Comparison of the melting properties of glass substrates for thin film transistor liquid crystal display and organic light-emitting diode

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ABSTRACT

The melting properties of two kinds of glass substrates for thin film transistor liquid crystal display (TFT-LCD) and organic light-emitting diode (OLED) were investigated. Chemical reaction process of the batches was similar for two substrates determined by DSC-TG test. The ascending behavior of bubbles with different fining agents of two substrates were studied by High-temperature imaging observation (HTO) test. Viscosity and surface tension for the glass melt were investigated. The results showed that tin dioxide (SnO2) exhibited better fining effect than stannous oxide (SnO), both for TFT-LCD and OLED substrates. For OLED substrate, it took more time to approximate the steady state for fining process due to its higher viscosity and higher surface tension. The molten resistance of these two substrates was also determined, which could provide some reference for the design of electrode in mass production. And the effect of grain size distribution of raw material silica sand on the melting quality of bulk glass samples was also developed. Silica sand with 150–200 mesh exhibited the best melting and fining effect.

1. Introduction

Glass substrates are used in display technologies, such as televisions, notebook computers, flat-panel desktop monitors, and portable electronic devices. These are mainly thin film transistor liquid crystal display (TFT-LCD) and organic light-emitting diode (OLED) applications [1–4]. In the preparation of display devices, some processes need 500–600 °C temperature treatment. Glass substrates should be free from thermal mismatch with film and free from thermal deformation during processing. Under high temperature, alkali metal ions will precipitate from the substrate glass and diffuse into the deposited film, which will degrade the film materials and shorten the display life. So glass substrate must be alkali-free glass, which means more difficulties in the melting and fining process than glass with alkaline. While compared with glass substrate for TFT-LCD, glass substrate for OLED is required to have minimum thermal shrinkage from heat processing during the manufacturing process, higher strain point and Young’s modulus with lower sagging than substrate for TFT-LCD is also needed. Higher thermal stability means more denser structure of glass network. For this kind of alkali free SiO2-B2O3-Al2O3-RO glass system, higher content of SiO2 and Al2O3 than conventional soda lime glass will be inevitable [5–8], which will increase the melting temperature of the glass batch.

In this study, we focused on the comparison of the melting properties of these two kinds of glass substrates. Chemical reaction process of the batch was tested by DSC measurement, while the melting and fining process of the batches were evaluated by High-temperature imaging observation (HTO) test. Furthermore, molten resistance, viscosity and surface tension for the glass liquid were also investigated. And finally, the effect of grain size distribution of main material silica sand on the melting quality of bulk glass samples was also studied.

2. Experimental procedure

2.1. Compositions of glass substrates

Compositions of TFT-LCD substrate and OLED substrate investigated in this study is described in Table 1[5,6]. The total SiO2 and Al2O3 amount was 76.5% (mass fraction) for TFT-LCD substrate, while 80% for OLED substrate.

2.2. High-temperature imaging observation for batch melting and fining tests

The High temperature imaging observation system (HTO) produced by glass service company of Czech Republic shown in Figure 1(a) was used in the test. The HTO system mainly included two parts: high temperature furnace body and image acquisition system. The high temperature furnace body was used to heat the glass batch by heating element of molybdenum...
The maximum heating temperature was 1600°C. The special-shaped crucible used for the test shown in Figure 1(b) was transparent observation crucible made of silica glass, with a Φ 30 × 500 mm hollow cylinder in the top for fixing and a 60 × 40 × 15 mm hollow cuboid in the bottom for holding the glass batch. And the wall thickness of the crucible is 3 mm. The glass batch of about 50 g placed in the crucible.

Table 1. Compositions of glass batches for TFT-LCD and OLED substrate.

| Sample            | Composition/wt.% |
|-------------------|------------------|
| SiO₂ | Al₂O₃ | B₂O₃ | MgO | CaO | SrO | BaO |
| TFT-LCD Substrate | 60.0  | 16.5  | 8.5 | 3.5 | 4.0 | 7.5 | 0   |
| OLED Substrate    | 61.0  | 19.0  | 2.0 | 2.8 | 5.0 | 2.0 | 8.0 |

Figure 1. (a) The visual appearance of the High Temperature Observation (HTO) furnace; (b) The visual appearance of the special-shaped crucible.

Figure 2. The heating procedure for HTO test.
was inserted into the furnace body and heated up with the heating procedure shown in Figure 2.

The image acquisition system recorded the melting state of the glass batch at different temperatures in the form of pictures. By the analysis of the collected pictures in the fixed melting area, with the length of about 15,000 μm and the height of about 12,000 μm as displayed in Figure 3, three groups of data could be obtained: the area fraction of bubbles in the total melting area, the mean bubble size, and the number of bubbles. In this test, the image acquisition system was set to record once every 20 s, and three pictures could be collected every 1 min. All the experiments were carried out under normal atmospheric pressure.

2.3. Bulk glass sample preparation

According to the compositions shown in Table 1, 400 g glass batch placed in a 500 mL platinum crucible was put into a Silicon Molybdenum Furnace to be heated. The melting procedure was as follows: (i) glass batch was heated from 25°C to 1100°C with a heating rate of 10.0 °C/min; (ii) the batch was continually heated from 1100°C up to 1650°C with a heating rate of 2.5°C/min and held for 3 h for fining process; (iii) the glass melt was then poured onto a copper plate to form the bulk sample with the size of 80 × 80 × 20 mm; (iv) the bulk sample was then put into a muffle furnace for annealing. The annealing procedure was as follows: held at 750°C for 2 hours and then cooled down to 80°C with a cooling rate of 1.5°C/min. For the test of viscosity, surface tension and molten resistance of glass, chemically pure reagents were employed for the preparation of glass samples, such as SiO₂, Al₂O₃, H₂BO₃, MgO, CaCO₃, SrCO₃, BaCO₃, SnO₂, SnO.

2.4. Measurement

2.4.1. DSC-TG test of glass batch

In this study, the differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis of glass batches were carried out on Netzsch STA499F5 thermal analyzer. DSC and TG tests could be employed to analyze the mass and heat changes in the process of chemical reaction between materials and silicate formation. About 20 mg of glass batch placed in a platinum crucible was heated up to 1400°C with a heating rate of 10°C/min under the protecting gas of N₂. The DSC and TG curves were recorded with the increase of temperature.

2.4.2. EDS (Energy-dispersive X-ray spectroscopy) test for bulk glass sample

The longitudinal bulk sample with the size of 20 × 20 × 5 mm was divided into 20 small regions (4 × 5 mm), which was then scanned by EDS to acquire the content of SiO₂. The uniformity of composition could be obtained by comparing the minimum and the maximum value of SiO₂ in the different positions of the sample.

2.4.3. Viscosity measurement for glass melt

The viscosity of the glass melt was monitored by rotating viscometer conducted on the Orton RSV-1600 system according to ASTM C965 [9]. The measured temperature varied from 1200°C to 1550°C, and the data were recorded in the cooling process with a cooling rate of 2°C/min.

2.4.4. Surface tension test for glass melt

Surface tension of the glass melt was measured by Sessile Drop method [10–12]. Figure 4(a) showed the diagram of the experimental setup. Details of the chamber for sample was also presented in the figure.

Figure 3. The fixed area for image acquisition analysis of HTO test.
Figure 4. (a) Experimental set-up for measuring surface tension of glass drop: 1. ellipsoid contour of the drop on the monitor; 2. CCD camera and imaging system; 3. horizontal electrical furnace; 4. platinum resistance wire; 5. alumina tube; 6. sample; 7. graphite supporting board; 8. thermocouple; 9. protecting gas (Ar); 10. lighting source; (b) Ellipsoid glass drop on the monitor.

Figure 5. (a) Experimental set-up for measuring the molten resistance of glass: 1. tubular high temperature furnace; 2. Alumina porcelain boat; 3. platinum electrode; 4. molybdenum silicide heating element; 5. glass liquid; 6. thermocouple; 7. Keithley 2410 digital multimeter; 8. power supply; 9. computer. (b) Top view of the crucible used for the measurement: 1. card slot for platinum electrode.
Horizontal electrical furnace with platinum resistance wound on an alumina tube was used for the test. The graphite supporting board was placed in the uniformity zone inside the alumina tube. A Pt-Rh thermocouple connected with the supporting board was used to measure the temperature. During the test, argon was continuously introduced to protect the glass droplet from the influence of oxidation or reduction atmosphere. At the same time, the graphite supporting board could also be protected from oxidation at high temperature.

Glass sample with the size of $1 \times 3 \times 1\ mm$ starts to soften after being heated in the furnace. The shape is naturally ellipsoidal due to the influence of gravity and surface tension as shown in Figure 4(b). The CCD camera projects the outer contour of the sample to the imaging system, and then fits it to get the volume of the droplet. Then, the density and surface tension of the glass drop at high temperature could be obtained. The measured range in this study was $1100 \sim 1400\ ^\circ C$.

2.4.5. Molten resistance measurement
Figure 5(a) shows the scheme of the setup for the molten resistance measurement of glass melt. The bulk glass samples were ground to powder with the size in the range of 0.425–0.850 mm, and then were filled into an alumina porcelain boat with the size of $55 \times 10 \times 15\ mm$. The volume of glass powder was about 80% of the porcelain boat. Two pieces of platinum electrodes were inserted at both ends of the porcelain boat and the electrode lead was led out of the furnace. The boat was then put into a tubular high temperature furnace and heated up to 1600°C for the melting of glass. When a DC voltage ($V$) is applied between the two electrodes, the current ($I$) flowing through the glass melt can be measured by the multimeter. According to Ohm’s law, the resistance of glass liquid can be derived by equation (1) as follows:

$$\rho = \frac{V \times d \times h}{I \times l}$$  \hspace{0.5cm} (1)

where $\rho$ is the resistance of glass melt, $V$ is the DC voltage, $d$ is the width of electrode, $h$ is the height of glass liquid in the boat which can be measured after the measurement, $I$ is the current measured with a Keithley 2410 digital multimeter connected to the platinum electrodes, and $l$ is the distance between two electrodes shown in Figure 5(b), which is a fixed value.

The resistance of glass melt was measured with the temperature decreasing from 1600°C to 1500°C with a cooling rate of 3°C-min$^{-1}$, and data was recorded every 1°C.

2.4.6. Test of gas composition of bubbles in bulk glass samples
For visible bubbles in the prepared bulk glass samples, gas composition of bubbles was determined using GIA 522 gas analysis system [13]. A rectangle sample type with $10 \times 10 \times 1.2\ mm$ with single bubble was prepared for the test.

3. Results and discussion
3.1. DSC-TG test for glass batches
Glass samples with compositions shown in Table 1 could be acquired from glass batches composed of reagent grade raw materials such as SiO$_2$, Al$_2$O$_3$, H$_3$BO$_3$, MgO, CaCO$_3$, SrCO$_3$, BaCO$_3$. The reaction process of the batches could be obtained by DSC-TG test displayed in Figure 6.

Firstly, for TFT-LCD substrate, the endothermic peak and mass loss of 5.56% in low temperature represented the evaporation and the decomposition of boric acid in 123.2°C, 148.2°C and 262.2°C, which could be expressed as $H_3BO_3 \rightarrow HBO_2 + H_2O$ and $2HBO_2 \rightarrow B_2O_3 + H_2O$. Secondly, the endothermic peak at 570.2°C with no mass loss referred to the crystal transition of SiO$_2$ from α - quartz to β - quartz [14]. The peaks at 758.2°C and 813.3°C were related to the decomposition reaction of CaCO$_3$ and the reaction between CaCO$_3$ and SiO$_2$, which could be expressed as CaCO$_3$ → CaO + CO$_2$↑ and CaCO$_3$ + SiO$_2$ → CaSiO$_3$ + CO$_2$↑ [15], and the release of CO$_2$ was responsible for the mass loss of 5.55% in TG curve. The next endothermic peak and mass loss at 943.6°C could be attributed to the decomposition reaction of SrCO$_3$ and the reaction between SrCO$_3$ and SiO$_2$ with the following formula: SrCO$_3$ → SrO + CO$_2$↑ and SrCO$_3$ + SiO$_2$ → SrSiO$_3$ + CO$_2$↑. When the temperature was higher than 1020°C, the mass loss was very slight, suggesting that the decomposition reaction of carbonate was finished till 1020°C. From this stage on, all the reactions were combination reaction between oxides, such as MgO + SiO$_2$ → MgSiO$_3$, CaO + SiO$_2$ → CaSiO$_3$ and SrO + SiO$_2$ → SrSiO$_3$. Finally, an exothermic peak occurred in 1261.1°C, which was related to the formation of mullite from Al$_2$O$_3$.

For OLED substrate, similar thermodynamic reaction process to TFT-LCD substrate was observed due to their similar compositions. However, the carbonate decomposition was completed at higher temperature for OLED substrate at about 1060°C compared to 1020°C for TFT-LCD substrate. This was due to the presence of BaCO$_3$ in OLED substrate batch. Higher alumina content led to the stronger exothermic peak in 1263.7°C, which meant that more energy would be put into the process of melting for OLED substrate batch.

3.2. HTO analysis for the batches
In mass production of glass industry, stannous oxide SnO and tin dioxide SnO$_2$ were both used as fining agent. SnO is a kind of redox fining agent, which can
absorb O₂ and release O₂ by changing the valence of tin ion. The fining mechanism is as follows: SnO reacts with oxygen to form SnO₂ when the temperature is lower than 800°C, and when the temperature is higher than 1400°C, the high valence SnO₂ releases O₂ through the decomposition, and the released O₂ diffuses into the bubbles in the glass melt, absorbing and merging other bubbles in the melt. Then, the bubbles increase and float, and finally ascend to escape from the glass melt. SnO₂ is also a kind of fining agent,
whose decomposition formula is as follows: $2\text{SnO}_2 \leftrightarrow 2\text{SnO} + \text{O}_2 \%$. The fining effect between them was studied.

Four glass batches were designed for HTO test. The first two compositions were TFT-LCD substrates, with different fining agent of SnO$_2$ (TFT-LCD substrate 1) and SnO (TFT-LCD substrate 2), respectively. The last two compositions are referred to OLED substrates, OLED substrate 1 for SnO$_2$, and OLED substrate 2 for SnO. The glass batches with the compositions shown in Table 1 were acquired from reagent grade raw materials such as SiO$_2$, Al$_2$O$_3$, H$_2$BO$_3$, MgO, CaCO$_3$, SrCO$_3$, BaCO$_3$, SnO$_2$ and SnO. The content of SnO$_2$ and SnO was the same for 0.2 wt.%

Figure 7 shows the changes of the area fraction of bubbles for four batches. It could be seen that the area fraction was lower with fining agent of SnO$_2$ than that with SnO, both for OLED and TFT-LCD substrates.

Firstly, for TFT-LCD substrate, in the first 30 min of holding time, the area fraction of batch 1 (with SnO$_2$) and batch 2 (with SnO) was almost the same. While with the extension of holding time to 30 minutes, the area fraction for batch 1 decreased faster than batch 2 and approximated to a relatively stable state from then on. After holding for 2 h, the area fraction for batch 1 and batch 2 were 25.3 and 41.7%, respectively. But when after 3 h of holding time for the fining process, batch 1 and batch 2 showed similar result, with 19.2 and 20.1%, respectively.

For OLED substrate, a better fining process with lower area fraction for SnO$_2$ was also found. And with efficient holding time for the fining, area fraction with SnO$_2$ fining agent could also be as low as TFT-LCD substrate (22.4%), while the fining effect was poor with SnO agent for OLED substrate.

From gradual decline to stabilization for the area fraction of bubbles, TFT-LCD substrate took about 120–130 min. While for OLED substrate, a steady downward trend for the area fraction was observed, and more time for stabilization was needed. Furthermore, both TFT-LCD and OLED substrates did not approximate to zero for the area fraction of bubbles, which meant that three hours of fining process was insufficient.

As a contrast, the glass batch with similar total SiO$_2$ and Al$_2$O$_3$ content to OLED substrate with $60\text{SiO}_2 - 20\text{Al}_2\text{O}_3 - 2\text{B}_2\text{O}_3 - 13.8\text{R}_2\text{O} (\text{Na}_2\text{O} + \text{K}_2\text{O}) - 4\text{RO} (\text{MgO} + \text{CaO}) - 0.2\text{SnO}_2$ which was a kind of cover glass for the substrate, was tested under the same heating procedure and holding time, and the same content SnO$_2$ was employed as fining agent. It could be found that alkali metal oxides could remarkably improve the fining process. The area fraction of bubbles approximated the steady line after about only 80 min, and the final value after 3 h fining process was 12.3%, less than two alkali free glass substrates. The ascending velocity of bubbles and holding time are closely related to the viscosity and surface tension of glass melt, which will be discussed in the following paragraph.

Figure 8 shows the change of the number of bubbles per square centimeter for four batches. At the first stage of holding time, bubbles were mixed together, and the image acquisition system could not distinguish the single bubble and no data was recorded until 110 minutes’
holding time. As shown in Figure 8, TFT-LCD substrate showed lower number of bubbles than OLED substrate. After holding for 3 hours, the number of bubbles per unit area of TFT-LCD substrate 1 with SnO₂ fining agent decreased from 124 cm⁻² to 50 cm⁻² with the holding time increasing from 110 minutes to 180 minutes, lower than that with SnO fining agent. While for OLED substrate, the number of bubbles per unit area was larger than TFT-LCD substrate, decreasing from 187 cm⁻² to 158 cm⁻², and lower number of bubbles could also be found for SnO₂ than SnO fining agent. Furthermore, for both TFT-LCD and OLED substrates, the image acquisition system could distinguish the single bubble at an earlier time for SnO₂ than for SnO agent, which suggested the faster escape of bubbles for SnO₂ agent. So it could be inferred from above that, the fining effect of agent judged by the number of bubbles was as follows: SnO₂ > SnO.

The mean bubble sizes of TFT-LCD substrate were larger than OLED substrate as shown in Figure 9. The mean bubble size of TFT-LCD substrate 1 with SnO₂ fining agent was in the range of 0.52 to 0.55 mm, a little bigger than that with SnO (0.46 to 0.54 mm). Larger bubble size suggested larger ascending velocity and faster escape of bubbles, and it indicated the fining effect between two fining agents was as follows, SnO₂ > SnO, which was consistent with the results discussed above. And for OLED substrate, the mean bubble size was in the range of 0.28 to 0.36 mm. The similar bubble size was found for both SnO₂ and SnO fining agent. Little effect of fining agents on the bubble size for OLED substrate might be related to its higher viscosity and surface tension of glass melt, which will be discussed in the following section.

In mass production of glass industry, both SnO and SnO₂ could achieve good fining effect. Cost of materials and storage conditions might influence the preferred choice of them. However, in this study, the fining effect of SnO was worse than SnO₂ according to the results discussed above. The reason might be as follows: at high temperature of 1600°C, the solid SnO was transformed into liquid SnO which might show significant volatility and the fining effect was poor. Furthermore, the thermal history of glass melts might have an impact on the fining effect. Since SnO and SnO₂ showed similar fining mechanism by O₂ release, and SnO reacts with oxygen to form SnO₂ below 800°C, the longer the glass melts stay below 800°C, the more Sn⁴⁺ ions will be created in the melts. Therefore, the conclusion in this study was based in the specific heating procedure and thermal history of glass melts as shown in Figure 2. In other words, if the heating procedure in this study shown in Figure 2 changed, such as smaller heating rate below 800°C or holding some time at 800°C, different results from above might be observed.

3.3. Viscosity and surface tension of glass melt

Figure 10 shows the curves of viscosity of TFT-LCD and OLED substrates in the range of 1100 ~ 1700°C measured by Orton RSV1600 viscometer. Sample TFT-LCD substrate and OLED substrate were both prepared with SnO₂ fining agent according to the compositions shown in Table 1 and the procedure described in

![Figure 9](image-url)  
**Figure 9.** Variation of mean bubble size with time for four batches.
Section 2.3. Data in the range of 1200 ~ 1550°C was the measured one, while data out of the range were fitted by the Vogel-Fulcher-Tamman (VFT) equation [16,17], \( \ln \eta = A + B/(T-T_0) \), where \( A, B, T_0 \) are constants and \( T \) represents temperature. Table 2 lists the fitted results. Figure 10 displays the comparison of the reference points in float mass production, including forming point of glass (\( T_f:10^{2} \text{ Pa·s} \)) and working point of glass (\( T_w:10^{3} \text{ Pa·s} \)). About 70 ~ 80°C higher for OLED substrate than TFT-LCD substrate in the forming process was observed. In addition, at 1600°C for the fining condition, they were \( 10^{1.65} \) Pa·s and \( 10^{1.40} \) Pa·s, respectively. Higher viscosity of OLED substrate glass melt was attributed to its denser structure enhanced by higher content of \( \text{Al}_2\text{O}_3 \).

**Table 2.** Constants \( A, B \) and \( T_0 \) of VFT equation.

| Constant | TFT-LCD substrate | OLED substrate |
|----------|-------------------|----------------|
| \( A \)  | -3.626            | -4.579         |
| \( B \)  | 6426.473          | 8352.198       |
| \( T_0 \) | 325.687           | 273.547        |

Figure 10. Viscosity of OLED and TFT-LCD substrate in the range of 1200 ~ 1550°C.

Figure 11. Density and surface tension of glass samples between 1100°C and 1400°C.
For the surface tension test, sample TFT-LCD substrate 1 was prepared with SnO₂ fining agent according to the procedure described in Section 2.3, while TFT-LCD substrate 2 was with SnO, as well as OLED substrate 1 and OLED substrate 2. Surface tension and the density of glass samples at the corresponding temperature of 1100 ~ 1400°C could be obtained by the test. Figure 11 displays the density and surface tension of samples with the interval of 50°C in this range. It could be seen that different fining agents had a little effect on the density and surface tension of glass samples in this range. Firstly, the density of glass melt at 1600°C could be fitted and derived according data between 1100°C and 1400 °C. Table 3 shows the fitted value at 1600°C. About 6% decrease of density at 1600°C compared to the value at room temperature could be observed.

Secondly, due to the test limit of the equipment, the surface tension test was only measured up to the maximum of 1400°C as shown in Figure 11. We found that the surface tension decreased by about 1% for every 100°C increase in temperature, then we assumed that the surface tension decreased by 2% for the value at 1600°C compared with the value at 1400°C, and the value at 1600 °C shown in Table 3 was derived by this way. At 1600°C, OLED substrate showed higher surface tension, about 365 mN/m compared to around 325 mN/m for TFT-LCD substrate. Larger surface tension will prevent the growth of bubbles, which was agreed with the results shown in Section 3.2.

The average ascending velocity of bubbles can be expressed as equation (2) [18],

\[
V = 2gr^2(\rho_{gl} - \rho_g)/9\eta_{gl}
\]

where \(V\) is the average ascending velocity of bubbles, \(r\) is mean bubble size, \(g\) is acceleration of gravity, \(\rho_{gl}\) is the density of glass liquid at 1600°C, \(\rho_g\) is the density of gas in bubbles, and \(\eta_{gl}\) is the viscosity of glass liquid at 1600°C.

Figure 12 shows the comparison of the average ascending velocity of bubbles calculated according to equation (2) and measured by HTO test for four batches. For TFT-LCD substrate, the bubble size of 0.50 mm was employed, and 0.30 mm for OLED substrate. There was some deviation between the theoretical value derived from equation (2) and the measured value based on the real bubbles. But the average ascending velocity of bubbles for TFT-LCD substrate was about four times higher than OLED substrate. Faster ascending of bubbles would lead to smaller area fraction and number of bubbles, and better fining could be realized.

| Table 3. Density and surface tension of glass melt. |
|---|---|---|---|
| Number | \(\rho_{1}/g\cdot cm^{-3} (25^\circ C)\) | \(\rho_{2}/g\cdot cm^{-3} (1600^\circ C)\) | \(\sigma_{m}/mN/m\) |
| TFT-LCD substrate 1 | 2.523 | 2.372 | 326.9 |
| TFT-LCD substrate 2 | 2.529 | 2.379 | 325.2 |
| OLED substrate 1 | 2.578 | 2.415 | 364.3 |
| OLED substrate 2 | 2.584 | 2.420 | 367.2 |

3.4. Molten resistance of glass melt

Electric assistant melting in mass production is based in the conductivity of glass melt at high temperature. By inserting the electrode in the bottom of melting tank to introduce the current into the glass melt, Joule heat generated between two electrodes under the
action of current can improve the temperature of the bottom glass melt and accelerate the melting of the batch, as well as the fining and homogenization of glass melt. Therefore, the resistance of glass melt has a great influence on the design of electrodes in mass production.

At high temperature, alkaline earth metal ions change from irregular thermal motion to directional movement under the action of electric field, which shows the conductivity of glass melt. The movement of alkali-earth ions in molten glass melt is affected by bond strength of M-O (M = Mg/Ca/Sr/Ba) and radius of alkaline earth metal ions. Figure 13 displays the molten resistance of two substrates in the range of 1500–1600°C. OLED substrate showed higher resistance than TFT-LCD substrate, probably owing to the different mobility for Ba$^{2+}$ and Sr$^{2+}$ judged by difference of the compositions. The radius of Ba$^{2+}$ is bigger than Sr$^{2+}$, which will make it more difficult to move in the network and cause the increase of resistance. Furthermore, compared to TFT-LCD substrate, more oxygen ion was incorporated by Al$^{3+}$ to form [AlO$_4$] tetrahedra in OLED substrate due to its higher Al$_2$O$_3$ content, and the free oxygen ion O$^{2-}$ was lower than that in TFT-LCD substrate. Then, the contribution to conduction from the carrier oxygen ion O$^{2-}$ decreased and the resistance increased for OLED substrate. With the decrease of temperature, the structure of glass network became denser, and the binding force between alkaline earth metal ions and network became stronger, which will bring more difficulties for the movement of alkaline earth metal ions and increase the resistance. For TFT-LCD substrate, with the decrease of temperature from 1600°C to 1500°C, the resistance increased from 44 to 90 Ω·cm, while faster increase was found for OLED substrate, from 97 Ω·cm to 208 Ω·cm. This faster increase with temperature decrease for OLED substrate was also related to its more denser network structure as a result of higher alumina content, as well as lower number of oxygen ion O$^{2-}$ as discussed above. The difference of resistance between the two glasses could provide some reference for the mass production, including the layout and dimensions of the electrodes.

3.5. Effect of grain size distribution on the melting quality of bulk glass samples

In order to investigate the influence of grain size distribution of the main raw material silica sand on the melting effect, a kind of the commercial silica sand with the original grain size shown in Table 4 was employed in this study. In the raw materials, big particles with the size in the range of 40 ~ 80 mesh accounted for more than 50%, which was not benefit

![Figure 13. Molten resistance of TFT-LCD and OLED substrates in the range of 1500 ~ 1600°C.](image)

| Table 4. Original grain size distribution of the commercial silica sand. |
|---------------------------------------------------------------|
|                  | < 40 mesh (>380 μm)/% | 40~80 mesh (180~380 μm)/% | 80~120 mesh (125~180 μm)/% | 120~150 mesh (100~125 μm)/% | > 150 mesh (<100 μm)/% |
| Commercial silica sand | 1.35                          | 53.83                        | 19.12                          | 10.83                          | 14.87                          |
for the fast melting. In this study, the original raw silica sand was classified into four kinds of particle size range, including 80 ~ 100 mesh, 80 ~ 120 mesh, 120 ~ 200 mesh and 150 ~ 200 mesh by standard vibrating screen. Figure 14 displayed the morphology of silica sand, most of which were sharp and angular particles. Then these four kinds of silica were used instead of reagent grade \( \text{SiO}_2 \) for the preparation of glass samples according to the compositions shown in Table 1 and procedure described in Section 2.3, while the other oxides were brought with chemically pure reagents and fining agent was \( \text{SnO}_2 \). As a contrast, the distribution of the reagent grade \( \text{SiO}_2 \) used for the measurements above was as follows: the particles with grain size smaller than 0.53 µm (>270 mesh) accounted for more than 90% and larger than 0.53 µm (<270 mesh) accounted for less than 10%.

Figure 15 shows the real images of bulk glass samples with visible bubbles, wherein Figure 15(a–d) in the top rows were TFT-LCD substrate samples, and Figure 15(e–h) in the bottom rows represented OLED substrate samples. Table 5 lists the number of bubbles and the composition uniformity of \( \Delta \text{SiO}_2 \) between different positions of samples. It could be observed from Figure 15 that with the decrease of particle size of silica sand (increasing mesh), the number of visible bubbles in the bulk glass sample gradually decreased, and the composition uniformity increased, both for TFT-LCD and OLED substrates. The samples prepared from the smallest particle size

**Figure 14.** The particle morphology of original raw silica sand.

**Figure 15.** Real images of bulk glass samples with visible bubbles.
Table 5. Bubbles in bulk glass samples with different silica sand grain size.

| Mesh | Number of bubbles/cm\(^2\) | ΔSiO\(_2\)/wt.% |
|------|-----------------------------|-----------------|
| 80 - 100 | TFT-LCD substrate 1.02 | ΔSiO\(_2\) difference of the maximum and minimum value of SiO\(_2\) between divided 20 small samples. |
| 80 - 120 | OLED substrate 5.71 | |
| 120 - 200 | TFT-LCD substrate 3.88 | |
| 150 - 200 | OLED substrate 4.84 | |

Table 6. Analysis of bubbles in bulk glass samples.

| Sample          | Gas composition/% | O\(_2\) | CO\(_2\) | H\(_2\) | N\(_2\) | Ar |
|-----------------|--------------------|---------|---------|--------|--------|----|
| TFT-LCD substrate | 97.862 | 0.476 | 0.385 | 1.260 | 0.017 | |
| OLED substrate   | 97.439 | 0.961 | 0.394 | 1.190 | 0.016 | |

4. Conclusion

The melting properties of TFT-LCD and OLED substrates were studied, and the results were as follows:

1. Chemical reaction of the batches for TFT-LCD and OLED substrates were similar, while the carbonate decomposition was completed at higher temperature for OLED substrate at about 1060°C compared to 1020°C for TFT-LCD substrate.
2. SnO\(_2\) showed better fining effect than SnO, both for TFT-LCD and for OLED substrates. Compared to alkaline glass, three hours’ fining process was not sufficient for TFT-LCD and OLED substrates. And it took more time for OLED substrate.
3. Silica sand with particle size in the range of 150 ~ 200 mesh exhibited the best melting quality in bulk glasses samples judged by the number of visible bubbles and ΔSiO\(_2\) between different positions of samples.
4. The molten resistance at 1600°C was 44 and 97 Ω·cm for TFT-LCD and OLED substrates, respectively. Faster increase of resistance with temperature decrease was observed for OLED substrate.

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Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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