Luminescence Properties of Ce\(^{3+}\) Doped Garnet 
Ca\(_2\)LaZr\(_2\)Al\(_3\)O\(_{12}\) Phosphors

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Abstract: A series of novel Ca\(_2\)LaZr\(_2\)Al\(_3\)O\(_{12}\): \(x\)Ce\(^{3+}\) garnet phosphors were obtained by conventional high temperature solid-state reaction. Crystal structure, phase purity, micromorphology as well as luminescence properties are studied via X-ray powder diffraction, scanning electron microscope and photoluminescence spectra including excitation and emission. Moreover, the mechanism of concentration quenching, thermal stability, fluorescent lifetime and quantum efficiency were investigated in detail. Under n-UV excitation, Ca\(_2\)LaZr\(_2\)Al\(_3\)O\(_{12}\): Ce\(^{3+}\) exhibits a broadband of blue emission at 440 nm approximately for maximum, corresponding to 5d-4f transition of Ce\(^{3+}\). Emission can keep 41% of initial intensity when temperature is promoted to 373 K according to temperature-dependence emission spectra. The internal quantum efficiency of the optimal specimen is 15% and with Ce\(^{3+}\) increasing, the color of emission transfers to light from dark blue at CIE.

Introduction

Compared with conventional lighting equipment, light emitting diodes (LEDs) have longer service life, superior quality of light source, higher quantum efficiency and the characteristic of environmental friendliness [1]. Based on these advantages, LEDs are gradually replacing traditional equipment in many fields, such as indicator, automobile headlight, display lighting and general illuminating [2, 3]. Nowadays, incorporating InGaN blue chip and yellow phosphor Y\(_3\)Al\(_5\)O\(_{12}\):Ce\(^{3+}\) is a pervasive method to encapsulate high quality white LEDs (WLED) [4]. However, lacking in the red component leads to the defects of high correlated color temperature (up to 7750 K) and low color rendering index (CRI, only about 75) [5]. As a result, the researchers suggested another solution: two or three phosphors are encapsulated together on n-UV LEDs chips. Differing from other trivalent rare ions, the 5d-4f transition at visible region of Ce\(^{3+}\) allows to be viewed for lower energy. Ground state is split into \(^2\)F\(_{5/2}\) and \(^2\)F\(_{7/2}\) by the reason of spin-orbit coupling and energy level difference is 2200 cm\(^{-1}\) approximately [6]. Luminescent spectrums are easily affected by crystal field for Ce\(^{3+}\) as 5d level is not shielded via 5s5p, So Ce\(^{3+}\) can emit wide spectra from ultraviolet to infrared region and vary from blue to yellow-orange at visible light mainly in different hosts due to various local coordination environment as well as lattice symmetry [7]. In recent years, garnet phosphors have attracted the attention of researchers because of their superior physical and chemical performances, such as appropriate hardness, excellent thermal conductivity and chemical stability [8]. There are many novel garnet phosphors have been explored, for example, red phosphors Ca\(_3\)Y\(_2\)Ge\(_3\)O\(_{12}\): Eu\(^{3+}\) [9], Y\(_3\)Mg\(_4\)Ge\(_3\)O\(_{12}\): Mn\(^{4+}\), Li\(^+\) [10], green phosphor Lu\(_3\)Al\(_5\)O\(_{12}\): Ce\(^{3+}\) [11], yellow phosphor Ca\(_2\)YZr\(_2\)Al\(_3\)O\(_{12}\): Ce\(^{3+}\) [12],...
Ce$^{3+}$[12] etc. Garnet structure is classified to isometric system with the general formula $A_3X_5O_{12}$ or $A_3B_2X_3O_{12}$. Only site A can be substituted by rare atom for the former, but A, B are all allowed to occupy for the latter. In addition, cation $A^{2+}$ surrounded by eight $O^{2-}$ anions forms a dodecahedron of $D_2$ symmetry point. B connects nearest six $O^{2-}$ ions forming octahedron of $C_3$ and X is usually tetrahedron coordination, similar to $[SiO_4]$, $[AlO_4]$ etc. Herein, A is occupied by alkaline earth metal $Ca^{2+}$, in which Ce$^{3+}$ substitution occurs.

In general, this work focuses on the synthesis and photoluminescence performances of $Ca_3LaZr_2Al_3O_{12}$: $x$Ce$^{3+}$ phosphors ($x = 0.01 \sim 0.08$) with CaF$_2$ flux. The phase composition is characterized by XRD and the luminescent properties are all investigate in detail, such as excitation and emission spectra, fluorescence lifetime, quantum efficiency and thermal stability etc.

**Experiment Section**

The garnet phosphors $Ca_3LaZr_2Al_3O_{12}$: $x$Ce$^{3+}$ (CLZA: $x$Ce$^{3+}$, $x=0.01$, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08) were prepared by the high temperature solid-phase reaction. First, raw materials including $Al_2O_3$ (99.99%), $CaCO_3$ (99%), $La_2O_3$ (99.9), $ZrO_2$ (99%), $CeO_2$ (99%) and CaF$_2$ (99%) were thoroughly ground for more than 15 minutes based on the stoichiometric proportions. Then, the mixture powders were heated at 1500$^\circ$C under reductive atmosphere (95%N$_2$-5%H$_2$) in a tubular furnace (GSL-1800) for 5 h. Lastly, the specimen bulk was ground into phosphor after cooling to room temperature naturally for further characterization. In this experiment, the phase composition was determined via a powder X-ray diffractometer (XRD, BRUKER AXS D8 Advance, Germany) using Cu-K$_{a1}$ radiation ($\lambda=1.5406$ Å), operating current 40 mA and voltage 40 kV. The morphology was observed by scanning electron microscopy (SEM, JEOL, JSM-IT300, Japan). The photoluminescence spectra were recorded by a fluorescence spectrophotometer (Japan, Hitachi F-4600) fitting a temperature control system and A 150 W xenon lamp is used as the excitation source. The diffuse reflection spectra were measured by an UV-Vis-NIR spectrophotometer with integrating sphere (Carry-7000, Agilent, America). The decay curve and fluorescent lifetime were tested by FL980 spectrofluorometer (Edinburgh, British) using picosecond pulsed laser.

**Results and Discussion**

**Phase composition and micromorphology**

Figure 1 shows the XRD patterns of CLZA: $x$Ce$^{3+}$($x=0.01$, 0.02, 0.04, 0.06) samples synthesized at 1500$^\circ$C, which match well with the PDF card #72-1970 (garnet $Ca_3Sc_2Ge_3O_{12}$) and homolog $Ca_2GdZr_2Al_3O_{12}$[13]. The diffraction pattern of CLZA belongs to isometric system can be determined
and the space group is indexed to the Ia3d. There is almost no impurity can are observed, which indicates that relatively pure garnet phosphors CLZL:xCe³⁺ have been obtained favourably. In addition, increasing the doping concentration of Ce³⁺ did not cause a change of the phase structure and the production of impurities. Simultaneously, Figure 1 shows the XRD pattern of the sample without CaF₂. The CLZA sample with flux has a purer phase than without because CaF₂ was melted in the calcination process and the surface tension of liquid could prompt particle coagulation as well as inter-particle sliding, which provided the impetus for contact reaction of particles and grain growth [14]. Besides, according to the information of PDF card, crystal indices have been marked on the corresponding diffraction peaks.

Gong [13] et al has already studied a series of the garnet crystal cell structure and coordination environments. In CLZA, Ca²⁺ or La³⁺ is connected to eight O²⁻, Zr⁴⁺ is linked to six O²⁻ and Al³⁺ coordinates with four O²⁻. R(Ca, Ce, La) = 1.12 Å, R(Ce, Ce, Ce) = 1.14 Å, R(Zr, Zr, Zr) = 1.06 Å, R(Zr, Ce, Ce) = 0.72 Å, on the basis of Hume-Rothery rule, the substituted sites of Ce³⁺ are estimated to be Ca²⁺ and La³⁺ [15]. [CaO₈] and [LaO₈] dodecahedrons share edges or corner to [AlO₄] tetrahedron and [ZrO₆] octahedron forms coordination polyhedron connection mode [16].

Figure 2 (a) (b) displays the SEM images of CLZA and CLZA: 0.04Ce³⁺, nearly spherical grains gathered forming polyhedrons of uniform particle and the size is between 3 µm and 6 µm. There is no obvious variation in size after doping Ce³⁺ and the crystallization degree is high. Crystal morphology was damaged more easily when grinding on account of the great hardness.

Figure 3. Diffuse reflectance spectra of CLZA and CLZA: 0.04Ce³⁺.
Photoluminescence Characteristics

The diffuse reflectance spectra were presented in Figure 3 CLZA host has an absorption at about 290 nm, which corresponds to the excitation peak of 250–300 nm. After doping Ce$^{3+}$, phosphor shows strong energy absorption over 350–450 nm (more than two absorbing sites) and the band gap is calculated to be 3.22 eV.

Figure 4 shows the excitation spectra (PLE) of CLZA phosphors adding different Ce$^{3+}$ concentrations. It presents two excitation bands including three peaks at 250 nm, 280 nm and 350 nm due to polymorphism of excited state of Ce$^{3+}$ in 4f orbital energy level possibly. In different coordination environment and lattice symmetry of hosts, the minimum 5d level position is different and it depends on two independent factors. First, nephelauxetic effect can cause the shift of 5d centroid. In addition, crystal field would lead 5d split into a certain width [17]. On account of the 4f $\rightarrow$ 5d transition of Ce$^{3+}$, the excitation spectrum displays a broad band that maximal intensity is about 350 nm ranging from 325 nm to 375 nm. With the increasing of Ce$^{3+}$, excitation intensity will fortify firstly when the concentration is lower than 4 mol%, then will decrease when more than 4 mol%. These results accord with emission spectra.

\[ D_q = \frac{1}{6} Z e^2 \frac{r^4}{R^5} \]  

Figure 5 exhibits the emission spectra of CLZA:xCe$^{3+}$ (0.01 ≤ x ≤ 0.08) under excitation 350 nm. A broad emission band over 380 nm to 600 nm can be viewed. The asymmetric emission band was divided into three fitting peaks locating 396 nm (25252 cm$^{-1}$, peak 2), 435 nm (22988 cm$^{-1}$, peak 1), 497 nm (20121 cm$^{-1}$, peak 3) by Gauss decomposition in Figure 5 inset. As Ce$^{3+}$ concentration increasing, the central emitting position shows obvious red-shift from 435 to 450 nm. The red-shift results of the electron transition from the higher 5d orbital energy to the lower, which generates an energy-decrease of excited state (5d) to ground state (4f). In short, the emission of Ce$^{3+}$ is effected by the 5d center position and split width, and Crystal field theory must be considered for the later. The value of crystal field splitting (Dq) is represented as equation (1) [18].where r is marked as the radius of wave function for 5d level, Z is the electrovalence of anion, R represents bond length between cation and ligand ion (O$^2$). After more Ce$^{3+}$ replacing Ca$^{2+}$ or La$^{3+}$, the distance of Ce-O is greater than Ca-O and La-O, so Dq and 5d level will decrease that leads to red-shift.
The reason why rare earth ions for phosphors possess the optimal doping concentration is that concentration quenching would happen if the doping amount is too high. Electronic transition from excited state to the ground state does not produce photons as the energy transfer to other activator ions forming countless non-radiative transition. Generally, concentration quenching can occur in conform to the three mechanisms: exchange interaction, multipole interaction and radiation reabsorption [19]. The critical radius ($R_c$) of quenching can be expressed as function (2), where $V$ represents cell volume ($V > 1945 \text{ Å}^3$ [14]), $x_c$ is the critical concentration ($x = 0.04$), $N$ is the number of cation for unit cell ($N = 8$). The $R_c$ is calculated to be more than 22.65 Å, so multipole interaction causes concentration quenching ($R_c > 5$ Å). Briefly, the quenching phenomenon will not occur when the distance of Ce$^{3+}$ is larger than $R_c$ [20].

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

Figure 5. Photoluminescence spectra of CLZA:$x$Ce$^{3+}$ varying Ce$^{3+}$ concentration and inset for Gauss decomposition.

Figure 6. The linear fitting of log($x$/Ce$^{3+}$) and log(I/I$^0$).
According to Dexter’s theory [21], the relationship between the concentration of activator and luminous intensity will be consistent with equation (3) when the concentration of Ce$^{3+}$ is large enough, where $K$ is a constant, $\theta = 6, 8, 10$ on behalf of the interaction of electric dipoles, electric dipole and quadrupole, quadrupoles, respectively. $\log(x/Ce^{3+})$ and $\log(I/x)$ show a linearity, which is fitted in Figure 6. The slope value ($-\theta/3$) is about -1.717, $\theta \approx 5.15$, closing to 6, so the mechanism of energy transfer is electric dipole-dipole interaction.

\[
\frac{I}{x} = K\left(1 + \beta x^{\theta/3}\right)^{-1}
\]  

(3)

Decay curves of different Ce$^{3+}$ concentration at room temperature monitored by 360 nm are described in Figure 7. Each curve matches the following equation (4) suitably [22].

\[
I(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)
\]

(4)

Where $I(t)$ represents the luminous intensity of t moment, $A$, $B_1$, and $B_2$ are constants, $\tau_1$ and $\tau_2$ are the long and short lifetimes for the bi-exponential function. Furthermore, the average lifetime ($\tau^*$) is calculated as follows (5). The measured lifetimes are 25.9, 26.2, 27.1, 28.1, 28.3, 28.0, 28.6, 28.4 ns with Ce$^{3+}$ gradient concentrations ($0.01 \leq x \leq 0.08$), respectively. It can be seen that lifetimes changes only slightly.

\[
\tau^* = \frac{B_1\tau_1^2 + B_2\tau_2^2}{B_1\tau_1 + B_2\tau_2}
\]

(5)

The quantum yield (QY) was measured and calculated according to the formula (6) [23]. $L_s$ is the integral-area of emission spectrum for sample. On the side, $E_R$ and $E_s$ represent the excitation integral-areas of blank and samples, respectively. The internal QY of the optimal sample is 15%, which should be improved for its practical application.

\[
\eta = \frac{\int L_s}{\int E_R \cdot \int E_s}
\]

(6)

In general, thermal stability is one of the significant parameters of quality for phosphors, because temperature has an obvious effect on the emission intensity [24]. Temperature-dependent emission spectra of Ce$^{3+}$-doped CLZA under 350 nm exciting are showed in Figure 8. The luminescence intensity decreases gradually when phosphor is heated and the emission intensity can maintain about 41% of the initial condition when the temperature is raised to 373 K. Configuration coordinate can be used to explain thermal quenching for high-temperature bring a promoting of vibrational energy and it
is higher than the intersection of ground and excited state. Then, activator is excited thermally and the interaction of phonon between ground and excited state generates non-radiation transition [25]. In addition, with the variation of temperature, the emitting center positions move to high energy region occurring blue-shift with the temperature increasing that can be explained by phonon-assisted tunneling and analyzed in configuration coordinate diagram. Thermal activation energy (ΔE) can also be estimated via the Arrhenius equation (7) [26], I_T and I_0 are the emitting intensities of temperature T and room-temperature. K is Boltzmann constant. The ln[(I_T/I_0)-1] shows a linear variation for 1/KT fitting in Figure 8 inset. The absolute value of slope is 0.344 eV, which equals activation energy ΔE.

\[ I_T = \frac{I_0}{1 + c \exp(-\frac{\Delta E}{KT})} \] (7)

Figure 8. Temperature-dependent spectra of CLZA:0.04Ce\(^{3+}\) ranging from 298 K to 448 K and inset of linear fitting of 1/KT and ln[(I_0/I_T)-1] to calculate ΔE.

The CIE chromaticity coordinates of CLZA: \(x\)Ce\(^{3+}\) (\(x\)=0.01, 0.03, 0.06, 0.08 corresponding to 1, 2, 3, 4) are shown in Figure 9. With the increasing of \(x\), the CIE coordinates were measured to be (0.1658, 0.1075), (0.1709, 0.1335), (0.1739, 0.1456) and (0.1841, 0.1709). It can be seen that the chromaticity coordinates displays a movement from the blue to pale blue, which has a well match to emission spectra. Tunable-wavelength can be obtained based on the given host by controlling Ce\(^{3+}\) concentration indicates that CLZA blue phosphor can be expected to applying to the business.

Conclusion
The new blue phosphorCa\(_2\)LaZr\(_2\)Al\(_3\)O\(_{12}\): Ce\(^{3+}\) was obtained via high temperature solid-state method, and the result from XRD analysis indicates this phosphor crystal vests in garnet structure of the isometric system. Ca\(_2\)LaZr\(_2\)Al\(_3\)O\(_{12}\): xCe\(^{3+}\) phosphors can be well excited by n-UV 350 nm and emit a wide band blue light center position at about 440 nm ranging from 380 to 650 nm. Optimal concentration of rare earth ions doping is 4 mol% and its quantum yield is 15%. Measuring thermal stability exhibits that emitting intensity can maintain only 41% at 373 K compared to room-temperature. These results indicates that Ca\(_2\)LaZr\(_2\)Al\(_3\)O\(_{12}\): Ce\(^{3+}\) has the potential used as a blue phosphor for white LEDs, but the luminescence properties still need to be improved.
Figure 9. CIE chromaticity diagram for CLZA: $x\text{Ce}^{3+}$ phosphors ($x = 0.01, 0.03, 0.06, 0.08$).

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