

**Performance improvement by alumina coatings on  $Y_3Al_5O_{12}$   
 $Ce^{3+}$  phosphor powder deposited using atomic layer deposition in a fluidized bed reactor**

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1                   **Performance improvement by alumina coatings on**  
2                    **$Y_3Al_5O_{12}:Ce^{3+}$  phosphor powder deposited using Atomic**  
3                   **Layer Deposition in a fluidized bed reactor**

4  
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18

19

20                   **Abstract:**

21                   To improve the thermal stability,  $Al_2O_3$  has been successfully coated on a  $Y_3Al_5O_{12}:$   
22                    $Ce^{3+}$  (YAG:Ce) phosphor powder host by using the Atomic Layer Deposition (ALD)  
23                   approach in a fluidized bed reactor. Transmission Electron Microscopy (TEM) and  
24                   Energy Dispersive X-ray spectroscopy (EDX) analysis indicate that coating an  $Al_2O_3$   
25                   thin layer by ALD is highly feasible. The luminescence properties (such as excitation  
26                   and emission as well as quantum efficiency and UV-absorption of the coated YAG:Ce  
27                   phosphor) were systematically analysed, with the further examination of the thermal  
28                   resistance characteristics. The  $Al_2O_3$  thin layer coating with precisely controlled  
29                   thickness by ALD can obviously improve the luminescence intensity and greatly  
30                   enhances the thermal stability of the YAG:Ce phosphor. It is suggested that the  
31                   alumina coating with tailoring thickness seems not only to act like a barrier to  
32                   decrease the thermal quenching, but also as a great help to promote the light  
33                   absorption and transfer.

34

35                   Key words: Atomic Layer Deposition (ALD), fluidized bed reactor, YAG:Ce,  
36                   phosphor, powder coating, thermal stability.

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## 41 1 Introduction

42 Inorganic luminescent materials, or phosphors, are commonly utilized for many  
43 applications such as monitors, fluorescent lamps, plasma displays, X-ray amplifier  
44 screens, Light Emitting Diodes (LEDs), and electroluminescent displays due to their  
45 cathodo-, photo-, X-ray- or electro-luminescence properties<sup>1-3</sup>. However, the  
46 instability of the phosphors against temperature, oxygen, water, acids, etc. remains a  
47 problem, which significantly hinders their processing, storage as well as the  
48 applications<sup>2</sup>.

49 Coating a phosphor with a protective layer has been proved to be an efficient  
50 approach to protect a phosphor from environmental attack<sup>4-12</sup>. Thus, several  
51 techniques have been explored to deposit coating layers on phosphor. Including 1)  
52 solid-state techniques such as rolling, milling, grinding of mixtures of phosphor  
53 powders with the precursor, followed by drying or a heat treatment if necessary; 2)  
54 liquid-phase techniques such as sol-gel<sup>4-6</sup>, emulsion<sup>7</sup>, hetero-coagulation<sup>8</sup>, and  
55 precipitation<sup>9</sup>; and 3) gas-phase techniques such as Chemical Vapor Deposition  
56 (CVD)<sup>10</sup>, Pulsed Laser Deposition (PLD)<sup>11</sup>, and Atomic Layer Deposition (ALD)<sup>12, 13</sup>.  
57 However, most of the conventional coating methods suffer from inhomogeneous  
58 and/or ununiformed coating layer deposition, which will have a negative effect on the  
59 optical properties<sup>6</sup>. Therefore, a closed thin film coating method is needed in order to  
60 protect phosphor particles while maintaining (or even improving) the optical  
61 properties.

62 ALD is well known for depositing thin films on a flat surface, but with the  
63 combination of a fluidized bed reactor, it can also be used for coating micro and  
64 nano-sized powders<sup>14</sup>. In such a fluidized bed reactor the particles are suspended in an  
65 upward gas flow so that good contact between gas and particles is ensured. Besides  
66 thin but nevertheless closed coating, another main advantage of ALD is that the  
67 thickness of a coated layer can be precisely designed by strictly controlling the  
68 number of ALD cycles. Thus, ALD can supply a uniform coating even on high surface  
69 area materials allowing a variation of thickness at an atomic resolution, all of which  
70 benefits ALD as a suitable method for homogeneous ultrathin layer deposition<sup>15</sup>. Li et  
71 al.<sup>16</sup> successfully deposited a 15 nm TiO<sub>2</sub> thin film on Cu<sub>2</sub>O-based photocathodes  
72 through ALD method after ALD coating of an appropriate 20 nm buffer layer of  
73 Ga<sub>2</sub>O<sub>3</sub> on Cu<sub>2</sub>O microcrystals. The high thermal resistance of Ga<sub>2</sub>O<sub>3</sub> allowed for the  
74 double coating at relatively high temperatures, resulting in a better photo-voltage of  
75 the whole active cathode. A thin 1.2 nm TiO<sub>2</sub> coating was performed by ALD on  
76 cobalt particles to prevent both leaching and sintering during aqueous-phase reactions.  
77 The TiO<sub>2</sub>/Co/TiO<sub>2</sub> composite showed a high catalysis activity for aqueous-phase  
78 hydrogenation reactions with excellent stability<sup>17</sup>. All above demonstrate that ALD  
79 techniques can produce continuous, pinhole-free oxide films with  
80 Angstrom-level-controllable thickness. Especially within a fluidized bed reactor, ALD  
81 shows high potential for depositing a protective thin layer coating on a phosphor  
82 particle without hurting the optical properties.

83 Many kinds of the oxides, such as Al<sub>2</sub>O<sub>3</sub><sup>18-20</sup>, SiO<sub>2</sub><sup>21, 22</sup>, TiO<sub>2</sub><sup>23, 24</sup>, ZnO<sup>25, 26</sup>, and  
84 ZrO<sub>2</sub><sup>27</sup> have been used as coating material in ALD processes. Among them, Al<sub>2</sub>O<sub>3</sub> is

85 considered to be a promising coating agent to enhance the resistance of the coated  
86 materials. For example, the capacity fading of  $\text{LiMn}_2\text{O}_4$  spinel as a battery material  
87 can be significantly reduced due to  $\text{Al}_2\text{O}_3$  coating and consistent discharge curves  
88 were found even after 50 charging/discharging cycles at an elevated temperature of  $55^\circ\text{C}$   
89 <sup>28</sup>. Ultrathin compact  $\text{Al}_2\text{O}_3$  layers deposited by ALD were also utilized to improve  
90 the ambient stability of quantum dot films<sup>29</sup> and organic-inorganic perovskite solar  
91 cells<sup>20</sup>. The results demonstrate that the stability of the solar cell against humidity was  
92 greatly enhanced without an obvious reduction in efficiency. Besides,  $\text{Al}_2\text{O}_3$   
93 demonstrates a unique affinity to a large variety of substrate<sup>14</sup>, together with its low  
94 deposition temperature, led to the judgments that depositing  $\text{Al}_2\text{O}_3$  as a coating via  
95 ALD in a fluidized bed reactor is a promising way to increase resistance against  
96 outside attacks resisted for phosphor materials like  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ .

97  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  (the trivalent cerium activated Yttrium Aluminate phosphor with  
98 Garnet structure, referred to as YAG:Ce), is a well-known luminescent material which  
99 has been broadly applied in the fields of flying spot scanner tubes in the past and  
100 white LED (WLED) devices nowadays. However, like most of the luminescence  
101 phosphors, YAG:Ce also suffers from the thermal instability, especially when used in  
102 practical WLED devices<sup>3</sup>. In this work, YAG:Ce phosphor powder is employed as  
103 model material to study the improvement of the thermal stability by  $\text{Al}_2\text{O}_3$  coating  
104 through ALD process performed in a fluidized bed reactor under atmospheric pressure.  
105 The impact of ALD cycle numbers on the thickness of the  $\text{Al}_2\text{O}_3$  layer is investigated,  
106 as well as the thermal and optical performance of YAG:Ce phosphor. It will be shown  
107 that the ALD method with a fluidized bed reactor using alumina as oxide coating  
108 materials could be a feasible way for the ultrathin film coating of YAG:Ce phosphors  
109 and apply a protective barrier for improving thermal resistance while maintaining the  
110 optical properties.

## 112 2 Experimental

### 113 2.1 Starting materials

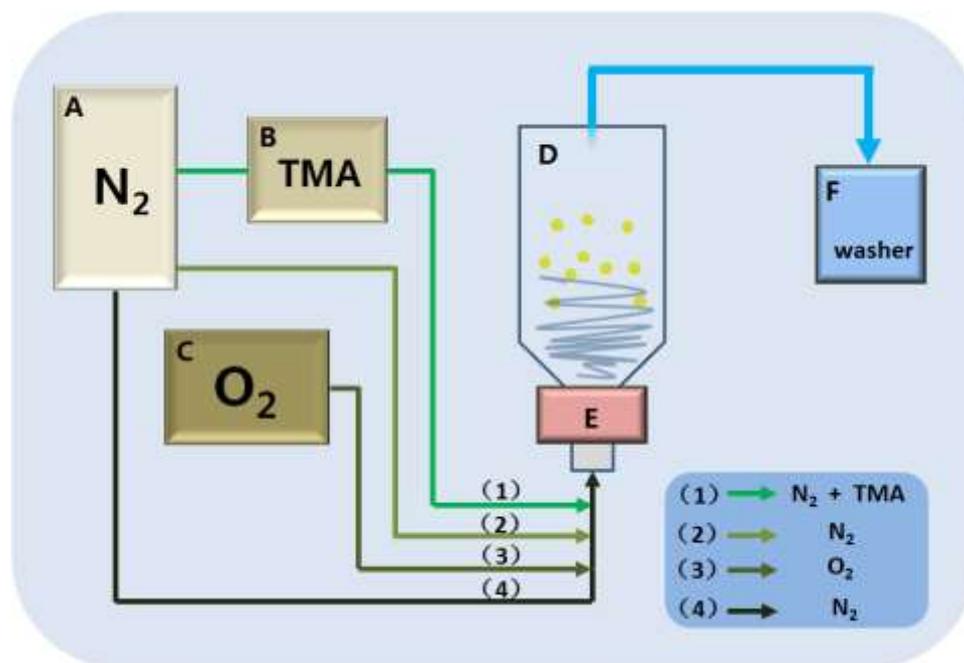
114 The YAG:Ce phosphor particles were obtained from Steady (Hunan Steady New  
115 Materials Company, China), which have a regular spherical morphology with highly  
116 concentrated particle size distribution between 6-15 micrometers.  
117 Tri-Methyl-Aluminium (TMA, semiconductor grade) was supplied by Akzo-Nobel  
118 HPMO in a 400mL VER-400 bubbler. The gas washers were filled with Kaydol oil,  
119 supplied by Sonneborn (Haarlem).

### 121 2.2 Sample preparation by ALD coating process in a fluidized bed reactor

122 A schematic illustration of the ALD set-up with a fluidized bed reactor for the  
123 alumina coating on YAG:Ce particle is shown in Fig. 1. From left to right, Part A is a  
124 nitrogen gas tank supplying a nitrogen flow. Part B is a bubbler filled with liquid  
125 TMA, through which nitrogen is bubbled to obtain a nitrogen flow with TMA vapor.  
126 Part C is a gas bottle filled with an  $\text{N}_2/\text{O}_2$  mixture (80%/20%). Part D is the Fluidized  
127 Bed Reactor (FBR), the main part of which is a glass column with 26 mm in internal  
128 diameter and 500 mm in length. Only less than one third volume of the column can be

129 filled with certain amount (100-120g) of phosphor particles, in order to guarantee  
130 enough space for the particles during fluidizing. The FBR is placed on a vibration  
131 table driven by two vibro-motors (Part E), which can produce a low amplitude  
132 vibration at a set frequency of 45 Hz to assist fluidization. The coating experiments  
133 were carried out at room temperature of about 25°C. And Part F represents the gas  
134 washers to neutralize TMA that might be released from the reactor.

135 Generally, one ALD cycle can be divided into four process steps: (1) TMA  
136 exposure, (2) purge with nitrogen gas, (3) oxygen exposure and (4) purge with  
137 nitrogen gas again. To begin with the whole ALD set needs to be purged with nitrogen  
138 for about 20 min before starting the first ALD cycle. For the first step of TMA  
139 exposure, nitrogen was purged through the reactant bubbler (Part B) filled with TMA  
140 and making a gas stream for carrying the reactant into the FBR (Part D) with a flow  
141 rate of 0.6 L/min (0.02 m/s superficial gas velocity). Subsequently, N<sub>2</sub> was pumped  
142 into the reactor to carry away the redundant TMA at the second step. After that,  
143 synthetic air was pumped into the reactor to oxidize TMA and form the Al<sub>2</sub>O<sub>3</sub> coating.  
144 Finally, the extra oxygen was blown away by N<sub>2</sub> and then a new cycle can be started.  
145 Duration of each step has been optimized as 3, 10, 3 and 10 minutes, respectively.  
146



147

148 Fig. 1 Schematic illustration of the ALD set-up and process: (A) nitrogen gas tank; (B) and (C)  
149 reactant tanks; (D) Fluidized Bed Reactor (FBR); (E) vibro-motors; (F) gas washers.

150 Effluent gases from the reactor were led through a double set of gas washers  
151 (Part F) filled with mineral oil. The gas streams containing TMA was led through  
152 separate gas washers to prevent reaction in the washers. Any TMA absorbed in the gas  
153 washers was neutralized after the experiment. The effluent from the gas washers was  
154 filtered using Pall Kleenpak pharmaceutical grade sterilizing filters to capture  
155 elutriated nanoparticles. The pressure at the outlet was atmospheric, meaning that the  
156 pressure in the column is slightly above atmospheric pressure. This is uncommon, as

157 most ALD is carried out at vacuum. More details about the reactor can be found in our  
158 previous work<sup>14</sup>.

159

### 160 **2.3 Characterization**

161 The crystalline phases and compositions of the prepared samples were examined  
162 by X-ray diffractometry (XRD) using a Bruker D4 Endeavor apparatus with a  
163 graphite- monochromatized Cu Ka radiation at 40 kV and 40 mA. The  $2\theta$  ranges of all  
164 the data sets are from 10 to 80° using step scan with a step size of 0.02° in  $2\theta$  and a  
165 counting time of 1s per step. The micro-morphology and elemental mapping of the  
166 samples were observed by using a JEOL/EO6500F Scanning Electron Microscope  
167 (SEM) combined with Energy Dispersive X-ray spectroscopy (EDX), the voltage of  
168 the EDX is 10KV and the spot size is 69  $\mu\text{m}$ . Cross section SEM combined with EDX  
169 was carried out on a FEI Nova Nano SEM for the  $\text{Al}_2\text{O}_3$  coated samples, besides the  
170 normal electric-beam for SEM, the equipment has an extra ion-beam for cut and mill  
171 the target samples. Moreover, Transmission Electron Microscopy (TEM) analysis was  
172 performed with an HRTEM JEOL 2010 high-resolution transmission electron  
173 microscope in combination with EDX spectroscopy and a GATAN digital micrograph  
174 with a slow-scan CCD camera.

175

### 176 **2.4 Optical properties**

177 A Perkin Elmer LS 50B spectrophotometer equipped with a Xe flash lamp as the  
178 excitation source was used to conduct diffuse reflectance and photoluminescence (PL)  
179 measurements. The reflection spectra were calibrated with the reflection of black felt  
180 (reflection 3%) and white barium sulfate ( $\text{BaSO}_4$ , reflection ~100%) in the  
181 wavelength region of 230-700 nm. The excitation and emission slits were set at 15 nm.  
182 All measurements were performed at room temperature.

183 The temperature dependent luminescence properties were measured by  
184 home-built equipment. The emission spectra were measured in air with the  
185 temperature increased from 300K to 600K. The emission spectrum was recorded from  
186 480 nm to 700 nm with an excitation wavelength of 460 nm came from a Xe flash  
187 lamp. The sample chamber was heated up with a rate of 10 K/min. The equipment  
188 was maintained for extra 5 min before each measurement to hold a constant  
189 temperature. The excitation and emission slits were set at 5 nm. Excitation spectra  
190 were automatically corrected for the variation in the lamp intensity by a second  
191 photomultiplier and a beam-splitter. All the spectra were measured with a scan speed  
192 of 100 nm/min.

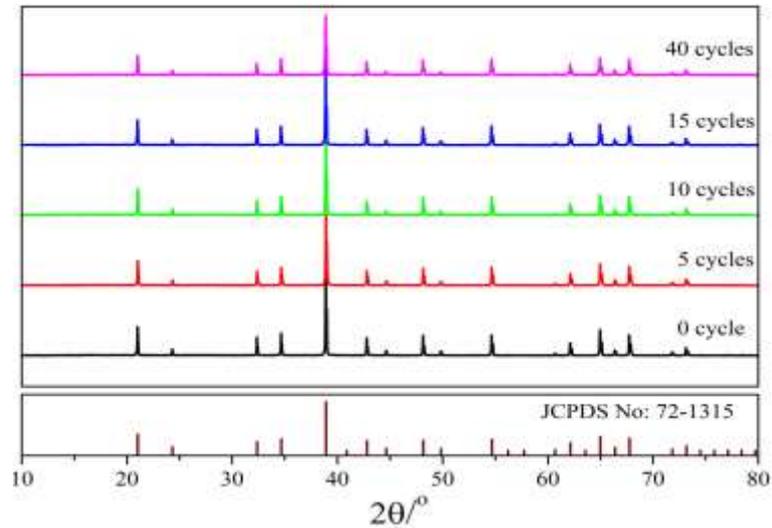
193

## 194 **3 Results and discussion**

### 195 **3.1 Phase composition**

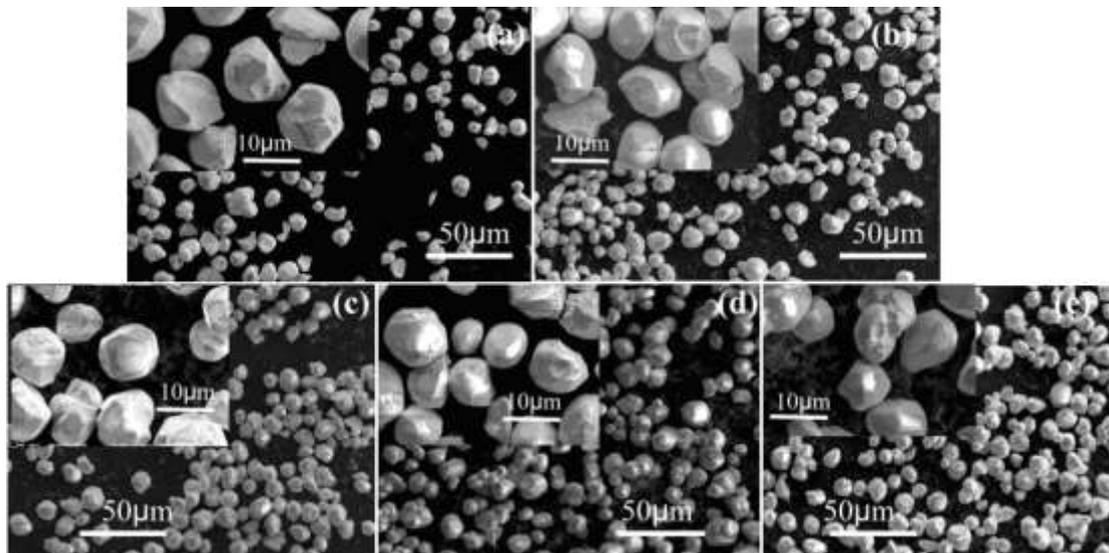
196 To study the impact of the ALD process on the phase composition of the selected  
197 phosphor material, uncoated and  $\text{Al}_2\text{O}_3$  coated Ce-doped YAG phosphor powders  
198 were examined by XRD. As shown in Fig. 2, the diffraction peaks of all obtained  
199 materials with or without coating are corresponding to  $\text{Y}_3\text{Al}_5\text{O}_{12}$  with the garnet  
200 structure (YAG) [Joint Committee on Powder Diffraction Standards (JCPDS) card No.

201 72-1315]. No obvious peak shifts or other impurity phases were detected after the  
 202 coating process, indicating that the sustainable ALD process has no obvious influence  
 203 on the phase and structure of the YAG:Ce phosphor. In addition, no diffraction peaks  
 204 characteristic for crystalline Al<sub>2</sub>O<sub>3</sub> were detected, suggesting that the Al<sub>2</sub>O<sub>3</sub> thin layer  
 205 should be amorphous phase since the crystalline phase of Al<sub>2</sub>O<sub>3</sub> is expected only  
 206 above 900°C<sup>30</sup>.  
 207



208  
 209 Fig.2 XRD patterns of the uncoated (0 cycle) and coated YAG:Ce phosphor powders after  
 210 different ALD cycles  
 211

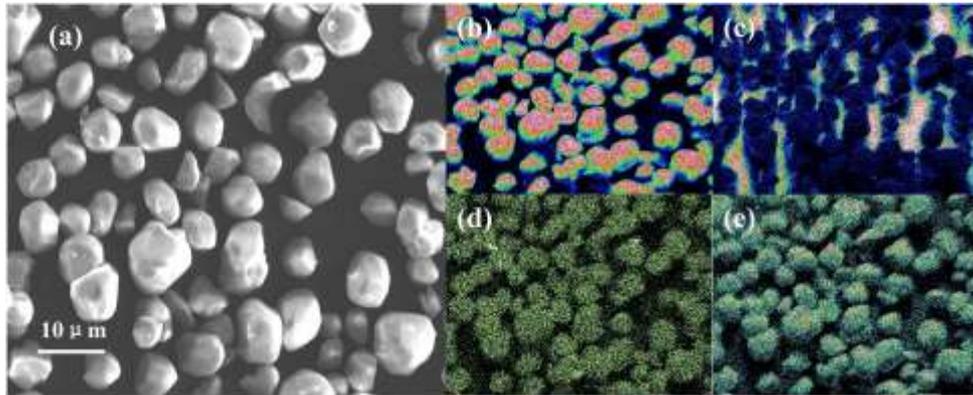
212 **3.2 Particle morphology**



213  
 214 Fig.3 SEM images of (a) the uncoated (0 cycle) and coated samples at different cycles (b) 5 cycles;  
 215 (c) 10 cycles; (d) 15 cycles; (e) 40 cycles under low and high magnification (insets)  
 216

217 SEM analysis was also carried out to investigate the influence of the ALD  
 218 process and alumina coating on the morphology of YAG:Ce particles. SEM  
 219 micrographs of the starting YAG:Ce sample [Fig. 3(a)] and Al<sub>2</sub>O<sub>3</sub> coated YAG:Ce

220 particles at various cycles [Fig. 3(b)-3(e)] are shown in Fig. 3. The obtained samples  
 221 with or without coating show similar micromorphology, all of which consist of  
 222 uniform and spherical-like particles with a size range of 6-15 $\mu\text{m}$  ( $D_{50} = 11 \mu\text{m}$ ). There  
 223 is no obvious difference between the coated and uncoated samples, implying that the  
 224  $\text{Al}_2\text{O}_3$  ALD coating process has no influence on the morphology of the YAG:Ce  
 225 particles, which should attribute to the ultrathin layer of the  $\text{Al}_2\text{O}_3$  coating that can not  
 226 be observed by normal SEM.  
 227



228  
 229 Fig. 4 SEM images of (a) YAG:Ce particle and corresponding elemental mapping of (b) Al, (c) Y,  
 230 (d) Ce and (e) O.  
 231

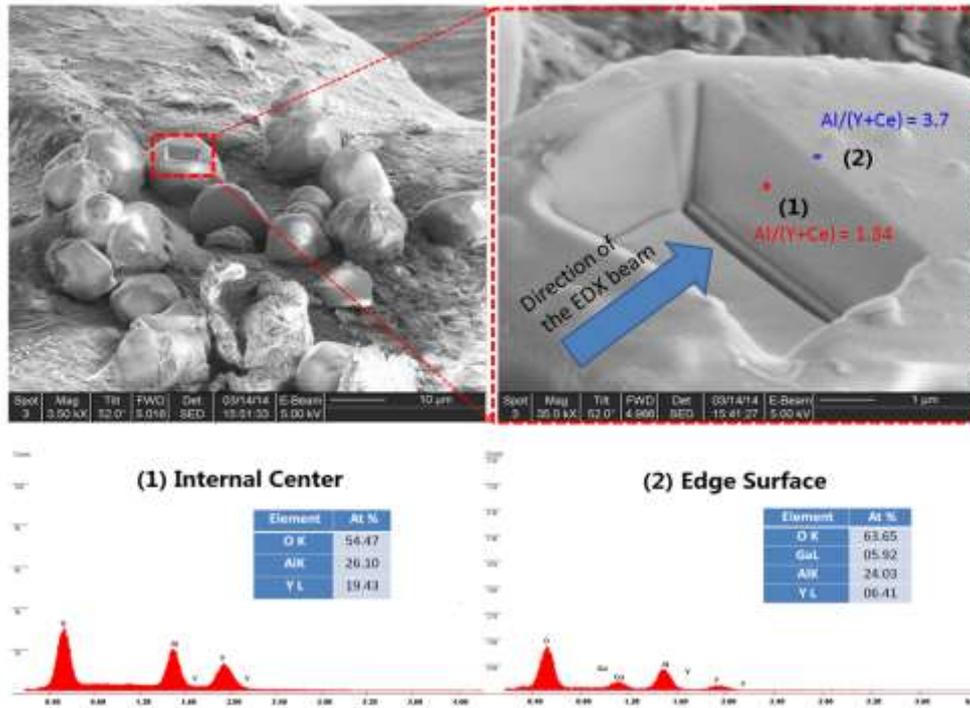
232 The elemental distribution of the coated YAG:Ce phosphor was mapped, as  
 233 illustrated in Fig. 4. Results indicate that the Y, Al, O and Ce elements are uniformly  
 234 distributed on the same particle, which confirms the uniform and homogeneous  
 235 coating of alumina via ALD process in fluidized bed. Meanwhile, EDX analysis with  
 236 SEM shows that the ratio of Al content divided by (Y + Ce) content grows from 1.38  
 237 to 1.76 along with the increase of number of ALD cycles, as shown in Table. 1, which  
 238 should be attributed to the increase of thickness of deposited  $\text{Al}_2\text{O}_3$  layers with adding  
 239 more ALD cycles. It needs to be mentioned that the ratio of  $\text{Al}/(\text{Y}+\text{Ce})$  measured by  
 240 EDX was relatively low compare to the ideal ratio (1.67) calculated for stoichiometric  
 241  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ . However, impurities and defects are generally formed during the  
 242 synthesis of  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and they exist within the crystals especially after doping with  
 243 other cations<sup>31,32</sup>.  
 244

245 Table 1. The dependence of the  $\text{Al}/(\text{Y}+\text{Ce})$  ratio on the number of ALD cycles, as obtained by  
 246 EDX.

Cycle(s)	0	5	10	15	40
$\text{Al}/(\text{Y}+\text{Ce})$	1.38	1.43	1.51	1.60	1.76

247  
 248 Furthermore, cross section SEM by dual beam was performed on the 40 cycles  
 249 coated sample, as shown in Fig. 5. The signal of Gacomes from the ions beam, which  
 250 was utilized to section the YAG:Ce particle. According to the EDX examination, the  
 251 ratio of  $\text{Al}/(\text{Y}+\text{Ce})$  at the surface (spot 2) turns out to be about 3.7, while that in the

252 bulk (spot 1) is about 1.34, which is in accordance with the Al/(Y+Ce) ratio  
 253 determined for the uncoated sample (Table. 1). A higher level of Al/(Y+Ce) ratio at  
 254 the surface than in the inner part of the particle, demonstrates that Al<sub>2</sub>O<sub>3</sub> had been  
 255 deposited on the surface of the phosphor particle and Al<sub>2</sub>O<sub>3</sub> thin layer coating with  
 256 ALD is highly feasible.  
 257



258  
 259 Fig.5 SEM cross section combined with EDX analysis of 40 cycles ALD coated YAG:Ce particle  
 260

261 To further study the thickness of the ALD coating, TEM images of the coated  
 262 samples were made. Unfortunately, the alumina layers covering the surface of the  
 263 YAG:Ce particles were too thin to be observed for 5 and 10 cycles coated samples.  
 264 But after 15 cycles of ALD coating, a 2 nm coating layer was detected and a clearer  
 265 layer with 5 nm thickness was found for the sample coated with Al<sub>2</sub>O<sub>3</sub> for 40 cycles  
 266 by ALD process, TEM images are shown in Fig. 6. Besides, the alumina coating  
 267 layers of both samples processed after 15 and 40 cycles were uniform, tight, and  
 268 homogeneous, indicating that the ALD process performed in a fluidized bed is a  
 269 promising approach for covering protective materials on phosphor particles.  
 270 The thickness of the coating layer on the particles after 15 and 40 cycles is about 2 nm  
 271 and 5 nm, respectively, from which the thickness of a single layer coating within one  
 272 cycle can be estimated to be about 0.13 nm.

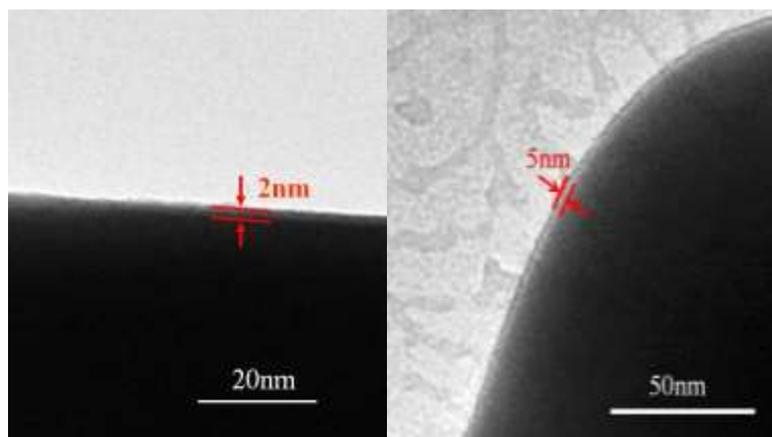


Fig. 6 TEM images of YAG:Ce particle coated with Al<sub>2</sub>O<sub>3</sub> by ALD: (a) 15 cycles and (b) 40 cycles.

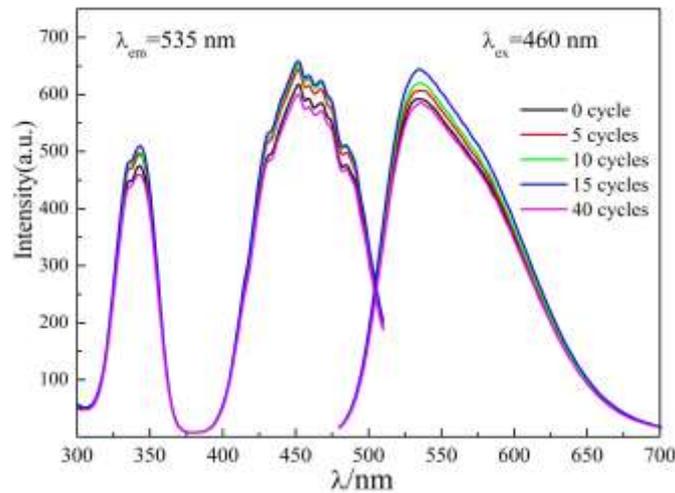
### 3.3 Luminescence properties

It has been confirmed that Al<sub>2</sub>O<sub>3</sub> is an appropriate material for thermal protection via ALD process<sup>33</sup>; however, it can also become an impeder for transfer of light, electrons, heat, humidity and so on<sup>34</sup>. Thus, the luminescence properties of coated and uncoated YAG:Ce phosphor powders were carefully investigated in order to optimize the ALD cycle numbers and alumina coating thickness. Fig. 7 displays the luminescence spectra of uncoated YAG:Ce powder and Al<sub>2</sub>O<sub>3</sub> coated YAG:Ce powders with different ALD cycle numbers. It can be seen that all samples, with or without coating, exhibit similar profiles of both excitation and emission bands with the same peak positions located at about 535 nm, indicating that the basic optical behavior of the phosphor has not been changed by the coating layer of alumina. The excitation spectra of all samples obtained upon monitoring 535 nm emission express two bands centered at around 450 nm and 350 nm respectively, which are corresponding to the transitions between the Ce<sup>3+</sup> ground state (<sup>2</sup>F<sub>5/2</sub>) and the 5d levels splitted by the crystal field with D<sub>2</sub> symmetry, which is in agreement with the report in the literature<sup>35</sup>. Upon 460 nm excitation, all the samples show a broad band emission with the maximum peaks located at about 535 nm, which is assigned to the transition of the lowest 5d state to the 4f ground state (<sup>2</sup>F<sub>5/2</sub>) of Ce<sup>3+</sup> ions.

Some experimental results from Zhang et al.<sup>36</sup> confirm that the optical absorption behavior of phosphor composite materials can be largely dependent on the amount of Al<sub>2</sub>O<sub>3</sub> compound. However, results achieved above indicate that the Al<sub>2</sub>O<sub>3</sub> coating has no obvious affection on the luminescence properties of the sample. The reason might be that the alumina-coating layer is too thin to affect the light diffusion.

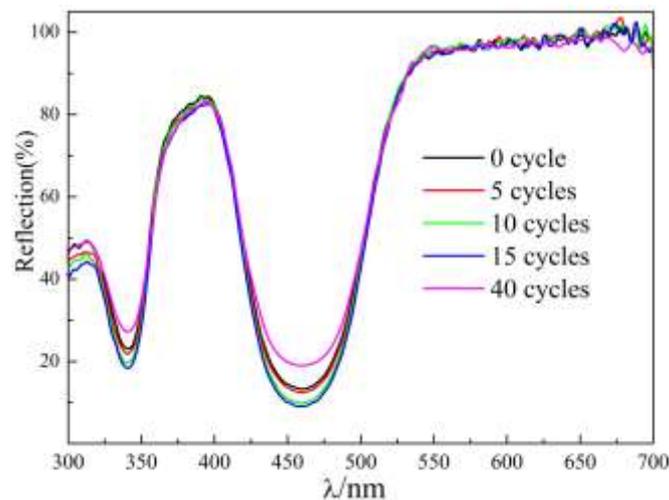
Nevertheless, the intensity of both excitation and emission bands show significant difference when comparing the uncoated and coated samples. The excitation and emission intensity continuously increase with increasing ALD cycle numbers, except for 40 cycles. After 40 cycles coating, the intensity dropped quite strongly and a value even lower than the uncoated phosphor was obtained. It can be concluded that alumina coating layer with controlled thickness of about 2 nm deposited via ALD process can benefit the luminescence properties, but too thick a coating will lower the excitation absorption as well as the emission radiation. The

307 enhancement of emission intensity can be attributed to an increased absorption  
 308 radiation, a larger quantum efficiency of absorbed radiation converted into emitted  
 309 radiation and an improved light outcoupling of emitted radiation. But when the  
 310 thickness of the covering went to 5 nm, the incident illumination and the emitted light  
 311 were largely obstructed by the over protective covering, thus the intensity of both  
 312 excitation and emission decreased rapidly.  
 313



314  
 315  
 316  
 317

Fig.7 Excitation and emission spectra of the uncoated and ALD coated YAG:Ce phosphor powder  
 (a) 0 cycle; (b) 5 cycles; (c) 10 cycles; (d) 15 cycles ; (e) 40 cycles.



318  
 319  
 320  
 321

Fig.8 Diffuse reflectance spectra of the uncoated (0 cycles) and  $\text{Al}_2\text{O}_3$  coated YAG:Ce samples for  
 different ALD cycles (5-40 cycles)

322 A further illustration about the increased absorption strength is provided by the  
 323 diffuse reflectance spectra of coated and uncoated samples as shown in Fig. 8. In  
 324 comparison with the uncoated YAG:Ce samples, the  $\text{Al}_2\text{O}_3$  coated ones with different  
 325 number of cycles exhibit similar absorption profiles and band widths, confirming that  
 326 the  $\text{Al}_2\text{O}_3$  coating material has no significant effect on the absorption characteristics of

327 YAG:Ce phosphor powder. As compared to the uncoated phosphor, the reflection  
 328 (around 340 and 455 nm) decreased (i.e. adsorption around 340 and 455 nm increased)  
 329 for higher number of ALD cycles, except for the 40 cycles sample (Table 2). All of the  
 330 above results are in agreement with the conclusion made from Fig. 7, further  
 331 confirming that the covering thickness of the alumina coating should be optimized  
 332 since a high amount of Al<sub>2</sub>O<sub>3</sub> can hamper the light absorption as well as the light  
 333 emission (Table 2).

334 The relative quantum efficiency is estimated by comparing the emission intensity  
 335 (EI) of the coated sample with that of the uncoated YAG:Ce phosphor powder from  
 336 the equation below:  
 337

$$QE(\text{coated}) = \left[ \frac{EI(\text{coated})}{EI(\text{uncoated})} \right] * \left[ \frac{A(\text{uncoated})}{A(\text{coated})} \right] * QE(\text{uncoated})$$

338

339 Here, “QE” refers to the relative quantum efficiency; “EI” refers to the integrated  
 340 area under the emission spectrum, which was obtained from the emission spectra in  
 341 Fig. 7; “A” refers to the absorption intensity at excitation wavelength of 460 nm,  
 342 which was calculated from the diffuse reflection spectra (A=1 - diffuse reflection for  
 343 semi-infinite thick samples). The QE of the uncoated phosphor was taken 1.00. The  
 344 calculated relative QE for the uncoated and coated samples are listed in Table. 2. The  
 345 emission intensity of the phosphors increased with the adding of cycle numbers, and  
 346 so does the relative quantum efficiency, with an exception of the 40 cycles coating  
 347 sample. The higher relative quantum efficiency is attributed to surface passivation  
 348 (resulting in less non-radiative transitions at defects) and easier extraction of the  
 349 emitted light. In summary, the results indicate that the coated YAG:Ce samples  
 350 processed with 10-15 cycles have better conversion abilities than the uncoated  
 351 material.

352

353 Table 2. The absorption of 460 nm (excitation radiation) and the relative quantum efficiency of  
 354 Al<sub>2</sub>O<sub>3</sub> coated versus uncoated YAG: Ce phosphor powders.

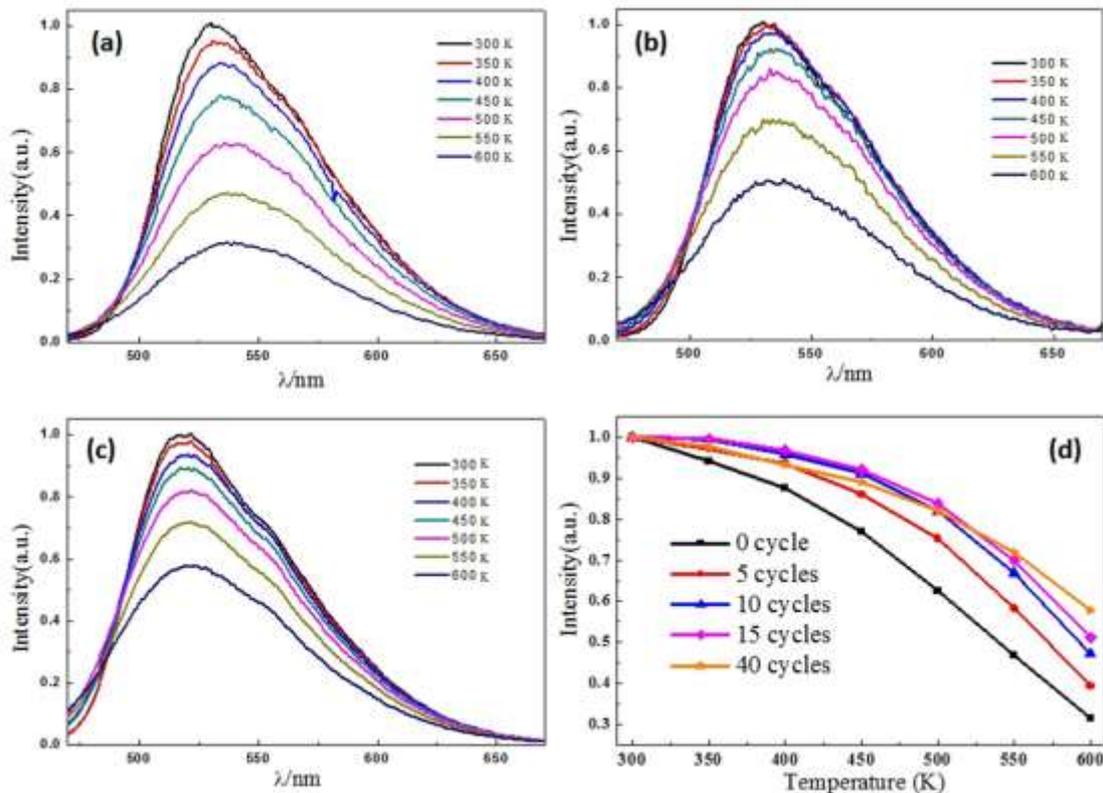
Number of coating cycles	Emission (arb. Units)	Absorption at 460 nm	Relative Quantum Efficiency
0 cycle	61639	0.93	1.00
5 cycles	63070	0.94	1.01
10 cycles	64222	0.94	1.03
15 cycles	66525	0.95	1.06
40 cycles	52938	0.93	0.96

355

### 356 3.4 Thermal stability

357 Fig. 9 displays the temperature-dependent emission spectra of the uncoated and  
 358 coated YAG:Ce phosphor powders prepared by ALD method, combined with the  
 359 summary of the dependence of the emission intensity in sample temperature (Fig.  
 360 9(d)). When compared with the uncoated YAG:Ce phosphor, the peak emission

361 wavelength of all the coated samples shows a red shift for higher sample temperature,  
 362 which can be explained by increased re-absorption due to more efficient energy  
 363 transfer at high temperature. When excited by 460 nm radiation, the integrated  
 364 emission intensities of all the samples continuously decreased with increasing sample  
 365 temperature from 300K to 600K, showing a typical thermal quenching behavior,  
 366 which is a normal phenomenon for all kinds of phosphors<sup>3</sup>. In comparison with the  
 367 uncoated sample, a remarkable development in temperature-dependent characteristic  
 368 of Ce<sup>3+</sup> emission of coated phosphors can be observed, demonstrating that the thermal  
 369 stability of YAG:Ce phosphor can be significantly improved by coating protective  
 370 alumina layers via ALD method.  
 371



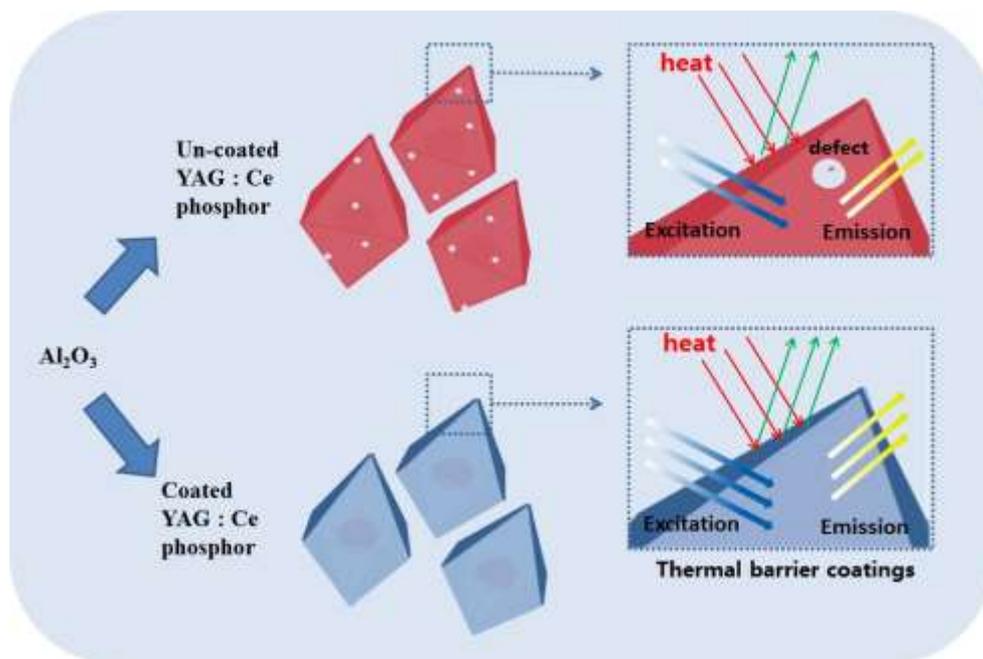
372  
 373 Fig.9 Temperature-dependent PL spectra for samples with various coating cycles: (a) uncoated, (b)  
 374 15 cycles, (c) 40 cycles, and (d) summarization of the PL intensity of all samples, under excitation  
 375 wavelengths of 460 nm.  
 376

377 Fig. 9(d) summarizes the emission intensity at different temperatures of all  
 378 samples according to the temperature-dependent emission spectra. The intensity was  
 379 normalized to that exhibited at room temperature for each sample. At the starting  
 380 temperature of 300K, all five samples are normalized as the same emission intensity  
 381 of about 100% for comparison. However, already after 50 degrees temperature  
 382 increment, remarkable changes have been observed for the alumina coated YAG:Ce  
 383 phosphor powders. More than 5% decrease was found for the uncoated phosphor,  
 384 while the intensity of the 5 cycles sample dropped only about 2% and the intensity of  
 385 samples with 10 and 15 cycles coating remained more or less constant. The thermal

386 stability of the coated phosphor has been remarkably improved even for only 5 ALD  
387 coating cycles, and for higher ALD cycle numbers, better thermal stability can be  
388 achieved. Especially at elevated temperature of 550K and 600K, the emission  
389 intensity of the uncoated phosphor dropped rapidly to 47% and 32%, while that of the  
390 40 cycles coated sample remained at a high value of 70% and 57%, respectively. The  
391 enhancement of thermal stability should be attributed to the effect of the thermal  
392 barrier coating of alumina formed by ALD process, which can keep the inner  
393 phosphor particles from directly exposure to the hot environment and protect  $Ce^{3+}$   
394 against oxidization to  $Ce^{4+}$ .

395 A phenomenon needs to be mentioned is that a lower relative emission intensity  
396 was exhibited by sample with 40 cycles coating than that of samples with 10 and 15  
397 cycles coating during the temperature range of 300K to 500K, indicating that high  
398 thickness alumina layer coatings might impede the luminescence properties of the  
399 phosphor below 550 K. It has been reported that  $Al_2O_3$  sometimes works like an  
400 insulator that can barrier the transfer of light, electrons or heat<sup>34</sup>. This conclusion is in  
401 accordance with the results of the luminescence property analysis discussed above.

402



403

404 Fig.10 Schematic diagram of enhancing of luminescence intensity coating  $Al_2O_3$  layer by ALD  
405 process in YAG:Ce host.

406

407 Fig. 10 schematically illustrates the mechanism of the enhancing emission  
408 intensity and thermal stability from the protective alumina layer for YAG:Ce phosphor.  
409 Firstly, coating the YAG:Ce phosphor powders with a thin  $Al_2O_3$  layer with an  
410 appropriate thickness can increase the quantum efficiency due to reduced number of  
411 surface defects, enhance the light absorption and form a thermal barrier coating.  
412 Secondly,  $Al_2O_3$  is kind of wide band gap oxide material, which could confine the  
413 inside excitation of the phosphor and suppress the ion-ion energy transfer (short range  
414 Forster transfer), ultimately decrease the non-radiative recombination. Finally, the

415 lack of Ce ion in the outer coating shell would effectively suppress the energy transfer  
416 from the inner part of the particle to the outside surface. Combined the above three, the  
417 quantum efficiency, emission intensity as well as thermal stability of the phosphor can  
418 be remarkably improved.

419

#### 420 **4 Conclusions**

421 The yellow-emitting YAG:Ce LED phosphor powders have been successfully  
422 coated with a thin Al<sub>2</sub>O<sub>3</sub> layer via the approach of fluidized bed reactor ALD. With  
423 the controllable deposition in the fluidized bed ALD reactor, designable thickness of  
424 the alumina-coating layer can be obtained. With the appropriate Al<sub>2</sub>O<sub>3</sub> coating layer  
425 thickness, an improvement of luminescence properties and thermal stability of the  
426 phosphor can be achieved without any change in bulk behavior. The uniform and  
427 stable Al<sub>2</sub>O<sub>3</sub> coating can reduce the number of surface defects of the phosphor  
428 particles and might enhance the quantum efficiency, consequently improving the  
429 optical performance. The thermal stability was improved gradually with the increase  
430 of the coating layer thickness, since the coated layer can act as a barrier to decrease  
431 the thermal quenching, resulting in high thermal resistance of the YAG:Ce material.  
432 For all the samples examined, the one with 15 cycles coating exhibited the best  
433 characteristics, from which can be concluded that the amount of the alumina coating  
434 needs to be precisely controlled.

435

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441

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