Preparation, crystal structure and photoluminescence properties of Ce^{3+} activated $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}$ phosphors for near-UV LEDs

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Abstract

A series of novel blue-green broadband emitting phosphors $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}:\text{Ce}^{3+}$ ($0 \leq y \leq 0.5$) were synthesized via the solid state reaction. The crystal structure and the photoluminescence properties were investigated for the application in white light-emitting diodes. The phosphors have two Ba^{2+} sites and one $\text{Y}(\text{Lu})^{3+}$ site with different coordination environment. These phosphors show the good absorption ranging from the ultraviolet to the blue region, the emission spectra contain both blue and green compositions, and the peaks can shift from 478nm to 493nm by changing the doped Lu^{3+} concentration, the mechanisms and reasons of the changes of the PL/PLE spectra, fluorescence decay curves and thermal quenching properties have also been studied in detail. The critical distance for Ce^{3+} ions in the $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$ host was calculated to be 23.85 Å and the energy transfer mechanism occurs among the nearest-neighbor ions. The above results indicate that $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}:\text{Ce}^{3+}$ is a good candidate as the blue-green component for near-UV LEDs.

1 Introduction

In the field of displays and lighting technology, white light-emitting diodes (w-LEDs) have been attracting more and more attention due to their high efficiency, good stability in physical and chemical properties, environmental friendliness and mercury-free properties, and w-LEDs become promising candidates to replace conventional incandescent and fluorescent lamps now.¹⁻⁵ There are several approaches to generate white light from chips and phosphors. One approach is to use the combination of blue LED chips with the yellow-emitting phosphors such as $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG), however, the obtained white light always exhibits poor color rendering in the visible spectrum because of the lack of red composition.⁶⁻⁸ An alternative way is to use the combination of a near-ultraviolet (NUV) LED chip with red, green, and blue (RGB) phosphors. Although this

type of white light could obtain a great color rendering by controlling the ratio of different phosphors, there are also some problems such as reabsorption phenomenon of blue-emission, different degradation rates of the phosphors, high expenses of the red and green phosphors (synthesis condition of high temperature and high pressure).⁹⁻¹¹ So decreasing the number of phosphors is a useful way to solve the problems. At present, there are two ways to achieve it. Firstly, using the energy transfer principle, the multicolor phosphors can be realized by co-doping sensitizers and activators into the same matrix,^{12,13} such as $\text{Sr}_{7.3}\text{Ca}_{2.7}(\text{PO}_4)_6\text{F}_2:\text{Eu}^{2+}, \text{Mn}^{2+}$,¹⁴ $\text{La}_5\text{Si}_2\text{BO}_{13}:\text{Ce}^{3+}, \text{Mn}^{2+}$,¹⁵ $\text{MgGd}_4\text{Si}_3\text{O}_{13}:\text{Ce}^{3+}, \text{Tb}^{3+}$,¹⁶ it always have a larger adjustable for the emission color, but the regulation and control are complicated and the energy efficiency is always low. Secondly, by doping the same rare earth ions in a multi-sites matrix, the different emission color from different luminescence centers are mixed up to form multicolor emission, such as $\text{Na}_2\text{TiSiO}_5$,¹⁷ $\text{MgAl}_2\text{O}_4:\text{Ti}^{18}$ $\text{Ca}_{15}\text{Si}_{20}\text{O}_{10}\text{N}_{30}:\text{Ce}^{3+}$.¹⁹ This is a relatively simple way due to the stable structure and the invariant ratio for the different sites. Meanwhile, the color of emission spectrum will be relatively complete, because the comprehensive manifestation of color comes from the superposition of the emission spectrum of different sites. As a result, several recent researches have focused on finding and designing multi-color-emitting phosphors with excellent properties, but there is not an ideal commercial phosphor for this way. So finding new multi-color-emitting phosphors is an important research direction for w-LEDs phosphors.

As a highly efficient activator with allowed 5d–4f transitions, the Ce^{3+} ion has been widely investigated because the emission and absorption spectra of Ce^{3+} ions consist of broad bands due to the transitions between the 4f¹ ground state and the crystal field components of the 5d excited state configuration. The energy of this transition is greatly affected by the coordination environment.²⁰⁻²⁴ To a certain degree, the optical properties of Ce^{3+} doped phosphors can be regulated and controlled by changing the environment around the activator ions.

Recently, aluminate-based phosphors have drawn much attention for their diverse crystal structures and great chemical and physical stabilities due to their strong and rigid frameworks.²⁵⁻²⁷ In 1999, A. M. Abakumov et al reported the crystal structure of $\text{Ba}_3\text{RM}_2\text{O}_{7.5}$ complex oxides (R = rare-earth elements M=Al, Ga),²⁸ from the report, we can find that the $\text{Ba}_3\text{RAl}_2\text{O}_{7.5}$ (R=Lu, Y) have a monoclinic P2/C unit cell, and there are two Ba^{2+} sites and one R^{3+} site with different coordination environments. This kind of structure which has multiple sites makes it a big

possibility to generate the luminescence centers of different colors. So we choose the $\text{Ba}_3\text{RAl}_2\text{O}_{7.5}$ ($\text{R}=\text{Lu}, \text{Y}$) for the investigation and synthesize a series of phosphors $\text{Ba}_3\text{RAl}_2\text{O}_{7.5}$ doped with Ce^{3+} . The crystal structure, luminescent property under NUV excitation, thermal quenching and the decay lifetime were investigated in detail for the use in near-UV LEDs.

2 Experimental

A series of Ce-doped $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}$ (BYLAO) were synthesized by a solid state reaction. The starting materials employed are BaCO_3 (A.R.), Y_2O_3 (A.R.), Al_2O_3 (A.R.), Lu_2O_3 (A.R.), CeO_2 (99.99%). The ingredients are mixed with the addition of moderate alcohol and then fired in alumina oxide crucibles at 1450°C for 6h in a reducing atmosphere (20% H_2 –80% N_2).

The phase structures of our samples were characterized by powder X-ray diffraction (XRD), using a Rigaku diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by a FLS-920T fluorescence spectrophotometer and the Xe 900 (450 W xenon arc lamp) is as the light source. The PL decay curves were measured by a FLS-920T fluorescence spectrophotometer, and the light source is an nF900 ns Flashlamp. The powder morphology of our samples was observed by a field emission scanning electron microscope (FESEM; S- 4800, Hitachi, Japan), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30, operated at 300 kV). The luminescence intensity in different temperature was measured by using an aluminum plaque with cartridge heaters; the temperature was measured by thermocouples inside the plaque and the temperature was controlled using a standard TAP-02 high-temperature fluorescence controller.

3. Results and discussion

3.1 Phase identification and crystal structure

Fig. 1 shows the XRD patterns of the obtained $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$ (BYAO), the Ce^{3+} doped BYAO ($0 \leq x \leq 0.06$) and Ce^{3+} doped BYLAO ($x=0.03$, $0 \leq y \leq 0.7$) samples. For the samples of $y \leq 0.5$, the XRD patterns of samples fit very well with the PDF card without the presence of obvious impurity diffraction peaks. With the further increase of the concentration of Lu^{3+} ($y > 0.5$), some unknown impurity phases were detected. The results mean that the Lu^{3+} ions could occupy the Y^{3+} sites of BYAO and formed the stable solid solution when the $y \leq 0.5$. In particular, with the increase of y , the peaks assigned to (321) (600) (020) and (002) crystallographic planes all obviously shift to

higher scattering angles. The (321) crystallographic planes has the strongest diffraction peak, and the (600), (020) and (002) crystallographic planes are perpendicular to a, b and c direction, respectively. On the basis of the Bragg equation $2d\sin\theta=n\lambda$, their interplanar spacings all gradually decrease with the increase of doped Lu^{3+} concentration, the changes also prove that the lattice constants(a, b, c) all become smaller.

According to the atomic coordinate,²⁸ the crystal structure of $\text{Ba}_3\text{RAl}_2\text{O}_{7.5}$ (R=Y, Lu) is given in the Fig. 2, which belongs to the monoclinic system (P2/C). The structure of $\text{Ba}_3\text{RAl}_2\text{O}_{7.5}$ (R=Y, Lu) consists of alternating octahedral Y(Lu) O_6 layers and corner-shared tetrahedral AlO_4 layers(Al_2O_7) along the c axis. Ba^{2+} ions and some oxide ions are accommodated in cavities for charge balance. There are two Ba^{2+} sites in the structure. The Ba(1) ions are in the Al_2O_7 layer, and the Ba(2) ions exist in the space between the Y(Lu) O_6 layer and Al_2O_7 layer. They are both co-ordinated by eight oxide atoms of Y(Lu) O_6 or Al_2O_7 units and by one single oxide atom, but the shapes of the BaO_9 polyhedrons centered on different Ba^{2+} atoms have apparent difference. When doping the activators ions, all the Y^{3+} (Lu^{3+}) and Ba^{2+} ions sites are possible for them to occupy, because the radius of Ce^{3+} ions (1.01Å, CN=6; 1.14Å, CN=8; 1.25Å, CN=10) is similar with the radius of Ba^{2+} (1.35Å, CN=6; 1.42Å, CN=8;), Lu^{3+} (0.86Å, CN=6; 0.97Å, CN=8;) and Y^{3+} (0.90Å, CN=6; 1.02Å, CN=8; 1.08Å, CN=9).

The morphology of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}:0.03\text{Ce}^{3+}$ is shown in Fig. 3a. The irregular nubby morphology of homogeneous dispersion has been observed. The particle size distribution of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$ has also been investigated by the program of Nano Measurer in Fig. 3b. The results indicate that the particle sizes of $\text{Ba}_3\text{Y}_{0.75}\text{Lu}_{0.25}\text{Al}_2\text{O}_{7.5}:0.03\text{Ce}^{3+}$ samples range from 0.5 μm to 4 μm and the average diameter is 1.776 μm . The corresponding EDX spectrum analysis (Fig. 3(c)) indicates that the product ($\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$) has a chemical composition of Ba, Y, Al, C, Cu and O, and the C and Cu peaks are resulted from the instrument, so there is no impurity element existing in our sample. A typical low-magnification TEM image is shown in Fig. 3d and the inset shows the HRTEM image. The interplanar spacings are measured to be 4.21Å and 3.92Å, which match well with the (301) and (020) interplanar distances of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$. These results show that well-crystallized $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}:\text{Ce}^{3+}$ samples have been obtained.

3.2 Photoluminescent properties

3.2.1 Photoluminescent properties of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}:\text{Ce}^{3+}$

Fig 4(a) shows the PLE spectra of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ monitored at different wavelengths. Monitored at 400nm, the PLE spectrum only shows one distinct excitation peak at around 325nm, increasing the monitored wavelength, the excitation spectrum becomes wide and covers the wavelength from 280nm to 400nm. Monitored at 480nm and 520nm, the spectra show the excitation peak at 368nm and some shoulders at around 310nm, 345nm and 380nm, respectively. Fig 4(b) shows the emission spectra of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ excited at different wavelengths. By changing the excitation wavelengths, the PL spectra have obvious variations. When the excitation wavelength is 300 nm, the emission band shows two broad bands at around 400nm and 478nm. As the excitation wavelength becomes longer, the broad band at 400nm of the emission spectrum becomes progressively weak and disappears at the excitation wavelength of 380nm. For the emission broad band at around 478nm, the intensity increases gradually and the peak moves to the longer wavelength side. Obviously, there exist site-selected excitations at around 478nm, so the Gaussian fitting was used for the emission spectrum excited at 368nm in Fig 4(c). The emission spectrum can be decomposed into four components with the maxima at 460nm, 483nm, 511nm and 543nm. It is accepted that the emission spectra of every Ce^{3+} site can be decomposed into two distinguished spectra with a theoretical energy difference value of about $2000\text{cm}^{-1}(\Delta E)$, which results from the transitions from the lowest 5d excited state to the $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ ground states. The above values can be divided into two groups with the $\Delta E_1 = 2170\text{ cm}^{-1}$ and $\Delta E_2 = 2287\text{ cm}^{-1}$, so the broad band at 478nm can be attributed to the emission of two kinds of emission centers (Ce2 and Ce3). Thinking about that there is also an emission peak at around 400nm (Ce1), so three emission centers are existed in the Ce^{3+} doped BYAO phosphors. Exactly, there are one Y^{3+} site and two Ba^{2+} sites. In addition, it can be found that the emission position of $\text{Ce}^{3+}(1)$ has a large-scale overlap with the excitation position of $\text{Ce}^{3+}(2)$ and $\text{Ce}^{3+}(3)$, the accordance of energy may cause the energy transfer from the $\text{Ce}^{3+}(1)$ to $\text{Ce}^{3+}(2)/\text{Ce}^{3+}(3)$. The results suggest that one Y^{3+} ions site and two Ba^{2+} ions sites all can be occupied by the Ce^{3+} ions.

In order to further demonstrate that there are multiple crystallographic sites for the Ce^{3+} ions, the fluorescence decay curves of Ce^{3+} monitored at 400nm, 460nm, 483nm, 511nm and 543nm with 330nm excitation wavelength in $\text{BYAO}: 0.03\text{Ce}^{3+}$ are measured, which are shown in Fig. 5. The decay processes of the sample are characterized by an average lifetime, τ , which can be calculated using the equation (1).^{29, 30}

$$\tau = \frac{\int_0^{+\infty} I(t) dt}{\int_0^{+\infty} I(t) dt} \quad (1)$$

where $I(t)$ is the luminous intensity at time t . Based on the equation (1), the lifetimes at 400nm, 458nm, 481nm, 511nm and 543nm are calculated to be 8.19ns, 32.15ns, 35.23ns, 33.24ns and 35.76ns, respectively. It is evident that they are different from each other, when the monitored emission wavelengths become longer, the average lifetime increases significantly at first and then has an obvious fluctuate. The photoluminescence lifetime strongly depends on the bonding strength between the activator and the coordinated oxygen anions through nonradiative relaxation, such as the energy transfer between the activators and the other neighbors ions, the multiphonon decay and so on,³¹ in addition, the energy transfer occurring from higher energy emission sites to lower energy emission sites further promotes the variation of decay time for the different wavelength, especially in the BYAO: Ce³⁺, the overlap of the excitation spectrum in the Ce³⁺(2)/Ce³⁺(3) sites and emission spectrum in the Ce³⁺(1) sites results in the very fast decay rate of Ce³⁺(1) sites.³² In conclusion, the variation of the decay times further validates that three emission bands exist in BYAO: Ce³⁺ phosphors.

The influence of the Ce³⁺ ions concentration on the luminescence properties was investigated. The emission spectra of Ba₃YAl₂O_{7.5} with varied Ce³⁺ concentrations under excitation at 368 nm are given in Fig. 6. With the increase of the Ce³⁺ concentration, the luminescence intensity increases first, and then the concentration quenching occurs when the Ce³⁺ concentration exceeds 0.03, and the emission peak positions of the Ba₃YAl₂O_{7.5}:xCe³⁺ phosphors shift from 473 to 487 nm. The red shift of the emission wavelength is attributed to the changes of the crystal field splitting and the Stokes shift caused by the changing lattices.^{33, 34}

According to the percolation model,^{35, 36} the concentration quenching of the compound has two different mechanisms: one is exchange interaction and the other is nonradiative energy transfer. The two energy transfer ways both strongly depend on distance between the sensitizer and activator. If the energy transfer results from the exchange interaction, the critical distance of the energy transfer between the activators should be shorter than 5 Å, which can be calculated according to the equation(2)³⁷

$$R_c = 2 \left[\frac{3V}{4\pi x_c N} \right]^{1/3} \quad (2)$$

where V is the volume of the unit cell, x_c is the critical concentration of activator ions, N is the

number of formula units per unit cell. For the BYAO: Ce³⁺ host, N = 4, x_c = 0.03 and V = 852.03 Å³, the obtained R_c is calculated to be 23.85 Å. It can be seen that the value of R_c is much larger than 5 Å, therefore, the energy transfer from the Ce³⁺ ions in Ba₃YAl₂O_{7.5}:xCe³⁺ phosphors does not belong to exchange interactions, but belong to nonradiative energy transfer. According to the theory of Dexter, the non-radiative energy transfer between the Ce³⁺ ions is caused by electric multipole–multipole interactions, and the strength of the interactions can be determined by the changes of the emission intensity. The emission intensity can be expressed by the equation (3) in the following:^{38, 39}

$$\frac{I}{x} = k[1 + \beta(x)^{\frac{\theta}{3}}]^{-1} \quad (3)$$

where x is the concentration of activator, the k and β are the constants under the same excitation and in the same host crystal, θ = 3 is corresponding to the energy transfer among nearest-neighbor ions, and θ = 6, 8, or 10 is corresponding to the energy transfer for dipole–dipole, dipole–quadrupole, or quadrupole–quadrupole interactions, respectively. Fig. 6(b) shows that the relationship between log(I/x_{Ce³⁺}) and log(x_{Ce³⁺}) is linear and the slope is calculated to be -1.09, so the value of θ is calculated to be 3.27, which is approximately equal to 3. The result indicates that the main mechanism of concentration quenching in the Ba₃YAl₂O_{7.5}:Ce³⁺ phosphors is the energy transfer among the nearest neighbor ions.

3.2.2 Photoluminescent properties of Ba₃Y_{1-y}Lu_yAl₂O_{7.5}: Ce³⁺

According to the investigation above, a blue-green light emission (the CIE coordinates of (0.1852, 0.3139) at the concentration quenching point) is obtained under the near UV excitation for the Ba₃YAl₂O_{7.5}: Ce³⁺. It is expected that the emission spectrum has a red shift to contain more green components and to make a balance between blue component and green component in the emission spectrum. An efficient method to shift the position of the Ce³⁺ emission band to longer wavelength is to replace part of the cations with smaller cations, the cationic substitution can change the crystal field strength around the activator ions and then influence the luminescence property. Thinking about that the Ba₃RAI₂O_{7.5} (R=Y, Lu) have the similar structure and the radius of Lu³⁺ is smaller than the radius of Y³⁺, the Lu³⁺ is selected for the replacement. Fig. 7 shows the excitation spectra and the emission spectra of Ba₃Y_{1-y}Lu_yAl₂O_{7.5}: 0.03Ce³⁺. The excitation peak positions have an obvious red shift from 368nm to 397nm with the y value changing from 0 to 0.5

monitored at 480nm (Fig. 8a), in addition, the shoulders and the peaks at around 345nm, 368nm and 380nm all obviously shift to longer wavelength, and the proportion of their intensity also has a bigger change, which makes the shapes of the excitation spectra become different and makes the peak positions of the excitation spectra change a lot. For the emission spectra, with the y value changing from 0 to 0.5, the shapes have no obvious changes and the peak positions of the emission spectra shift from 478nm to 493nm. Moreover, the emission intensity gradually decreases with the increase of the Lu^{3+} concentration, which is relative to the different crystallinity and the lattice variation. (Fig. 8b). The internal quantum efficiencies (QE) of $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ ($y=0$ to 5) are measured to be 44%, 43%, 43%, 39% and 37% excited at the maximum excitation wavelength. Fig. S1 shows the Gaussian fitting of the emission spectra of $\text{Ba}_3\text{Y}_{0.7}\text{Lu}_{0.3}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$, the emission spectra both can be decomposed into four components, the peak positions are 461nm, 486nm, 515nm and 545nm for $y=0.3$, 461nm, 490nm, 518nm and 547nm for $y=0.5$, Compared with the Gaussian fitting data of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ (Fig.4), it can be found that all the Gaussian fitting compositions have a red shift with the increase of Lu^{3+} concentration.

To understand the performance of the luminescence for $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: \text{Ce}^{3+}$, a probable schematic diagram is shown in Fig. 9. When the Lu^{3+} ions replace part of the Y^{3+} ions, the $\text{Y}(\text{Lu})\text{O}_6$ octahedral becomes more compact due to the smaller radius of Lu^{3+} , and the replacement produces a series of subtle structural changes, as a result, the lattice constant a, b and c all become smaller and smaller with the increase of the doped Lu^{3+} concentration, the changes of lattice constants can be demonstrated from the shifts of different XRD diffraction peaks. Accordingly, we can reasonably consider that all the Ce^{3+} sites become more compact and the average distances from the central ion to its ligands become smaller when increasing the Lu^{3+} concentration. The changes of the Ce^{3+} ions corresponding coordination environment cause the variation of the excitation and emission spectrum due to three reasons. First, the crystal field splitting of the d-level is smaller for Ce^{3+} on a larger cationic site. When increasing the doped Lu^{3+} concentration, the gradually smaller lattice constants make the position of the 5d state shifts to lower energies. As a result, the peaks or the shoulders positions of the excitation spectrum and the peak positions of the emission spectra all have a red shift. The second reason for the shift of the emission to lower energies is the Stokes shift. The Stokes shift is related to the ease of relaxation of the excited ion

in the lattice. When the lattice constant becomes smaller, the change will promote the shrinkage of Ce^{3+} ions in the excited state compared to the ground state, and then the peaks of the emission spectra will have a red shift. Thirdly, thinking about that the $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}$ has more than one cationic site, the intensity ratio of the different emission centers are not completely coincident when changing Lu^{3+} concentration, which can be reflected in the Gaussian fitting data of $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}$ (Fig.4 and Fig.S1), it also causes the shift of the excitation and emission peaks.^{33,34,40,41} In addition, the stronger crystal field splitting and the larger Stokes shift result in the decrease of probability of the electron transition from excited level to the ground level, which also make the intensity have a decrease.^{42,43} (Fig.8b)

In order to deeply understand the changes of the luminescence property for $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}$: 0.03Ce^{3+} , the fluorescence decay curves were measured. Fig. 10 shows the PL decay curves of $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}$: 0.03Ce^{3+} monitored at 480nm, on the basis of equation (1), the average luminescence lifetimes of Ce^{3+} were evaluated to be 35.11, 31.56, 28.92, 26.23, 23.08 and 22.56 ns with $y=0, 0.1, 0.2, 0.3, 0.4$ and 0.5 , the lifetimes decrease gradually with the increase of Lu^{3+} ions. The change of the decay lifetimes can be contacted with the changes of lattice dimension. When increasing the rate of the Lu^{3+} , the lattice constants become smaller and smaller, (Fig.1) the crystal structure get to more compact. Therefore the activators Ce^{3+} will have a higher density in the vicinity, which makes the energy transfer brisker under the higher Lu^{3+} concentration due to the shortened average distance of activators, moreover the tiny changes of the bond lengths and angles of the Ce^{3+} with the coordinated oxygen anions are also important roles for the changes of lifetimes.

3.2.3 Temperature-dependent PL properties

Thermal quenching is one of the important technological parameters for the phosphors used in near-UV LEDs. Generally, the thermal stability of phosphors is closely related to the rigidity of the crystal, the component elements, the Stokes shift, the energy band structure and so on. Fig.11(a) and Fig.11(b) show the temperature dependence of luminescence property for $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$: 0.03Ce^{3+} and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}$: 0.03Ce^{3+} under 375nm excitation with the temperature range of 25-250°C. We can observe that the emission intensity decreases when increasing the operating temperature. It is accepted that the decrease of emission intensity is resulted from the thermal quenching, which is due to the thermal activation through the intersection point of the excited

states and ground states. Fig. 11(c) displays the comparison of the thermal quenching for $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$, $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and the commercial $(\text{Ba}, \text{Sr})_2\text{SiO}_4: \text{Eu}^{2+}$ green phosphor. The $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: \text{Ce}^{3+}$ shows the comparable thermal stability to the $(\text{Ba}, \text{Sr})_2\text{SiO}_4: \text{Eu}^{2+}$. For the $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$, the emission intensity of the peak position at 150°C remains 50.3% and 44.2% of their corresponding initial, and the intensity of the commercial $(\text{Ba}, \text{Sr})_2\text{SiO}_4: \text{Eu}^{2+}$ decreases to 48.2% of that measured at room temperature at 150°C , thus, the thermal quenching property of $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: \text{Ce}^{3+}$ is acceptable. The peak positions of the emission spectra show no obvious shift with the increase of temperature in the data, and the color coordinates could stay stabilized when the phosphors are used in the environment with large fluctuations of temperature.

In order to understand the temperature dependence of emission intensity and to determine the activation energy for thermal quenching, the Arrhenius equation (equation (4)) was fitted to the thermal quenching data of the $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ phosphors.⁴⁴

$$I_T = \frac{I_0}{1 + c \exp\left(-\frac{\Delta E}{kT}\right)} \quad (4)$$

In equation (4), I_0 is the emission intensity at room temperature, I_T is the intensity at different temperatures, ΔE is activation energy of thermal quenching, c is a constant for a certain matrix, and k is the Boltzmann constant (8.629×10^{-5} eV). Fig. 11(d) plots the relationship between $\ln[(I_0/I_T)-1]$ and $1000/T$ for the $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ phosphors, which is linear with slopes of -3.72 and -3.47. According to equation (4), the activation energy ΔE of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ phosphors are calculated to be 0.321 eV and 0.299 eV. For the phosphors with the bigger activation energy, the electrons could easily jump into the ground levels from the excited levels via the radiationless transition, which causes the better thermal stability of the phosphors, it can be found that the change of the activation energy coincides with the measured results of thermal stability. From the analysis and discussion above, the relative position of the 5d energy level of the Ce^{3+} for the $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}$ samples in the configurational coordinate diagram is shown in the Fig. 12. Because of the smaller lattice constant, the bigger crystal field splitting makes the 5d energy levels of Ce^{3+} for the $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}$ have a lower position than that for the $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$. The red

shift of the peaks of the excitation and emission spectra also reflects the changes, and on the other hand, the large Stokes shift causes the right shift of the 5d energy level in the configurational coordinate diagram. After these changes, the distance between the crossing point of the ground and the excited states and the bottom of the excited 5d energy level (the activation energy ΔE) obviously reduce, so the change of the data for activation energy is in accord with the theoretical analysis.

3.2.4 CIE coordinates of BYAO: Ce^{3+} and BLYAO: Ce^{3+}

Fig. 13(a) shows the variation of the CIE chromaticity coordinate of the BYAO: 0.03Ce^{3+} and BLYAO: 0.03Ce^{3+} under excitation at 380 nm. The CIE coordinates are calculated and summarized in Table 1. The results indicate that the emission light can be modulated in a large range of blue-green colors with changing the doping content of Lu^{3+} ions. Under the lamp of 365nm, the related changes of the colors are visibly observed by the photographs of some samples. These results suggest that it is possible to regulate the emission color and the proportion of blue component and green component by the replace of Lu^{3+} ions.

The color properties of BLYAO: Ce^{3+} are compared with some excellent phosphors materials, including YAG: Ce^{3+} , low silica aluminosilicate glasses(LSCAS: Ce^{3+}), BAM: Eu^{2+} and $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$,^{45,46} Table 2 shows the excitation and emission peak, overlapping spectrum region, correlated color temperature(CCT), position u' and v' of the CIE 1976 $u' v'$ color diagram and the x, y coordinates in the CIE 1931 color diagram of the different phosphors. The optimal excitations of these samples(except YAG) are located in the near UV region. Compared with other phosphors, the BLYAO: 0.03Ce^{3+} phosphor has a relatively wide emission spectrum 400-650nm, which contains large blue and green compositions. The results reflect that the multi-sites phosphor is effective for expanding the width of emission spectra, and then decreasing the phosphor number in the w-LEDs. In addition, when changing the Lu^{3+} concentration, the integral color property could be regulated in a wide blue-green range, the CCT of BLYAO: Ce^{3+} could change from 20189K to 10970K, the CIE coordinate is adjacent to the white light area. In order to obtain the self-fabricated w-LED lamp, the red light emission composition is needed for obtaining the warm light emission. We choose the $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5} : 0.03\text{Ce}^{3+}$ ($y = 0.3$) sample to fabricate the w-LED mixing with (Sr,Ca)AlSiN₃: Eu^{2+} red phosphor and 370 nm GaN chip. We adjust the weight rate of two phosphors, a warm white light could be obtained and its CIE coordinate(x, y),

CCT and Ra are (0.3746, 0.3593), 4014K and 82. Its patterns, emission spectrum and CIE coordinates are shown in Figure 13.

4. Conclusions

We have successfully synthesized a series of solid solutions $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ ($0 \leq y \leq 0.5$) and investigated the structure and luminescence properties. The obtained $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}$ phosphors have a broad excitation band ranging from 300 to 430 nm, which matches perfectly with the emission of NUV LED chips. The emission spectra contain both blue and green compositions, and with the increase the Lu^{3+} content, the emission hue can be modulated in a large range of blue-green colors, the shift of the emission spectra can be explained from the increasing crystal field splitting, the larger Stokes shift and the multiple crystallographic sites. The energy transfer between the Ce^{3+} ions occurs among nearest-neighbor ions. The changes of fluorescence decay curves and thermal quenching for different Lu^{3+} concentration have also been analyzed in detail. All these results indicate that the $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: \text{Ce}^{3+}$ phosphor is a potential candidate for n-UV LED applications.

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Figure captions

Fig. 1 The XRD patterns of the BYAO, BYAO: Ce^{3+} and BYLAO: Ce^{3+} samples.

Fig. 2 The crystal structure of $\text{Ba}_3\text{RAl}_2\text{O}_{7.5}$ and the coordination environment of the Ba^{2+} ions.

Fig. 3 (a)SEM micrograph of SYAO, (b)The particle size distribution of SYAO. (c)EDS of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$. (d)TEM image of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$ (the inset shows the HRTEM image).

Fig. 4 (a) The PLE spectra of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ monitored at different wavelengths. (b) The PL spectra of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ excited at different wavelengths (c) The Gaussian fitting of the emission spectrum of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ excited at 370nm.

Fig. 5 Fluorescence decay curves monitored at 400nm, 458nm, 481nm, 511nm and 545nm with the excitation wavelength of 330 nm for $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$.

Fig. 6 (a) PL (excited at 370 nm) spectra of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}$ with varying Ce^{3+} concentrations; inset shows the peak of the emission spectra as a function of the Ce^{3+} content; (b) The emission intensity as a function of the Ce^{3+} content ;inset shows the dependence of $\log(I/x)$ on $\log(x)$.

Fig. 7 The excitation spectra monitored at 480nm and the emission spectra excited at 375nm of $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: \text{Ce}^{3+}$.

Fig. 8 The changes of excitation peaks positions, emission peak positions and the emission intensity with the different doped Lu^{3+} concentration.

Fig. 9 The schematic diagram of the changes of the excitation and emission spectra for $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ ($0 \leq y \leq 0.5$)

Fig.10 Fluorescence decay curves monitored at 485nm with the excitation wavelength of 375 nm for $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ ($0 \leq y \leq 0.5$).

Fig.11 (a) Temperature-dependent PL spectra of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ phosphor. (b) Temperature-dependent PL spectra of $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ phosphor. (c) The intensity vs. temperature for $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$, $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and the commercial $(\text{Ba}, \text{Sr})_2\text{SiO}_4: \text{Eu}^{2+}$. (d) The Arrhenius fitting of the emission intensity of $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ phosphors.

Fig. 12 Configurational coordinate diagram of the ground state and split excited state of Ce^{3+} , showing the change of the activation energy for $\text{Ba}_3\text{YAl}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ and $\text{Ba}_3\text{Y}_{0.5}\text{Lu}_{0.5}\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$.

Fig. 13 The CIE coordinates of BLYAO: 0.03Ce^{3+} and white LEDs fabricated by $\text{Ba}_3\text{Y}_{1-y}\text{Lu}_y\text{Al}_2\text{O}_{7.5}: 0.03\text{Ce}^{3+}$ ($y = 0.3$) and $(\text{Sr}, \text{Ca})\text{AlSiN}_3: \text{Eu}^{2+}$. (inset: The PL spectra of fabricated w-LEDs composed of a 370 nm NUV chip (GaN)).

Table 1 Comparison of the CIE chromaticity coordinates for BLYAO: 0.03Ce³⁺ phosphors excited at 380 nm.

Sample	y(the doped Lu ³⁺)	CIE coordinates (x, y)
1	0	(0.1852, 0.3139)
2	0.1	(0.193, 0.336)
3	0.2	(0.197, 0.3427)
4	0.3	(0.1978, 0.3719)
5	0.4	(0.2053, 0.3864)
6	0.5	(0.2099, 0.3992)

Table 2 The excitation and emission peak, overlapping spectrum region, correlated color temperature(CCT), position u' and v' of the CIE 1976 u' v' color diagram and the x, y coordinates in the CIE 1931 color diagram of the different phosphors.

	BLYAO:Ce	YAG:Ce	LSCAS:Ce	BAM:Eu	BSO:Eu
Excitation peak (nm)	350-400	445	405	350	365
Emission peak(nm)	478-493	546	525	451	503
Spectrum region(nm)	400-650	480-700	450-670	400-550	450-600
Position u' v'	(0.1158, 0.4417)- (0.1136, 0.4737)	(0.46, 0.52)	(0.17, 0.53)	(0.1613, 0.2004)	(0.0758, 0.5118)
Position x, y	(0.1852, 0.3139)- (0.2099, 0.3992)	(0.46, 0.53)	(0.33, 0.46)	(0.1487, 0.0821)	(0.16, 0.48)
Temperature (K)	20189-10970	3450	5350	5349	11058

Normalized Intensity (a.u)