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Luminescent low temperature co-fired ceramics for high power LED package

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ABSTRACT

A kind of luminescent low temperature co-fired ceramics (LTCC) for high power LED package was developed. CBS ($CaO—B_2O_3—SiO_2$) glass-ceramic doped with Eu^{3+}, Bi^{3+} was prepared by sol–gel process and its sintered bodies were characterized by fluorescence spectrophotometer, X-ray diffraction (XRD), scanning electron microscopy (SEM). It is found that the optimal sintering temperature for this glass-ceramic is 875 °C, and the major phases of this material are $CaSiO_3$, CaB_2O_4 and SiO_2. The glass-ceramic possesses good yellow-red emission under 395 and 465 nm excitation, excellent dielectric properties: $\varepsilon_r = 3.94$, $\tan\delta < 0.002$ at 1 MHz. Thus, this material is supposed to be used as the LTCC substrate material for the application in white LED packaging.

1. Introduction

Nowadays, heat dissipation management is a big challenge for high power light-emitting diodes (LEDs) packaging. Currently, a very important method for solving this problem is to use low-temperature co-fired ceramics (LTCC) as a substrate. Selecting an appropriate ceramic which can be co-fired with the conductive materials (such as Ag, Cu and Au) at the temperature less than 900 °C and then obtaining multi-component, or embedding the passive components in multilayer circuit boards become the inevitable requests for this trend [1–3]. The LTCC materials are mainly added with an appropriate amount of sintering additives (low melting point oxides or low melting point glasses) to the dielectric ceramics system, by the mechanism of liquid-phase sintering to promote the material densification [4,5]. For example, the sintering temperature of the $CaO—B_2O_3—SiO_2$ system will be lowered to 900 °C by adding B_2O_3, Bi_2O_3 or others [6–8].

However, due to the phosphor coating layer materials around the LED chip are meanly high thermal resistance composites of epoxy or silicone, it is hard to solve heat transfer problem by only using LTCC substrate. In this study, we develop an efficient light-emitting LTCC material. Our design is to directly sinter phosphor in LTCC, thus the chip can be embedded into the LED lamp in the future. In this way, the new material system can be used in the white LED packaging for improving light extraction, solving heat transfer problem and the manufacturing process will be simplified [9–11].

2. Experimental procedure

A simple sol–gel method was utilized to prepare $CaO—B_2O_3—SiO_2$: Eu^{3+}, Bi^{3+} glass powder. Analytical reagent-grade $CaCO_3$, $Si(OC_2H_5)_4$(TEOS), C_2H_5OH, H_3BO_3, Eu_2O_3 (99.99%), Li_2CO_3 and Bi_2O_3 were chosen as starting materials. The molar ratio of $CaCO_3$ to TEOS and B_2O_3 was 1.5:6:5. $CaCO_3$, Eu_2O_3, Li_2CO_3 and Bi_2O_3 were dissolved in HNO_3 and H_3BO_3 was dissolved in distilled water. Then TEOS was dissolved in C_2H_5OH and a volume ratio of C_2H_5OH to TEOS was 4:1. The two solutions were mixed and stirred for 2 h at 75 °C to form gels. At this time, the pH value was adjusted to be ~2 by use of HNO_3 and a mole ratio of H_2O to TEOS was 20:1. The glass powder was prepared by heating the formed gel in an oven at 95 °C for 8 h and at 600 °C for 3 h in a furnace. The powder was milled with a mixture of agate balls in different diameters of 5–30 mm to obtain an average particle size of less than 5 μm. After being mixed and milled for 24 h, the several materials would be very uniform in compositional distribution. Then, the glass powder prepared above was mixed with an amount of polyvinyl alcohol (PVA, 10 wt%), uniaxially pressed under a pressure of 20 MPa to obtain the green compacts with diameters of 10 mm and thicknesses of 1.5 mm, and then sintered in air at different temperatures for 3 h.

Photoluminescence excitation (PLE) and photoluminescence (PL) spectra were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer. The microstructures were observed by scanning electron microscopy (SEM SSX-550). The phase composition of the obtained samples was characterized by X-ray diffraction (XRD S7000) with Cu Kα radiation. The dielectric properties were measured by impedance analyzer (HP 4278A Network Analyzer) at 1 MHz. The bulk densities of the sintered sample were measured by the Archimedes method. The thermal expansion coefficient of the sample was measured by thermal analyzer (NETZSCH DIL 402 PC). The flexural strength was tested by electronic universal testing machine (EHF-10L).

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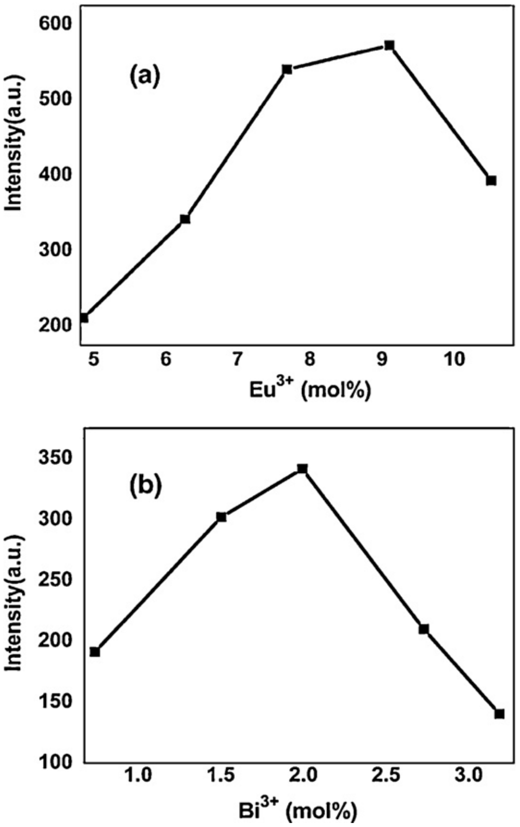

Fig. 1. (a) Effect of Eu^{3+} concentration on the luminescence intensity of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$ LTCC. (b) Effect of Bi^{3+} concentration on the luminescence intensity of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$ LTCC.

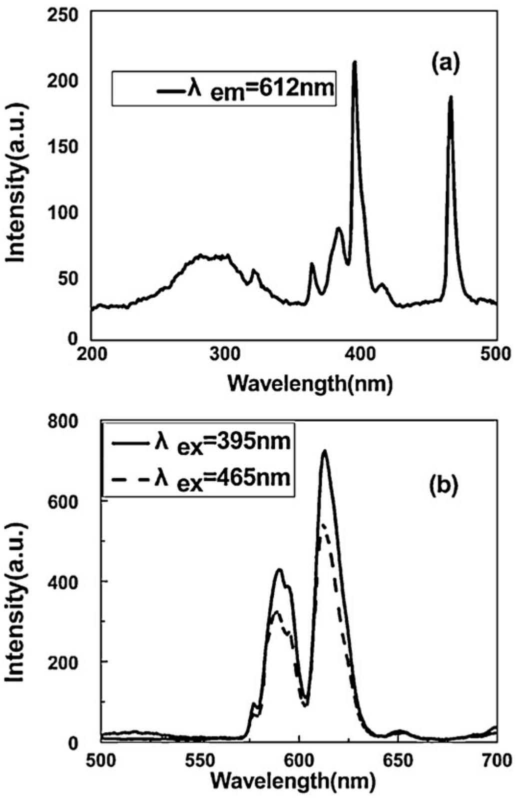

Fig. 2. (a) Excitation spectra of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$. (b) Emission spectra of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$.

3. Result and discussion

The dependences of luminescence intensity of $^5D_0 \to {}^7F_2$ (612 nm) transition, monitored under 465 nm, on Eu^{3+} concentration (x) in $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: Eu^{3+}, Bi^{3+} LTCC are shown in Fig. 1(a). The yellow-red emission intensity of LTCC increases with increasing Eu^{3+} concentration, maximizing at about $x = 9$ mol% and then the intensity decreases gradually owing to the energy transfer between the neighboring Eu^{3+} ions, which was corresponding to the quench of the emission of Eu^{3+} [12,13]. While the luminescence intensity is also sensitive to the concentration of compensator ions, such as Bi^{3+} [14]. When the doped amount of Eu^{3+} is 9 mol%, Bi^{3+} ions have the best charge compensation effect. The results show that the emission intensity reaches the maximum when the Bi^{3+} content is about 2 mol% concentration as shown in Fig. 1(b).

As shown in Fig. 2(a), the excitation spectrum (monitored at 612 nm) of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$ shows a broad band expanding from 200 to 350 nm which was from the charge transfer between the Eu^{3+} and its surrounding oxygen atoms, and a group of sharp-lines such as $^7F_0$–$^5L_6$ line at around 395 nm and $^7F_0$–$^5D_2$ line at around 465 nm, which are coupled well with the characteristic emission from UV-LED and blue LED, respectively. Fig. 2(b) shows the emission spectrum of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$ (sintered at 875 °C for 3 h) under 395 and 465 nm excitation. The emission spectrum shows several emission bands at 585 nm, 612 nm, and 650 nm, corresponding to the electric dipole $^5D_0 \to {}^7F_1$, $^5D_0 \to {}^7F_2$, and $^5D_0 \to {}^7F_3$ transition of Eu^{3+} respectively, while the emission intensity at 612 nm is stronger than the others.

The color coordinates ($x = 0.62301$, $y = 0.37565$) of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$ in the CIE 1931 chromaticity diagram is represented in Fig. 3, which indicate that

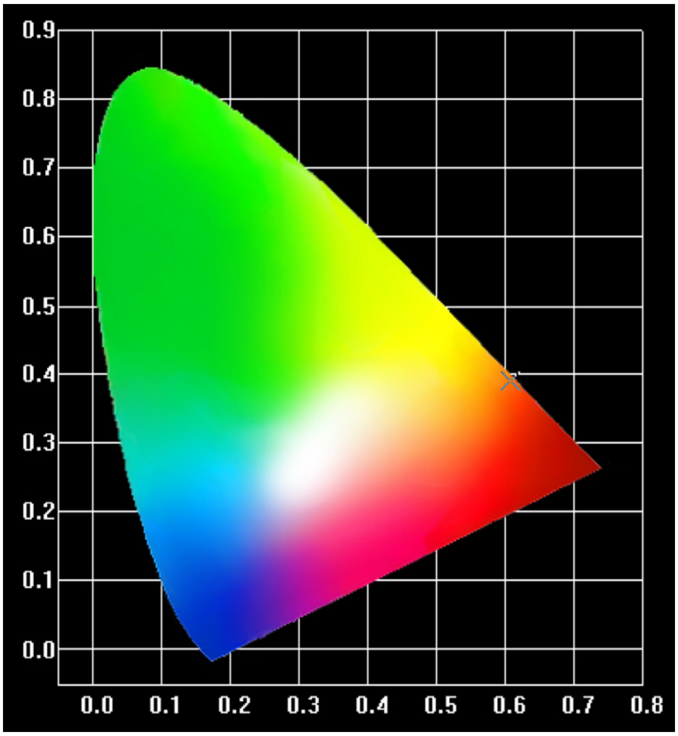

Fig. 3. Color coordinates of $\mathrm{CaO{-}B_2O_3{-}SiO_2}$: $0.09Eu^{3+}$, $0.02Bi^{3+}$ in CIE chromaticity diagram. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

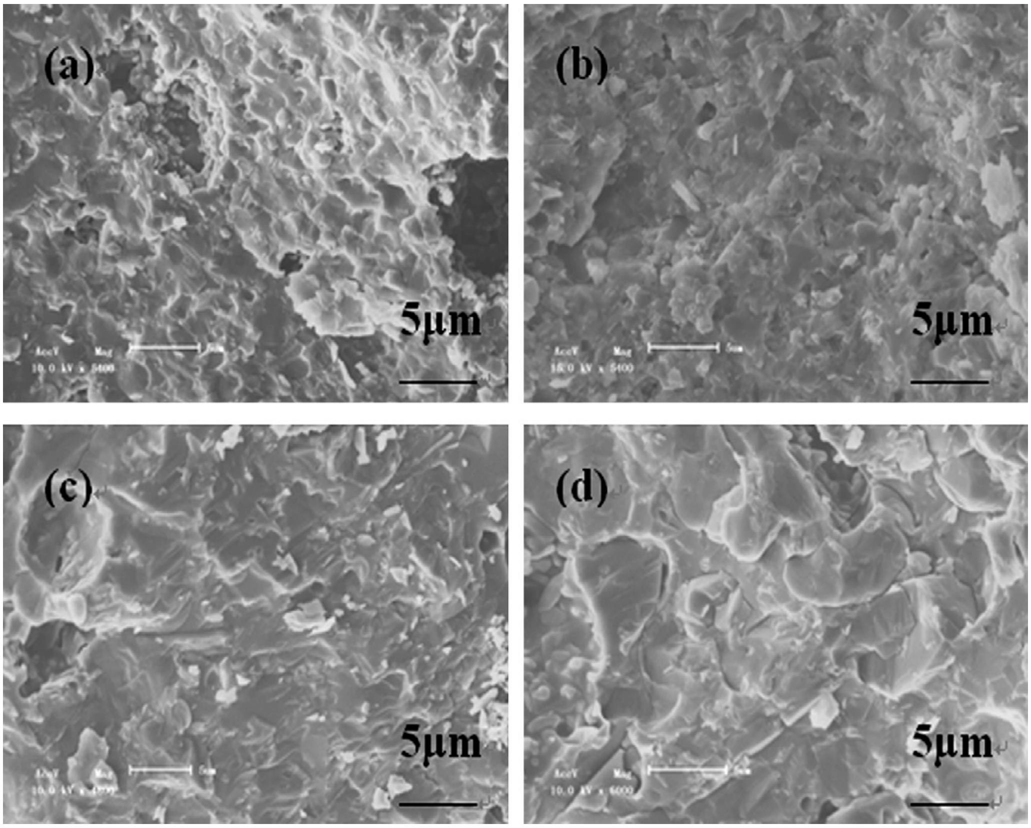

Fig. 4. SEM photographs of fractured sections of the samples sintered at different temperature: (a) 825 °C, (b) 850 °C, (c) 875 °C and (d) 900 °C.

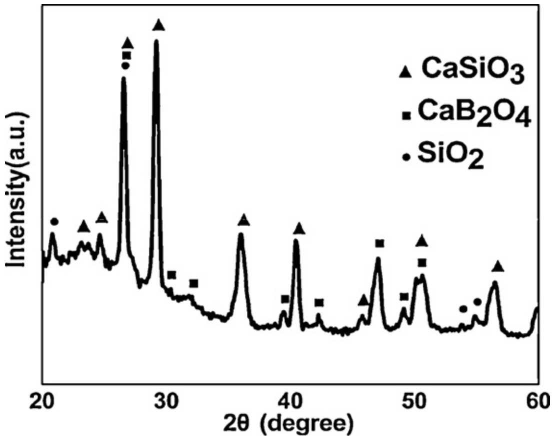

Fig. 5. XRD spectra of the sample sintered at 875 °C.

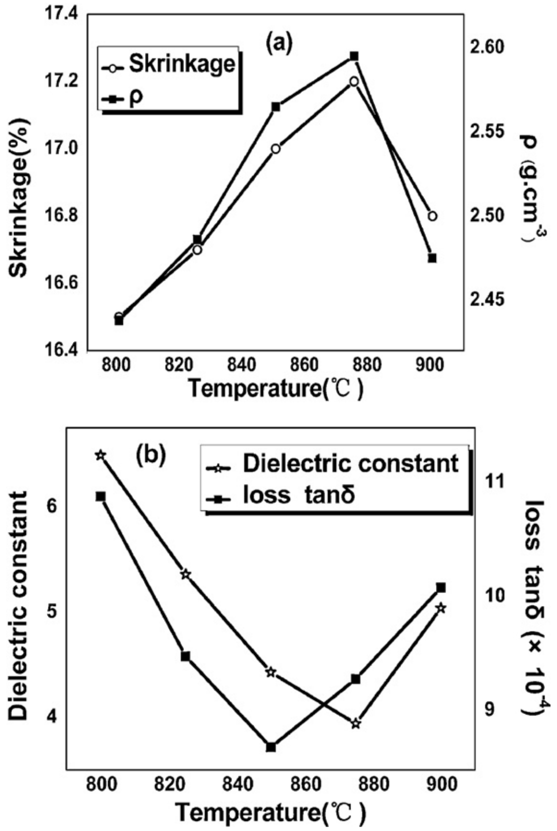

Fig. 6. The properties of the sample sintered at different temperatures. (a) Shrinkage and density. (b) Dielectric properties.

$CaO—B_2O_3—SiO_2$: $0.09Eu^{3+}$, $0.02Bi^{3+}$ glass-ceramics will be useful as yellow-red luminescence materials [14,15].

Fig. 4 shows the SEM photographs of the fracture surface of the samples sintered at different temperatures. It seems that the particles are only partially sintered together at 825 °C, many connected open pores could be seen. With the sintering temperature increasing, the glass softening occurs, mobility increases, the opening-connected pores gradually become similar. When the sintering temperature is up to 850 °C, the pores would be covered by a large number of glass phases. However, there is still a certain amount of cross-sections at the existence of large-size pores. When the sintering temperature is further increased to 875 °C, there are only a small amount of sample cross-sections of small and scattered closed pores, and the densification of the sample reaches the maximum.

Fig. 5 shows the XRD patterns of the sample sintered at 875 °C which the maximum density was achieved. It is indicated that the glass-ceramic is mainly composed of crystalline phases of $CaSiO_3$, CaB_2O_4 and SiO_2 [16,17]. In addition, there is no peak related to Eu^{3+} and Bi^{3+} indicating the doping ions cannot form new phase at the synthesis temperature.

Fig. 6(a) is the curves of shrinkages and densities of the sample sintered at different temperatures. The results demonstrate that shrinkage of the samples increases with the sintering temperature gradually increased, and reach the maximum at 875 °C. Meanwhile, the densities of the samples also increase gradually with the sintering temperature increasing. At 875 °C, the samples reach the maximum degree of compaction with shrinkage rate about 17% and density of about 2.6 g cm^{-3}.

For microelectronic packages, the requirements of high signal transmission speed and low loss at high frequency are substrate materials of low dielectric constant (ε_r) and loss ($\tan\delta$). According to the plots of Fig. 6(b), $CaO—B_2O_3—SiO_2$: Eu^{3+}, Bi^{3+} compacts reached a minimum of dielectric value ($\varepsilon_r = 3.94$ and $\tan\delta = 9.3 \times 10^{-4}$ (1 MHz)) in the range of 825–875 °C, which was a better result than the dielectric properties of $CaO—B_2O_3—SiO_2$ glass-ceramic [18]. In this investigation, the presence of Eu^{3+} and Bi^{3+} in the composition may improve sintering behavior.

4. Conclusions

We prepared $CaO—B_2O_3—SiO_2$ system low temperature co-fired ceramics doped with Eu^{3+}, Bi^{3+} and studied the luminescence properties, sintering characteristics, microstructure, phase composition, dielectric properties, as well as dielectric loss and other features. The best contents of Eu^{3+} and Bi^{3+} in the system glass-ceramics are 9 mol% and 2 mol%. They can achieve maximum densification sintering at 875 °C. The sintered samples have a low dielectric constant $\varepsilon_r = 3.94$, a low dielectric loss $\tan\delta < 0.002$, lower coefficient of thermal expansion ($7.6 \times 10^{-6}\,K^{-1}$), a high flexural strength (140 MPa). The main properties of this material have reached the requirements of LTCC technology. So the material can be applied as ceramic substrates, resonators and other electronic devices as well as in other areas of microelectronic packaging materials, including the white LED packaging.

Acknowledgments

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