation correction (CDC-CC) was also used here. Originally, the detail procedure of these methods were explained in Refs. [24] and Refs. [25], for DV-Xα and DVME methods respectively.

3. Results and discussion

The pressure dependency on the MO of $\alpha$-Al$_2$O$_3$: Mn$^{4+}$ is shown in Figure 1. It was calculated based on clusters which (a) neglecting the effect of lattice relaxation and (b) taking into account the effect of lattice relaxation based on CASTEP code. The conduction bands (CB) are distinguished by dashed black lines which composed predominantly of aluminum orbitals 3s, 3p, and 3d. Whereas the solid black lines mark the valence bands (VB) that consisting predominantly of oxygen orbitals 2p. In this case, the highest value of VB is set up at zero. The solid blue lines represent the $t_{2g}$ orbitals, while the $e_g$ orbitals are represented by dashed red lines. Here, the $t_{2g}$, $e_g$, and CB lines are fitted by polynomial function. In the case of no-relax clusters, the $t_{2g}$ and $e_g$ orbitals increase from 1.565 to 2.323 eV and from 3.838 to 5.499 eV, respectively. The 10$Dq$ increase from 2.272 to 3.176 eV, where the conduction band increase from 10.626 to 14.291 eV. On the other hand, the $t_{2g}$ and $e_g$ orbitals rise from 0.560 to 1.593 eV and from 2.548 to 4.240 eV, respectively, in the case of CASTEP clusters. The crystal field splitting 10$Dq$ increase from 1.988 to 2.775 eV, while the conduction band increase from 7.272 to 12.946 eV. Here, we can also see that the bandgap between the highest $e_g$ orbital and lowest CB becomes smaller in the calculations based on CASTEP clusters. The bandgaps for no-relax and CASTEP clusters increase from 6.784 to 8.787 eV and from 4.702 to 8.367 eV. However, here the lattice-relaxation effect was dominant in the clusters with lower pressure.
The calculated multiplet energies of Mn$^{4+}$ in α-Al$_2$O$_3$ under pressure as shown in Figure 2. They are emission R, R’, and B lines which correspond to the transition energies from $^2$E, $^2$T$_1$, and $^2$T$_1$ states to...
the ground state $^4A_2$, respectively. The U and Y absorption bands refer to transition energies from the ground state $^4A_2$ to $^4T_2$ and $^4T_{1a}$ states, respectively. The experimental data for 0 GPa was obtained from Ref. [26]. The R-line was observed at ca. 1.84 eV, while the U-band was observed at ca. 2.64 eV. In our calculations based on no-relax clusters neglecting the CDC-CC correction, all of the emission R-, R'-, B-lines and the absorption U-, Y-bands increase from 1.92 to 1.98 eV, from 2.08 to 2.14 eV, from 3.05 to 3.19 eV, from 2.84 to 3.56 eV and from 3.90 to 4.72 eV for pressure from 0-113 GPa. On the other hand, based on no-relax clusters with taking into consideration the CDC-CC correction for the same pressure, the emission R- and R'-lines decrease from 1.75 to 1.55 eV and from 1.90 to 1.72 eV, respectively. But increase from 2.78 to 3.36 eV for B-line. The absorption U- and Y-bands rise from 2.52 to 2.65 eV and from 3.46 to 4.33 eV, respectively. In the calculations based on CASTEP clusters neglecting the CDC-CC correction for pressure from 0-120 GPa, all of the multiplet energies increase from 1.69 to 1.95 eV, from 1.88 to 2.10 eV, from 2.74 to 3.14 eV, from 2.14 to 3.16 eV and from 3.14 to 4.29 eV for R-, R', B-, U-, and Y-bands respectively. When the CDC-CC correction was taken into account, the emission R-, R', and B-lines decrease from 1.81 to 1.65 eV, from 2.012 to 1.76 eV, from 2.87 to 2.70 eV. The absorption bands rise from 2.17 to 2.96 eV and from 3.18 to 3.94 eV for U- and Y-bands, respectively, for the same pressure.

When we consider lattice relaxation using CASTEP code, however, the zero pressure theoretical energies of R-line and U-band were underestimated. The increasing pattern in absorption energies was mainly due to the increasing crystal field splitting, which was strongly related to the local structure. The two types of bond lengths in α-Al$_2$O$_3$ at zero pressure were 1.871 and 1.993 Å for $d_1$ and $d_2$, respectively. As shown in Figure 3(a), they decrease continuously up to 1.695 and 1.806 Å at 113 GPa. After the
Mn^{4+} substitution, the Mn-O bond length $d_1$ decrease from 1.919 to 1.764 Å, the $d_2$ decrease from 1.987 to 1.848 Å. Next, in the case of emission energies, they decrease mainly due to the decreasing of effective Coulomb integral ($J_{el}$), the Coulomb integrals for atomic orbital ($J_{AO}$), the molecular orbital ($J_{MO}$), and the effective Coulomb integral ($J_{eff}$) are all seen in Figure 3. The $J_{AO}$ was obtained from the weighted Racah parameters, while the $J_{MO}$ was obtained for each impurity orbital $t_{2g}$ and $e_{g}$ states. The $J_{eff}$ was acquired from the multiplication of $J_{AO}, c$ factor, and the orbital deformation parameter $\lambda$ [27,28]. Our calculations show that the $J_{AO}$ increase from 24.22 to 24.65 eV, $J_{MO}$ for $t_{2g}$ and $e_{g}$ increase from 17.67 to 19.56 eV, and from 17.47 to 18.37 eV, respectively. Therefore, as the ratio of $J_{AO}$ and $J_{MO}$, $\lambda$ of $t_{2g}$ and $e_{g}$ slightly increase from 0.73 to 0.79 eV and from $\lambda$ 0.72 to 0.75 eV, respectively. The $c$ factors, which are coefficient determined as the consistency between one-electron and many-electron approach, decrease for no-relax and CASTEP clusters from 0.9171 to 0.8043 and from 1.06347 to 0.84586 eV, respectively. Thus we obtained $J_{eff}$ of $t_{2g}$ and $e_{g}$ decrease from 18.79 to 16.54 eV and from 18.58 to 15.54 eV, respectively.

4. Conclusion
In this work, we established a practical energy diagram of $\alpha$-Al$_2$O$_3$: Mn$^{4+}$ under pressure. However, since there are limited number of observed data, the results in this work are just our predictions. During the calculations, we consider two types of clusters i.e., no-relax and CASTEP clusters. They consist of one Mn$^{4+}$ ion, 14 Al$^{3+}$ ions and 48 O$^{2-}$ ions. We also investigated the effect of energy correction, CDC-CC. This work shows that (1) the absorption energies rise as the increasing pressure in all computational conditions, and (2) only the calculations combining both the effect of lattice relaxation and CDC-CC correction give the multiplet energy patterns comparable to ruby. We reproduced the R-line energy excellently. However, it could be possible to further increase the underestimation of the calculated U-band energy by different method of lattice-relaction effect estimation.

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