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# Calculations of the Racah parameter $B$ for Mn$^{4+}$ and Mn$^{2+}$ ions doped in CaAl$_2$O$_4$

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**Abstract.** The luminescent materials CaAl$_2$O$_4$:Mn$^{4+}$ and CaAl$_2$O$_4$:Mn$^{2+}$ were synthesized by solid state reaction method. The red luminescence of CaAl$_2$O$_4$:Mn$^{4+}$ shows an asymmetric broad band peaking at 650 nm, respectively to the characteristic luminescence of Mn$^{4+}$ ions. The emission spectrum of CaAl$_2$O$_4$:Mn$^{2+}$ shows a broad green emission band centering at 545 nm respectively to the characteristic luminescence of Mn$^{2+}$ ions. By doping different outer shells in the same host lattice, the ionic interaction between ions and the host lattice are also different. The differences are reflected in Racah parameter $B$, and the nephelauxetic effect $\beta$. The $\beta$ coefficient of CaAl$_2$O$_4$:Mn$^{4+}$ is small, indicating that its orbitals expand greatly, the interaction force between Mn$^{4+}$ and the host lattice is greater than that of Mn$^{2+}$.

## 1. Introduction

Nowadays, luminescent materials are being studied and applied widely in engineering and in daily life. Therefore, more and more group of materials are being synthesized, especially transition metal doped aluminate materials. The luminescent wavelength of doped ions depends on the strength of crystal field. In weak crystal field, the emission spectrum of Mn$^{2+}$ shows a broad band in the green, while in strong crystal field, the emission spectrum is from the orange to red. In weak crystal field, Mn$^{4+}$ emits infrared radiation while in strong crystal field, it emits light in the red spectral range [1, 2]. The Racah parameter $B$ or the nephelauxetic effect $\beta$ must be determined to better understand the interaction between the doped ions and the crystal field. However, almost no works has been done to compare crystal field force of a host lattice when doped with different valences ions. Therefore, to understand clearly these crystal field forces, we compares the crystal field of Mn$^{2+}$ doped and Mn$^{4+}$ doped in CaAl$_2$O$_4$ (CAO) host lattice.

## 2. Experiments

The CAO materials (CAO:Mn$^{2+}$ or CAO:Mn$^{4+}$) were synthesized by solid state reaction. Commecial powders of Al$_2$O$_3$, B$_2$O$_3$, CaCO$_3$, and MnO$_2$ with purity of 99.9% were use as precursors. These precursors are weighted by molar ratio and mixed with 4 *weight* percent B$_2$O$_3$ (used as fluxing agents). The mixtures are well grinded for two hours by using an agate pestle and mortar. Then, the mixtures were anneled at 1250 $^{\circ}$C for 2h. The formation of CAO:Mn$^{2+}$ is described by following chemical reaction:

$$(1\text{-}x)\,CaCO_3 + Al_2O_3 + x\,MnO_2 \rightarrow Ca_{(1\text{-}x)}Al_2O_4{:}x Mn^{2+} + CO$$
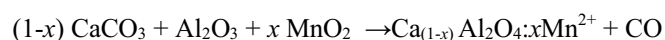
The CAO:$Mn^{4+}$ sample is annealed in the air environment. Particularly, the CAO:$Mn^{2+}$ was annealed in an environment in which CO gas is used as the reductant to generate $Mn^{2+}$ from $Mn^{4+}$. In the synthesis of CAO:$Mn^{2+}$, coal pellets are put in the bottom of the crucible to continuously generate CO.

The X-ray difraction (XRD) spectra at room temperature were measured by using the diffractometer Bruker D8-Advance at Faculty of Chemistry, Hanoi University of Science. Photoluminescence (PL) and Photoluminescence excitation (PLE) spectra were measured by Flourescent spectrometer FL3-22 Horiba at Duy Tan University, Vietnam. Samples were measured at room temperature and a 450W Xenon lamp was used to excite the sample.

## 3. Results and Discussion

### 3.1. X-ray diffraction
XRD pattern of CAO:$Mn^{2+}$ (2 mole%) and CAO:$Mn^{4+}$ (2 mole%) are shown in Figure 1. Characteristic peaks of $CaAl_2O_4$ with $2\theta$ angle of 22º, 30º, 35.5º, 37.5º shows that $CaAl_2O_4$ phase are the dominating phase, the $Ca_3Al_2O_6$ phase virtually does not exist. With low Mn doping concentration, XRD pattern of CAO:$Mn^{2+}$ (2 mole%) and CAO:$Mn^{4+}$ (2 mole%) do not change compared with based-material $CaAl_2O_4$ (not shown). $CaAl_2O_4$ has orthorhombic crystal structure and its lattice parameters are $a = 8.740$ Å, $b = 8.100$ Å, $c = 15.130$ Å và $\alpha = \gamma = \beta = 90º$ .
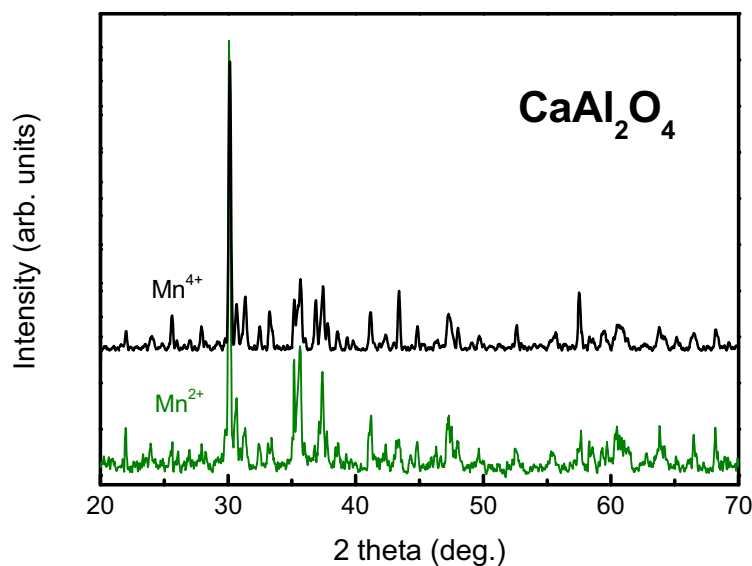


**Figure 1.** X-ray diffraction of CAO:$Mn^{2+}$ (2 mole%) and CAO:$Mn^{4+}$ (2 mole%).

### 3.2. Photoluminescence and Photoluminescence excitation spectrum of CAO:$Mn^{2+}$
The PL and PLE spectrums of CAO:$Mn^{2+}$ (2 mole%) were measured at the wavelengths $\lambda_{ex} = 425$ nm and $\lambda_{em} = 545$ nm, respectively, shown in Figure 2. PLE spectrum shows narrow peaks at wavelengths of 456, 426, 385 and 360 nm. The emission spectrum showed a broad band peaked at 545 nm. This peak is attributed to the spin-forbidden $^4T_{1g}(^4G)$ to $^6A_{1g}$ [2]. In addition there is a low-intensity peaks at ~650 nm, correspond to luminescence characteristic of a small amount of $Mn^{4+}$. Because during the synthesis of material, not all of $Mn^{4+}$ ions had been reduced to $Mn^{2+}$.

PLE peaks of $Mn^{2+}$ correspond to the transition from ground state $^6A_1$ to excited states of $^4T_{2g}(^4G)$, $^4E(^4G)$'$^4A_{1g}(^4G)$, $^4T_{2g}(D)$, $^4E(D)$ [3]... There is a narrow and high intensity peak at 425 nm because according to Tanabe-Sugano (T-S) diagram, the ground level $^6A_1$ and the excited levels $^4E(^4G)$' $^4A_1(^4G)$

are illustrated in two virtually parallel lines (Figure 3). The transition from $^6A_1$ to $^4E(D)$ is shown at the wavelength of 360 nm in Figure 2.
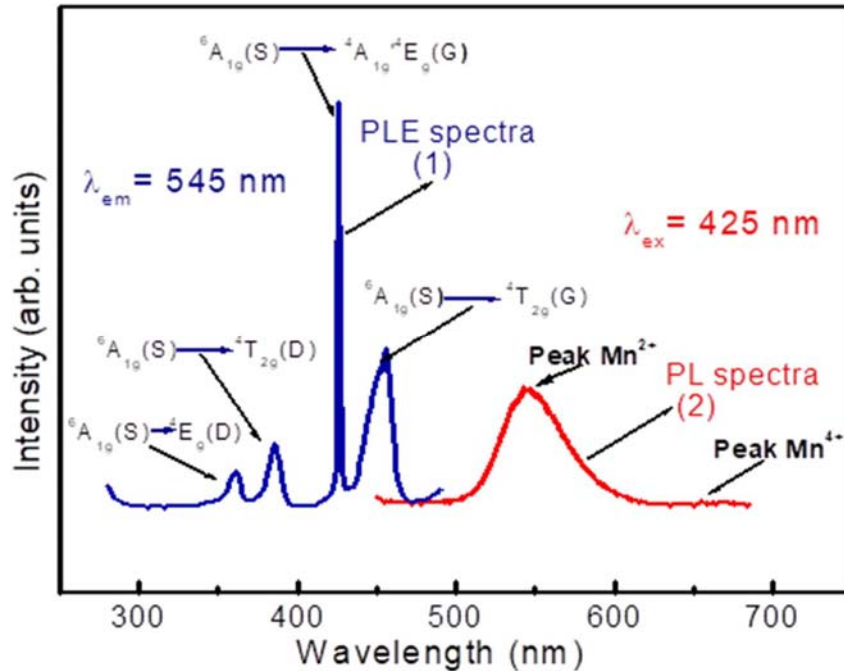


**Figure 2.** PLE and PL spectra of CAO:$Mn^{2+}$

The Racah parameter can be determined by the following formula [4]:

$$\upsilon_1 = E\,[^4E(^4G)\text{'}\,^4A_1(^4G)] - E\,[(^6A_1)] \tag{1}$$

$$= 10B+5C$$

$$\upsilon_2 = E\,[^4E(D)] - E\,[(^6A_1)] \tag{2}$$

$$= 17B+5C$$

By subtracting (1) by (2), we have

$$\upsilon_2 - \upsilon_1 = 7B. \tag{3}$$

We have $\upsilon_2 = 27777$ cm$^{-1}$, and $\upsilon_1 = 23474$ cm$^{-1}$. Substituting $\upsilon_1$ and $\upsilon_2$ into (3), we found that $B = 615$ cm$^{-1}$ and $C = 3464$ cm$^{-1}$. The nephelauxetic effect $\beta$ is calculated by the formula $\beta = B/B_0$, where $B_0 = 785$cm$^{-1}$ [4, 5] is the Racah parameters for free $Mn^{2+}$ ion. By substituting the $B$ and $B_0$ (as mentioned above), we find that $\beta = 0.78$.

From PLE spectrum, we obtained transition energy from $^6A_1$ to $^4T_{2g}(^4G)$ is $\upsilon_3 = 22123$ cm$^{-1}$. T-S diagram (Figure 3) can be used to determine splitting parameters $Dq$. We draw a line, parallel to the vertical axis ($E$) and it intersects excited state levels of $^4T_{2g}(^4G)$, $^4E(^4G)$' $^4A_1(^4G)$, $^4T_{2g}(D)$, $^4E(D)$ at ordinates: 22123, 23474, 25974, and 27777 cm$^{-1}$, respectively and intersects the horizontal axis ($Dq$) at 650cm$^{-1}$. Therefore $Dq = 650$cm$^{-1}$ or the crystal field of $Mn^{2+}$ doped CAO is $\Delta = 6500$ cm$^{-1}$ ($\Delta = 10Dq$).
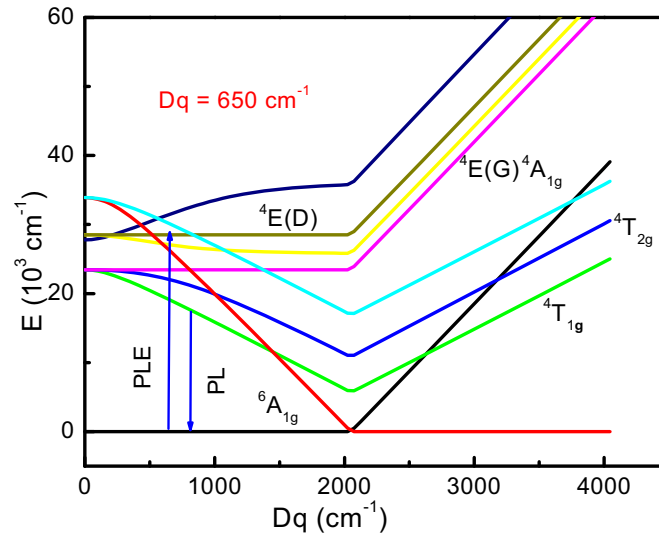
**Figure 3.** Determine *Dq* from T-S diagram [3]

### 3.3. Photoluminescence and Photoluminescence excitation of CAO:Mn$^{4+}$

PL and PLE spectra of CAO:Mn$^{4+}$ are shown in Figure 4. The PLE spectra has two broad band with peaks at 450 and 328 nm, correspond to the transition from the ground state $^4A_2$ to excited states $^4T_1$ and $^4T_2$ of Mn$^{4+}$ ions. The PL spectrum reveals peaks at 643, 650 and 668 nm which are due to the $^2E$ to $^4A_2$ states transition of Mn$^{4+}$ ions. In addition, there is a low intensity peak at 545 nm, correspond to the luminescent characteristic of a small amount of Mn$^{2+}$. Because during the synthesis process, some Mn$^{4+}$ ions are reduced to Mn$^{2+}$.
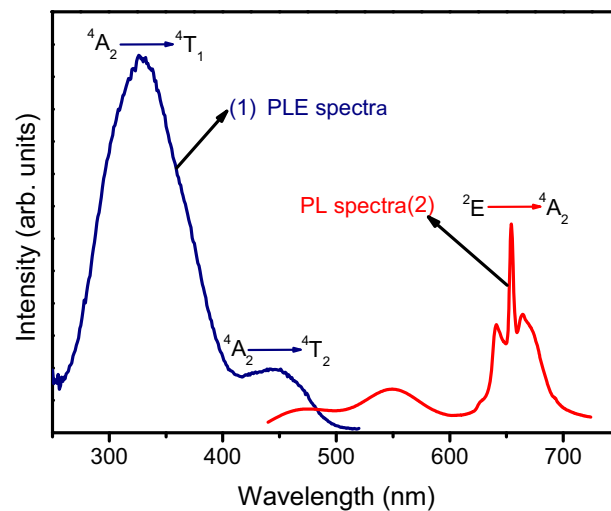


**Figure 4.** PL and PLE spectra of CAO:Mn$^{4+}$ with $\lambda_{ex} = 450$ nm and $\lambda_{em} = 650$ nm

*Determine Racah parameter B  from diagrams and formula.*

The wavelength $\lambda = $ 450 nm and $\lambda = $ 328 nm correspond to wavenumbers of $v_1 = $ 22222 cm$^{-1}$  and $v_2 = $ 30487 cm$^{-1}$, respectively. The ratio between $v_2$ and $v_1$ is $v_2/v_1 = 1.37$ [5, 6]. From the Figure 5, we determined that $\Delta/B = 27.4$. From the Figure 6 (T-S diagram with only necessary levels indicated), we draw a line parallel to $E/B$ axis at position $\Delta/B = 27.4$. It intersects $^4T_{2g}$ level curve at $A$. From $A$, we draw the a line parallel to $\Delta/B$ axis and its intersects $E/B$ axis at $E/B = 27,4$. From $E = 22222$ cm$^{-1}$, we found that $B = 811$cm$^{-1}$, $\Delta = 22222$ cm$^{-1}$ and $Dq = 222$ cm$^{-1}$ [7] (the $v$ and $E$ signs could be used interchangably).
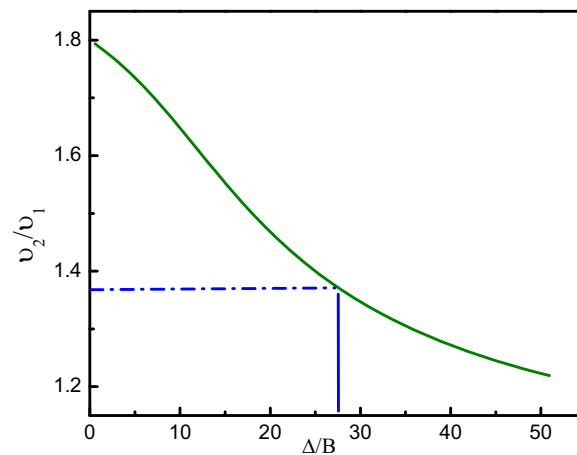


**Figure 5.** The relationship between $v_2/v_1$ and $\Delta/B$ [8].

From the formula $B = \dfrac{2v_1^2 + 2v_2^2 - 3v_1v_2}{15v_2 - 27v_1}$ [8, 9] we found that $B = 808$ cm$^{-1}$. The nephelauxetic effect coefficient $\beta = B/B_0$, where $B_0 = 1160$cm$^{-1}$, [9] is the Racah parameters for free Mn$^{4+}$ ions. The calculated coefficient is $\beta = 0.7$. The small $\beta$ indicates that the $d$-orbitals of Mn$^{4+}$ ions expands greatly.
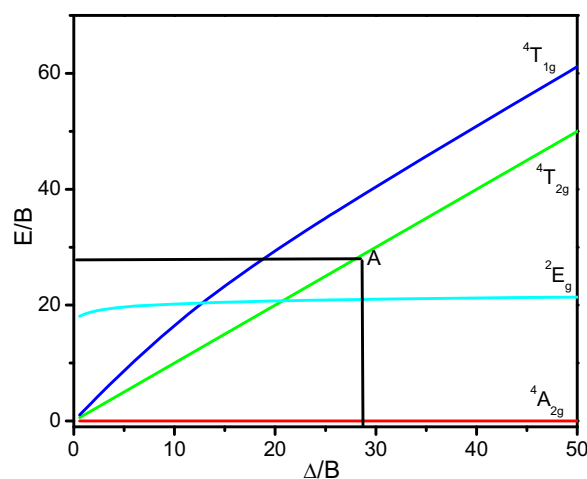


**Figure 6.** Determination of $B$ for $d^3$ configuration from T-S diagram.

## 4. Conclusion

Based on the experimental photoluminescence excitation spectrum are provided to calculate the Racah parameter $B$ and the nephelauxetic effect $\beta$. Various methods have been applied to determine the $B$ parameter, the nephelauxetic effect coefficient $\beta$, as well as crystal field $Dq$ or $\Delta$. For the same CAO host lattice, the expansion coefficient of $d$-orbilals when it is doped with $Mn^{2+}$ is smaller than when it is doped with $Mn^{4+}$, indicating that the outer electron shell of $Mn^{4+}$ expands greatly. The small values of coefficient $\beta$ (= 0.7) mean that should strong interaction between the ligand field with the $d$-orbitals of $Mn^{4+}$ ions. For electrons in $d^3$ configuration ($Mn^{4+}$), both calculation methods yield similar $B$ parameters. The crystal field force of CAO:$Mn^{4+}$, and CAO:$Mn^{2+}$ are $\Delta = 22222$ cm$^{-1}$ and $\Delta = 6500$ cm$^{-1}$, respectively. Therefore, the crystal field of CAO doped with $Mn^{4+}$ is 3.4 times greater than that of CAO doped with $Mn^{2+}$. The researchers have deliberately control the content of $Mn^{2+}$ or $Mn^{4+}$ by adding reductant to the reagents when they are sintered.

## References

[1]  Blasse G, and Geiabmaier B C 1994 *Luminescent Materials* (Springer-Verlag, Berlin)
[2]  Andre Bleise, Holger Winkler and Thomas Jüstel 1999 *On the Luminescence of Mn$^{4+}$ and Mn$^{2+}$* (University of Applied Sciences Münster, Stegerwaldstrabe 39, D-48565)
[3]  Yukito Tanabe and Satoru Sugano 1954 On the absorption spectra of complex Ions *J. Phys. Soc. Jpn.* **9** 753-766
[4]  Adam Bartecki and Krzysztof Kurzak 1981 *Calculations of the Racah Parameter B and Crystal Field Parameters $D_s$ and $D_t$ for $d^2$, $d^3$, $d^7$, $d^8$ -Metal Complexes* vol 24 no 5-6 (Bulletin de l'académie polonaise des sciences serie le des sciences chimiques)
[5]  König E *The Nephelauxetic Effect — Calculation and Accuracy of the Interelectronic Repulsion Parameters*, (Zeitschrift Für Naturforschung, pp.175-212)
[6]  Wei Q 2010 Investigations of the Optical and EPR Spectra for Cr$^{3+}$ Ions in Diammonium Hexaaqua Magnesium Sulphate Single Crystal, *Acta Phys. Pol.* Vol. 118
[7]  Casalboni M, Ciafardone V, Giuli G, Izzi B, Paris E and Prosposito P 1996 An optical study of silicate glass containing ions Cr$^{3+}$ and Cr$^{6+}$, *J. Phys. Cond. Matter* 8 9059–9069
[8]  Richard L 1963 Electronic spectra of transition metal complexes, *J. Chem. Edu.* 40 (3), pp 135.
[9]  Simon A, Vander Sluis J H and Biedenhan L C 1954 *Tables of the racah coefficients* (Yale University New Haven Connecticut).