Influence of Ca^{2+} , Ba^{2+} Ions on the Structure and Luminescent Properties of Ce^{3+} Doped Strontium Chlorine Aluminate Blue Phosphor

Yue Lu, Xu Li*, Yue Dong, Zhenzhen Ma, Tengxuan Hou, Dian Jiao, Qinglin Guo, Li Guan*,

Feng Teng

*Hebei Key Laboratory of Optic-electronic Information Materials, Hebei University,
Baoding 071002, China*

Abstract

A series of Ce^{3+} doped $\text{M}_3\text{Al}_2\text{O}_5\text{Cl}_2$ ($\text{M}=\text{Ca}^{2+}$, Sr^{2+} and Ba^{2+}) phosphor were synthesized by traditional solid phase reaction method and their optical properties were studied. XRD patterns show the phase formation of $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$. The excitation spectra of $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Ce}^{3+}$ phosphors indicated that it can be excited by near UV light between 250-375 nm, which is matched well with the ultraviolet (UV) chip. The emission spectra are an asymmetry broad band centered at 442 nm. The fluorescence lifetime of $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Ce}^{3+}$ phosphor was calculated as 56.65 nS. The effect of the concentration of Ce^{3+} ions was investigated in detail and the quenching mechanism was given. The energy band and densities of state of $\text{M}_3\text{Al}_2\text{O}_5\text{Cl}_2$ were calculated by in the software CASTEP for the first time. The influence of Ca^{2+} and Ba^{2+} on the emission spectra of $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Ce}^{3+}$ are investigated. The results indicated that this $\text{M}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Ce}^{3+}$ can be a better blue emitting candidate phosphor.

Keywords: Luminescence; Energy band; Densities of state; Phosphor; LED

1. Introduction

Due to its efficiency, longer lifetime, low pollution, and mercury free, white

* Corresponding author. Tel.: No.180 Wusi East Road. Baoding City, Hebei Province, P. R. C, +86 312 5049678; fax: +86 312 5079352. Email address: fteng@bjtu.edu.cn (F. Teng).

light-emitting diode (w-LED) is considered as a promising generation light source.^[1,2] The w-LED fabricated by the normal method of integrating an InGaN blue LED chip and a yellow-emitting phosphor has unfavorable color rendering index (CRI) due to the absence of the red light. With the development of semiconductor technology, the mode combining near ultraviolet (n-UV) or UV GaN chip with tricolor phosphors is introduced, which has tunable color temperature (CT), CRI and high conversion efficiency^[3, 4].

The Ce^{3+} ion is very useful as an activator for solid state chemistry on account of its high sensitivity to the chemical environment. The spectra of absorption and emission of Ce^{3+} ions ordinarily take on broad bands ascribe to the transition between the ground state of the $4f$ configuration and the lower excited states that caused by the $5d$ configuration crystal field split. The emission of Ce^{3+} can vary in the visible region for $5d$ electrons are affected by the neighboring anion ligand in the compounds.

Halophosphate-based blue phosphors doped with rare earth ions such as $(\text{Ca}, \text{Sr}, \text{Ba})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$ have been widely applied to the blue phosphor of plasma display panel and UV based white LED^[5,6]. Many researchers works on other phosphors that can emit blue light, for example $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ phosphor^[7], $\text{LiSrPO}_4:\text{Eu}^{2+}$ phosphor^[8], $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ phosphor^[9], $\text{Ba}_5\text{SiO}_4(\text{F},\text{Cl})_6:\text{Eu}^{2+}$ phosphor^[10] *etc.* The emission peaks of the above phosphors excited by UV light located at blue light region, thus they are beneficial to the development of UV based white LED. In addition, the $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$ phosphor doped Ce^{3+} and Eu^{2+} ions could be excited by near-ultraviolet and emit orange light.^[11]

In this paper, a series of blue phosphor $\text{M}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Ce}^{3+}$ (MAOC- Ce^{3+}) were synthesized and their structure and luminescence properties were described in detail.

2. Experimental

The original materials were calcium carbonate (CaCO_3 , A.R.), strontium carbonate (SrCO_3 , A.R.), barium carbonate (BaCO_3 , A.R.), calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, A. R.), strontium chloride ($\text{SrCl}_2 \cdot 4\text{H}_2\text{O}$, A. R.), barium chloride (BaCl_2 , A. R.), alumina (Al_2O_3 , A. R.) and cerium oxide (CeO_2 , 99.9%). A stoichiometric ($\text{M}/\text{Al}/\text{O}/\text{Cl}=3/2/5/2$) mixture was weighed and completely mixed in the agate mortar. Then the preparation material was put into alumina crucibles and sintered at 1300 °C for 4h under reducing atmosphere. Ultimately, the sintered samples need cool to room temperature and then ground into powder again for further measurement.

The crystal structures of the samples were collected on a Bruker D8 X-ray powder diffractometer with a CuK α radiation (40 kv, 40 mA).. A Hitachi F-7000 spectro-photometer with Xe (150 W) lamp excitation source was used to record the fluorescence spectra. The measurement of luminescence lifetime was conducted by utilizing an Edinburgh FLS920 luminescence spectrometer by the excitation source of 370-nm pulse laser radiation (nano-LED). The whole measurements were operated at ambient temperature.

3. Results and Discussion

3.1 X-ray diffraction analysis

The XRD pattern of the $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2\text{:Ce}^{3+}$ (SAOC- Ce^{3+}) with various Ce^{3+} molar fraction (0.005, 0.006, 0.0075, 0.008, 0.009) as shown in Fig. 1, in which the molar fraction is the ratio of Ce^{3+} and Sr^{2+} ions. The diffraction peaks are in line with the JCPDS card 80-0564, which illuminates the pure phase $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$ is obtained. $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$ possess orthorhombic structure with $P212121(19)$ space group and the crystal lattice parameters of $a = b = c = 0.9422$ nm, and $V = 0.83643$ nm³. The lattice constants of SAOC- Ce^{3+} are a little smaller than those of the single SAOC phase due

to the radius of Ce^{3+} ions (0.1034 nm) are smaller than that of Sr^{2+} ions (0.1102 nm).

The crystal structure of SAOC is drawn using Materials Studio 7.0 according to the data of the ICSD (see Fig. 2).^[12] It can be seen that there are three different strontium ions lattice sites in this diagram, in which the different sizes of green balls represent the Sr I, Sr II and Sr III. The different Sr^{2+} ions are coordinated by different numbers of oxygen and chlorine ions.

3.2 The Photoluminescence (PL) of SAOC- Ce^{3+} phosphor

It is well known that the excitation and emission of Ce^{3+} ions are related to the transition between $4f$ electrons and $5d$ levels. Moreover, the $4f$ electron configuration has two ground states ($^2F_{5/2}$ and $^2F_{7/2}$) and the $5d$ levels can split into various energy levels in the effect of different host matrix.^[13] Fig.3 gives the PL spectra of the SAOC- Ce^{3+} phosphor compound by conventional solid phase reaction method with the calcinations temperature at 1300 °C. For monitoring the emission of 442 nm, the excitation spectrum takes on two peaks broad band from 240~400 nm centered at 283 and 332 nm, which are corresponding to the $4f$ - $5d$ transition of Ce^{3+} ions.

The PL emission spectra of the SAOC- Ce^{3+} phosphor excited by 283nm and 332 nm are given in the right of Fig.4(a). The emission spectra are an asymmetry broad band centered at 442 nm range from 375 to 525 nm. Compared with the full width at half maximum (FWHM) of the PL spectrum of YAG: Ce^{3+} (100 nm), the FWHM of SAOC- Ce^{3+} is smaller (82 nm), which could be considered as similar. The emission peaks are located at 442 nm, which illuminate this phosphor can emit well blue light.

The emission spectrum excited by 332 nm could be approximately fitted to three Gauss curves peaked at 427, 458 and 493 nm, respectively. It can be seen from Fig.4 (a) that the fitting curve is well matched with the experimental curve. The consequences illuminate that there exist three luminescent centers of Ce^{3+} ions in the

SAOC lattice, which is related to the three Sr^{2+} ions lattice sites. The Ce^{3+} center with shorter $\text{Ce}^{3+}\text{-O}^2$ distance will give a longer emission when the crystal environments are parallel^[14].

Fig.4 (b) shows the configuration coordinate diagram curve and energy transfer between Ce^{3+} ions in SAOC and the corresponding excitation and emission wavelength. When Ce^{3+} ions occupies the Sr(I) site ,its emission intensity reaches the maximum and would be weaken when it occupies the Sr(II) and Sr(III). There is energy transfer between the different sites.

In the literature [15], L.G. Van Uitert illuminated the position in energy (E) of the lower d -band edge for Ce^{3+} in a simple three-dimensional structure, which could be calculated using an empirical formula (Eq. 1):

$$E = Q[1 - (V / 4)^{1/V} 10^{-(n \cdot ea \cdot r)/8}](\text{cm}^{-1}) \quad (1)$$

In this formula, Q represents the energy position for the lower d -band for the free ions (50000 cm^{-1} for Ce^{3+} ions); V is the valence of the activator cation and V is +3 here; n is the coordination numbers of anions; ea is the electron affinity of the atoms that form anions (is in electron volts (eV)); r is the radius of the host cation replaced by the activator cation (is in Ångstroms). Generally, the values of ea vary with the crystal cohesion and outward (s^2) polarization *etc.* surrounding of Ce^{3+} ion. The value of ea for $(\text{Al}_2\text{O}_5)^{4-}$ and Cl^- are 2.19 eV and it is taken to be the smaller. The ions radius of Sr^{2+} is 1.12 Å ^[15]. If the Eq. (1) takes the logarithm, Eq. (2) will be obtained.

$$n = -80[\lg(1 - E / Q) / (V / 4)^{1/V}] / (ea \cdot r) \quad (2)$$

The calculated values according to Eq.(2) are obtained and shown in Table 1. As can be seen, the theoretical values are in agreement with the experimental values, and the difference could be ascribed to the subtle change in the crystal field around the

Ce³⁺ ions. Sr²⁺ ions have 6, 7 and 8 three kinds of coordinate in the SAOC crystal, which is matched with the crystal structure in Fig.2.

3.3 The impact of the molar fraction of Ce³⁺ ions on the SAOC-Ce³⁺ phosphor

Fig.5 gives the relation between molar fraction of Ce³⁺ and the intensity of the emission peak of SAOC-Ce³⁺ phosphor. When the molar fraction of Ce³⁺ is 0.0075, the PL intensity reaches the maximum; however, it would decrease with the molar fraction increase due to the concentration quenching. In accordance with the mechanisms of concentration quenching of Ozawa and Jaffe ^[16], the relationship between luminescent intensity (I_{ob}) and activator concentration (c) could be denoted by the Eq (3):

$$I_{ob} / c = A[1 + \beta(c)^{\theta/3}]^{-1} \quad (3)$$

In this formula, A and β is constant; the value of $\theta/3$ equals to the slope of the curve in a double logarithm coordinates using $\lg x$ and $\lg(I/x)$ as abscissa and ordinate. It denotes the dipole-dipole ($d-d$), quadrupole - quadrupole ($q-q$) and dipole - quadrupole ($d-q$) reciprocity when θ equals to 6, 8 and 10, respectively. As the inset of Fig.5 shown, the slope is 2.06741 and the value of θ is about 6, which manifests that $d-d$ interaction is the quenching mechanism of Ce³⁺ in SAOC-Ce³⁺.

3.4 The decay lifetime of the SAOC-Ce³⁺ phosphor

Decay curves of SAOC-Ce³⁺ phosphor with 0.0075 mol⁻¹ Ce³⁺ ions is measured and shown in Fig.6. The decay curves could be fitted with a simple function (Eq. 4) [17]:

$$I(t) = I_o + A_0 \exp(-t / \tau) \quad (4)$$

In Eq. 4, I is the luminescence intensity, t represents the time, τ is the decay lifetimes, and A_0 is the corresponding fitting parameters. According to Eq. (4), the lifetime τ

extracted from the fitted curve is about 56.65 nS. As it is known, the allowed $5d-4f$ transition of Ce^{3+} ions occurs within less than a microsecond and our consequence is reasonable for it, which demonstrates that the lifetime of this kind of phosphor is short enough and it could qualified to the extensive applications in displays and lighting.

3.5 The electric structure of $\text{M}_3\text{Al}_2\text{O}_5\text{Cl}_2$

First principle calculation was carried out by the software CASTEP^[18]. A Vanderbilt-type ultra-soft pseudopotential formalism and exchange-correlation function founded on the generalized gradient approximation (GGA) in the scheme of Perdew- Burke- Eruzerhof (PBE) were applied to calculate the band structure and density of state. The energy band structures of $\text{Ca}_3\text{Al}_2\text{O}_5\text{Cl}_2$, $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$ and $\text{Ba}_3\text{Al}_2\text{O}_5\text{Cl}_2$ are respectively shown in Fig.7 (a), (b) and (c). It can be seen that $\text{M}_3\text{Al}_2\text{O}_5\text{Cl}_2$ belongs to indirect optical band gap materials and the gap between the conduction band minimum (CBM) and the valence band maximum (VBM) is respectively about 4.489, 4.233 and 4.106 eV. Thus, $\text{M}_3\text{Al}_2\text{O}_5\text{Cl}_2$ could be a category of good host due to the large band gaps and the possibility of the luminescence quenching would be minimized significantly. Thanks to the large band gap both the ground and excited states could be well accommodated within the band gap. Fig.4 illuminates the total and partial densities of states of $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$. The Cl 3p, O 2p states dominate the top of the valence band and the conduction band is mainly composed of Al 3p and Sr 5s states. The $\text{Ca}_3\text{Al}_2\text{O}_5\text{Cl}_2$ and $\text{Ba}_3\text{Al}_2\text{O}_5\text{Cl}_2$ have similar densities of states to $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2$.

3.5 The influence of matrix materials on the luminescence of SAOC-Ce^{3+}

phosphor

In order to investigate the effect of matrix on the luminescent properties, a series of Ce^{3+} doped phosphors with different cation are prepared. Fig.9 shows the emission spectra of these phosphors. It can be seen that all the emission of MAOC- Ce^{3+} ($\text{M}=\text{Ca}$, Sr and Ba) have the similar peak besides the center of peaks are located at 434, 442 and 450 nm, respectively. The red shift of the emission spectra is observed with the decrease of electro-negativity of cations.

4. Conclusions

In conclusion, Ce^{3+} doped MAOC phosphor was successfully synthesized using the traditional solid phase reaction method. There are two different excitation peaks located at 283 and 332 nm in PL spectra of SAOC: Ce^{3+} phosphor, respectively. The phosphor could be excited by 332 nm UV light and emit blue light centered at 442 nm. The optimum molar fraction of Ce^{3+} ions in SAOC: Ce^{3+} is 0.0075 and the concentration quenching is caused by $d-d$ interaction of Ce^{3+} ions. The decay of SAOC: Ce^{3+} curve indicated that the lifetime of this phosphor is 56.65 ns. The energy band structure showed that the MAOC are broad gap materials. The emission spectra shift blue with the change of the alkaline earth in the matrix. The results indicated that MAOC- Ce^{3+} phosphor was a good candidate for near UV or blue light-based white LED.

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Fig.1 XRD patterns of $\text{Sr}_3\text{Al}_2\text{O}_5\text{Cl}_2:\text{Ce}^{3+}$ with different Ce^{3+} concentration. (a) 0.005, (b) 0.006, (c) 0.0075, (d) 0.008, (e) 0.009.

Fig.2 (Color online) Crystal structure of SAOC.

Fig.3 (Color online) The excitation and emission spectra of $\text{SAOC}:\text{Ce}^{3+}$ phosphor.

Fig.4 (Color online) (a) Gauss fitting curve of the emission spectra of $\text{SAOC}:\text{Ce}^{3+}$ phosphor excited by 332 nm. (b) Schematic of luminescence process.

Fig.5 (Color online) The relation between luminescent intensity of $\text{SAOC}:\text{Ce}^{3+}$ and the Ce^{3+} molar fraction. (The inset is the relation of $\lg x$ and $\lg(I/x)$).

Fig.6 (Color online) Decay curve of $\text{SAOC}:\text{Ce}^{3+}$ excited at 332 nm and monitored at 442 nm.

Fig.7 Energy band structure of MAOC. (M=Ca (a), M=Sr (b) and M=Ba (c))

Fig.8 Total and partial densities of states of MAOC. (M=Ca (a), M=Sr (b) and M=Ba (c)).

Fig.9 (Color online) Emission spectra of $\text{MAOC}:\text{Ce}^{3+}$ (M=Ca, Sr and Ba) phosphor.

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1 The calculated values of position in energy of the lower d-band edge for Ce^{3+} occupying different crystallographic sites

n(actual)	ea/eV	$r(\text{Å})$	$E(\text{cm}^{-1})$	$n(\text{calculated})$	$\lambda_{\text{ex}}/\text{nm}$
8	2.19	1.12	23419	7.59	427
7	2.19	1.12	21834	6.77	458
6	2.19	1.12	20283	6.01	493