

Calculations of the Racah parameter B for Mn^{4+} and Mn^{2+} ions doped in CaAl_2O_4

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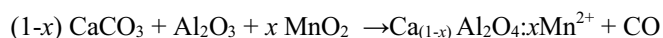
Abstract. The luminescent materials $\text{CaAl}_2\text{O}_4:\text{Mn}^{4+}$ and $\text{CaAl}_2\text{O}_4:\text{Mn}^{2+}$ were synthesized by solid state reaction method. The red luminescence of $\text{CaAl}_2\text{O}_4:\text{Mn}^{4+}$ shows an asymmetric broad band peaking at 650 nm, respectively to the characteristic luminescence of Mn^{4+} ions. The emission spectrum of $\text{CaAl}_2\text{O}_4:\text{Mn}^{2+}$ 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 β . The β coefficient of $\text{CaAl}_2\text{O}_4:\text{Mn}^{4+}$ 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 β 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_2O_4 (CAO) host lattice.

2. Experiments

The CAO materials ($\text{CAO}:\text{Mn}^{2+}$ or $\text{CAO}:\text{Mn}^{4+}$) were synthesized by solid state reaction. Commercial powders of Al_2O_3 , B_2O_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_2O_3 (used as fluxing agents). The mixtures are well grinded for two hours by using an agate pestle and mortar. Then, the mixtures were annealed at 1250 °C for 2h. The formation of $\text{CAO}:\text{Mn}^{2+}$ is described by following chemical reaction:



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 diffraction (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 Fluorescent 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 2θ angle of 22° , 30° , 35.5° , 37.5° shows that CaAl_2O_4 phase are the dominating phase, the $\text{Ca}_3\text{Al}_2\text{O}_6$ 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 $a = 8.740 \text{ \AA}$, $b = 8.100 \text{ \AA}$, $c = 15.130 \text{ \AA}$ và $\alpha = \gamma = \beta = 90^\circ$.

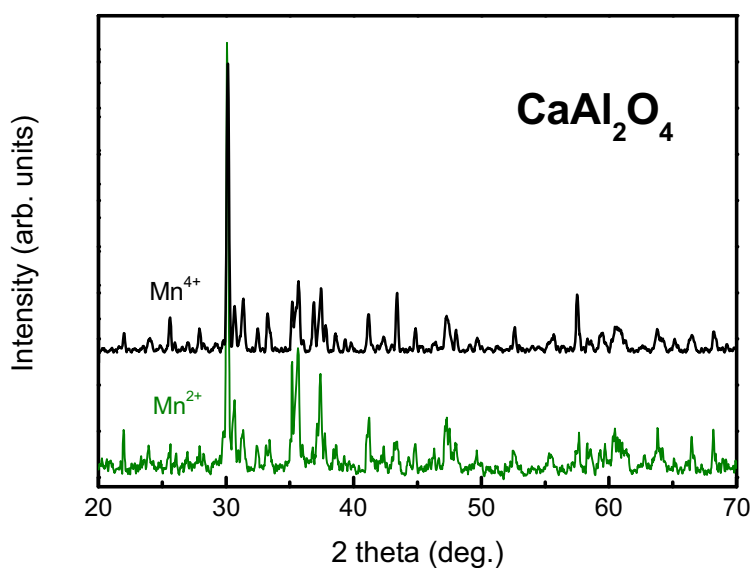


Figure 1. X-ray diffraction of CaO:Mn^{2+} (2 mole%) and CaO:Mn^{4+} (2 mole%).

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 $\lambda_{\text{ex}} = 425 \text{ nm}$ and $\lambda_{\text{em}} = 545 \text{ nm}$, 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 $\sim 650 \text{ nm}$, 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.

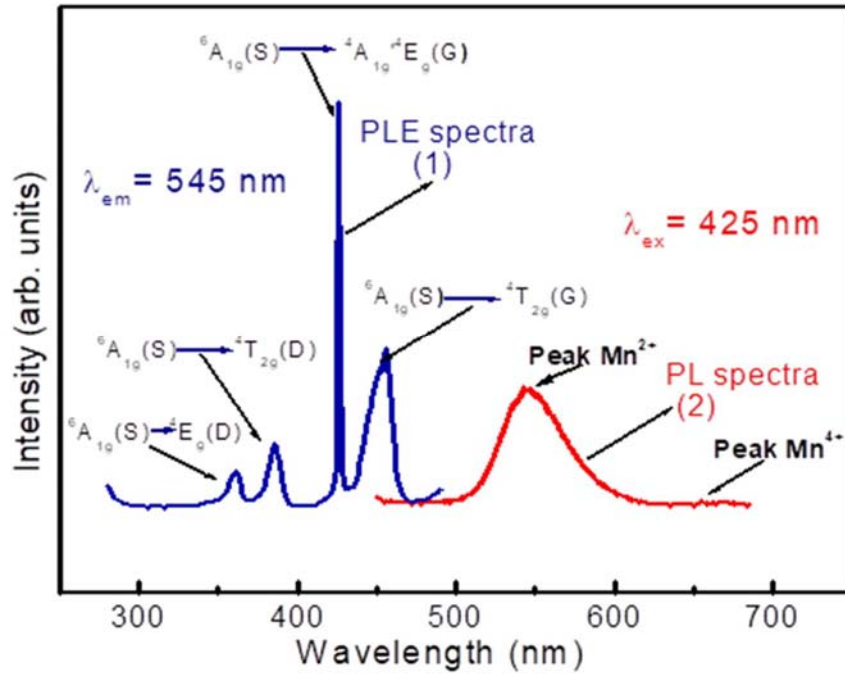


Figure 2. PLE and PL spectra of CAO:Mn²⁺

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

$$v_1 = E[{}^4E({}^4G), {}^4A_1({}^4G)] - E[({}^6A_1)] \quad (1)$$

$$= 10B + 5C$$

$$v_2 = E[{}^4E(D)] - E[({}^6A_1)] \quad (2)$$

$$= 17B + 5C$$

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

$$v_2 - v_1 = 7B. \quad (3)$$

We have $v_2 = 27777 \text{ cm}^{-1}$, and $v_1 = 23474 \text{ cm}^{-1}$. Substituting v_1 and v_2 into (3), we found that $B = 615 \text{ cm}^{-1}$ and $C = 3464 \text{ cm}^{-1}$. The nephelauxetic effect β is calculated by the formula $\beta = B/B_0$, where $B_0 = 785 \text{ cm}^{-1}$ [4, 5] is the Racah parameters for free Mn²⁺ 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 $v_3 = 22123 \text{ cm}^{-1}$. 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 650 cm^{-1} . Therefore $Dq = 650 \text{ cm}^{-1}$ or the crystal field of Mn²⁺ doped CAO is $\Delta = 6500 \text{ cm}^{-1}$ ($\Delta = 10Dq$).

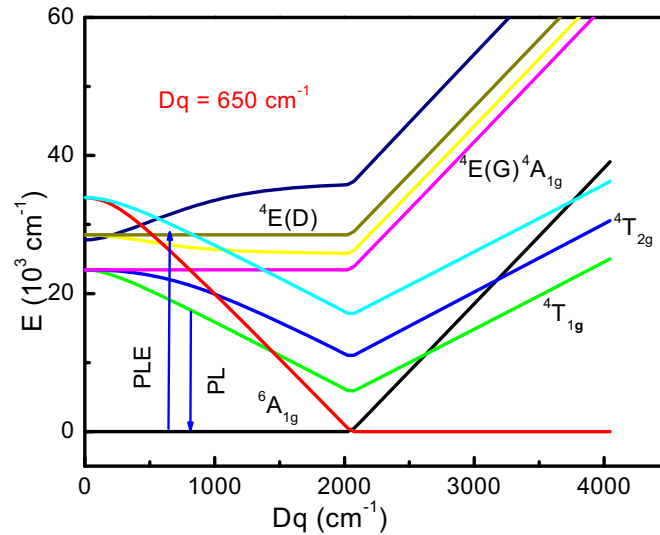


Figure 3. Determine Dq from T-S diagram [3]

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+} .

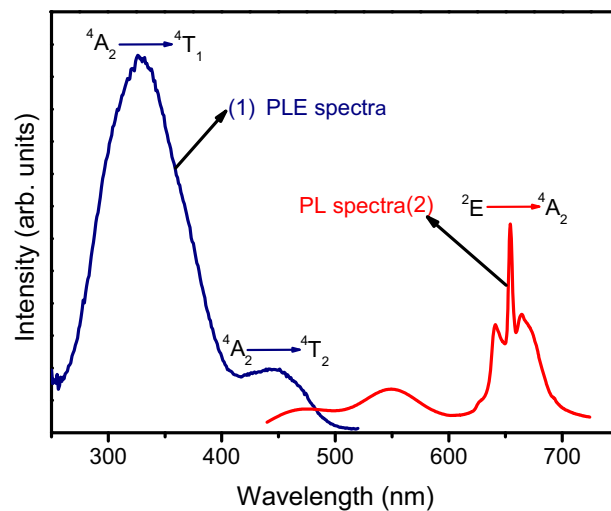


Figure 4. PL and PLE spectra of CAO:Mn^{4+} with $\lambda_{\text{ex}} = 450 \text{ nm}$ and $\lambda_{\text{em}} = 650 \text{ nm}$

Determine Racah parameter B from diagrams and formula.

The wavelength $\lambda = 450$ nm and $\lambda = 328$ nm correspond to wavenumbers of $\nu_1 = 22222$ cm^{-1} and $\nu_2 = 30487$ cm^{-1} , respectively. The ratio between ν_2 and ν_1 is $\nu_2/\nu_1 = 1.37$ [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 Δ/B axis and its intersects E/B axis at $E/B = 27.4$. From $E = 22222$ cm^{-1} , we found that $B = 811 \text{ cm}^{-1}$, $\Delta = 22222$ cm^{-1} and $Dq = 222$ cm^{-1} [7] (the ν and E signs could be used interchangeably).

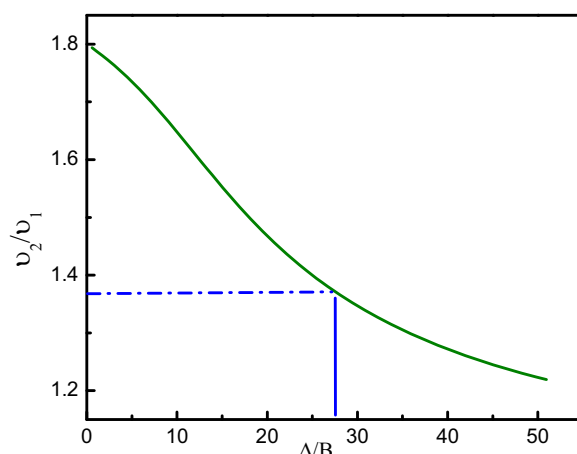


Figure 5. The relationship between ν_2/ν_1 and Δ/B [8].

From the formula $B = \frac{2\nu_1^2 + 2\nu_2^2 - 3\nu_1\nu_2}{15\nu_2 - 27\nu_1}$ [8, 9] we found that $B = 808$ cm^{-1} . The nephelauxetic effect coefficient $\beta = B/B_0$, where $B_0 = 1160 \text{ cm}^{-1}$, [9] is the Racah parameters for free Mn^{4+} ions. The calculated coefficient is $\beta = 0.7$. The small β indicates that the d -orbitals of Mn^{4+} ions expands greatly.

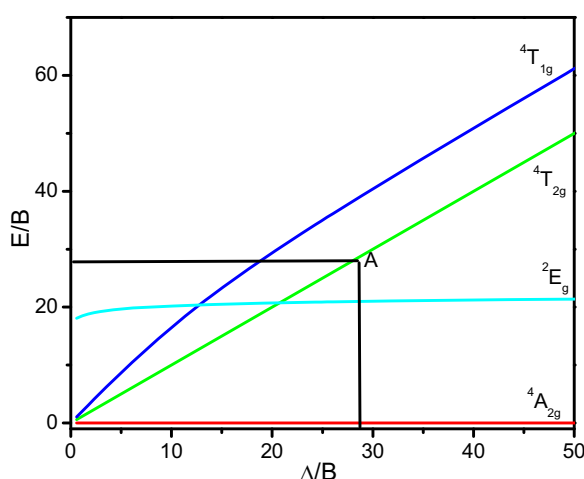


Figure 6. Determination of B for d^3 configuration from T-S diagram.

4. Conclusion

Based on the experimental photoluminescence excitation spectrum are provided to calculate the Racah parameter B and the nephelauxetic effect β . Various methods have been applied to determine the B parameter, the nephelauxetic effect coefficient β , as well as crystal field Dq or Δ . For the same CAO host lattice, the expansion coefficient of d -orbitals 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 β ($= 0.7$) mean that should strong interaction between the ligand field with the d -orbitals of Mn^{4+} ions. For electrons in d^5 configuration (Mn^{4+}), both calculation methods yield similar B parameters. The crystal field force of CAO: Mn^{4+} , and CAO: Mn^{2+} are $\Delta = 22222\text{ cm}^{-1}$ and $\Delta = 6500\text{ cm}^{-1}$, 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

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