Research on the structure and luminous property of CaO-MgO-SiO_2- Al_2O_3-TiO_x luminous glass

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It was found that blast furnace slags emit yellow light under UV light excitation. By simulating the components of blast furnace slags, CaO-MgO-SiO_2- Al_2O_3-TiO_x (CMSAT) emission glass was designed and prepared to explore the relation between the emission characteristics and the structure of blast furnace slags. Through XRD, FT-IR and DSC analyses, the network structure were investigated, and luminous properties were explored by PL spectra analyses. It is to explore a new approach of direct functional materials of the complex silicates system.

(Received April 13, 2015; accepted April 5, 2016)

Keywords: Blast furnace slags, Luminescent glass-ceramics CMSAT, Network structure, Thermal stability

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1. Introduction

Water-quenching blast furnace slags include 95% to 97% of amorphous vitreous with network structures [1]. Their components are basically stable, comprised of 35~44 wt% CaO, 32~42 wt% SiO_2, 6~16 wt% Al_2O_3, 4~13 wt% MgO and a trace of oxides for Fe, Mn, and Ti. As all are main matrix and light-emitting central ions of luminous crystal silicates. And we found that blast furnace slags yellow under UV-light excitation. Nowadays there are plenty of researches on preparation of glass ceramics from blast furnace slags for glass with microcrystal possesses mechanical property, good thermal resistance, low expansion and high strength. [3-6] But, to date, there is few researches on direct preparation of luminescent glass with microcrystal form blast furnace slags.

Based on this interesting phenomena, simulating the composition and structure of blast furnace slags, CMSAT was designed and prepared to study Ti^{4+} ions concentration, network structure impacting on the luminescent characteristics. DSC analyses was performed for the thermal stability of luminescent glass of CMSAT.

2. Experimental

All reagents are analytical reagents. In accordance with ratio in Table 1, CaO, SiO_2, Al_2O_3, MgO and TiO_2 were mixed and ground thoroughly. Then the mixtures were put in 20 ml corundum crucible. At the heat rate of 3℃/min, the reactants were heated to about 1400 °C (the melting temperature of blast furnace slags is 1250~1400 °C) in silicon molybdenum furnace and kept for 2 hours. One of the following preparation method can be selected to develop CMSAT emission glass. First, the glass liquid was quenched by water and dried at 120℃ for 2 hours in drying oven, and the glass particles were collected. Second, the glass liquid was put into ductile iron mold and preserved at temperature lower than glass transition temperature for 2 hours to eliminate the inner stress of glass(the annealing temperature set in accordance with the glass transition temperature by DSC analysis of water-quenched blast furnace slags), and then begin to cool in the furnace. At last, the glass sheet was obtained from the mold, ground and polished. Specific preparation processes are shown in Fig. 1.

Table 1. The compositions of CMSAT(mol%)

Number	SiO_2	CaO	Al_2O_3	MgO	TiO_2
CMSA	34.10	45.13	10.54	10.23	0
CMSAT	33.762	44.683	10.431	10.125	1.0

The structure of CMSAT was carried out using American Thermo Nicolet 6700 Fourier transform infrared spectrometer (FT-IR). The glass particles should be ground to about 10 μm powder, combined with KBr crystals and pressed into one Φ10 mm wafer, which was used to detect infrared spectrum in the range of 400-2000cm^{-1}. The absorption spectrum of sample was tested by Germany Jena Company SPECORD PLUS UV-Vis spectrophotometer, slit width 0.5 nm, scanning range 190-600 nm, scanning speed 50 nm/ min. The emission spectrum of CMSAT glass powder was carried out by Japan Hitachi F-4600 fluorescence spectrometer, slit width 2.5 nm, 150 W Germax lamp used as excitation light source, photomultiplier tube voltage 500V, scanning speed 240 nm/ min. The differential scanning calorimetry (DSC) analysis of CMSAT was checked by Germany Netzsch company STA449C simultaneous thermal analyzer, argon gas protection, the speed rate of increasing temperature 10 °C/min, scanning temperature range from room temperature to 1400 °C. All experiments were done at room temperature.

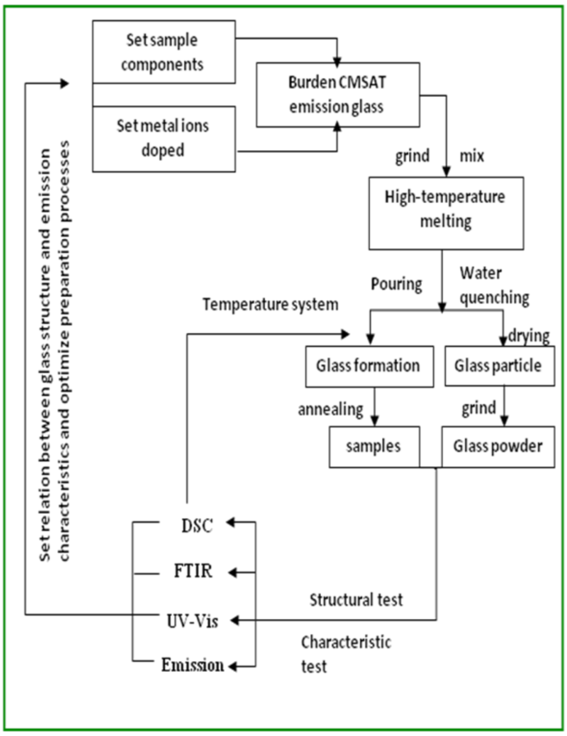

Fig. 1. Preparation processes of CMSAT

3. Results and discussion

In the network structure of CMSAT glass, SiO_2 exists as $[SiO_4]$ tetrahedrons and Al_2O_3 forms $[AlO_4]$ tetrahedrons. In the general, if $(R_2O+RO)/Al_2O_3>1$ in silicates glass, Al^{3+} ions are considered as occupying the core of $[AlO_4]$ tetrahedrons so act as network forming ions in CMSAT glass [7]. MgO and CaO act as network modifiers. Ti ions mostly present in the octahedral and tetrahedral gaps of the network structure and do not participate in the network structure for they own larger ionic radii and their content is low in the CMSAT glass. The infrared absorption of the glass is primarily attributed to the vibration of the binding bond between cations and anions in anionic groups. So the infrared spectrum is dominated by network forming system, basically not affected by a little of cations as network modifiers. [8] Therefore, in the aluminum silicates glass system, the coordination states of Al^{3+} and Si^{4+} ions can reflect the change of the glass network to a certain extent.

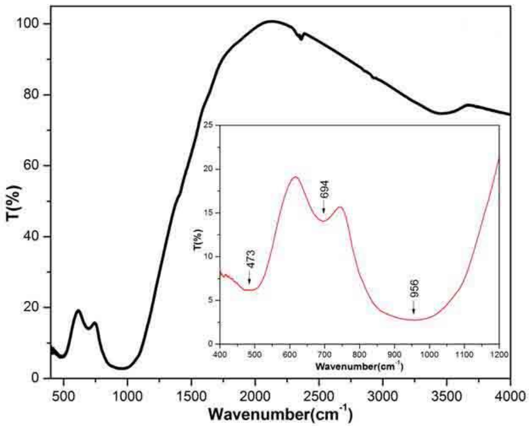

Fig. 2. IR spectrum of CMSAT in the range of 400~4000cm^{-1}

Fig. 2 depicts the infrared spectrum of CMSAT glass. There are several weak absorption bands in range of 2000-2500 cm^{-1} and at 3500 cm^{-1} or so, ascribed to water or O-H group owning a series of vibration [8, 9]. The right insert figure of Fig. 3 presents that there three strong and wide absorption peaks in the range of 400-1200 cm^{-1}. The strongest absorption band lies among 750-1200 cm^{-1}, of which the main peak is at about 956 cm^{-1}. The second strong absorption presents among 400-600 cm^{-1}, of which the main peak is at about 473cm^{-1}. Among 620-750 cm^{-1} exists one weak absorption band, of which the main peak is at about 694 cm^{-1}.

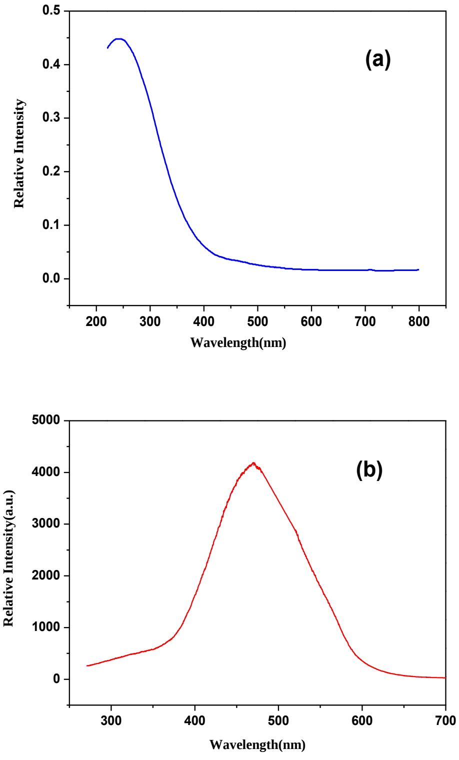

Fig. 3. UV-VIS absorption spectrum of CMSAT(a) and emission spectra of a CMSAT (λ_{ex}=250nm)(b)

Referring to the infrared spectra of calcium (magnesium) aluminosilicate glass system [8, 10-13] and alkali metal / alkaline earth metal silicate glass system [14-19], it is concluded from the research of calcium aluminosilicates glass and calcium silicates glass that, three obvious characteristic bands among 400-1200cm^{-1}, are considered as the characteristic bands of [SiO_4] tetrahedrons and [AlO_4] tetrahedrons. That is to say that these characteristic bands indicate the changes and characteristics of glass network structure including [SiO_4] tetrahedrons and [AlO_4] tetrahedrons. Due to the network structure of CMSAT glass composed of [SiO_4] tetrahedrons and [AlO_4] tetrahedrons, the 400-600cm^{-1} absorption band is ascribed to the bending vibration of Si-O-Si, Si-O-Al, O-Si-O and Si-O^{-1} bond, the 620-750cm^{-1} absorption band attributed to the bending vibration of Si-O-Si and Si-O^{-1} bond and the stretching vibration of Si-O-Al and Al-O-Al bond, and the 750-1200cm^{-1} absorption band considered as the asymmetric bending vibration of Si-O-Si, Si-O^{-1} and Al-O^{-1} bond.

In summary, the network structure of CMSAT is mainly constituted by [SiO_4] tetrahedrons and [AlO_4] tetrahedrons. [SiO_4] and [AlO_4] groups share the top corner oxygen. Ca^{2+}, Mg^{2+} and Ti ions come into the network gaps of [SiO_4] tetrahedrons and [AlO_4] tetrahedrons, and form Si-O-R or Al-O-R(R=Ca,Mg,Ti).

Fig. 3 (a) presents the absorption spectrum of CMSAT. There is the strong and wide band at below 400 nm, of which the main peak situates at about 250 nm. So 250 nm is selected as excitation wavelength. Fig. 3(b) indicates the emission spectrum of CMSAT glass by excitation at 250 nm. The emission band covers the range of 250-620 nm from the characteristic emission of Ti^{4+} ions, of which the main peak lies at 470 nm, its width at half maximum (FWHM) 129 nm. Compared to Ti^{4+} ions' luminescent property, the luminescent ability of silicates matrix is weaker and can be ignored. So adjusting Ti^{4+} ions concentration (T0-0.5 mol%, T1-1.0 mol%, T2-2.0 mol%, and T3-3.0 mol%) is performed to explore the luminescent characteristics of CMSAT. With Ti^{4+} ions introduced into CaO-MgO-SiO_2-Al_2O_3 matrix, the emission ability of CMSAT strengthens obviously. So it is thought that blast furnace slags yellowing is mostly ascribed to transition metals ions' occurrence and trend such as Ti^{4+} ions, of which the optimistic doped amount is 1 mol% in Fig. 4(a)(obtaining the same results under 235 nm, 250 nm, or 280 nm excitation). The shorter excitation wavelength (280 nm→250 nm →235 nm), the stronger emission intensity (1460 a.u. in Fig. 4(b) →4510a.u. in Fig. 4(c)→4830 a.u. in Fig. 4(a)). This phenomenon is consistent to the photoluminescence spectra of CMSAT1 under 235 nm, 250 nm, or 280 nm excitation in Fig. 4(d).

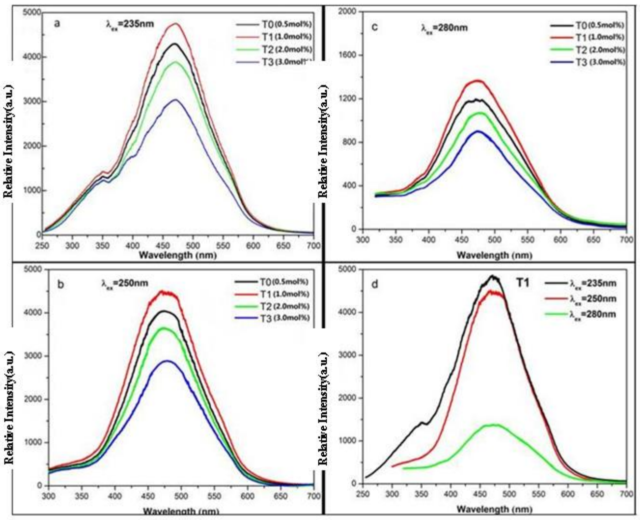

Fig. 4. The emission spectra of CMSAT under different T^{4+} concentration

Fig. 5 shows DSC curve of CMSAT glass. There are six temperature transition points, such as T_g (endothermic peak), T_c(crystallization onset temperature points), T_{P1}(exothermic crystallization peak), T_{P2}(exothermic crystallization peak), T_{m1} (endothermic melting peak), and T_{m2}(endothermic melting peak). T_g lies at 748℃, endothermic peak, which is glass transition point temperature. T_{P1} and T_{P2} present at 1048℃ and 1077℃, respectively, exothermic peaks. According to the phase diagram of CaO-10 wt %Al_2O_3-MgO-SiO_2 and CaO-Al_2O_3-10 wt%MgO-SiO_2 [20-25], at T_{P1}, calcium aluminum Melilites (2CaO • Al_2O_3 • SiO_2), akermanites (2CaO • MgO • 2SiO_2) and metastable phase merwinites (3CaO •MgO •2SiO_2) present. At T_{P2}, calcium aluminum Melilites (2CaO • Al_2O_3 • SiO_2), akermanites (2CaO • MgO • 2SiO_2), wsollastonites (CaO • SiO_2) and oblique wollastonites (2CaO • SiO_2) begin to form. To two endothermic peaks, Fredericci [7] and Gan [21] thought that the endothermic peak at T_{m1} is attributed to akermanites melting and the endothermic peak at T_{m2} is ascribed to calcium aluminum Melilites melting.

Table 2. DSC analysis of CMSAT glass

	T_g(℃)	T_c(℃)	T_{P1}(℃)	T_{P2}(℃)	T_{m1}(℃)	T_{m2}(℃)
CMSAT	748	937	1048	1077	1287	1322

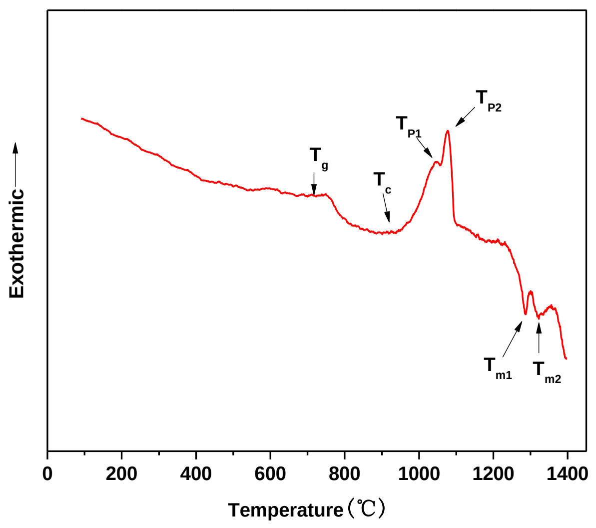

Fig. 5. DSC curve of CMSAT

The stability of glass is defined as the resistance ability in losing transparent state during re-heating processes, especially close to or slightly above the range of glass transition temperature (T_g) [26]. It is a common method to express the thermal stability of the glass expressed by the difference between crystallization starting temperature and glass transition temperature ($\Delta T = T_c - T_g$). The biggest ΔT value corresponds to the best the thermal stability of the glass [27]. ΔT value is calculated as follows and the results are listed in Table 2.

$$\Delta T = T_c - T_g = 937 - 748 = 189℃$$

$$K_{gl} = (T_c - T_g)/(T_{m1} - T_{P1}) = (937 - 748)/(1287 - 1048) = = 0.7908$$

The calculated result is $\Delta T \geq 100℃$ [28].

That means CMSAT glass with good thermal stability.

According to the above analyses, the softening temperature is about 748℃. Due to the nucleation temperature of the CMSAT glass higher than its softening temperature [7], so the annealing temperature should be controlled below the temperature (748℃).

4. Conclusions

CMSAT glass was prepared with the doping amount of 1 mol% Ti ions by simulation the components and network structure of blast furnace slags. CMSAT's network structure is mainly composed of by $[SiO_4]$ tetrahedrons and $[AlO_4]$ tetrahedrons, which share the top corner oxygen. Ca^{2+}, Mg^{2+} and Ti^{4+} ions come into the network gaps of $[SiO_4]$ tetrahedrons and $[AlO_4]$ tetrahedrons, forming Si-O-R or Al-O-R(R=Ca,Mg,Ti), which maintains CMSAT's stable network structure. So CMSAT glass possesses better emitting characteristics. In the PL spectrum, there is one broad peak at 470 nm excited by 235 nm light, its HWHM 136 nm. And CMSAT glass possesses better thermal stability. In the future, this method plays an important role in developping $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$-Rare earth oxides luminous glass for LED illumination and display applications.

Acknowledgments

The authors are grateful for Anhui Provincial Natural Science Foundation of Education Agency of PR China (No.KJ2011Z032), and Anhui Provincial Natural Science Foundation of Science and Technology Agency (No. 1408085ME78) of PR China.

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