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Growth and characterization of air annealing Tb-doped YAG:Ce single crystal for white-light-emitting diode

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ABSTRACT: We report the preparation of transparent Ce and Tb co-doped Y₃Al₅O₁₂ single crystal by the Czochralski method. The characterization of the resulting single crystal was accomplished by using X-ray powder diffractometer, scanning electron microscopy and energy dispersive X-ray spectroscopy. Absorption peak of the single crystal at about 460 nm has been obtained from ultraviolet-visible absorption spectrometer and their intensity is changed with different annealing condition. Its optical properties also have been investigated using fluorescence spectrometer. What’s more, its photoelectric parameters were studied by LED fast spectrometer. The constructed single crystal based white-light-emitting diode exhibits a high luminous efficiency of 140.89 lm/W, and a correlated color temperature of 4176 K as well as a color rendering index of 56.7, which reveal the prominent feasibility of the present single crystal material in white-light-emitting diode application.

Keywords: White LED; Crystal growth; X-ray powder diffractometer; Optical properties

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1. Introduction

Nowadays, the white-light-emitting diode (WLED), as a new type of luminescent source, has played a crucial role in applications of indicator, backlight, automobile headlight and general illumination [1-7], not only due to its excellent properties such as low heat, energy-saving, long lifetime, high luminous efficiency, but also owing to it is environmentally benign. The current leading commercial WLED combines an InGaN blue-emitting chip with a Ce:YAG yellow-emitting phosphor packed on the chip surface using epoxy resin or silicone [8-11] because of the lowest manufacturing costs at present and the capability to promote high light yield. Ce:YAG phosphor can efficiently convert InGaN-based blue LED radiation into a very broad intense yellow emission band due to the 5d-4f transition of Ce$^{3+}$ ions and shows a maximum absorbance in the blue region. A mixture of yellow emission with the non-absorbed blue emission from blue LED results in white light [12-17]. In recent years, Ce:YAG phosphor as a substrate material has attracted considerable attention for LED [18]. The optical properties of YAG powder doped with transition metal (Mn, Cr and Fe) [19-20] and rare-earth ions (Ce, Eu and Tb) [21-30] have been studied for applications in phosphor. However, WLED based on a blue LED chip plus YAG:Ce yellow phosphor has many disadvantages, such as poor color rendering index property, blue/yellow color separation and lacking of red component in the spectra of this kind of LED. Therefore this kind of LED can't fully meet the illumination requirements.

To solve this problem, an innovative inorganic material, YAG single crystal, has been investigated recently as a relative optimal fluorescent conversion material for LED, not only due to its high thermal conductivity, stable physical and chemical performance and mature growth process, but also due to the fact that it is a suitable host lattice for investigating the optical characteristics of doping ions such as Ce, Pr, Mn and Sm [31-36]. However, in mostly previous studies, there are very few reports on ions co-doped in YAG single crystal in order to complement the lacking of red component in the white light spectra and achieve certain modification effect.

In this work, we propose Ce and Tb ions co-doped in YAG single crystal by Czochralski method. Mainly due to the characteristic luminescence peaks of Tb$^{3+}$ ion locat at 492, 545, 585 and 625 nm, which are contributed to the transition of $^5D_4 \rightarrow \ ^7F_6$, $^5D_4 \rightarrow \ ^7F_5$, $^5D_4 \rightarrow \ ^7F_4$ and $^5D_4 \rightarrow \ ^7F_3$. The crystal structure and photoelectric properties of Ce,Tb:YAG single crystal were characterized.
Meanwhile the most important factor affecting the emission applications of YAG single crystal is annealing, which has been documented by the authors [37]. Hence, the single crystal was annealed in air atmosphere in order to improve its optical properties.

2. Experimental details

2.1. Synthesis

The raw materials of Y$_2$O$_3$ (99.999%), Al$_2$O$_3$ (99.99%), CeO$_2$ (99.99%) and Tb$_2$O$_7$ (99.99%) were prepared for Tb-doped Ce:YAG single crystal growth. The stoichiometric ratio is $Y_{3-x-y}Al_5O_{12} : Ce_xTb_y$ ($x=0.06$, $y=0.08$).

Then they were initially mixed thoroughly and compressed into pieces and calcined at 1200 °C for 24 h. Afterwards, they were loaded into Ir crucible. The crystal was grown by the radio frequency (RF) heating CZ pulling method. The temperature was controlled by a precision temperature controller with a precision of ± 0.5 °C. The melt temperature was kept at 1950 ± 5 °C, which should be favorable for starting the growth. A (111) diffraction direction YAG seed was used to dip the center of the melt surface and start the pulling progress. The pulling rate and the rotation rate were 1-2 mm/h and 10-20 rpm, respectively. The growth time was approximately 30-40 h. After lowering temperature, the single crystal could be obtained. Its diameter is about 29 mm, the entire length is about 120 mm. Fig. 1 shows photograph of as-grown Ce,Tb:YAG single crystal by Czochralski method. The as-grown Ce,Tb:YAG single crystal is transparent with bright yellow coloration which is characteristic for the Ce-doped crystals. However, with the augment of Ce,Tb:YAG crystal length, rare earth ions doped concentration increases. Therefore, in order to reduce the error, the position located at 17-18 cm of steel ruler was choosed to cut the crystal with size of 10 mm × 10 mm × 0.5 mm and annealed them in air atmosphere.

2.2. Characterization

The crystal structure was analyzed by D8 X-ray diffractometer produced in Germany Bruker, Cu target, $\lambda=0.15406$ nm, an accelerating voltage of 40 kV, with the scan range of 10°-80° and scan step of 0.02 (°)/s. The sample for scanning electron microscopy (SEM) analysis was prepared by crushing single crystal into pieces and spread the powder onto a conductive carbon tape. The SEM analysis was performed in a FEI Quanta 250F with low vacuum mode (in order to reduce the charging effect), and the energy dispersive X-ray spectroscopy (EDS) analysis was done with an
EDAX detector and TEAM software. Absorption spectra of the crystal sample was tested by PerkinElmer spectrometer type lambda 950, the measurement wavelength range was 200-800 nm. Fluorescence spectra and photoluminescence lifetime decay were measured by HORIBA Jobin Yvon FluoroMax-4, the best detection wavelength range was 200-950 nm, the Xe lamp as the excitation source, the type for lasers was 454N, emission wavelength was 535 nm, slit width was 0.5 nm. Photoelectric parameters were surveyed by EVERFINE HAAS-2000 type fast spectrometer. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. XRD analysis of the single crystal

Fig. 2 displays all the diffraction crystal plane could match well with the standard card (JCPDS No.33–0040), no other phase impurities were present in the sample, which indicated that Ce,Tb ions co-doped YAG was well-crystallized and had no effect on the crystal structure of YAG. In addition, YAG single crystal is a cubic crystal system, point group is O_h(10)-I_a3d, lattice parameters are a=b=c=1.2008 nm. According to the XRD test data, the crystal structure of Ce,Tb:YAG is body centered cubic so that its lattice parameters can be obtained by the following equation:

\[
sin^2 \theta = \frac{\lambda^2}{4a^2 (h^2 + k^2 + l^2)}
\]

Where \(\lambda\) is the wavelength of X-ray, \((h k l)\) is Miller index, \(\theta\) is the diffraction angle and \(a\) is the lattice parameter. it can figure out that a=1.2001 nm, which is smaller compared with YAG single crystal. As the diameter of the doped rare earth ion decreases, the surface area ratio and surface pressure of each atom of YAG unit cell will increase, then, chaos of internal system will also increase resulting in the lattice parameters decrease.

3.2. SEM and EDS analysis

Fig. 3a shows a backscattered SEM image of single crystal sample and EDX spectrum. In the backscattered image the contrast could reflect the atomic number difference. Meanwhile it can be seen that the single crystal was mainly composed of Y, Al, Ce and Tb four elements and the stoichiometric ratio was 43:52:2:3, which indicated that Tb ions could enter into the dodecahedral site of the YAG lattices to complement the lacking of red component in the white light spectrum of
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the blue LED chip plus pure YAG:Ce single crystal [35]. Fig. 3b reveals EDS elemental mapping of Y, Al, Ce and Tb marked as different colors, which are homogeneously distributed in the single crystal. and the size of these particles are quite uniform. What’s more, no O rich regions were found due to the limited resolution of EDS detector in SEM.

3.3. Absorption spectra of the single crystal

Fig. 4a indicates that the absorption spectra of Ce,Tb:YAG single crystal showed the same change trend under different annealing temperature, which had four similar locations of peaks, only the absorption intensity varied at 800 °C, 1000 °C and 1200 °C. The absorption intensity enhanced obviously after annealing in air atmosphere. Simultaneously according to Fig. 4b, the absorption spectra of Ce,Tb:YAG single crystal through different annealing time revealed the same change curve, except that the absorption intensity of the samples changed remarkably at 1000 °C for different time in air atmosphere. What's more, the absorption intensity of the samples increased initially with time increased. But when the sample was annealed at 1000 °C for 48 h, the absorption intensity instead began to decrease.

3.4. Fluorescence spectra of the single crystal

According to Fig. 4, we can see that Ce,Tb:YAG single crystal has a intense absorption peak located at 460 nm. Therefore we choose 460 nm wavelength monochromatic light as the excitation source to test the emission spectra of Ce,Tb:YAG single crystal as shown in Fig. 5.

Fig. 5a presents the emission spectra of Ce,Tb:YAG single crystal samples at different annealing temperature. All the peaks of the luminescence bands of Ce ions and Tb ions before and after annealing in air were 535 nm under excited at 460 nm, but the emission intensity varied significantly at 800 °C, 1000 °C and 1200 °C. The emission intensity enhanced obviously after annealing in air atmosphere. Fig. 5b shows that the emission intensity of the samples changed remarkably at 1000 °C under different annealing time in air atmosphere. The emission intensity increased clearly after annealing at 1000 °C for 10 h and 24 h in air atmosphere, but it instead decreased after annealing at 1000 °C for 48 h in air atmosphere.

3.5. Energy level structure of Ce\(^{3+}\) and Tb\(^{3+}\) ions

Fig. 6a presents schematic energy level diagrams of Ce\(^{3+}\) and Tb\(^{3+}\) ions, energy level of Tb\(^{3+}\) ions hasn’t entirely drawn up in order to handle conveniently. For Ce:YAG single crystal, Ce\(^{3+}\)
ions can enter into the dodecahedral site of the YAG lattices to take the place of Y$^{3+}$ ions which are symmetrical. Ground state of Ce$^{3+}$ ions which possess [Xe] 4f$^1$ electronic structure of inert gas can split into $^2F_{5/2}$ and $^2F_{7/2}$ doublet state because of spin-coupling. Due to 4f energy level can be blocked in internal layer, therefore crystal field has a little effect on it, but radial wave function of 5d electron locates outside of the closed shell of 5s$^2$5p$^6$, thus, crystal field has a intense effect on 5d state. Under the effect of crystal field, the gap between 4f and 5d energy level becomes narrow, 5d state can also occur energy level splitting, the division of the energy level will form energy band. When Ce$^{3+}$ ions are under excited at 460 nm, electrons from the 4f ground state are excited to the 5d excited state [38-42], most excited electrons immediately transfer back from 5d excited state to 4f ground state to emit a broad band spectra of yellow-green light [43]. 5d excited state energy band of Ce$^{3+}$ ions is lower than $^5D_3$ energy level of Tb$^{3+}$ ions, but higher than their $^5D_4$ energy level, thus energy can transmit from 5d excited state energy level of Ce$^{3+}$ ions to $^5D_4$ energy level of Tb$^{3+}$ ions through radiative or non-radiative transition, then transmit to ground state to make Tb$^{3+}$ ions luminescence [44].

For further analysis of the energy transmission mechanism of Ce$^{3+}$ and Tb$^{3+}$ ions, the comparison of photoluminescence lifetime decay behaviors of the Ce:YAG and Ce,Tb:YAG single crystal is carried out, as exhibited in Fig. 6b. As expected, Ce:YAG single crystal shows a single-exponential decay and the fitting yields a decay time of 60 ns. The lifetime in nanosecond order is one of the characteristics of the Ce$^{3+}$ electric-dipole allowed 5d-4f transition. However, interestingly, the decay time of Ce,Tb:YAG single crystal only reaches 56 ns, which indicates that there are extra excited state energy loss, further proving that energy transfer occurs in Ce,Tb:YAG co-doped system.

3.6. Effect of annealing on photoelectric parameters of as-grown Ce,Tb:YAG single crystal

As we all know, Lumens per watt (lm/W) is a commonly used metrics for evaluating light sources. The concentration of the Ce and Tb ions and F color centers would influence the luminous flux of the crystal panels. We have annealed the samples under air atmosphere for reducing the negative effect of F color centers. Table 1 lists the lumens per watt for samples annealing in air atmosphere under different temperature and time testing at 20 mA.

Table 1 shows that luminous efficiency of Ce,Tb:YAG single crystal enhanced
obviously after annealing in air atmosphere with different annealing temperature. When annealing temperature reached at 1000 °C, luminous efficiency reached the maximum, then began to decrease as annealing temperature increased. It also reveals that luminous efficiency of Ce,Tb:YAG single crystal enhanced initially after annealing in air atmosphere at 1000 °C with different annealing time. As annealing time reached at 24 h, luminous efficiency reached the maximum. Then when annealing time continued to increase at 48 h, luminous efficiency instead began to decrease maybe due to annealing time was so long that lattice structure of the single crystal sample was destroyed. Therefore choosing appropriate annealing temperature and time becomes necessary because they can influence photoelectric performance of Ce,Tb:YAG single crystal and the ideal annealing condition is 1000 °C for 24 h.

3.7. White illuminant performance of Ce,Tb:YAG single crystal

A photograph of the LED encapsulation jig is shown in Fig. 7a, which is used to fix blue LED chip. Then a photograph of a transparent Ce,Tb:YAG single crystal and blue LED is exhibited in Fig. 7b, in which it can be seen that the single crystal had good transparency, with the letters under it clearly visible. When the single crystal was packaged with a blue-emitting LED chip, a transparent single crystal WLED was obtained as is shown in Fig. 7c.

4. Conclusions

The properties of Ce:YAG single crystal have been improved by co-doped Tb ions using the Czochralski method. The emission spectra of the single crystal consists of a peak around 535 nm under excited at 460 nm. Compared to the emission spectra of Ce:YAG single crystal, the emission of Ce,Tb:YAG single crystal has been improved to the yellow-green range, the optimal annealing condition is annealing in air atmosphere at 1000 °C for 24 h. The SEM and EDS analysis shows the single crystal is mainly composed of Y, Al, Ce and Tb four elements, which are homogeneously distributed in the single crystal. and the size of these particles are quite uniform. The photoluminescence lifetime decay of Ce:YAG and Ce,Tb:YAG single crystal indicates that energy transfer exists in Ce,Tb:YAG co-doped system. Meanwhile through the photoelectrical parameters test report of Ce,Tb:YAG single crystal, it can be seen that its
luminous efficiency, color rendering index, color temperature has come close to commercialize WLED mainstream level at present, which can be expected to be an ideal candidate for generating white light.

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Associated content

Supporting data. Photograph of single crystal furnace and its internal growth structure, luminous efficiency curve of slice at different annealing temperature with current (I) changes, luminous efficiency curve of slice at different annealing time with current (I) changes. See supplementary material at [URL will be inserted by ELSEVIER].

Notes

The authors declare no competing financial interest.

References

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Figure and table caption:

**Table 1.** Lumens per watt (lm/W) for samples annealed at different temperature and time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lumens per watt (lm/W)</th>
<th>I_A(mA)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>140.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 °C 10h annealing in air</td>
<td>151.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 °C 10h annealing in air</td>
<td>153.37</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>1000 °C 24h annealing in air</td>
<td>165.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 °C 48h annealing in air</td>
<td>153.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200 °C 10h annealing in air</td>
<td>139.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** Photograph of as-grown Ce,Tb:YAG single crystal by Czochralski method.

**Fig. 2.** XRD pattern of Ce,Tb:YAG single crystal.

**Fig. 3.** (a) backscattered SEM image of single crystal sample and EDX spectrum, (b) EDS elemental mapping of Y, Al, Ce and Tb, respectively, in single crystal fragments.

**Fig. 4.** Absorption spectra of Ce,Tb:YAG single crystal. (a) at different annealing temperature, (b) at different annealing time.

**Fig. 5.** Emission spectra of Ce,Tb:YAG single crystal. (a) at different annealing temperature, (b) at different annealing time.

**Fig. 6.** (a) Schematic energy level diagrams of Ce^{3+} and Tb^{3+} ions, (b) Photoluminescence lifetime decay of Ce:YAG and Ce,Tb:YAG single crystal.

**Fig. 7.** Photographs of (a) the LED encapsulation jig, (b) a transparent Ce,Tb:YAG single crystal and blue LED, (c) transparent single crystal WLED in operation.

**Fig. S1.** Photograph of single crystal furnace and its internal growth structure.

**Fig. S2.** Luminous efficiency curve of slice at different annealing temperature with current (I) changes.

**Fig. S3.** Luminous efficiency curve of slice at different annealing time with current (I) changes.
Graphical abstract
In this work, we evaluated its highlights as shown below:

- We report preparation of transparent Ce,Tb:YAG single crystal by Czochralski method.
- The effect of annealing on Ce,Tb:YAG single crystal had been investigated.
- The Ce,Tb:YAG single crystal after annealing exhibited better optical performance.
- The Ce,Tb:YAG single crystal could be used as an ideal candidate for WLED.