Thermal stability of luminous YAG: Ce bulk ceramic as a remote phosphor prepared through silica-stabilizing valence of activator in air*

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A prototype of YAG: Ce ($Y_3Al_5O_{12}$) luminous bulk ceramic as a remote phosphor for white LED illumination was fabricated in air through a strategy of silica addition. With increasing the amount of silica in a specific range, the opaque sample turns to be semi-transparent. The precipitation of crystals is verified to be in pure YAG phase by X-ray diffraction (XRD). Beyond the limit of silica amount, the dominant phase of YAG crystal is found to coexist with a small amount of newly-formed $Y_2Si_2O_7$, Al_2O_3 and the amorphous phase. The YAG crystals are with a grain size of approximately 2 μm and distribute evenly. The YAG hosts after structural modification via addition of silica result in yellow band emission of 5d → 4f transition peaked around 535 nm as excited by a blue LED, owing to the self-reduction of Ce^{4+} to Ce^{3+} even in the absence of reductive atmosphere.

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The heat dissipation problem arises due to development of high power lighting-emitting diodes (LEDs), possibly leading to the degradation of epoxy and the light decay of phosphors[1]. As an effective solution, a new variety of phosphor named as remote phosphor emerges to improve the uniformity of angular-dependent correlated color temperature (CCT) and to lessen thermal attack to the luminous layers, compared with the conventional remote phosphor coating structures[2-5]. Furthermore, all inorganic remote phosphors are also expected to be further developed to take place of YAG:Ce/silicone luminosity, which are in YAG:Ce bulk ceramic and glass-ceramic forms. For instance, YAG:Ce glass-ceramic, YAG: Ce single crystal and optical ceramics were prepared with complex technology and equipment by Cherepy[6] and Mihóková[7], respectively. Zych[8] prepared YAG:Ce transparent ceramic material via hot-isostatic pressing equipment, which is very expensive. However, the sintering temperature of traditional YAG:Ce ceramics is so high that the harsh preparation leads to high cost[8-10]. So we report a process of preparing bulk YAG remote phosphors by just sintering at 1400 °C under air through adding silica. The addition of silica to the YAG host is important to achieve the desired photoluminescence (PL), so a series of experiments are carried out to focus on the role of silica addition. After adding a suitable amount of silica, a distinct broad yellow-green band emission peaked at 535 nm is observed, which is featured for Ce^{3+} in its 5d → 4f transition[11]. However, very little attention is paid to the valence state of Ce in YAG host with the addition of silica, which is probably due to the ease of reduction of Ce^{4+} to Ce^{3+} from YAG host in reductive atmospheres, like CO, H_2 and the invisible observation of unreduced Ce^{4+} in YAG host. In the respects of valence stability, abnormal valance state of lanthanide ions has been widely observed[12,13] in some specific matrix of particle, film or glass phosphors, i.e., some divalent states can be stable even under oxidizing conditions and trivalent states can also exist in reductive atmosphere.

As to specific valence state of Ce^{3+}/Ce^{4+}, some approaches were explored on the invisibility of Ce^{4+} with PL characterization[14-21]. Herein, we demonstrate that the addition of silica promotes the reduction of Ce^{4+} to Ce^{3+} in air atmosphere. Meanwhile, the addition of silica promotes the formation of phase-pure YAG host. Eventually, a better thermal stability for YAG: Ce remote phosphor is achieved compared with that for YAG: Ce commercial phosphors blended with epoxy or silicone.

The samples were prepared by high-temperature solid state synthesis procedure. Raw materials of Y_2O_3 (99.99%, 100 nm), Al_2O_3 (99.9%, 200 nm), SiO_2 (99.9%, 80 nm) and CeO_2 (99.99%, 100 nm) are all in high purity and nanometer particles. In accordance with YAG: Ce formula, raw materials were weighed and ground manually with the aid of small amounts of ethanol to form slurries. The slurries of starting materials were dispersed with pestle grinding for half an hour, and then dried at 70 °C for half an hour, followed by pressing them into tablet sample and sintering the tablet in a muffle furnace at 1400 °C for 5 h in air. Finally the samples were naturally cooled down to room temperature. In particular, for comparing with YAG:Ce remote phosphor samples, the samples of $(SiO_2)_{0.75}$:$Y_{2.97}Al_5O_{12}$:0.03Ce and $(SiO_2)_{2.25}$:$Y_{2.97}Al_5O_{12}$:0.03Ce were prepared with the same procedure.

The phase of YAG:Ce remote phosphors was examined via X-ray diffraction (XRD, Rigaku D/max-2500/pc, $\lambda_{CuK\alpha}$ = 1.54062 nm, Japan). The crystal structure of YAG: Ce remote phosphors was measured by the scanning electronic microscope (SEM) (JSM-6700F JEOL/ Japan). The reflection spectrum of samples was measured by TU-1901 plus dual beam UV-VIS spectrophotometer. The emission spectrum of samples was obtained via Shimadzu RF-5301 fluorescent spectrophotometer which is equipped with Xe lamp, and the slits of excitation and emission are set at 1.5 nm and 3.0 nm, respectively. All of above measurements were carried out at room temperature. The thermal stabilities of YAG: Ce remote phosphors were measured at gradually rising temperatures on an EX-1000 exciting spectra and thermal quenching analyzer for phosphors.

According to Fig.1(a), it is uniform and intact for YAG growth in the YAG ceramic, and the average size is approximately 2 μm. Fig.1(b) demonstrates that YAG crystals with a grain size of approximately 2 μm are dispersed unevenly in the glass-ceramic.

Fig.2 shows the XRD patters of $(SiO_2)_{0.75}$:$Y_{2.97}Al_5O_{12}$: 0.03 Ce (YAG:Ce bulk ceramic) and $(SiO_2)_{2.25}$:$Y_{2.97}Al_5O_{12}$:0.03Ce (YAG:0.03Ce glass-ceramic) which were both sintered at 1400 °C for 5 h in air. It is confirmed that by XRD measurements, only YAG crystal can be detected in the $(SiO_2)_{0.75}$:
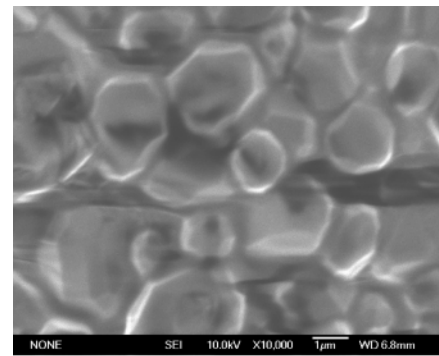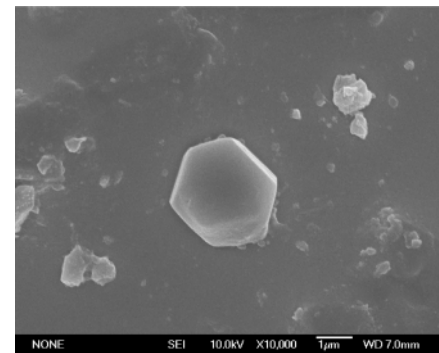
Fig.1 SEM images of (a) $(SiO_2)_{0.75}$:$Y_{2.97}Al_5O_{12}$:0.03 Ce and (b) $(SiO_2)_{2.25}$:$Y_{2.97}Al_5O_{12}$:0.03 Ce

$Y_{2.97}Al_5O_{12}$:0.03 Ce, and major phase YAG crystal is precipitated in the $(SiO_2)_{2.25}$:$Y_{2.97}Al_5O_{12}$:0.03 Ce (YAG:Ce glass-ceramic), but impure phases of $Y_2Si_2O_7$, Al_2O_3 and the amorphous phases occur. At the same time, the results indicate that the XRD measurement corresponds to each micro-particle in the SEM image.

The role of silica addition is generally regarded as a mineralizing agent and a catalyst to enhance the activity energy of reaction. Induced by silica, the formation of liquid phases increases the contact area between particles of reactants so as to lower the reaction activation energy and increase the reaction rate, which leads to the formation of pure phase of YAG with suitable stoichiometric ratio of $(SiO_2)_{0.75}$:$Y_{2.97}Al_5O_{12}$:0.03Ce only at 1400 °C. Furthermore, the YAG formation temperature in the present work is found to be much lower than that in the conventional solid-state synthesis procedure. As the stoichiometric ratio is set to be $(SiO_2)_{2.25}$:$Y_{2.97}Al_5O_{12}$:0.03Ce, some impure phases and more liquid amorphous phases occur, which is detrimental to the crystallization of the YAG glass-ceramics since excess silica can react with Y_2O_3 to yield $Y_2Si_2O_7$. The associated reaction can be described as

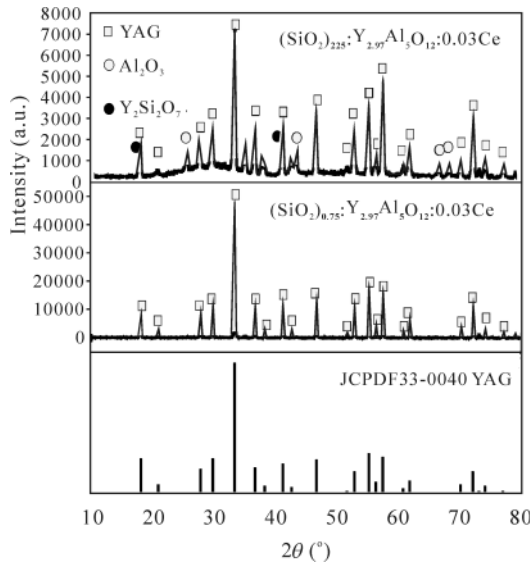$$2SiO_2 + Y_2O_3 \rightarrow Y_2Si_2O_7 . \tag{1}$$

Fig.2 XRD patterns

Fig.3 depicts the diffuse reflection spectra. The absorption edge of energy level for YAG:Ce is estimated to be at 465 nm[19,22], which corresponds to the first excitonic absorption, and the broad absorption band of Ce^{3+} in YAG: Ce remote phosphors from about 410 nm to 510 nm can be ascribed to the transitions from the ground state 4f of Ce^{3+} to its excited state. The absorption of Ce doped $(SiO_2)_{0.75}$:$Y_{2.97}Al_5O_{12}$ (YAG bulk ceramic) host is relatively stronger than that of Ce doped $(SiO_2)_{2.25}$:$Y_{2.97}Al_5O_{12}$ (YAG glass-ceramic). Therefore, the results indicate that the absorption capability of YAG remote phosphors host exhibits virtually the same spectrum features compared with that of YAG phosphors host, which is helpful to induce an efficient emission for Ce^{3+} in the YAG remote phosphors host.
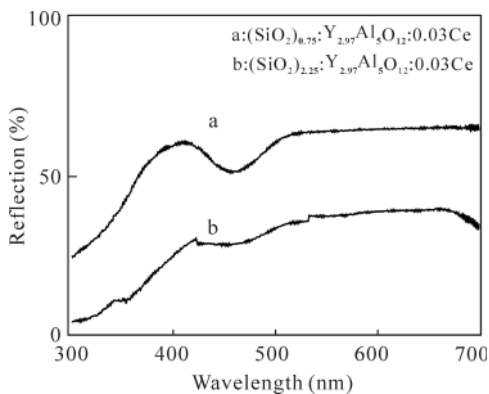

Fig.3 Diffuse reflection spectra

In Fig.4, the Ce doped $(SiO_2)_{0.75}$:$Y_{2.97}Al_5O_{12}$ (YAG bulk ceramic) spectrum is stronger than that of the Ce doped $(SiO_2)_{2.25}$:$Y_{2.97}Al_5O_{12}$ (YAG glass-ceramic). The result demonstrates that the Ce^{3+} ions incorporated in the YAG remote

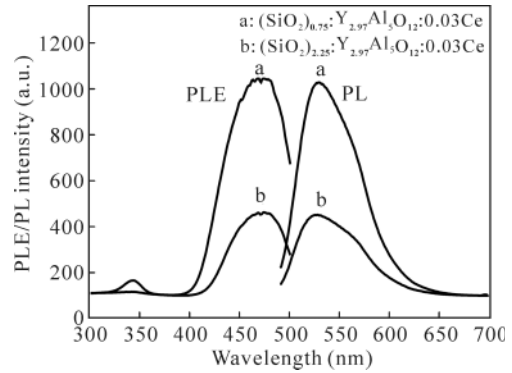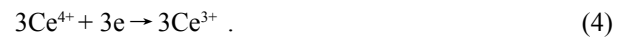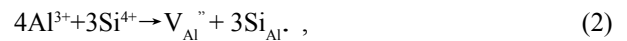phosphors (YAG bulk ceramic and YAG glass-ceramic) were sintered at 1400 °C under air atmosphere.

Fig.4 PLE monitored at 535 nm and PL excited at 465 nm

Three Si^{4+} ions tend to substitute for four Al^{3+} ions owing to similar radius of Si^{4+} ion and Al^{3+} ion, and at the same time, the charge compensation is indispensable to keep charge balance[13]. Therefore one cation vacancy defect with negative charges of V_{Al}'' and three $Si_{Al}·$ defects occur. The cation vacancy acts as a donor of electron while the Ce^{4+} is an acceptor of electron. Upon thermal stimulation, the electron in the vacancy defect V_{Al}'' is transferred to Ce^{4+}, leading to a reduction of Ce^{4+} ions to Ce^{3+} ions. A charge balance process can be expressed as

$$4Al^{3+}+3Si^{4+} \rightarrow V_{Al}'' + 3Si_{Al}· \, , \tag{2}$$

$$V_{Al}'' \rightarrow V_{Al} + 3e \, , \tag{3}$$

$$3Ce^{4+} + 3e \rightarrow 3Ce^{3+} \, . \tag{4}$$

YAG crystal cell consists of 24 Y ions, 40 Al ions and 96 O ions. 1 Y ion and 8 coordinated O ions construct dodecahedron, 16 Al ions and 6 coordinated O ions construct octahedron, and 24 Al ions and 4 coordinated O ions construct tetrahedron. The YAG crystal cell is the connection which links dodecahedron, octahedron and tetrahedron[10]. Rare earth ions with low valence can be attained easily in air atmosphere if one of four conditions is met with the requirements of appropriate structure (SiO_4 tetrahedron, AlO_4 tetrahedron or AlO_6 octahedron)[23]. As long as the YAG host is modified to a proper structure, the Ce^{3+} ion is stable in air.

According to Fig.5, the PL relative intensities for YAG: Ce bulk ceramic and YAG:Ce glass-ceramic have the same trend when the temperature is gradually raised. However, the PL relative intensity for YAG:Ce bulk ceramic has more advantages than that of the YAG:Ce commercial phosphors which are blended with resin or silicone. In general, YAG: Ce commercial phosphors have higher quantum efficiency than YAG:Ce bulk ceramic remote phosphors. However,

YAG: Ce commercial phosphors must be blended with resin or silicone, making initial intensity somewhat weaker than that of YAG: Ce bulk ceramic owing to the dispersion of light. A compensation of quantum efficiency is achieved by keeping the phosphor further from the temperature-raised chips so as to lessen the degradation and decay of luminescence. The result demonstrates that YAG: Ce remote phosphors have better heat dispersion and thermal stability than YAG: Ce commercial phosphors blended with silicone.
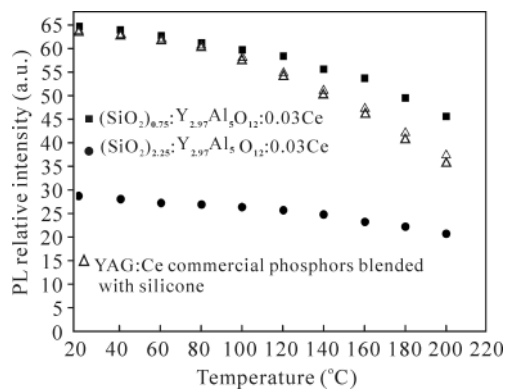

Fig.5 Thermal stabilities

In conclusion, we sinter YAG:Ce remote phosphors via high temperature solid state synthesis procedure at 1400 °C in air, and the addition of silica leads to the formation of luminous center of Ce^{3+} and YAG:Ce remote phosphors. The results demonstrate that YAG: Ce remote phosphors have better heat dispersion and thermal stability than YAG:Ce commercial phosphors blended with resin or silicone. It is expected that this newly developed YAG:Ce remote phosphors are promising candidates for the realization of organic-free and long-life power white LED devices.

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