

## Energy level diagram of lanthanide ions in calcium aluminosilicate phosphors

Sơ đồ năng lượng của các ion lanthanide trong vật liệu phát quang calcium aluminosilicate

Ho Van Tuyen<sup>a,b\*</sup>, Nguyen Ha Vi<sup>a,b</sup>, Nguyen Thi Thai An<sup>a,b</sup>  
Hò Văn Tuyền<sup>a,b\*</sup>, Nguyễn Hạ Vi<sup>a,b</sup>, Nguyễn Thị Thái An<sup>a,b</sup>

<sup>a</sup>Institute of Research and Development, Duy Tan University, Danang, 550000, Vietnam

<sup>a</sup>Viện Nghiên cứu và Phát triển Công nghệ Cao, Trường Đại học Duy Tân, Đà Nẵng, Việt Nam.

<sup>b</sup>The Faculty of Natural Sciences, Duy Tan University, Danang, 550000, Vietnam.

<sup>a</sup>Khoa Khoa học Tự nhiên, Trường Đại học Duy Tân, Đà Nẵng, Việt Nam.

(Ngày nhận bài: 03/7/2020, ngày phản biện xong: 22/7/2020, ngày chấp nhận đăng: 17/9/2020)

### Abstract

Calcium aluminosilicate ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) phosphors doped with  $\text{Ln}^{3+}$  (1 mol%) ions (Ln: Eu, Ce, and Tb) were prepared by the solid-state reaction at high temperature. Photoluminescence (PL), photoluminescence excitation spectra (PLE) of  $\text{Ce}^{3+}$  and  $\text{Eu}^{3+}$  ions in  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  material have been studied and used to predict the lowest f-d transition energies as well as charge transfer energies of lanthanides in  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  host lattice. From PLE spectra data, the host referred binding energy (HRBE) diagram of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  material has been constructed to present the energy levels position of all lanthanide ions relative to the valence and conduction bands. The obtained energy levels diagram has been checked by comparison the calculation energy the experimental energy of  $\text{Tb}^{3+}$  ions from the excitation spectra of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tb}^{3+}$  material and HRBE scheme has also been used to estimate the possibility of the energy transfer process between several lanthanides in  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  materials.

**Keywords:** HRBE diagram; lanthanide ions; calcium aluminosilicate.

### Tóm tắt

Vật liệu calcium aluminosilicate ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) pha tạp các ion  $\text{Ln}^{3+}$  (1 mol%) (Ln: Eu, Ce, và Tb) được chế tạo bằng phương pháp phản ứng pha rắn ở nhiệt độ cao. Phổ phát quang (PL), phổ kích thích phát quang (PLE) của ion  $\text{Ce}^{3+}$  và  $\text{Eu}^{3+}$  trong vật liệu  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  đã được nghiên cứu và sử dụng để tiên đoán năng lượng của chuyển dời f-d thấp nhất cũng như năng lượng truyền điện tích của các ion lanthanide trong mạng nền  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ . Từ dữ liệu phổ PLE, giản đồ năng lượng (HRBE) của  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  đã được xây dựng để biểu diễn vị trí các mức năng lượng của ion lanthanide so với vùng dẫn và vùng hóa trị của mạng nền. Giản đồ năng lượng HRBE được đánh giá bằng cách so sánh năng lượng tiên đoán với giá trị thực nghiệm thu từ phổ kích thích của  $\text{Tb}^{3+}$  trong  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  và đồng thời giản đồ HRBE cũng được sử dụng để xem xét khả năng của quá trình truyền năng lượng giữa một số ion lanthanides trong vật liệu  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ .

**Từ khóa:** Giản đồ năng lượng HRBE; lanthanide ions; calcium aluminosilicate.

\* Corresponding Author: Institute of Research and Development, Duy Tan University, Danang, 550000, Vietnam; The Faculty of Natural Sciences, Duy Tan University, Danang, 550000, Vietnam.

Email: hovantuyen@gmail.com, hovantuyen@duytan.edu.vn

## 1. Introduction

Lanthanide ions doped silicate hosts have been studied for a long time, such as  $\text{Sr}_2\text{MgSiO}_7$  [1],  $\text{M}_3\text{MgSi}_2\text{O}_8$  (M: Ba, Ca, Sr) [2] and  $\text{M}_2\text{Al}_2\text{SiO}_7$  (M: Sr, Ca) [3, 4] in which the luminescent materials based on  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  (CAS) host containing lanthanide ions have been widely used in light-emitting diodes, and laser [5-7]. A lot of studies dealing with luminescent feature, long-persistent, energy transfer, and thermoluminescence of the lanthanides doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  are available in literatures [6-12], however, there is no report mentioning to the energy levels position of the lanthanide ions in this host lattice. It is known that luminescent properties of lanthanide ions in a specific compound are influenced by their 4f and 5d energy levels position comparing to the valence and conduction bands of that compound [13, 14]. Hence, predicting position of 4f and 5d energy levels of a specific lanthanide ion in a host material is very important for the estimation of the application possibilities of this material when it is doped with this ion. Position of 4f state of all divalent and trivalent lanthanide ions in the specific compound can be generally predicted from photoluminescence excitation spectra (PLE) of a lanthanide ion by using the charge transfer model [15]. According to this model, the 4f ground states position for all  $\text{Ln}^{2+}$  and  $\text{Ln}^{3+}$  ions can be constructed based on the charge transfer energy ( $E^{\text{CT}}$ ) of a lanthanide because the relative energy position of the 4f ground state of these ions is weakly influenced by the nature of the host materials and is almost unchanged in the series of lanthanides. Among  $\text{Ln}^{3+}$  ions, the  $\text{Eu}^{3+}$  ion are widely used as a reference ion to determine  $E^{\text{CT}}$  because its charge transfer spectrum often occurs at low energy. To locate the 5d levels position, the lowest 4f $\rightarrow$ 5d excitation energy ( $E_{\text{fd}}$ ) of the  $\text{Ce}^{3+}$  ion is often used because of its simple PLE spectra and low energies and then the 5d levels of all other

lanthanide ions can be predicted by using the charge transfer and chemical shift model [16, 17].

In our knowledge there has been no literature presenting of the energy levels of lanthanide ions in  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  material by the spectroscopic technique. In this work, therefore, the host referred binding energy (HRBE) scheme for all lanthanide ions doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  material was constructed by using information from PLE spectra of  $\text{Eu}^{3+}$  and  $\text{Ce}^{3+}$  ions doped this compound. The obtained energy level diagram was confirmed by comparison of the calculation data with the experimental data of  $\text{Tb}^{3+}$  ions doped  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphors.

## 2. Experiment

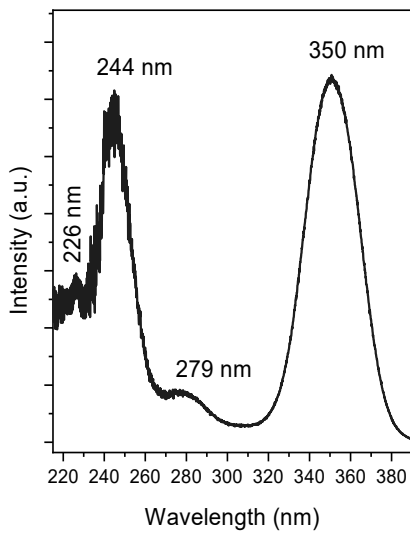
Calcium aluminosilicate  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  materials doped with  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Ce}, \text{Eu}, \text{Tb}$ ) ions (1 mol%) were synthesized by the solid-state reaction at 1280°C for 1 h. Ingredients used to synthesize phosphors include of  $\text{CaCO}_3$  (AR),  $\text{Al}_2\text{O}_3$  (AR),  $\text{SiO}_2$  (Sigma),  $\text{CeO}_2$  (Merck),  $\text{Tb}_2\text{O}_3$  (Sigma), and  $\text{Eu}_2\text{O}_3$  (Merck). They were weighed according to the nominal compositions of samples and mixed homogeneously for 2 h. The mixture was calcined at 1280°C for 1 h in air and then it was cooled to room temperature to obtain final sample. Photoluminescence (PL) and PLE spectra were measured at room temperature using a spectrophotometer (FL3-22; Horiba Jobin-Yvon) with Xenon -450W lamp.

## 3. Results and discussion

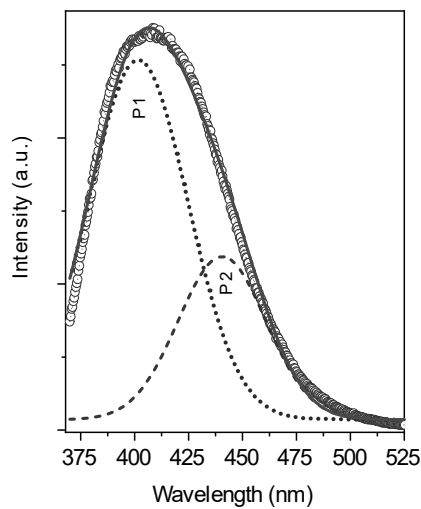
### 3.1. Luminescent properties of $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$ and $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu}^{3+}$ samples

Fig. 1 presents PLE spectrum in the 240-390 nm region of  $\text{Ce}^{3+}$  doped CAS material recorded at the emission wavelength of 420 nm. The PLE spectrum with a broad band includes of four excitation bands centered at 350 nm, 279 nm, 244 nm and 226 nm, which are

attributed to the electron transitions from the 4f ground state to the 5d ( $J = 1, 2, 3, 4, 5$ ) excited states of  $Ce^{3+}$  ions [14]. These bands are similar to the observed excited transitions of  $Ce^{3+}$  ions in the same compound in literature [18] (bands locating at 350, 307, 278, 244 and 226 nm) except for the band at 307 nm. The excitation band peaking at 350 nm (3.54 eV) is the lowest 4f→5d transition of  $Ce^{3+}$  ions in this materials, and energy  $E_{fd}$  ( $Ce^{3+}$ , CAS) of this transition will be used to determine the  $E_{fd}$  ( $Ln^{3+}$ , CAS) for the other lanthanide ions, that contribute to energy levels diagram in next section.



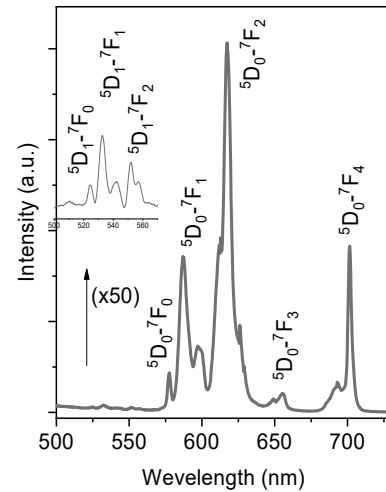
**Fig. 1.** Photoluminescence excitation spectrum of  $Ce^{3+}$  ions in  $Ca_2Al_2SiO_7$  material.



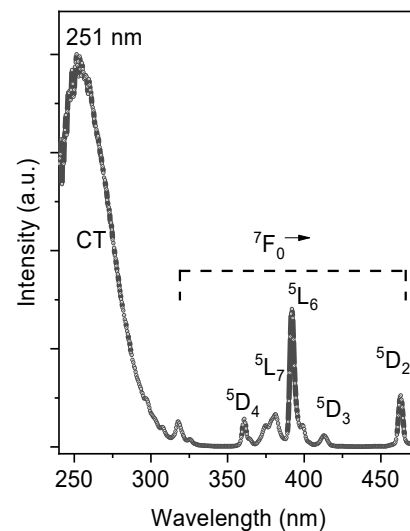
**Fig. 2.** Photoluminescence spectrum of  $Ce^{3+}$  ions in  $Ca_2Al_2SiO_7$  material

Photoluminescence spectrum of  $Ce^{3+}$  ions in  $Ca_2Al_2SiO_7$  material under excitation at 350 nm

is presented in Fig. 2, and it shows a broad band in the 350-500 nm region. This broad band is contributed of two emission bands P1 and P2 peaked at 403 nm (3.07 eV) and 440 nm (2.82 eV), which corresponds to  $Ce^{3+}$  transitions from the lowest 5d excited state to the 4f ground state levels  $^2F_{7/2}$  and  $^2F_{5/2}$ , respectively. Generally, two levels are typically separated by an energy of  $\sim 0.25$  eV corresponding to the spin-orbital interaction energy [14, 19]. In the case of CAS material in this work, this splitting energy is  $\sim 0.25$  eV which is just equal to the theoretical result and also similar to other results of 0.25~0.27 eV [20, 21].



**Fig. 3.** Photoluminescence spectrum of  $Eu^{3+}$  ions doped  $Ca_2Al_2SiO_7$  material.



**Fig. 4.** Photoluminescence excitation spectrum of  $Eu^{3+}$  ions doped  $Ca_2Al_2SiO_7$  material.

PL spectrum of  $\text{Eu}^{3+}$  ions doped CAS material under the excitation radiation of 394 nm at room temperature is presented in Fig. 3. It includes of five sharp peaks locating at 578 nm, 588 nm, 617 nm, 655 nm and 702 nm, which are the electron transitions from the excited  $^5\text{D}_0$  level to the ground states  $^7\text{F}_J$  ( $J = 0, 1, 2, 3, 4$ ), respectively. In addition, several weak peaks are also observed in the 500-570 nm region (the inset in Fig. 3), derived from the transitions between  $^5\text{D}_1$  excited level and the ground states  $^7\text{F}_0$ ,  $^7\text{F}_1$  and  $^7\text{F}_2$  of  $\text{Eu}^{3+}$  ions. PLE spectrum of  $\text{Eu}^{3+}$  recorded at the emission wavelength of 617 nm is shown in Fig. 4. The excitation spectrum consists of several sharp peaks in the 310 -480 nm region and a broad band in the 240 - 310 nm. These sharp peaks are the excitation transitions from the ground  $^7\text{F}_0$  state to the excited levels of  $\text{Eu}^{3+}$  ions:  $^7\text{F}_0 \rightarrow ^5\text{D}_2$  (463 nm),  $^7\text{F}_0 \rightarrow ^5\text{D}_3$  (412 nm),  $^7\text{F}_0 \rightarrow ^5\text{L}_6$  (392 nm),  $^7\text{F}_0 \rightarrow ^5\text{L}_7$  (381 nm) and  $^7\text{F}_0 \rightarrow ^5\text{D}_4$  (361 nm) transitions, in which the  $^7\text{F}_0 \rightarrow ^5\text{L}_6$  transition reaches the highest intensity. While, the broad band centered at 251 nm (4.94 eV) is due to the charge transfer transition between the  $\text{Eu}^{3+}$  ions and the host lattice. Energy of the charge transfer  $E^{\text{CT}}$  of  $\text{Eu}^{3+}$  ions relatives to the energy difference  $E_{\text{Vf}}$  of electron transfer from the top of the valence band to the ground state of  $\text{Eu}^{2+}$  ions in the same compound and  $E_{\text{Vf}}$  is used to build the energy level scheme of lanthanide ions in CAS host in the next section.

### 3.2. The energy levels diagram for lanthanide ions in $\text{Ca}_2\text{Al}_2\text{SiO}_7$

In this section, the host referred binding energy (HRBE) diagram of all lanthanide ions in  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  material will be constructed by using the Dorenbos model which includes the redshift and charge transfer energies. Besides, the predicted energy of the  $f \rightarrow d$  transition of  $\text{Tb}^{3+}$  ions from the energy levels diagram was compared to the experimental energy of

$\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tb}^{3+}$  sample to verify the consistence of the obtained energy levels scheme.

#### 3.2.1. Predicting the energies of the $f-d$ transitions for $\text{Ln}^{3+}$ and $\text{Ln}^{2+}$ ions in $\text{Ca}_2\text{Al}_2\text{SiO}_7$

In  $\text{Ln}^{3+}$  ions doped CAS phosphors, the lowest  $4f \rightarrow 5d$  transition energies  $E_{\text{fd}}(\text{Ln}^{3+}, \text{CAS})$  of the  $\text{Ln}^{3+}$  ions are shifted toward the lower energy (redshift) in the comparison with those of corresponding  $\text{Ln}^{3+}$  free ions. According to the redshift model, the redshift value  $D(\text{Ln}^{3+}, \text{CAS})$  is the same for all lanthanides in the same compound but it depends on the compound and it relates to the energies of the lowest  $4f \rightarrow 5d$  transitions of  $\text{Ln}^{3+}$  ions as below [17, 22]:

$$E_{\text{fd}}(\text{Ln}^{3+}, \text{CAS}) = E_{\text{fd}}(\text{Ln}^{3+}, \text{free}) - D(\text{Ln}^{3+}, \text{CAS}) \quad (1)$$

where  $E_{\text{fd}}(\text{Ln}^{3+}, \text{free})$  and  $E_{\text{fd}}(\text{Ln}^{3+}, \text{CAS})$  are the energies of the lowest  $4f \rightarrow 5d$  excited state of free  $\text{Ln}^{3+}$  ion and corresponding  $\text{Ln}^{3+}$  ion in  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ , respectively. The values of  $E_{\text{fd}}(\text{Ln}^{3+}, \text{free})$  for all lanthanides have been found in literature [17]. From PLE spectrum of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$  in Fig. 1, the  $E_{\text{fd}}(\text{Ce}^{3+}, \text{CAS})$  energy is determined to be 3.54 eV and hence the  $D(\text{Ln}^{3+}, \text{CAS})$  is 2.57 eV. By using Eq.1 and the  $D(\text{Ln}^{3+}, \text{CAS})$  result, the  $E_{\text{fd}}(\text{Ln}^{3+}, \text{CAS})$  values of other lanthanide ions are obtained and presented in column 6 in Table 1. For  $\text{Tb}^{3+}$  ions,  $E_{\text{fd}}(\text{Tb}^{3+}, \text{CAS})$  energies were predicted two values, which correspond to the spin-allowed and spin-forbidden transitions of the  $\text{Tb}^{3+}$  in CAS materials. Two values will be used to compare to the experimental values in next section to evaluate the obtained energy levels diagram.

**Table 1.** Charge transfer energies ( $E^{CT}(\text{Ln}^{3+}, \text{CAS}) \equiv E_{\text{Vf}}(\text{Ln}^{2+}, \text{CAS})$ ), the lowest 4f→5d energies ( $E_{\text{fd}}$ ) for  $\text{Ln}^{3+}$  and  $\text{Ln}^{2+}$  ions in CAS host (in eV).  $n$  is the number of electrons in the 4f configuration in trivalent lanthanides.

Ln	$n$	$E_{\text{Vf}}(\text{Ln}^{2+}, \text{CAS})$	$E_{\text{fd}}(\text{Ln}^{2+}, \text{CAS})$	$E_{\text{Vf}}(\text{Ln}^{3+}, \text{CAS})$	$E_{\text{fd}}(\text{Ln}^{3+}, \text{CAS})$
La	0	10.55	-2.36	-	.....
Ce	1	9.07	-1.07	3.51	3.54
Pr	2	7.81	0.14	1.67	5.05
Nd	3	7.37	0.51	0.17	6.34
Pm	4	7.28	0.54	-0.26	6.66
Sm	5	6.19	1.58	-0.46	6.76
Eu	6	4.94	2.80	-1.73	7.92
Gd	7	9.50	-1.62	-3.06	9.22
Tb	8	8.15	-0.23	1.85	4.32-5.17*
Dy	9	7.21	0.75	0.42	6.02
Ho	10	7.34	0.83	-0.67	7.07
Er	11	7.52	0.70	-0.61	6.97
Tm	12	6.66	1.53	-0.44	6.92
Yb	13	5.37	2.80	-1.49	8.12
Lu	14	-	-	-2.74	9.42

\* Two energies corresponding to the 4f→5d allowed transition and the 4f→5d forbidden transition of  $\text{Tb}^{3+}$  ions

In the case of  $\text{Ln}^{2+}$  ions, energy  $E_{\text{fd}}(\text{Ln}^{2+}, \text{CAS})$  of the lowest 4f→5d transitions are estimated with the same formula as  $E_{\text{fd}}(\text{Ln}^{3+}, \text{CAS})$ . In which, the  $D(\text{Ln}^{2+}, \text{CAS})$  redshift relates to the  $D(\text{Ln}^{3+}, \text{CAS})$  through the following equation [17]:

$$D(\text{Ln}^{2+}, \text{CAS}) = 0.64 * D(\text{Ln}^{3+}, \text{CAS}) - 0.233 \quad (2)$$

Using Eq. 2,  $D(\text{Ln}^{2+}, \text{CAS})$  is found to be 1.41 eV, thus the  $E_{\text{fd}}(\text{Ln}^{2+}, \text{CAS})$  energies of all  $\text{Ln}^{2+}$  ions in CAS host are determined and indicated in column 4 of Table 1.

### 3.1.2. Predicting the $E_{\text{Vf}}(\text{Ln}^{2+}, \text{CAS})$ , $E_{\text{Vf}}(\text{Ln}^{3+}, \text{CAS})$ energies and HRBE diagram of the lanthanides in CAS materials

It is well known that the energy needed to transfer an electron from the valence band to a trivalent lanthanide impurity in a compound is called the charge transfer energy  $E^{CT}$ . The  $E^{CT}$  energy of a trivalent lanthanide ion provides information on the locations of the ground state of the corresponding divalent lanthanide ion

relative to the top of the valence band in the same compound [22, 23].

$$E_{\text{Vf}}(\text{Ln}^{2+}, \text{CAS}) = E^{CT}(\text{Ln}^{3+}, \text{CAS}) \quad (3)$$

The  $E^{CT}(\text{Eu}^{3+}, \text{CAS})$  was determined as 4.94 eV from the excitation spectrum of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu}^{3+}$  in Fig. 4, this energy is also  $E_{\text{Vf}}(\text{Eu}^{2+}, \text{CAS})$  of  $\text{Eu}^{2+}$  ions. It is possible to predict the  $E_{\text{Vf}}(\text{Ln}^{2+}, \text{CAS})$  for all other divalent lanthanides in CAS host using the obtained  $E_{\text{Vf}}(\text{Eu}^{2+}, \text{CAS})$  and the energy difference  $\Delta E_{\text{Vf}}(\text{Ln}^{2+}, \text{Eu}^{2+})$  in ref. [24], results are shown in column 3 in Table 1.

Similarly to the  $E_{\text{Vf}}(\text{Ln}^{2+})$  of divalent lanthanides, the energy of the ground states  $E_{\text{Vf}}(\text{Ln}^{3+})$  of the trivalent lanthanides can be located by measuring the  $E^{CT}$  energy of the tetravalent lanthanides  $\text{Ln}^{4+}$  ions. However, there is too little available information on such transitions of  $\text{Ln}^{4+}$  in literature. Instead, the position of the ground state  $E_{\text{Vf}}(\text{Ln}^{3+})$  of trivalent lanthanides can be estimated based on the Coulomb correlation energy  $U(6, \text{CAS})$ ,

which is known as the energy difference between the ground state energy of  $\text{Eu}^{2+}$  and that of  $\text{Eu}^{3+}$  [17]:

$$U(6, \text{CAS}) = E_{Vf}(\text{Eu}^{2+}, \text{CAS}) - E_{Vf}(\text{Eu}^{3+}, \text{CAS}) \quad (4)$$

In addition, the  $U(6, \text{CAS})$  value relates to centroid shift  $\varepsilon_C(\text{Ce}^{3+}, \text{CAS})$  of  $\text{Ce}^{3+}$  ions in CAS host through expression [17]:

$$U(6, \text{CAS}) = 5.44 + 2.834 * e^{\frac{-\varepsilon_C(\text{Ce}^{3+}, \text{CAS})}{2.2}} \quad (5)$$

The centroid shift  $\varepsilon_C(\text{Ce}^{3+}, \text{CAS})$  is the shift of the barycenter of  $5d_i$  levels of  $\text{Ce}^{3+}$  ions in CAS host comparing to gaseous  $\text{Ce}^{3+}$  and determined by the following equation [22]:

$$\varepsilon_C(\text{Ce}^{3+}, \text{CAS}) = 6.35 - \frac{1}{5} \sum_{i=1}^5 E_{fd_i}(\text{Ce}^{3+}, \text{CAS}) \quad (6)$$

Where 6.35 eV is the average energy of the  $5d_i$  levels in gaseous  $\text{Ce}^{3+}$ , and  $E_{fd_i}(\text{Ce}^{3+}, \text{CAS})$  are the f-d excited transition energies of  $\text{Ce}^{3+}$  in CAS host which are obtained from the PLE spectrum in Fig. 1 and literature 19. Using Eq. 6 and Eq. 5, the values of  $\varepsilon_C(\text{Ce}^{3+}, \text{CAS})$  and  $U(6, \text{CAS})$  are found to be 1.83 and 6.67 eV, respectively. Hence, with the known energies of  $E_{Vf}(\text{Eu}^{2+}, \text{CAS})$  and  $U(6, \text{CAS})$ , the values  $E_{Vf}(\text{Ln}^{3+}, \text{CAS})$  can be predicted for all other lanthanides in CAS host by using Eq. 4. The results of  $E_{Vf}(\text{Ln}^{3+}, \text{CAS})$  are shown in column 5 in Table 1.

The energy differences between the 4f ground state energy of  $\text{Ln}^{2+}$  ions with that of  $\text{Eu}^{2+}$  ( $\Delta E_{4f}(\text{Ln}^{2+}, \text{Eu}^{2+})$ ) and between the 4f ground state energy of  $\text{Ln}^{3+}$  ions with that of  $\text{Ce}^{3+}$  ( $\Delta E_{4f}(\text{Ln}^{3+}, \text{Ce}^{3+})$ ) are given in [17]. Therefore, the  $E_{4f}(\text{Ln}^{2+}, \text{CAS})$  and  $E_{4f}(\text{Ln}^{3+}, \text{CAS})$  energy values for all lanthanides are calculated and presented in the columns 3 and 5 of Table 2. Combining the  $E_{4f}(\text{Ln}^{2+}, \text{CAS})$  and the  $E_{fd}(\text{Ln}^{2+}, \text{CAS})$  values, the value of  $E_{5d}(\text{Ln}^{2+}, \text{CAS})$  energies with respect to the top of the valence band of all divalent lanthanides is calculated by the following expression:

$$E_{5d}(\text{Ln}^{2+}, \text{CAS}) = E_{4f}(\text{Ln}^{2+}, \text{CAS}) + E_{fd}(\text{Ln}^{2+}, \text{CAS}) \quad (7)$$

The  $E_{5d}(\text{Ln}^{2+}, \text{CAS})$  energies are found by using Eq. 7 and presented in columns 4 of Table 2. Similar to the  $E_{5d}(\text{Ln}^{2+}, \text{CAS})$ , the energy of  $E_{5d}(\text{Ln}^{3+}, \text{CAS})$  energies of all trivalent lanthanides are also determined by the same equation and shown in columns 6 of Table 2. These energies combining the band gap ( $E_g$ ) of this host which is 6.5 eV [25] are used to construct a host referred binding energy diagram (HRBE) in Fig. 5 that shows the location of the  $4f^n$  and  $4f^{n-1}5d$  levels of all divalent and all trivalent lanthanide impurities relative to the top of the valence band of CAS host material.

**Table 2.** The energy levels position of 4f and 5d states for divalent and trivalent lanthanides comparing to the top of the valence band; All energies are in eV.

Ln	n	$E_{4f}(\text{Ln}^{2+})$	$E_{5d}(\text{Ln}^{2+})$	$E_{4f}(\text{Ln}^{3+})$	$E_{5d}(\text{Ln}^{3+})$
La	0	10.55	8.19	....	....
Ce	1	9.07	8.00	3.51	7.05
Pr	2	7.81	7.95	1.67	6.72
Nd	3	7.37	7.88	0.17	6.51
Pm	4	7.28	7.82	-0.26	6.40
Sm	5	6.19	7.77	-0.46	6.30
Eu	6	4.94	7.74	-1.73	6.19
Gd	7	9.50	7.88	-3.06	6.16
Tb	8	8.15	7.92	1.85	6.17
Dy	9	7.21	7.96	0.42	6.44

Ho	10	7.34	8.17	-0.67	6.40
Er	11	7.52	8.22	-0.61	6.36
Tm	12	6.66	8.19	-0.44	6.48
Yb	13	5.37	8.17	-1.49	6.63
Lu	14	....	....	-2.74	6.68

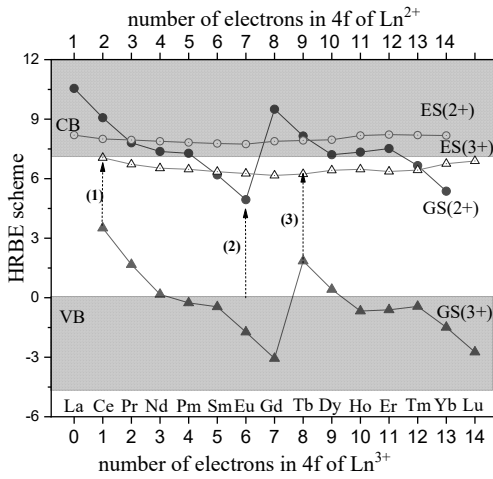


Fig. 5. The HRBE scheme of lanthanide ions in CAS host lattice

To check correctness of the obtained energy levels scheme of CAS host material, the PL and PLE spectra of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tb}^{3+}$  sample are measured and presented in Fig. 6 and Fig. 7. The PL spectrum under excitation at 368 nm ( ${}^7\text{F}_6 \rightarrow {}^5\text{D}_3$  transition) includes four strong emission peaks locating at 490, 544, 587 and 622 nm (Fig. 6), which are assigned to the emission transitions from the  ${}^5\text{D}_4$  excited level to the ground states  ${}^7\text{F}_J$  ( $J = 6, 5, 4, 3$ ) of  $\text{Tb}^{3+}$  ions, respectively. The excitation spectrum with several sharp intense peaks in the 300-400 nm region characterizes to the f-f excitation transitions of the  $\text{Tb}^{3+}$  ions, in which the strongest intensity at 368 nm is the  ${}^7\text{F}_6 \rightarrow {}^5\text{D}_3$  excitation transition. To obtain the f-d excitation transition of  $\text{Tb}^{3+}$  ions, the excitation spectrum was measured in the 220-300 nm short wavelength region as shown in Fig. 7. It indicates an intense band locating at 241 nm (5.14 eV) and a weaker band at 284 nm (4.36 eV) that are the f-d excitation transitions of  $\text{Tb}^{3+}$  ions from the 4f ground state to two 5d excited states (the first fd spin-allowed and spin-forbidden transitions) [26]. These energies

coincide with the calculation energies to be 5.17 eV (240 nm) and 4.32 eV (287 nm) as shown in Table 1 and it indicates that the obtained energy scheme can be used well to predict the energy levels position of lanthanides doped CAS host.

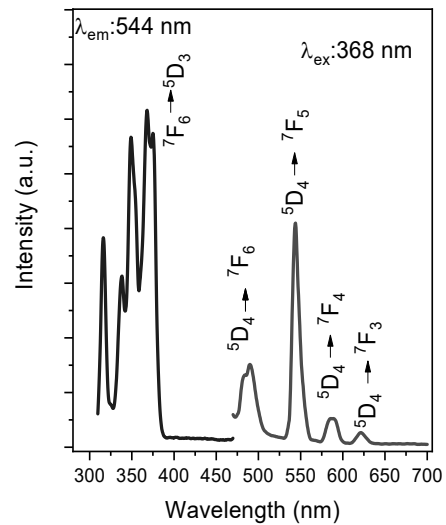


Fig. 6. PL and PLE spectra in the 300-475 nm of  $\text{Tb}^{3+}$  ions in CAS materials.

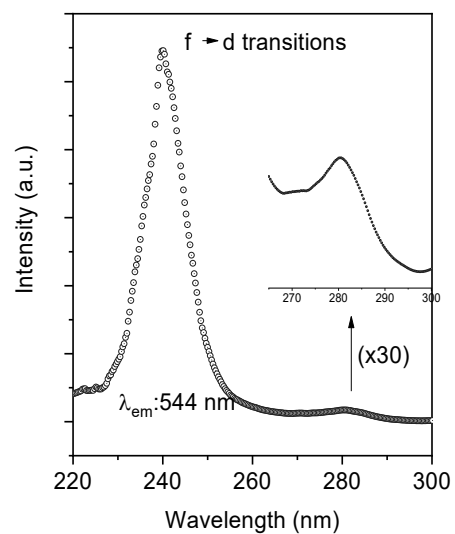


Fig. 7. PLE spectrum in the 220-300 nm region of  $\text{Tb}^{3+}$  ions in CAS materials.

The energy level diagram allows a better understanding of some luminescence process in lanthanide ions doped CAS. As can be seen from the Table 1, the predicted value of the lowest 4f-5d transition of  $\text{Eu}^{2+}$  ion is 2.80 eV, while the lowest 5d-4f transition value of  $\text{Ce}^{3+}$  ions is 2.82 eV, therefore, the energy transfer process from  $\text{Ce}^{3+}$  to  $\text{Eu}^{2+}$  ions is possible in CAS material.

#### 4. Conclusions

Luminescent properties of  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  phosphors doped with  $\text{Ln}^{3+}$  (1 mol%) ions (Ln: Eu, Ce, and Tb) were studied through photoluminescence and photoluminescence excitation spectra. The host referred binding energy diagram of lanthanide ions doped CAS material has been constructed using the lowest f-d transition energy of  $\text{Ce}^{3+}$  ions as well as charge transfer energy of  $\text{Eu}^{3+}$  ions. The obtained energy levels diagram has been checked by comparing the calculation energy and ??? the experimental energy of  $\text{Tb}^{3+}$  ions from the excitation spectra of CAS: $\text{Tb}^{3+}$  sample and it indicates that the HRBE scheme can well predict the energy levels position of lanthanides doped CAS host.

#### Acknowledgment

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.03-2018.323.

#### References

- [1] Y.H. Lin, Z.L. Tang, Z.T. Zhang, X.X. Wang, J.Y. Zhang, Prepa-ration of a new long afterglow blue-emitting  $\text{Sr}_2\text{MgSi}_2\text{O}_7$ - based photoluminescent phosphor, *Journal of Materials Science Letters*, 20 (2001) 1505-1506.
- [2] Y. Yonesaki, TakahiroTakei, NobuhiroKumada, NobukazuKinomura, Crystal structure of  $\text{Eu}^{2+}$ -doped  $\text{M}_3\text{MgSi}_2\text{O}_8$  (M=Ba, Sr, Ca) compounds and their emission properties, *Journal of Solid State Chemistry*, 182 (2009) 547-554.
- [3] M. Kimata, The structural properties of synthetic Sr-gehlenite,  $\text{Sr}_2\text{Al}_2\text{SiO}_7$ , *Zeitschrift für Kristallographie - Crystalline Materials*, 167 (1984) 103-116.
- [4] M.A. Bouhifd, G. Gruener, B.O. Mysen, P. Richet, Premelting and calcium mobility in gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) and pseudowollastonite ( $\text{CaSiO}_3$ ), *Physics and Chemistry of Minerals*, 29 (2002) 655-662.
- [5] P. Yang, X. Yu, H. Yu, T. Jiang, X. Xu, Z. Yang, D. Zhou, Z. Song, Y. Yang, Z. Zhao, J. Qiu,  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Bi}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}$ : A potential single-phased tunable-color-emitting phosphor, *Journal of Luminescence*, 135 (2013) 206-210.
- [6] G. Tiwari, N. Brahme, R. Sharma, D.P. Bisen, S.K. Sao, S.J. Dhoble, A study on the luminescence properties of gamma-ray-irradiated white light emitting  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Dy}^{3+}$  phosphors fabricated using a combustion-assisted method, *RSC Advances*, 6 (2016) 49317-49327.
- [7] P.L. Boulanger, J.-L. Doualan, S. Girard, J. Margerie, R. Moncorge, B. Viana, Excited-state absorption of  $\text{Er}^{3+}$  in the  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  laser crystal, *Journal of Luminescence*, 86 (2000) 15-21.
- [8] Q. Zhang, J. Wang, M. Zhang, W. Ding, Q. Su, Enhanced photoluminescence of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu}^{3+}$  by charge compensation method, *Applied Physics A*, 88 (2007) 805-809.
- [9] P. Yang, X. Yu, H. Yu, T. Jiang, D. Zhou, J. Qiu, Effects of crystal field on photoluminescence properties of  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Eu}^{2+}$  phosphors, *Journal of Rare Earths*, 30 (2012) 1208-1212.
- [10] G. Tiwari, N. Brahme, R. Sharma, D.P. Bisen, S.K. Sao, S. Tigga, Luminescence properties of dysprosium doped di-calcium di-aluminium silicate phosphors, *Optical Materials*, 58 (2016) 234-242.
- [11] N.M. Son, D.T. Tien, N.T.Q. Lien, V.X. Quang, N.N. Trac, T.T. Hong, H.V. Tuyen, Luminescence and Thermal-Quenching Properties of Red-Emitting  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Sm}^{3+}$  Phosphors, *Journal of Electronic Materials*, 49 (2020) 3701-3707.
- [12] H. Jiao, G. Zhang, P. Wang, Q. Chen, L. Liu, C. Limao, Y. Wang, Crystal structure refinement, photoluminescence properties and energy transfer of multicolor tunable  $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Tm}^{3+}, \text{Dy}^{3+}$  for NUV white-light-emitting diodes, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 229 (2020) 117942.
- [13] P. Dorenbos, A.H. Krumpel, E. van der Kolk, P. Boutinaud, M. Bettinelli, E. Cavalli, Lanthanide level location in transition metal complex compounds, *Optical Materials*, 32 (2010) 1681-1685.
- [14] A.H. Krumpel, E. van der Kolk, D. Zeelenberg, A.J.J. Bos, K.W. Krämer, P. Dorenbos, Lanthanide 4f-level location in lanthanide doped and cerium-lanthanide codoped  $\text{NaLaF}_4$  by photo- and thermoluminescence, *Journal of Applied Physics*, 104 (2008) 073505.
- [15] P. Dorenbos, Systematic behaviour in trivalent lanthanide charge transfer energies, *J. Phys.: Condens. Matter* 15 (2003) 8417-8434



- [16] P. Dorenbos, Modeling the chemical shift of lanthanide 4f electron binding energies, *Physical Review B*, 85 (2012).
- [17] P. Dorenbos, Ce<sup>3+</sup> 5d-centroid shift and vacuum referred 4f-electron binding energies of all lanthanide impurities in 150 different compounds, *Journal of Luminescence*, 135 (2013) 93-104.
- [18] N. Kodama, T. Takahashi, M. Yamaga, Y. Tani, J. Qiu, K. Hirao, Long-lasting phosphorescence in Ce<sup>3+</sup>-doped Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> and CaYAl<sub>3</sub>O<sub>7</sub> crystals, *Applied Physics Letters*, 75 (1999) 1715-1717.
- [19] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer, Berlin, Germany, 1994.
- [20] H.H. Lin, Y.Y. Wu, H.Y. Chen, The Luminescence and Energy-Transfer of Ce<sup>3+</sup>, Tb<sup>3+</sup> Activated Sr<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, *Adv. Mater. Res.*, 399-401 (2012) 1169-1174.
- [21] C.-K. Chang, T.-M. Chen, Sr<sub>3</sub>B<sub>2</sub>O<sub>6</sub>:Ce<sup>3+</sup>,Eu<sup>2+</sup>: A potential single-phased white-emitting borate phosphor for ultraviolet light-emitting diodes, *Appl. Phys. Lett.*, 91 (2007) 081902.
- [22] P. Dorenbos, A Review on How Lanthanide Impurity Levels Change with Chemistry and Structure of Inorganic Compounds, *ECS J. Solid State Sci. Technol.*, 2 (2013) R3001-R3011.
- [23] P. Dorenbos, The Eu<sup>3+</sup> charge transfer energy and the relation with the band gap of compounds, *J. Lumin.*, 111 (2005) 89-104.
- [24] P. Dorenbos, Lanthanide charge transfer energies and related luminescence, charge carrier trapping, and redox phenomena, *Journal of Alloys and Compounds*, 488 (2009) 568-573.
- [25] P. Dorenbos, Valence stability of lanthanide ions in inorganic compounds, *Chemistry of Materials*, 17 (2005) 6452-6456.
- [26] P. Dorenbos, The 4f<sup>n</sup>-4f<sup>n-1</sup>5d transitions of the trivalent lanthanides in halogenides and chalcogenides, *J. Lumin.*, 91 (2000) 91-106.