Synthesis, luminescence and energy transfer of Ca$_3$GdNa(PO$_4$)$_3$F: Ce$^{3+}$, Tb$^{3+}$ phosphor with novel apatite structure

Lin-Yan Xie$^{1, 5}$, Ning-Zhe Zhuo$^{2, 5}$, Na Zhang$^{1, 5}$, Wen-Hui Du$^{1}$, Yue-Hua Zhu$^{1, 5}$, Shao-Wen Cheng$^{6}$ and Hai-Bo Wang$^{7}$

$^{1}$ College of Material Science and Engineering, Nanjing Tech University; Nanjing 210009, People’s Republic of China
$^{2}$ Institute of Electronic and Photonic Materials of Light Industry, Nanjing 210015, People’s Republic of China
$^{3}$ Research Institute of Electronic and Photonic Materials, Nanjing Tech University, Nanjing 210015, People’s Republic of China
$^{4}$ College of Energy Science and Engineering, Nanjing Tech University, Nanjing 211816, People’s Republic of China

E-mail: wanghaibo88@163.com

Keywords: high-temperature solid-state reaction, Ca$_3$GdNa(PO$_4$)$_3$F:Ce$^{3+}$, Tb$^{3+}$, luminescence, energy transfer

Abstract

A series of Ce$^{3+}$/Tb$^{3+}$ singly doped and Ce$^{3+}$/Tb$^{3+}$ co-doped Ca$_3$GdNa(PO$_4$)$_3$F phosphors were synthesized via high temperature solid-state reaction in a reductive atmosphere. The crystal, luminescence properties, energy transfer mechanism and thermal stability of the samples were investigated in detail. The Ce$^{3+}$ doped phosphors can be excited in the range from 250 to 330 nm. The Ce$^{3+}$/Tb$^{3+}$ co-doped phosphors exhibit characteristic emission of Ce$^{3+}$ and Tb$^{3+}$ simultaneously under the excitation of 301 nm. In addition, the energy transfer efficiency from Ce$^{3+}$ to Tb$^{3+}$ reaches as high as 78.6% when the doping amount of Tb$^{3+}$ is 0.20. The mechanism of energy transfer between Ce$^{3+}$ and Tb$^{3+}$ ions is demonstrated to be a dipole–dipole interaction. The luminescence characteristics show that this phosphor can be a platform for modeling a new phosphor and application in the solid-state lighting field.

1. Introduction

Apatite compounds are regarded as important phosphor matrix materials due to their excellent thermal and chemical stability. Among them, Ca$_3$(PO$_4$)$_2$F is the simplest apatite structure and the first apatite compound proved to have P6$_3$/m space group. On the basis of Ca$_3$(PO$_4$)$_2$F, apatite fluorescent materials with very rich compositions were obtained by changing the types of cations, anion groups and channel atoms in the crystal [1]. In apatite compound crystals, there are usually two cationic crystal lattices, which are locally symmetric at C$_3$ point (4f lattices) and locally symmetric at C$_5$ point (6h lattices). These two crystal lattice sites can be replaced by rare earth elements, because the 4f and 6h lattice sites have different requirements on the radius and valence state of substituted ions, which often make apatite phosphors with special spectral characteristics [2].

Green phosphors are useful to obtain white light source with high color rendering in the field of illumination [3]. It is also advantageous to obtain the display effect of high color purity in the display field. In recent years, many green phosphors based on apatite crystals have been reported. For example, the green phosphor Ca$_9$La$_9$(SiO$_4$)$_{12}$(PO$_4$)$_2$O$_2;0.01$Eu$^{2+}$ prepared by Xia [4], its emission peak of 500 nm was emitted from the 4f and 6h positions occupied by Eu$^{2+}$, and the quantum efficiency was 57.73%. Besides, Tian [5] prepared fluorescent powder Ca$_9$Sr(PO$_4$)$_8$Cl$_2$:Ce$^{3+}$, Tb$^{3+}$ by high temperature solid phase method. Based on the effective energy transfer between Ce$^{3+}$ and Tb$^{3+}$, the green emission peak of Tb$^{3+}$ at 541 nm was significantly increased, and the energy transfer efficiency of Ce$^{3+}$ → Tb$^{3+}$ was up to 76%. However, no relevant reports have been reported on the study of green phosphor with apatite structure Ca$_3$GdNa(PO$_4$)$_3$F as matrix. Based on the efficient energy transfer between Ce$^{3+}$ and Tb$^{3+}$, it is expected that new green fluorescent materials with apatite structure can be obtained by mixing Ce$^{3+}$ and Tb$^{3+}$ in the Ca$_3$GdNa(PO$_4$)$_3$F matrix. As the emission wavelength of semiconductor chips is gradually extended to short-wave UV and deep UV [6], this kind of fluorescent powder has the potential to be used in the solid-state lighting field in the future.
Considering the difference of valence state and radius of each cation, the substitution of two Ca\(^{2+}\) coordination polyhedra respectively.

As shown in figure 1. XRD patterns of \(\text{Ca}_3\text{Gd}_1-x\text{Na}(\text{PO}_4)_3\text{FxCe}^{3+}/\text{yTb}^{3+}\) (a) and magnified patterns in the region 31.8°~32.2°(b).

A series of phosphors \(\text{Ca}_3\text{Gd}_1-x\text{Na}(\text{PO}_4)_3\text{FxCe}^{3+}/\text{yTb}^{3+}\) (0 ≤ \(x\) ≤ 0.14, 0 ≤ \(y\) ≤ 0.28) were prepared by a high temperature solid-state reaction. Then the energy transfer process and mechanism of Ce\(^{3+}\), Tb\(^{3+}\) co-doped phosphor \(\text{Ca}_3\text{Gd}_{0.92-y}\text{Na}(\text{PO}_4)_3\text{F:0.08Ce}^{3+}/\text{yTb}^{3+}\) (0 ≤ \(y\) ≤ 0.28) were discussed, and the emission spectrum CIE chromaticity diagram was drawn.

2. Experimental

2.1. Materials and synthesis

Powder samples of \(\text{Ca}_3\text{Gd}_1-x\text{Na}(\text{PO}_4)_3\text{FxCe}^{3+}/\text{yTb}^{3+}\) phosphors were prepared by a high temperature solid-state reaction. \(\text{CaCO}_3\) (AR), \(\text{Na}_2\text{CO}_3\) (AR), \(\text{NH}_4\text{H}_2\text{PO}_4\) (AR), \(\text{NH}_4\text{F}\) (AR), \(\text{CeO}_2\) (99.99%) and \(\text{Tb}_2\text{O}_3\) (99.99%) were used as the raw materials and weighed in a proper stoichiometric ratio with a 10% excess of fluorine for the loss at high temperature. The raw materials were fully mixed and ground in an agate mortar, and the mixture was placed into an alumina crucible and was heated at 1200 °C for 1 h in a reducing atmosphere with flowing gas.

2.2. Characterization

The phase purity of the phosphor was checked by powder x-ray diffraction (D/Max-rA 9kw, Japan) with Cu K\(\alpha\) radiation (\(\lambda = 0.15406\)nm) from 15°~80°(2\(\theta\)). XRD data for the Rietveld refinement were performed using the computer software: general structure analysis system (GSAS). The particle morphology and microstructure of the samples were examined by scanning electron microscopy (SEM) using a JSM-7610F instrument with a voltage of 10kV. The photoluminescence spectra was recorded on a RF-6000 (Shimadzu corporation, Japan) luminescence spectrometer. The excitation light source was xenon arc lamp, and the spectral scanning step was 1 nm.

3. Results and discussion

As shown in figure 1 (a), the peaks of all samples conform to the standard card of \(\text{Ca}_5(\text{PO}_4)_3\text{F}\), and no additional peaks of other impurities are found in the diffraction patterns. The phenomenon indicates high purity of the matrix material \(\text{Ca}_3\text{GdNa}(\text{PO}_4)_3\text{F}\) [7].

\(\text{Ca}1\) forms a tetrahedral structure with 9O coordination points [8] in \(\text{Ca}_5(\text{PO}_4)_3\text{F}\) crystal (figure 2), which is a locally symmetric 4f lattice position at \(\text{Ca}_1\) point. \(\text{Ca}2\) coordinates with 6O and 1F to form a decahedral structure, which is a locally symmetric 6h grid position at \(\text{Ca}_2\) points. The O and P in the crystal coordinate to form the structure of \((\text{PO}_4)_3\text{F}^{2-}\) tetrahedron, which is connected with the common edges and angles of \(\text{Ca}1\) and \(\text{Ca}2\) coordination polyhedra respectively.

We can achieve the radius of each cation in different coordination environments [9] from table 1. Considering the difference of valence state and radius of each cation, the substitution of two \(\text{Ca}^{2+}\) by \(\text{Gd}^{3+}\) and...
Na⁺ had occurred [10]. Matrix crystal Ca₃GdNa₃(PO₄)₃F was obtained after being replaced by Gd³⁺ and Na⁺. In this matrix, Ce³⁺ and Tb³⁺ activators were introduced. Ce³⁺ and Tb³⁺ replaced Gd³⁺ in the matrix to form replacement solid solution [11] due to the need to keep valence balance. Figure 3. shows Ca₃Gd₀.72Na₀.28(PO₄)₃F:0.08Ce³⁺,0.20Tb³⁺ samples have irregular micromorphology with relatively smooth surface and particle size ranging from 6 ∼ 14 μm.

The emission spectra of the as-prepared samples Ca₃Gd₁₋ₓNaₓ(PO₄)₃F:xCe³⁺, where 0 ≤ x ≤ 0.14 as shown in figures 4(a), (b). Upon the excitation of 301 nm, its emission spectral intensity enhances with the increasing of the doping concentration of Ce³⁺ [12]. The spectral intensity reaches the highest, when the doping of Ce³⁺ is 0.08. The doping amount of Ce³⁺ continues to increase, the concentration quenching phenomenon begins to appear, and the spectral intensity decreases accordingly. Figure 5(a) shows that when the single content of Ce³⁺ is 0.08, the phosphor has a broadband excitation spectrum from the 4f → 5d transition of Ce³⁺ at 250 nm–330 nm, and the optimal emission wavelength is 301 nm, at which time the broadband emission presents an asymmetric peak [13]. Gaussian fitting was performed on the emission spectrum, and two peaks appeared at 334.47 nm and 358.73 nm. After Ce³⁺ is excited, a 5d → 4f transition emission occurs, and 4f splits into 2F₅/₂ and 2F₇/₂. Therefore, the emission spectrum comes from Ce³⁺ occupying the same crystal lattice position. High valence and low ion radius are the most likely to replace likely to replaces the lattice site of 6h crystals with shorter coordination bonds and smaller volume. According to the coordination ion radius in table 1, it can be seen that Ce³⁺ replaces Gd³⁺ and occupies the lattice site of 6h [14], and then emits light. Figure 5(b) shows that when the single dosage of Tb³⁺ is 0.20, the characteristic emission of Tb³⁺ at 542 nm is monitored.

In figure 5(c), the emission peak of 542 nm green light was monitored, and the excitation intensity of Ce³⁺ and Tb³⁺ co-doped phosphors at 301 nm was much higher than that of single doped Tb³⁺ phosphors at 301 nm. Then 301 nm ultraviolet light is the best excitation wavelength of Ce³⁺, and the spectra of figures 3(a) and (b)

![Figure 2. The crystal structure of Ca₅(PO₄)₃F along the c-axis direction (a) and the coordination environment of Ca1 (b) and Ca2 (c).](image)

**Table 1. Ionic radii (nm) for given coordination number (CN).**

| Ion    | Sites | Symmetry | Ionic radius (nm) CN = 7 | Ionic radius (nm) CN = 9 |
|--------|-------|----------|--------------------------|--------------------------|
| Ca²⁺   | 4f / 6h | C₃v/C₃  | 0.106                    | 0.118                    |
| Gd³⁺   | 4f / 6h | C₃v/C₃  | 0.100                    | 0.1107                   |
| Na⁺    | 4f / 6h | C₃v/C₃  | 0.112                    | 0.124                    |
| Ce³⁺   | 4f / 6h | C₃v/C₃  | 0.107                    | 0.1196                   |
| Tb³⁺   | 4f / 6h | C₃v/C₃  | 0.098                    | 0.1095                   |
have a significant overlap, so it can be speculated that there is an energy transfer of Ce\(^{3+}\) \(\rightarrow\) Tb\(^{3+}\) in phosphor Ca\(_3\)Gd\(_{0.72}\)Na\((PO_4)_3F:0.08Ce^{3+},0.20Tb^{3+}\).

As the Tb\(^{3+}\) doping increases, the 355nm broadband emission peak intensity decreases (figure 6(a)). The narrow-band emission peaks in the emission spectrum come from the electron transition of Tb\(^{3+}\)\[^{15}\], including the spectral peaks of 376 nm, 413 nm, 435 nm and 455 nm radiated by the electron transition of the high-excited energy level \(^5D_3 \rightarrow ^7F_J\)\((J = 6, 5, 4, 3)\), and the spectral peaks of the low-excited energy level \(^5D_4 \rightarrow ^7F_J\)\((J = 6, 5, 4, 3)\) radiated by the electron transition of 488nm, 542nm, 582nm and 620nm. Energy transfer efficiency (\(\eta_T\)) can be expressed by [16]:

\[
\eta_T = 1 - \frac{I_S}{I_{S0}}
\]  

(1)

Among them, \(I_S\) and \(I_{S0}\) represent the luminescence intensity of sensitizer Ce\(^{3+}\) when doped with Tb\(^{3+}\) and without Tb\(^{3+}\), respectively. The energy transfer efficiency of Ce\(^{3+}\) \(\rightarrow\) Tb\(^{3+}\) can reach 78.6%, when the doping concentration of Tb\(^{3+}\) reaches 0.20.

Dexter and Schulman suggest that the distance \(R_c\) between Ce\(^{3+}\) ion and Tb\(^{3+}\) can be estimated using the equation [17]:

\[
R_{Ce-Tb} = 2\left[3V/(4\pi x_c N)\right]^{1/3}
\]  

(2)

Where \(V\) is the volume of the unit cell volume, \(x_c\) is the critical concentration, which refers to the total concentration of Ce\(^{3+}\) and Tb\(^{3+}\) when the energy transfer efficiency between Ce\(^{3+}\) and Tb\(^{3+}\) reaches 50% (from figure 6). \(N\) is the number of sites that the Ce\(^{3+}\) ions can occupy in the unit cell \((N = Z \times 2)\) and of doped ions.
In case of Ca$_3$GdNa(PO$_4$)$_3$F:xCe$^{3+}$, yTb$^{3+}$ phosphor, $V = 0.52371$ nm$^3$, $N = 2$, and $x_c = 0.18$. Upon inserting the value in equation (2), $R_c$ value is determined to be $1.41$ nm $> 0.5$ nm, therefore the energy transfer mainly occurs through multiple dipole interactions from Ce$^{3+}$ to Tb$^{3+}$.
To summarize, Ce$^{3+}$ is an important luminescent center in Ca$_3$Gd$_{1-y}$Na$_y$PO$_4$:Ce$^{3+}$, Tb$^{3+}$, and Ce$^{3+}$:Tb$^{3+}$ phosphors. The energy transfer process can be effectively controlled by adjusting the doping ratio of Ce$^{3+}$ and Tb$^{3+}$. The energy transfer efficiency from Ce$^{3+}$ to Tb$^{3+}$ ions was 78.6% for Ca$_3$Gd$_{0.92}$Na$_{0.08}$PO$_4$:Ce$^{3+}$, which was higher than that of Ca$_3$Gd$_{0.72}$Na$_{0.20}$PO$_4$:Ce$^{3+}$, Tb$^{3+}$ with a lower doping ratio of Tb$^{3+}$. The purity of green light at 542 nm increased monotonously when the Tb$^{3+}$ doping amount was increased. The relative brightness stability and color coordinate stability of the phosphors were determined according to GB/T 23595.4-2009 national standard for Ca$_3$Gd$_{0.72}$Na$_{0.20}$PO$_4$:Ce$^{3+}$, 0.20Tb$^{3+}$ prepared under optimal conditions (1200℃, 1 h). Calculated according to formula (4)–(6):

$$B_h = B_0 - B_0 / B_0 \times 100$$  \hspace{1cm} (4)

Where $\Delta B_h$ is relative brightness thermal stability(%), $B_0$ and $B_h$ represent the relative brightness(%) of the sample after heat treatment and heat treatment.

$$\Delta X_h = X_h - X_0$$ \hspace{1cm} (5)

$$\Delta Y_h = Y_h - Y_0$$ \hspace{1cm} (6)

Among them, $\Delta X_h$ and $\Delta Y_h$ are the stability of color coordinates, $X_0$ and $Y_0$ are the unheated color coordinates, and $X_h$ and $Y_h$ are the heat processed color coordinate. After testing and calculation, $\Delta B_h$ value is determined to be 2.56% < 5%, and $(\Delta X_h, \Delta Y_h) = (0.0003, 0.0006)$, which is also far less than national standard 0.0015. These data indicate that Ca$_3$Gd$_{0.72}$Na$_{0.20}$PO$_4$:Ce$^{3+}$, 0.20Tb$^{3+}$ phosphors have good thermal properties and can be used in solid-state lighting.

4. Conclusions

To summarize, Ce$^{3+}$ and Tb$^{3+}$ singly doped and co-doped Ca$_3$GdNa$_2$PO$_4$:Ce$^{3+}$, Tb$^{3+}$ phosphors were successfully prepared and investigated. In Ca$_3$Gd$_{1-y}$Na$_y$PO$_4$:Ce$^{3+}$, the Ce$^{3+}$ tent to replace Gd$^{3+}$ on 6$h$, and the broad emission band centered at 355 nm was observed with optimal Ce$^{3+}$ concentration being 0.08. We observed the energy transfer in the Ca$_3$Gd$_{0.92}$Na$_{0.08}$PO$_4$:0.08Ce$^{3+}$, yTb$^{3+}$ (0 ≤ y ≤ 0.28) phosphors.

![Figure 7. Dependence $I_{so} / I_s$ of Ce$^{3+}$ on $C_{ce Tb}$, $C_{Ce Tb}$, and $C_{Ce Tb}$ in Ca$_3$Gd$_{0.92}$Na$_{0.08}$PO$_4$:yTb$^{3+}$ (0 ≤ y ≤ 0.28) phosphors.](image)
interaction. The phosphor emitted bright green light and had good thermal stability. All the above results demonstrated that Ca$_3$GdNa(PO$_4$)$_3$:Fe$^{3+}$,Ce$^{3+}$,Tb$^{3+}$ can be a platform for modeling a new phosphor and application in the solid-state lighting field.

Acknowledgments

The authors would like to acknowledge the financial support in part from the National Key R&D Program of China (Grant Nos. 2017YFB0404300, 2017YFB0404301) and the Natural Science Foundation of Jiangsu Province (Grant No. BK20171128).

ORCID iDs

Lin-Yan Xie https://orcid.org/0000-0003-1732-5410
Ning-Ze Zhuo https://orcid.org/0000-0001-5761-6496
Wen-Hui Du https://orcid.org/0000-0002-9441-6597

References

[1] Zhili D and White T J 2003 Acta Crystallographica. Section B, Structural Science 59 1–16
[2] Li G, Zhao Y, Tian Y, Quan Z and Lin J 2015 J Chem. Commun. 52 3376–9
[3] Yu G, Liu W, Zhang W, Li W, Huang Y and Qiu K 2019 J. Alloys Compd. 784 1003–10
[4] Xia Y, Liu Y, Huang Z, Fang M, Molokheev M and Meil L 2016 J. Mater. Chem. C 4 4675–83
[5] Feng L, Tian Y, Wang F, Cui C, Shi Q and Huang P 2015 J. Mater. Sci. 51 2841–9
[6] Xiong R, Liu W, Yuan X, Liu J, Song J and Liang Y 2015 Acta Phys. Sin. 64 247801
[7] Wu X, Bai W, Hai O, Ren Q, Lin F and Jiao Y 2018 Optics & Laser Technology 107 46–53
[8] Bale W F 1940 American Journal of Roentgenology 43 735
[9] Berry L G, Mason B and Dietrich R V 1983 Mineralogy, Concepts, Descriptions, Determinations. (San Francisco: W. H. Freeman) 550–1
[10] Guo Y, Moon B K, Choi B C, Jeong J H, Kim J H and Choi H 2016 Ceram. Int. 42 18324–32
[11] Yang Z, Yu Y, Zhang G, Ji C, Bu H, Xu D and Sun J 2018 J. Mater. Sci., Mater. Electron. 29 7203–12

Figure 8. The CIE chromaticity diagram of Ca$_3$Gd$_{0.92-y}$Na(PO$_4$)$_3$:0.08Ce$^{3+},y$Tb$^{3+}$ (0 ≤ y ≤ 0.28) phosphors.
[12] Guo Q, Wang Q, Jiang L, Liao L, Liu H and Mei L 2016 Physical Chemistry Chemical Physics 18 15545–54
[13] Ma X, Zhou W, Zhang Z, Wang X, Zhang B and Guo Y 2018 J. Lumin. 199 82–6
[14] Xia Y, Chen J, Liu Y, Maxim S M, Guan M, Huang Z and Fang M 2016 Dalton Trans. 45 1007–15
[15] Li S, Guo N, Liang Q, Ding Y, Zhou H, Ouyang R Z and Lv W 2018 Spectrochim. Acta, Part A 190 246–52
[16] Liu H, Guo Q and Mei L 2016 Ceram. Int. 42 16579–83
[17] Bao C, Liu Z, Zhang W, Li W and Qiu K 2019 Ceram. Int. 45 23592–9
[18] Guo Q, Zhao C, Jiang Z, Liao L, Liu H, Yang D and Mei L 2017 Dyes Pigm. 139 361–71