

Controllable precipitation and photoluminescence of efficient green-emitting crystalline phase from luminescent CaO-SiO₂ glass-ceramic system*

TIAN Hua (田华)^{1,2,3}, WANG Da-jian (王达健)^{2,3}, and LIU Ji-wen (刘技文)^{1,2,3**}

1. School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

2. School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China

3. Tianjin Key Laboratory for Photoelectronic Materials and Devices, Tianjin University of Technology, Tianjin 300384, China

(Received 29 August 2011)

©Tianjin University of Technology and Springer-Verlag Berlin Heidelberg 2012

A new kind of glass-ceramic phosphor, which contains crystalline phases with green emissions, is explored. The glass-ceramic is prepared through semi-melt-quenching procedure with a nominal composition of (Ca_{0.99}Eu_{0.01})₃Si₂O₇. The green-emitting crystals are precipitated and identified to be β-Ca₂SiO₄: Eu²⁺ which is responsible for 510 nm-peaked much broader band emissions holding at 1550 °C for half an hour. In terms of the available light scattering theory, the appearance of opaque is discussed by closely associating with size and morphology of luminous β-Ca₂SiO₄ crystalline phase in glass.

Document code: A **Article ID:** 1673-1905(2012)01-0037-3

DOI 10.1007/s11801-012-1113-4

With the increasing demand of high output power of phosphor-converted light-emitting-diodes (pc-LEDs) to meet sufficient brightness and luminous flux in general lighting field, thermal management of device packaging has become critical. Great efforts have been made to maintain the luminescent stability of chip and powder phosphors in service, and metals or ceramic parts with high heat coefficient are generally used in packaged LED structure^[1-4]. An optional strategy by using bulk-crystallized glass-ceramic phosphor instead of powder phosphor installed with LED chip has been proposed, and it not only increases the resistance of phosphor to thermal degradation, but also improves the distribution of light extraction in such a plane-like source^[5,6]. In general, the crystals are easily precipitated on the surface upon heat-treatment of glass. To form bulk-crystallized glass-ceramic, some nucleating agents as “seeds” have to be added to the glass system prior to the melting process. But the nucleating agent can absorb the incident photon energy through absorption, reflection, self-lattice resonance and the energy dissipation around phase boundary^[7,8], eventually leading that part of photonic energy does not contribute to the radiation within the glass-ceramic bulk.

The approaches to bulk crystallized glass-ceramic phosphor without adding external additives have drawn much attention, such as utilizing phase separation to materialize high-luminous glass-ceramic phosphor^[9]. However, some unique ceramic systems may exhibit non-seeded bulk-crystallized behaviors. For instance, Tanabe et al^[10] described a new bulk-crystallized glass-ceramic, which consists of both Ca₂SiO₄ and Ca₃Si₂O₇ crystals by using a frozen sorbet process.

We examine the crystallization behaviors of powder phosphors of CaO - SiO₂ binary system, and observe that Ca₂SiO₄ is easily formed as an intermediate phase in the synthesis process of calcium silicate. In this paper, we concentrate on a green-emitting glass-ceramic phosphor of Eu²⁺ activated calcium silicate in the nominal composition of (Ca_{0.99}Eu_{0.01})₃Si₂O₇, which is precipitated with β-Ca₂SiO₄ and SiO₂ crystal phases to form glass-ceramic by one step of quenching the semi-melt liquid instead of previous two steps of quenching the homogeneous pure molten liquid and following heat treatment.

Glass-ceramic sample is prepared by the procedure of quenching the semi-melt liquid in a nominal composition of

* This work has been supported by the National Natural Science Foundation of China (Nos.50872091 and 21076161), and the Key Discipline of Materials Physics and Chemistry of Tianjin (Nos.2006ZD30 and 10SYSYJC28100).

** E-mails: djwang@tjut.edu.cn; jwliu@tjut.edu.cn

$(\text{Ca}_{0.99}\text{Eu}_{0.01})_3\text{Si}_2\text{O}_7$. The starting materials of CaCO_3 (99%), nanometer-sized SiO_2 (99.99%) and Eu_2O_3 (99.99%) are mixed thoroughly in an agate mortar, and then subjected to be precalcined at 1300 °C in a furnace for 3 h in air and cooled to the room temperature. The precalcined powders are mixed with NH_4Cl in an amount of 3 wt%, pressed into a pellet, placed in a platinum crucible, and re-fired at 1300 °C for 6 h under carbon powder surroundings. And then the temperature is increased to 1550 °C rapidly, which is in the solid-liquid (SL) two-phase region of CaO-SiO_2 binary phase diagram shown in Fig. 1^[11], and maintained for 0.5 h. The semi-molten mixture is cast on a preheated brass plate followed by annealing to reduce the residual stress in the sample. The sample exhibits opaque yellow-green color.

Photoluminescence (PL) and PL excitation (PLE) of the glass-ceramics are acquired on a fluorescence spectrophotometer (FL3-2-IHR320-NIR-TCSPC, USA) with a xenon lamp (Xe-lamp) (450 W) as excitation source. The structure of the glass-ceramics is observed with the scanning electron microscopy (SEM) (JEOL JSM-6700F, Japan). Crystallization behaviors of the glass-ceramic are characterized by the X-ray diffraction (XRD) on a D/max-2500/pc diffraction meter (Rigaku, Japan) with the scattering angle range of $10^\circ \leq 2\theta \leq 90^\circ$ at a step of 0.01 with $\lambda_{\text{CuK}\alpha} = 1.54062$ nm. All of these measurements are carried out at room temperature.

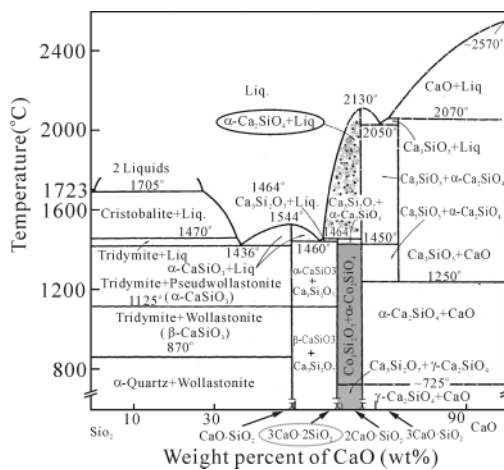


Fig.1 CaO-SiO_2 binary phase diagram^[11]

Fig.2 shows the XRD patterns of the sample. The diffraction patterns correspond to those of $\beta\text{-Ca}_2\text{SiO}_4$ (PDF#83-0461) and those of partially crystallized glassy phase are centered at $2\theta \approx 21^\circ$. So the sample we obtained is a direct glass-ceramic phosphor (named as GC sample) by using the method of quenching semi-mett liquid. In particular, diffraction peaks at $2\theta = 21.417^\circ$ and $2\theta = 27.6^\circ$ are ascribed to those of high-temperature cubic $\alpha\text{-SiO}_2$ (PDF # 85-0621) and low-temperature orthorhombic $\beta\text{-SiO}_2$ (PDF # 86-1563), respectively.

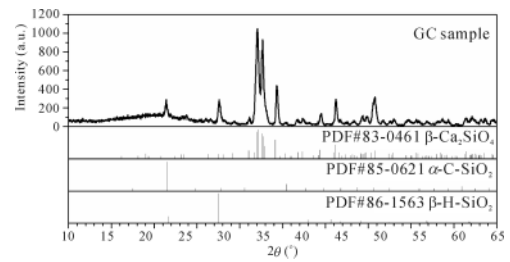


Fig.2 XRD patterns of the glass-ceramic sample

Fig.3 shows PL and PLE spectra of GC sample together with those of $\beta\text{-Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ powdered phosphor for comparison. It is observed that the broad band emission of glass-ceramic sample is centered around 510 nm, which can be stimulated effectively by near UV to the blue-violet light in the range of 300–440 nm with the peak at 365 nm. Differences between the spectra of powdered phosphor and GC sample are that the PL spectrum for powder phosphor is peaked at 505 nm with a full width at half maximum (FWHM) of 75 nm, while for GC sample it is peaked at 510 nm with a FWHM of 122 nm, and the intensity of PLE spectrum of GC sample by blue-violet light is enhanced compared with the powder sample.

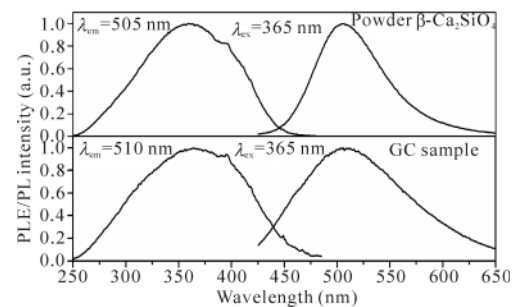
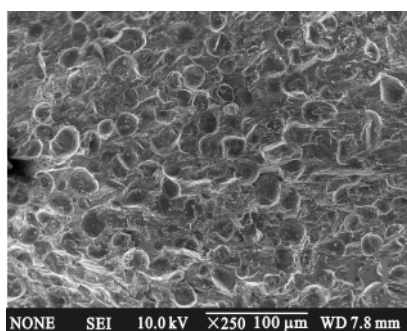


Fig.3 PLE/PL spectra of the glass-ceramic sample and the $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ powder phosphor for comparison

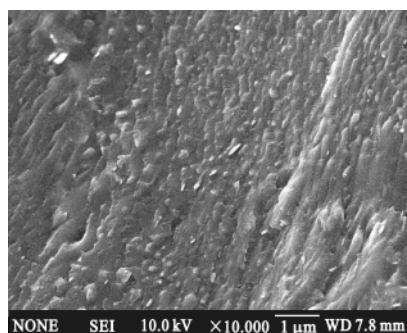
Fig.4 shows the SEM images of GC sample. As shown in Fig.4(a), a large number of spherical particles are distributed uniformly with the mean size around 30 μm in the glass matrix. Fig.4(b) shows the morphology around spherical particles, which exhibits that many elongated particles in average size of several hundred nanometers and much smaller spherical particles appear in the glass matrix.

The occurrence of the precipitated crystals as mentioned above could be interpreted from the CaO-SiO_2 binary phase diagram (Fig. 1). It is recognized that when the ratio of starting materials is in a composition of $3\text{CaO} \cdot 2\text{SiO}_2$, the mixture of $\alpha\text{-Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ and nanometer-sized $\alpha\text{-SiO}_2$ powders in high crystallinity is obtained as precalcined in air at 1300 °C for 3 h followed by re-fired at 1300 °C for 6 h with carbon powder. Increasing the temperature rapidly to 1550 °C, i.e. SL two-phase region of “Liq.+ $\alpha\text{-Ca}_2\text{SiO}_4$ ” in CaO-

SiO₂ binary phase diagram, the raw material is semi-melted and hold for 0.5 h, and part of the nanosized unreacted α -SiO₂ and resultant α -Ca₂SiO₄:Eu²⁺ are melted and decomposed into individual ions of Ca²⁺, Eu²⁺, Si⁴⁺ and O²⁻. Once quenched from the high-temperature in SL region, the glass matrix is formed, consisting of [SiO₄] island-like tetrahedrons connected by Ca²⁺ and Eu²⁺ ions. A large number of unmelted α -Ca₂SiO₄:Eu²⁺ spherical particles in mean size of 30 μ m and unmelted nano α -SiO₂ spherical particles are surrounded by sticky amorphous glass. Another part of SiO₂ single crystal particles, in the form of cubic in average size of several hundred nanometers, are precipitated from glass matrix in sheet shape to reduce the elastic strain, as the silicon-rich liquid is quenched simultaneously. The phase of α -Ca₂SiO₄ is eventually transformed into the metastable phase of β -Ca₂SiO₄, and a part of high-temperature α -SiO₂ is transformed into a stable phase of β -SiO₂ in the process of rapid cooling to room temperature.



(a) Spherical particles



(b) Morphology around spherical particles

Fig.4 SEM images of GC sample

The emission spectrum of GC tends to be wider than that of powder. As heated in the SL region for a short duration of 0.5 h, the particles of β -Ca₂SiO₄ are not melted instantly owing to delay of heat transfer. Most of Eu²⁺ ions remain in the unmelted β -Ca₂SiO₄ crystal particles, and a small part of them are melted together with β -Ca₂SiO₄ crystal particles into the glass. The emission of Eu²⁺ in both β -Ca₂SiO₄ crystal par-

ticles and glass matrix makes the emission spectrum of GC broaden. The phenomenon, which is the excitation spectrum of GC is broader than that of the powder sample, indicates that the glass matrix can transfer excitation energy to the Eu²⁺ effectively.

For glass-ceramic, in terms of Rayleigh scattering theory, there exists a positive relationship between τ and k^8R^7 , where τ represents turbidity, $k=2\pi/\lambda$ is wave vector and R is grain radius^[12]. Due to the mean size of Ca₂SiO₄ spherical particles in GC sample is about 30 μ m which is much larger than the wavelength of visible incident light, the sample is opaque.

The efficient green-emitting glass-ceramic sample precipitated with Ca₂SiO₄:Eu²⁺ crystals is obtained through the method of quenching semi-melt liquid in terms of a SL two-phase region of CaO-SiO₂ binary phase diagram in nominal composition of (Ca_{0.99}Eu_{0.01})₃Si₂O₇ instead of homogenized molten liquid. The opaque appearance of the sample is determined by the size of Ca₂SiO₄:Eu²⁺ spherical particles around 30 μ m precipitated in the glass matrix based on the Rayleigh scattering theory. Broad band emission of the sample centered around 510 nm can be stimulated effectively by near ultraviolet (UV) to the blue-violet light in the range from 300 nm to 440 nm, which can make the sample potential for phosphor-converted high-power LEDs.

References

- [1] X. B. Luo and S. Liu, IEEE T Adv. Packaging **30**, 475 (2007).
- [2] S. Liu, J. H. Yang, Z. Y. Gan and X. B. Luo, Int. J. Therm. Sci. **47**, 1086 (2008).
- [3] R. H. Horng, C. C. Chiang, Y. L. Tsai, C. P. Lin, K. Kan, H. I. Lin and D. S. Wu, Electrochem Solid St **12**, H222 (2009).
- [4] M. Arik and A. Setlur, Int. J. Energ. Res. **34**, 1195 (2010).
- [5] S. Fujita, A. Sakamoto and S. Tanabe, IEEE J. Sel. Top. Quant. **14**, 1387 (2008).
- [6] S. Tanabe, S. Fujita, A. Sakamoto and S. Yamamoto, Glass Sci. Technol. **78**, 33 (2005).
- [7] A. Arvind, A. Sarkar, V. K. Shrikhande, A. K. Tyagi and G. P. Kothiyal, J. Phys. Chem. Solids **69**, 2622 (2008).
- [8] L. Cormier, O. Dargaud, N. Menguy, G.S. Henderson, M. Guignard, N. Trcera and B. Watts, Cryst. Growth Des. **11**, 311 (2011).
- [9] H. Hijiya, T. Kishi and A. Yasumori, J. Ceram. Soc. Jpn. **117**, 120 (2009).
- [10] T. Nakanishi and S. Tanabe, IEEE J. Sel. Top. Quant. **15**, 1171 (2009).
- [11] E. M. Levin and H. F. McMurdie, Phase Diagrams for Ceramists, Supplement, 104 (1975).
- [12] S. Hendy, Appl. Phys. Lett. **81**, 1171 (2002).