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A novel Ce\(^{3+}\) activated Lu\(_3\)MgAl\(_3\)SiO\(_{12}\):Ce phosphor was synthesized and found to crystallize in the garnet structure. The crystal structure of synthesized phosphors has been characterised by X-ray diffraction and refined with Rietveld refinements. Both room and high temperature photoluminescence spectra are utilized to investigate the luminescence properties and crystal field splitting. The high temperature quenching of these phosphors and quantum efficiency (QE) are also studied using both the prepared YAG:Ce and commercial YAG:Ce phosphor named P46-y3 as reference. Upon excitation by blue light, the composition-optimized Lu\(_3\)MgAl\(_3\)SiO\(_{12}\):Ce phosphor exhibited strong yellow light with a high QE of 81.2% and better thermal stability than that of commercial phosphor. The results indicate that Lu\(_3\)MgAl\(_3\)SiO\(_{12}\):Ce phosphor can serve as a candidate phosphor for blue chip LEDs.

1. Introduction

The development of efficient white light-emitting diodes (w-LEDs) has provided tremendous potential in reducing energy use by replacing conventional lighting source, such as fluorescent or incandescent lamps.\(^{1,4}\) The most common method to create white light is partially converting the blue light from InGaN chip in Y\(_3\)Al\(_3\)O\(_{12}\):Ce\(^{3+}\) (YAG:Ce) phosphor to yellow. Although the path of white light realization is inexpensive and efficient, it has poor color rendering properties due to the deficiency of the red component limiting its application in some field.\(^{5,7}\) like in-home lighting which takes up the majority of the lighting market. To meet the requirements for general illumination lighting, two major modifications have been developed. One is the modification of the YAG:Ce system, including co-doping rare earth ions (Pr\(^{3+}\), Sm\(^{3+}\), Eu\(^{2+}\), etc.)\(^{5,10}\) or transition metal ions (Mn\(^{2+}\)),\(^{11}\) which could increase red component, as well as substituting host components by other ions (Y\(^{3+}\) substituting by Tb\(^{3+}\), Gd\(^{3+}\),\(^{9,10,12,13}\) Al\(^{3+}\) substituting by Mg\(^{2+}\)-Si\(^{4+}\) or Mg\(^{2+}\)-Ge\(^{4+}\),\(^{14}\) and O\(^{2-}\) substituting by N\(^{2-}\),\(^{15,16}\) etc.) to change the crystal field strength or covalence. The problem is the enhancement of the red component efficiency is not obvious, and almost all bright and thermal stability of modification YAG:Ce is obviously declined. The other is exploring novel red phosphors which are usually based on Eu\(^{3+}\) doped nitride.\(^{15,16}\) However, these phosphors require critical preparation conditions like high temperature, high pressure and expensive raw materials, etc. Besides, they have to be blended with YAG:Ce phosphor to make white lamps, possibly leading to variations during lamp manufacturing. In principle, using a single phosphor rather than two or three could help to reduce sort of this variability.

The host of commercial YAG:Ce phosphor belongs to garnet structure, and currently, garnet structure is almost the only oxide host for Ce\(^{3+}\) doped that could absorb blue light and emit from green-yellow to orange-red light.\(^{5,17-23}\) The general stoichiometric formula of the garnet structure is [A\(_i\)]\([B\(_{2m}\)](C\(_{3n}\)O\(_{12}\)), where A, B, and C are dodecahedral, octahedral and tetrahedral coordination, respectively. In this structure, Ce\(^{3+}\) occupies A site and emits from green to orange light through varying crystal field strength and covalent characteristic, because the energy position of the lowest Ce\(^{3+}\) 5d level could be justified by changing the crystal field strength around Ce\(^{3+}\) and the covalency of Ce\(^{3+}\)-O\(^{2-}\). Thus, it is possible and valid to modify the typical garnet composition to obtain a significant red-shift emission spectrum by enhancing the crystal field strength surrounding of Ce\(^{3+}\) or decreasing covalent interaction between the oxygen anions and A ions (A\(^{3+}\)-O\(^{2-}\)). In principle, an increased diameter of the A site results in an increased crystal field strength of Ce\(^{3+}\). In contrast, an increase in the average diameter of B or C sites results in a decrease covalent interaction between A\(^{3+}\)-O\(^{2-}\). These provide a simple design rules for Ce\(^{3+}\) luminescence in garnet hosts. For example, Mg\(^{2+}\)-Si\(^{4+}\) substitution on the B and C sites, respectively, leads to Ce\(^{3+}\) emission band shift to the longer wavelength. However, further red shift of the emission is limited by garnet phase instability due to the competition of apatite structure forming, and leads to lower efficiencies at room temperatures.\(^{2}\) As a consequence, there are rare reports on larger amount substitution of Mg\(^{2+}\)-Si\(^{4+}\) pairs in YAG:Ce. However, smaller dodecahedral A cations substitution can strengthen the garnet phase stability.\(^{28}\) Under the guidance of above principles, if we induce larger amount Mg\(^{2+}\)-Si\(^{4+}\) pairs into YAG host, smaller Lu\(^{3+}\) should be in place to substitute Y\(^{3+}\) to keep stability. In other words, Lu\(^{3+}\) based garnet host Lu\(_3\)MgAl\(_3\)SiO\(_{12}\) should be more stable than Y\(^{3+}\) based Y\(_3\)MgAl\(_3\)SiO\(_{12}\).\(^{24}\) and Ce\(^{3+}\) activated Lu\(_3\)MgAl\(_3\)SiO\(_{12}\) could be expected with better luminescence properties (Shown in Figure S1-S3).
In a practical sense, phosphors should not only have redder spectra for lower correlated color temperature (CCT) and high color rendering index (CRI) but also have high QE and thermal stability for warm white LED phosphors. The aim of this work is to investigate Ce\textsuperscript{3+} activated Lu\textsubscript{3}MgAl\textsubscript{12}SiO\textsubscript{12} garnet phosphor, and discuss its synthesis, crystal structure and luminescence properties in \textit{w}-LEDs use.

2. Experimental methods

Using the conventional high temperature solid-state reaction method Lu\textsubscript{3}MgAl\textsubscript{12}SiO\textsubscript{12}:xCe (Lu\textsubscript{3-x}Ce\textsubscript{x}MgAl\textsubscript{12}SiO\textsubscript{12}, x = 0.04, 0.06, 0.07, 0.08, 0.09, 0.10) phosphors were prepared. The starting materials (Lu\textsubscript{2}O\textsubscript{3}, 99.99%, CeO\textsubscript{2}, 99.99%, 4MgCO\textsubscript{3}·Mg(OH)\textsubscript{2}·5H\textsubscript{2}O, A.R., Al\textsubscript{2}O\textsubscript{3}, A.R. and H\textsubscript{2}SiO\textsubscript{4}, A.R.) were all weighed out as the desired stoichiometry and thoroughly mixed using an agate mortar with small amount of ethanol. The mixtures were first fired using BN crucibles at 800 °C for 2h then at 1500 °C for 6h in 5% H\textsubscript{2} + 95% N\textsubscript{2} atmosphere. Finally, the samples were cooled to room temperature in the furnace, and then ground in an agate mortar. All samples are yellow body color.

YAG:Ce was also synthesized as a reference by solid-state reaction with 1 wt% BaF\textsubscript{2} as flux at 1500 °C for 6h in 5% H\textsubscript{2} + 95% N\textsubscript{2} atmosphere. Powder X-ray diffraction (XRD) data were collected on a Rigaku D/MAX-2400 powder X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å) operating at 40 kV and 60 mA. Step scans were performed from 5 to 110° 2θ and a step size of 0.02 . Generally, the lattice parameter of Lu\textsubscript{3}MgAl\textsubscript{12}SiO\textsubscript{12} space group, and lattice constants were refined as a = 11.9421 Å.

Powder X-ray diffraction (XRD) patterns were fitted by Rietveld refinements using MAUD software. Excitation (PLE) and emission (PL) spectra were measured by HORIBA JOBIN YVON Fluorlog-3 spectrophotometer system. The QE was measured by a FLS-920T fluorescence spectrophotometer. High temperature luminescence intensity measurements were carried out by using an aluminum plaque with cartridge heaters; the temperature was measured by thermocouples inside the plaque and controlled by a standard TAP-02 high temperature fluorescence controller. All measurements are taken at room temperature unless otherwise mentioned.

3. Results and Discussion

3.1 Crystal structure analysis of garnet phase

Fig. 1 shows a Rietveld refinement of XRD patterns of Lu\textsubscript{3}MgAl\textsubscript{12}SiO\textsubscript{12}:0.06Ce phosphor. The initial structural model of the actual structure of Lu\textsubscript{3}MgAl\textsubscript{12}SiO\textsubscript{12}:0.06Ce phosphor was constructed with crystallographic data previously reported for Y\textsubscript{3}Al\textsubscript{12}O\textsubscript{19} (JCPDS Card No. 33-0040). The refinement result shows the pattern matched well with the model regardless of the minor apatite impurity peaks, corresponding to I\textit{a}\textit{3d} (No.230) space group, and lattice constants were refined as a = 11.9421 Å. The lattice parameter of Lu\textsubscript{3}MgAl\textsubscript{12}SiO\textsubscript{12}:Ce phosphor is smaller than YAG (12.066 Å),\textsuperscript{6} which is likely due to the smaller size of Lu\textsuperscript{3+} vs Y\textsuperscript{3+}. Nevertheless, it’s larger than Lu\textsubscript{3}Al\textsubscript{12}O\textsubscript{19} (LuAG, 11.912 Å), due to lager size of Mg\textsuperscript{2+} vs Al\textsuperscript{3+}. The Rietveld refinement of Lu\textsubscript{3}MgAl\textsubscript{12}SiO\textsubscript{12}:Ce phosphor (Table 1) shows that the 24c, 16a, 24d and 96h Wyckoff sites are occupied by Ce/Lu, Mg/Al\textsubscript{11}, Si/Al\textsubscript{2} and O, respectively. However, occupancies of all ions are slightly less than expected from the nominal composition.
distributed on the tetrahedral sites, shown in green color. The (Ce/Lu)O₈ dodecahedrons are connected with (Mg/Al)O₈ octahedrons by their shared edges, while are connected with part of (Si/Al₂)O₄ tetrahedrons by one O atom, and the other tetrahedrons by edges. In fact, every (Ce/Lu)O₈ dodecahedron is surrounded by four (Ce/Lu)O₈ dodecahedrons, four (Mg/Al)O₈ octahedrons and six (Si/Al₂)O₄ tetrahedrons, which means that every coordination O²⁻ of Ce³⁺ is shared by four cations, two Lu³⁺, one Mg/Al and one Si/Al₂. Thus, the photoluminescence of Ce³⁺ is not only affected by (Ce/Lu)O₈, but also by (Mg/Al)O₈ and (Si/Al₂)O₄.

To make sure all obtained samples are garnet structure, a quicker scan XRD is used. Fig. 3 shows the XRD patterns of the obtained Lu₃MgAl₃SiO₁₂:xCe phosphors. All samples are in agreement with the garnet structure, and it is hard to find impurity phases under the condition of quicker scan. Combined with Rietveld refinement, we believe that there is bare amount of impurity phases in obtained Lu₃MgAl₃SiO₁₂:xCe phosphors. The influence on photoluminescent properties of bare amount of impurity phases will be discussed later. In addition, the activator up to 0.10 does not cause any significant change in the structure.

![Fig. 3 XRD patterns of Lu₃MgAl₃SiO₁₂:xCe phosphor.](image)

### 3.2 Luminescence properties of Lu₃MgAl₃SiO₁₂:Ce phosphor

As expected for a garnet host, the lowest Ce³⁺ 4f⁴-5d⁴ absorption transition is in the blue spectral region, leading to a green-yellow to orange color. The excitation spectra of Lu₃MgAl₃SiO₁₂:0.06Ce phosphor and com-YAG:Ce (P46-y3) are shown in Fig. 4a. For both phosphors, the spectral was measured for the Ce³⁺ emission band maximum. Both excitation spectra exhibit two excitation bands of Ce³⁺, one 5d band between 370 nm to 500 nm, and the other 5d band level between 300 nm to 360 nm, which corresponds to the two lowest 5d levels of Ce³⁺ (5d⁴ and 5d⁵ bands, respectively). The intensity of 5d² band is less than two times as much than that of 5d⁴ band due to symmetry selection rules. ²⁵,²⁶ And the ratio of 5d⁴ band intensity divided 5d² band is 2.80 and 2.73 for Lu₃MgAl₃SiO₁₂:0.06Ce phosphor and P46-y3, respectively. The similar ratio of these two phosphors indicates the same symmetry between Lu₃MgAl₃SiO₁₂:0.06Ce and YAG:Ce phosphors.

It is difficult to analysis of the Ce³⁺ 5d crystal field splitting of Lu₃MgAl₃SiO₁₂:0.06Ce phosphor at room temperature due to the secondary phase excitation bands obscure the higher energy Ce³⁺ 5d levels of garnet, seen the wide band range from 250 nm to 380 nm in Fig. 4a. But it is known, Ce³⁺ doped garnet phosphors have much better thermal stability than Ce³⁺ doped silicate apatite or oxysilicate. ²⁷-²⁹ Thus it is possible to obtain pure garnet excitation spectra at higher temperature like 250 °C. According to above, a perfect excitation spectrum was obtained at 250 °C, shown in Fig. 4b. From high temperature excitation spectrum, the splitting between the lowest two Ce³⁺ 5d levels in Lu₃MgAl₃SiO₁₂:0.06Ce phosphor is ~ 7468 cm⁻¹, smaller than that of ~ 7600 cm⁻¹ in YAG:Ce, ⁵ expecting better thermal stability than that of YAG:Ce. However, this is larger than that of LuAG:Ce for ~ 6430 cm⁻¹. ³⁰ In Ce³⁺ activated garnet structure, the splitting of the 5d state can be related to a T₄₂g₂E₂ parity splitting due to the distortion of the cubic coordination into a dodecahedron with D₂₅ symmetry. ³²,³³ Lu₃MgAl₃SiO₁₂:0.06Ce phosphor compared with YAG:Ce phosphor, smaller size of dodecahedral Lu³⁺ gives a more cubic environment of Ce³⁺, resulting in a reduction crystal field strength around Ce³⁺ than Y-based garnet, revealing smaller crystal fields splitting. While compared with LuAG:Ce, Mg²⁺-Si⁴⁺ substitution Al³⁺ results in inherent disorder in the host lattice and obtaining stronger crystal fields splitting. ³⁷ Besides, the position of the lowest Ce³⁺ 4f⁴-5d⁴ absorption transition is at higher energy in Lu₃MgAl₃SiO₁₂:0.06Ce phosphor than YAG:Ce (460 nm), while its very close to that of Lu₃Al₂O₁₂:Ce³⁺ (Lu₃AG:Ce) (~450 nm) phosphor, ³⁰,³¹ which may be due to the same electronegativity because of the same Lu³⁺ ions in dodecahedral sites.

Excitation into the absorption band at 450 nm gives a typical asymmetric garnet luminescence band with maxima of ~560 nm, although not so red as that for P46-y3, but redder than that for prepared YAG:Ce. The emission is red shifted of ~835 nm compared to non-doped YAG:Ce, shown in Fig. 4c. However, UV excitations lead to the blue emission band. Among the phases present in these samples, Ce³⁺ doped silicate apatite or oxysilicate ²⁷-²⁹ should correspond to the blue region. The deep blue emission from the impurity phases can be absorbed by the garnet in these samples, leading to garnet luminescence and spurious UV peaks in the garnet excitation spectra. In addition, the relative intensity of the blue band compared to garnet yellow band also indicates that Ce³⁺ has reduced solubility in the garnet under these synthesis conditions, supporting the above Rietveld refinement results. Fortunately, Ce³⁺ doped silicate apatite or oxysilicate can barely absorb blue light. Thus the effect of bare amount of impurity phases on emission spectra can be ignored when under blue light excitation.
It has considerable influence on the light output and color rendering performance, especially for blue LED. Thus, the thermal stability plays an important role in ensuring a high efficiency of phosphor-converted blue chip LEDs. Fig. 6 gives temperature-dependent photoluminescence spectra for optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor. With increase temperature from 20 °C to 250 °C, the shape seems the same with very little blue shift (560 nm in 20 °C vs 558 nm for 250 °C), which can be explained by faster quenching of low energy emission band if compared to its high energy counterpart, like in CaY$_2$Al$_2$SiO$_{12}$:Ce$^{3+}$ garnet phosphor. This is an agreement with the asymmetric emission band, shown in Fig. 4c. The inset of Fig. 6 is the brightness vs temperature for Lu$_3$MgAl$_2$SiO$_{12}$:0.06Ce phosphor excited by 450 nm and in comparison to P46-y3 excited by 460 nm. It is clearly seen that the thermal stability of the luminescence of Lu$_3$MgAl$_2$SiO$_{12}$:0.06Ce phosphor is greater than that of P46-y3. When the temperature was increased to 150 °C, emission intensity of optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor dropped to only 81.1% of its initial intensity, while that of P46-y3 decreased to 68.0%. The higher thermal stability of synthesized optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor indicates that it can be good candidate yellow phosphor for blue chip LEDs. Also, it is expected that the thermal stability of this new phosphor can be further enhanced by improved preparation conditions, which can restrain apatite structure forming. The better thermal stability of novel garnet phosphor can be explained as following. Lu$_3$MgAl$_2$SiO$_{12}$ and YAG have same garnet crystal structure. Ce$^{3+}$ occupies Lu and Y sites. Both are dodecahedral coordination. Thus, we can assume that when these two phosphors undergo high temperature, factors are similar beyond the atom’s weight. As Lu is more weight than Y, the agitation range radius R$_1$ is smaller than R$_2$, schematic diagram showed in Fig. 7. Larger R causes to more energy lose, resulting in worse thermal stability. From the aspect, if phosphors have same crystal structure, Lu-based phosphors should have better thermal stability than that for other rare-earth ions based phosphors.
prepared YAG:Ce will get highest CCT, which cannot be phosphor, YAG:Ce and P46qy3 phosphors are shown in Fig. 8. Combined with blue chip LEDs, can give single phosphor convert shown optimized Lu3 of P46qy3, and introducing high CRI. Above analysis results connection of excitation wavelength and CIE chromaticity coordinates will meet with blackbody radiation in a bit, which is the CCT value. From this figure, blue LED chip combined with prepared YAG:Ce will get highest CCT, which cannot be accepted by many domain. While this new garnet phosphor, when combined with blue chip LEDs, can give single phosphor convert white light LEDs (pc-w-LEDs) with lower CCTs (∼5500 K) than that of P46-y3, and introducing high CRI. Above analysis results show optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor has great potential application in blue chip LEDs.

**Fig. 7 Schematic diagram for thermal agitation of Lu$^{3+}$ and Y$^{3+}$ based garnet phosphors, R$_1$ and R$_2$ are the agitation range radii of Lu$^{3+}$ and Y$^{3+}$ based garnet phosphors, respectively.**

The commission International de l’Eclairage (CIE) chromaticity coordinates and CCTs for optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor, YAG:Ce and P46-y3 phosphors are shown in Fig. 8. ① and ② are excitation wavelength of each phosphor. ③, ④ and ⑤ are the CIE chromaticity coordinates of each other. The connection of excitation wavelength and CIE chromaticity coordinates will meet with blackbody radiation in a bit, which is the CCT value. From this figure, blue LED chip combined with prepared YAG:Ce will get highest CCT, which cannot be accepted by many domain. While this new garnet phosphor, when combined with blue chip LEDs, can give single phosphor convert white light LEDs (pc-w-LEDs) with lower CCTs (∼5500 K) than that of P46-y3, and introducing high CRI. Above analysis results show optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor has great potential application in blue chip LEDs.

**Fig. 8 The CIE chromaticity coordinates and CCTs for optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce, YAG:Ce and P46-y3 phosphors.**

4. Conclusion

We have presented the preparation and luminescence characterization of Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor for blue chip LEDs. XRD Rietveld refinement results show that Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor is in garnet structure, and Ce$^{3+}$ occupy Lu$^{3+}$ sites on the dodecahedral sites, Mg and Al1 are randomly distributed on the octahedral sites, and Si and Al2 are randomly distributed on the tetrahedral sites. (Ce/Lu)$_3$O$_4$ dodecahedron is surrounded by four (Ce/Lu)$_3$O$_4$ dodecahedron, four (Mg/Al1)O$_6$ octahedrons and six (Si/Al2)O$_4$ tetrahedrons. The excitation and emission spectra show this new garnet phosphor can be excited efficiently by 450 nm and emit yellow color with higher luminescence intensity and room temperature QE. The temperature-dependent photoluminescence spectra show the optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor has better thermal stability than commercial YAG:Ce phosphor P46-y3, when the temperature was increased to 150 °C, the emission intensity of only dropped to 81.1% of its initial intensity, while that of P46-y3 decreased to 68.0%. The CIE chromaticity coordinates suggest that when combined with blue chip, this new garnet phosphor can give single phosphor convert white light LEDs with lower CCTs (5500 K) and high CRI. All of these characterizations indicate the optimized Lu$_3$MgAl$_2$SiO$_{12}$:Ce phosphor is a good candidate yellow phosphor for blue chip LEDs.

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Novel Ce$^{3+}$ activated Lu$_3$MgAl$_3$SiO$_{12}$ garnet phosphor for blue chip light-emitting diodes with excellent performance

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The design, synthesis, and photoluminescence of a novel Lu$_3$MgAl$_3$SiO$_{12}$:Ce$^{3+}$ garnet phosphor for potential warm-white LED applications is reported.