Optical properties of wavelength-tunable green-emitting color conversion glass ceramics*

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Color conversion glass ceramics are prepared by cosintering borosilicate glass frits and green 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ phosphors. The crystal structures, the influence of Ga concentration on the photoluminescence (PL), and reliability properties of the color conversion glass ceramics are investigated. The PL emission wavelengths of 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics show blue shift from 545 nm to 525 nm with increasing Ga content (x value) under excited at 460 nm. Reliability test results show that the quantum yield (QY) of 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics decreases from 70.60% to 59.06% with x value increasing from 0.15 to 0.35 under the ambient condition of 85 °C/RH85% for the exposure time of 168 h. And the quantum yield (QY) of 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics decreases from 65.13% to 52.23% after being soaked into boiled water for 4 h. The finding reveals that the addition of Ga can deteriorate the reliability of the color conversion glass ceramics.

Keywords: color conversion glass ceramic, photoluminescence wavelength, quantum yield, reliability property

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1. Introduction

White light-emitting diodes (WLEDs) have been widely used in the luminescence market due to their being environmentally friendly, long lifetime and low energy consumption features.[1–4] The current commercial WLED commonly use epoxy resin or silicone to combine a blue chip with Ce:YAG phosphors.[5,6] However, the use of epoxy resin and silicone may easily degrade the long-term reliability of the WLED because of their poor thermal conductivity and thermal stability.[7] Consequently, inorganic materials such as Ce:YAG color conversion glass ceramics have drawn extensive attention in recent years as practical alternatives to organic polymer binders.[8,9] The current preparation process of color conversion glass ceramics include glass crystallization and the cosintering of a simple mixture of phosphors and matrix glass powders.[10,11] Compared with glass crystallization, the cosintering route is considered to be promising future in LED application because of its easy process and readily combining different kinds of phosphors.[12]

In previous studies, the color rendering index (CRI) of white LEDs was approximately 70, which is lower than the requirements of commercial illumination.[13] At present, the emission peak of InGaN blue-emitting chip varies from 450 nm to 480 nm. Adjusting the emission wavelength of Ce:YAG converter to match the blue LED chips, it is possible to obtain white light with high CRI. The CRI can be improved by using green and red converters to enhance high-fidelity lighting.[14] The applications of green-emitting phosphors with different emission wavelengths in LED have been explored.[15] Therefore, wavelength-tunable green-emitting conversion glass ceramics are required.

In this paper, borosilicate glasses and 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ (x value is 0.15, 0.2, 0.25, 0.3, and 0.35, respectively) phosphors are cosintered to prepare color conversion glass ceramics. The crystal structures and the influences of Ga concentration on the PL properties of the color conversion glass ceramics are investigated. For WLED application, a color conversion glass ceramic should maintain its PL performance although it would be affected by the heat generated by the operation of LED chips and the humidity in the air.[16,17] In this paper, we investigate the quantum yields before and after reliability test of the glass ceramics, respectively.

2. Experiment

Precursor glass with the composition "B_2O_3–SiO_2–ZnO–BaO–Na_2O" was prepared by a conventional melting–

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quenching method. The relative chemicals were mixed thoroughly and melted in air at 1100 °C for 1 h. The melt was quickly poured into a cold copper mould and cooled down to room temperature. The glass was milled to powder with a d_{50} of 15 μm using a ball grinder, and then mixed with 3 wt% YAG ($0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$; YAP4454-L, RayPower, China) phosphors with a d_{50} of 13 μm thoroughly. Then, the mixture was fired at 650 °C for 20 min in air and cooled naturally with the furnace. The sintered body was then polished to a thickness of 1 mm.

The crystal structures of the color conversion glass ceramics were analyzed by the x-ray diffraction (XRD; Rigaku, Ultima IV, Japan) with Cu Ka radiation ($k = 0.154178$ nm) over a 10°–60° 2θ range, at a scanning rate of 0.02°/step and 4°/min. Microstructures of the color conversion glass ceramics were studied using a scanning electron microscope (SEM, Phenom pro). The photoluminescence (PL) spectra and quantum yield were measured by Hitachi F-7000 spectrofluorometer and the integrating sphere with using a Xenon lamp as the light source. To investigate the reliability of the glass ceramics, the crystal structures and quantum yield of the glass ceramics were measured again after being stored in a chamber with high temperature and high-humidity (85 °C/RH 85%) for 168 h. To directly examine humidity resistance of the glass ceramics, each sample of $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics was inserted into a beaker containing 50 ml of deionized water which was heated to boiling. Then the boiling solution was hold and stirred at 120 rpm for 4 h. After that, the quantum yield of these glass ceramics were measured again at room temperature.

3. Results and discussion

Figure 1 shows the $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramic samples with different x values. On increasing the Ga content, the color of the glass ceramic gradually turns green.

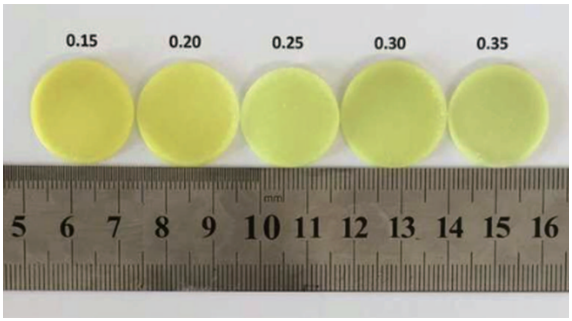


Fig. 1. (color online) Photographs of the $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics with different x values.

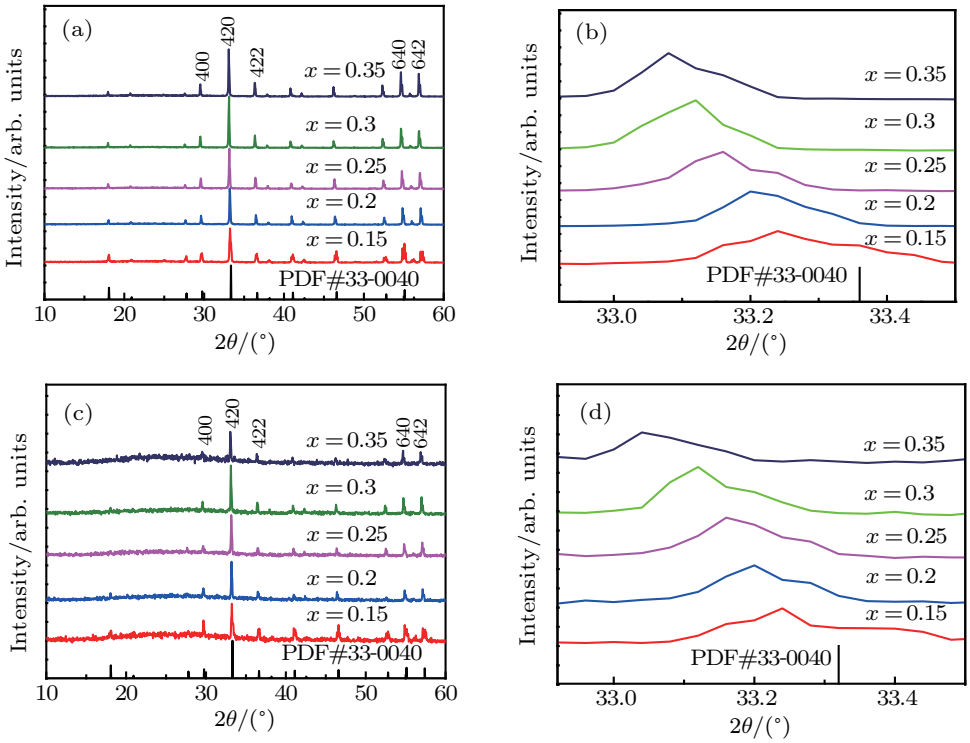


Fig. 2. (color online) XRD patterns of $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ phosphors and color conversion glass ceramics: (a) XRD of phosphors; (b) magnified XRD of phosphors; (c) XRD of the glass ceramics; (d) magnified XRD of the glass ceramics.

Figures 2(a) and 2(c) present the XRD analyses of $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ phosphors and the color conversion glass ceramics. Comparing the patterns of the phosphors, it is clearly observed that the color conversion glass ceramics do not change the host structure and diffraction of the YAG. The phosphors in the glass matrix present the high intensities of the diffraction peaks and no broad bands in the background of the diffraction patterns. Figures 2(b) and 2(d) show mag-

nified XRD patterns of the phosphors and glass ceramics, in a range of $2\theta = 32.6°$–$33.6°$ for each x value, where the (420) plane main diffraction peaks shift to lower angles in reference to the YAG PDF card. As the Ga concentration increases, the peaks are shifted to lower angles, which show that Ga substitution induces the lattice parameter to increase. We also calculated the lattice constants of $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics against x value as shown in Fig. 3. The lattice constants increase with x value increasing, because Al^{3+} ions (0.535 Å) are replaced by larger Ga^{3+} ions (0.62 Å) in the YAG structure.[18] Meanwhile, the substitution of Ga^{3+} ions for Al^{3+} ions therefore modify the local crystal field symmetry around Ce^{3+} ions in the host lattice, and thereby affecting PL properties of the color conversion glass ceramics.

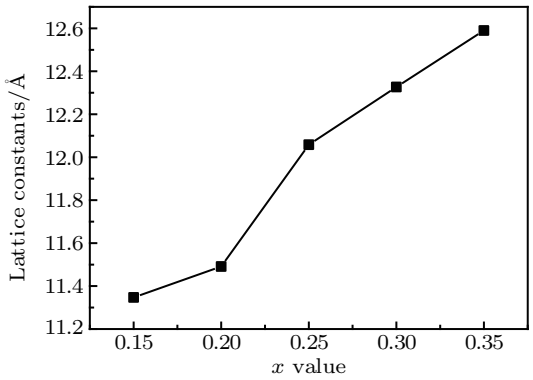


Fig. 3. Lattice constants of $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics against x value.

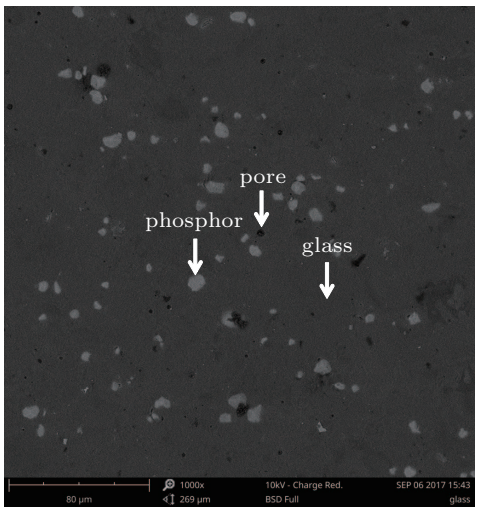


Fig. 4. SEM image of the glass ceramic sample.

Scanning electron microscopy (SEM) observations on the color conversion glass ceramic sample evidently display that the phosphor particles are homogeneously dispersed in the glass matrix as shown in Fig. 4. Figure 5 displays the PL spectra of the $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics with different Ga content values excited at 460 nm, of which the CRIs are more than 75. The Ce^{3+} emissions are observed to be blue-shifted with increasing Ga content. With the x value increasing from 0.15 to 0.35, the emission peak of Ce^{3+} is shifted from 545 nm to 525 nm. Accordingly, we can conclude that Ga^{3+} substitution reduces the splitting of Ce^{3+} ionic 5d levels and elevates its lowest excited state energy level of 5d. The studies showed the deviation from cubic site symmetry becomes smaller when Al^{3+} is replaced by Ga^{3+}.[19] Therefore, the energy difference between the lowest 5d sublevel and the ground state of 4f configuration of Ce^{3+} is larger, which makes the emission band of the glass ceramic blue-shifted. As shown in Figs. 5 and 6, the PL intensitied and quantum yields of the glass ceramics decrease as Ga content increases.

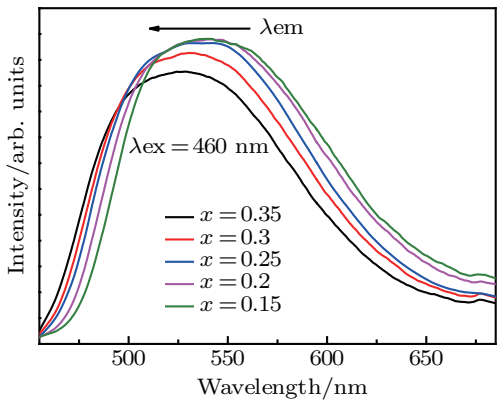


Fig. 5. (color online) PL spectra of the $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics excited at 460 nm.

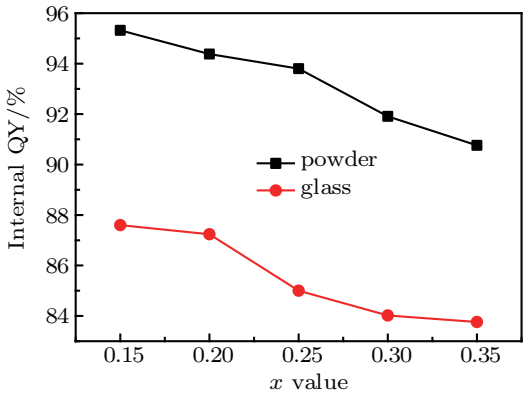


Fig. 6. (color online) Plots of internal quantum yield versus x value for $0.06Ce:Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ powders and glass ceramics.

To investigate the reliabilities of the glass ceramics, the crystal structures and quantum yields of the glass ceramics are measured again after being stored in a chamber with high temperature and high-humidity (85 °C/RH 85%) for 168 h. Compared with the XRD patterns of samples before being exposed to high-temperature and high-humidity (85 °C/RH 85%) in a chamber, the XRD patterns of all five glass ceramics after being exposed are little changed. As shown in Table 1, the values of 2θ of five main diffraction peaks before and after being exposed indicate that the lattice structures of glass ceramics are not modified under the exposure condition. Figure 7 displays internal QYs of the five glass ceramics before and after reaching the ambient condition of 85 °C/RH

85 % for the exposure time of 168 h. The quantum yield of 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramic decrease from 70.60% to 59.06% with x value increasing from 0.15 to 0.35 under the ambient condition of 85 °C/RH85% foran exposure time of 168 h. Figure 8 shows internal QYs of the five glass ceramics before and after being soaked into deionized water for 4 h. The quantum yield of 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ glass ceramics decrease from 65.13% to 52.23% with x value increasing from 0.15 to 0.35 after being soaked into boiled water for 4 h. The results suggest that the addition of Ga can deteriorate the reliability properties of the color conversion glass ceramics.

Table 1. Values of 2θ of five main diffraction peaks of the glass ceramics.

Samples	Condition	2θ				
		(400)	(420)	(422)	(640)	(642)
0.06Ce:$Y_{2.94}(Al_{0.85}Ga_{0.15})_5O_{12}$	before exposing	29.681	33.246	36.522	54.880	57.163
	after exposing	29.684	33.242	36.526	54.886	57.160
0.06Ce:$Y_{2.94}(Al_{0.8}Ga_{0.2})_5O_{12}$	before exposing	29.687	33.202	36.482	54.884	57.122
	after exposing	29.685	33.204	36.482	54.885	57.126
0.06Ce:$Y_{2.94}(Al_{0.75}Ga_{0.25})_5O_{12}$	before exposing	29.646	33.162	36.484	54.806	57.086
	after exposing	29.644	33.160	36.480	54.802	57.048
0.06Ce:$Y_{2.94}(Al_{0.7}Ga_{0.3})_5O_{12}$	before exposing	29.562	33.128	36.448	54.728	57.006
	after exposing	29.553	33.123	36.426	54.720	57.002
0.06Ce:$Y_{2.94}(Al_{0.65}Ga_{0.35})_5O_{12}$	before exposing	29.522	33.048	36.368	54.682	56.884
	after exposing	29.485	33.006	36.323	54.644	56.845

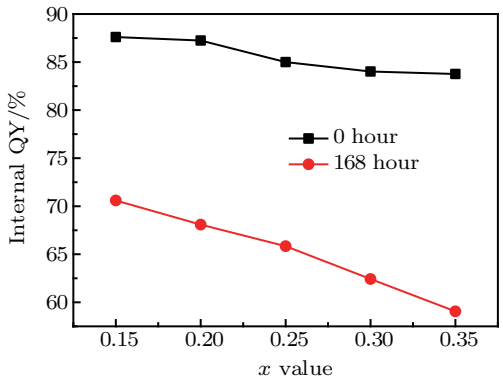


Fig. 7. (color online) plots of internal QY versus x value for five glass ceramics before and after the ambient condition of 85 °C/RH 85% for the exposure time of 168 h.

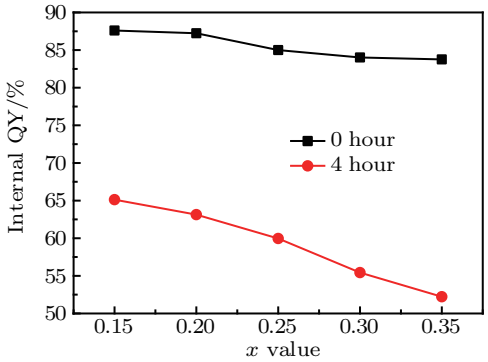


Fig. 8. (color online) Plots of internal QY versus x value for five glass ceramics before and after the soaking into boiled water for 4 h.

4. Conclusions

Wavelength- tunable 0.06Ce: $Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ (x = 0.15–0.35) color conversion glass ceramics are successfully prepared by cosintering borosilicate glass frits and green 0.06Ce:$Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ phosphors. For 0.06Ce: $Y_{2.94}(Al_{1-x}Ga_x)_5O_{12}$ (x = 0.15–0.35) glass ceramics, PL emission peaks are shifted from 545 nm to 525 nm after Ga ions have replaced Al ions under the excitation of 460 nm. Meanwhile, the investigations of reliability properties of the glass ceramics show that the addition of Ga can deteriorate the reliability properties of the color conversion glass ceramics.

References

[1] Guo X, Liu Q L, Li C, Liu B, Dong J and Shen G D 2015 *Chin. Phys. B* **24** 068505

[2] Feng B, Deng B, Liu L G, Li Z C, Feng M X, Zhao H M and Sun Q 2017 *Acta Phys. Sin.* **66** 047801 (in Chinese)

[3] Fu M, Wen S S, Xia Y Y, Xiang C M, Ma B X and Fang F 2017 *Acta Phys. Sin.* **66** 048501 (in Chinese)

[4] Chen D Q, Xu W, Zhou Y, Zhong J S and Li S C 2017 *J. Mater. Chem. C* **5** 738

[5] Xu W, Chen D Q, Yuan S, Zhou Y and Li S C 2017 *Chem. Eng. J.* **317** 854

[6] Zhou Y, Chen D Q, Tian W D and Ji Z G 2015 *J. Am. Ceram. Soc.* **98** 2445

[7] Iqbal F, Kim S and Kim H 2017 *Opt. Mater.* **72** 323

[8] Yie H, Kim S, Kim Y and Kim H 2017 *J. Non-Cryst. Solids* **463** 19

[9] Tsai C C 2015 *Optik - International Journal for Light and Electron Optics* **126** 655

[10] Chen D Q, Xiang W D, Liang X J, Zhong J S, Yu H, Ding M Y, Lu H W and Ji Z G 2015 *J. Eur. Ceram. Soc.* **35** 859

[11] Zhu Q Q, Wang X J, Wang L, Hirosaki N, Nishimura T, Tian Z F, Li Q, Xu Y Z, Xu X and Xie R J 2015 *J. Mater. Chem. C* **3** 10761

[12] Jeong H J, Huh C, Lim T Y, Kim J H, Lee M J, Jeon D W, Hwang J H, Park T H and Shin D W 2015 *J. Non-Cryst. Solids* **423–424** 25

[13] Zhu Q Q, Xu X, Wang L, Tian Z F, Xu Y Z, Hirosaki N and Xie R J 2017 *J. Alloys Compd.* **702** 193

[14] Han K, Lee S, Choi Y, Im W and Chung W 2016 *J. Non-Cryst. Solids* **445–446** 77

[15] Yang B B, Zou J, Wang F C, Zhang C Y, Xu J Y, Li L and Sun L H 2016 *J. Mater. Sci.-Mater. Electron.* **27** 3376

[16] Ji E K, Song Y H, Lee M J and Yoon D H 2015 *Mater. Lett.* **157** 89

[17] Zhong J S, Chen D Q, Zhou Y, Wan Z Y Ding M Y and Ji Z G 2016 *J. Eur. Ceram. Soc.* **36** 1705

[18] Shannon R D 1993 *J. Appl. Phys.* **73** 348

[19] Pan Y X, Wu M M and Su Q 2004 *J. Phys. Chem. Solid* **65** 845