FULL PAPER

Comparison and low-temperature sintering mechanism of “K₂O–Na₂O” and “Li₂O–K₂O–Na₂O” fluxes on the porcelain building tiles

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The “K₂O–Na₂O” binary and “K₂O–Na₂O–Li₂O” ternary flux systems on the densification behaviors of the porcelain building ceramic were analyzed. The results showed that when K₂O and Na₂O content were equivalently replaced by Li₂O content, the sintering temperature of “K₂O–Na₂O–Li₂O” flux samples was reduced to 1090–1130°C, which is lower than that of “K₂O–Na₂O” binary flux sample (1130–1160°C). The corresponding sintering temperature range of the ternary flux sample is widened from 30 to 40°C, and thus the bending strength of the ternary flux sample is increased by 3.5%. The energy spectrometer system and “K₂O–Na₂O–Li₂O” ternary frit simulation results indicate ternary flux sample has more Al₂O₃ and SiO₂ content in glass phase than those of the binary flux sample, however, the alkaline oxide contents are higher than those of ternary flux sample. For binary flux samples, “K₂O–Na₂O” fluxes melt themselves due to low melting point and thus suddenly appear a large amount of the liquid phase and have no time to dissolve Al₂O₃ and SiO₂ contents, resulting in low glassy viscosity of the sample. However, when Li₂O content equivalently replace K₂O and Na₂O contents for the ternary flux sample, they would appear high glassy viscosity steeply, due to the formation of low eutectic mixture melted with high Al₂O₃ and SiO₂ contents. Combined with X-ray powder diffraction patterns and scanning electron microscope images, the ternary flux samples have more crystallite phase, smaller porosity and pore size than those of binary flux samples. Therefore, the properties of the ternary flux samples are superior to those of binary flux samples.

Key-words : Porcelain building ceramic tile, Low-temperature sintering mechanism, “K₂O–Na₂O–Li₂O” ternary flux, “K₂O–Na₂O” binary flux

1. Introduction

Due to its excellent bending strength, corrosion and stain resistance, porcelain building ceramics have been considered as one of the most important decorative materials.¹ Nowadays, porcelain building ceramics are usually fired at 1160–1200°C. It not only consumes a lot of raw materials and fuels, but also emits a large amount of carbon dioxide (CO₂) waste gas, which aggravates the earth “Greenhouse Effect” and seriously pollutes environment.² Therefore, how to save energy and consumption for ceramic industry has already been a hot topic.

It is known that many factors e. g. fuels kinds, firing temperature and time, composition etc greatly affect the properties of the porcelain building tiles.³⁻¹⁷ Among these factors, reducing the sintering temperature by adding “K₂O–Na₂O” fluxes is the most common method of the existing technology, because it can significantly reduce the emissions of CO₂ and other waste gas. However, this method has the following technical defects: the sintering temperature range becomes narrow only about 20°C, which makes the product easy to deform and brittleness and thus could not guarantee the product’s performance in the large-scale production process.¹²⁻¹⁴

In the previous work,¹⁴⁻¹⁷ our research group has reduced the firing temperature by adjusting the types and quantities of multi-component fluxes e. g. “K₂O–Na₂O–Li₂O” ternary fluxes. And the porcelain building ceramics were prepared at low temperature of 1090–1130°C. This brings us an inspiration: what is the melting behavior of “K₂O–Na₂O–Li₂O” ternary fluxes at different firing temperatures, and how does it affect the reaction densification process of building porcelain ceramic, keeping its the physical and chemical properties unchanged? Although effects of firing temperature on the properties of the sample with “K₂O–Na₂O” were studied in our previous paper,¹⁸ it has not been reported that why is it difficult to keep the ceramic tiles with good properties at low firing temperature using K₂O–Na₂O binary fluxes. Therefore, the

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behavior of the binary and ternary fluxes on the densification process and their low-temperature sintering law of the porcelain building ceramic were compared and analyzed in detail.

2. Experimental

2.1 Samples preparation

Table 1 is chemical composition of the raw material by X-ray Fluorescence (XRF, PANalytical B.V., Holland). Particle size of the final raw materials powder is 120–160 μm. Table 2 shows sintering properties of raw materials. Batches (Table 3) were milled in a fast ball milling for 12 min. using alumina balls as grinding media. The resultant slurry was dried at 80 °C to 3–7 % water. The dried powder uniaxially pressed at 10 MPa in a steel die and 850–1170 °C following a fast firing process. Square tiles (6 g each) of 41 mm × 11 mm × 7 mm were prepared for properties measurements. And circular tiles (16 g each) of φ 50 mm × 10 mm were used to characterize the shrinkage measurements.

2.2 Characterization

The sintering properties of the samples were evaluated by the firing shrinkage, water absorption, bulking density according to Archimedes law. The final results are averaged for five samples under the same conditions. The firing shrinkage, \( L_s \) (%), is such as Eq. (1).

\[
L_s = \frac{L_b - L_a}{L_b} \times 100 \%
\]

(1)

\( L_b \) and \( L_a \) are the diameter (mm) of the green and fired samples, respectively. The water absorption was measured, boiling in water for 3 h and soak for an additional 24 h at ambient temperature. Water absorption, \( W_a \) (%), of the fired samples has been determined by means of the following equation:

\[
W_a = \frac{W_c - W_b}{W_b} \times 100 \%
\]

(2)

The bulking density, \( B_d \) (g/cm³), is such as Eq. (3).

\[
B_d = \frac{W_c - W_d}{W_c} \times 100 \%
\]

(3)

\( W_a \) and \( W_c \)-the mass of dry and water-saturated fired sample in the air, respectively. \( W_d \)-the mass of watersaturated fired sample in the water.

Table 1. Average chemical composition of the raw materials

| Chemical composition | Extra-white potash sand (wt%) | Zhiji porcelain sand (wt%) | Ball clay (wt%) | Composite clay (wt%) | Jiangning feldspar (wt%) | Sodium feldspar (wt%) | Lithium porcelain stone (wt%) |
|----------------------|------------------------------|---------------------------|----------------|---------------------|-------------------------|------------------------|-----------------------------|
| Li2O                | 74.7                         | 74.04                     | 51.14          | 68.64               | 71.46                   | 70.32                  | 19.68                       |
| SiO2                | 16.67                        | 16.70                     | 33.87          | 20.16               | 14.24                   | 17.79                  | 19.68                       |
| Al2O3               | 5.94                         | 3.48                      | 0.70           | 1.89                | 7.07                    | 2.75                   | 3.46                        |
| K2O                 | 2.88                         | 0.66                      | 0.42           | 0.47                | 3.30                    | 7.30                   | 2.32                        |
| Na2O                | 1.06                         | 0.41                      | 0.10           | 0.09                | 1.51                    | 0.53                   | 0.38                        |
| CaO                 | 0.47                         | 0.71                      | 0.15           | 0.20                | 1.07                    | 0.15                   | 0.13                        |
| MgO                 | 0.02                         | 0.10                      | 0.07           | 0.40                | 0.02                    | 0.02                   | 0.01                        |
| TiO2                | 0.16                         | 0.59                      | 0.47           | 1.00                | 0.15                    | 0.11                   | 0.09                        |
| Fe2O3               | 1.28                         | 3.14                      | 12.56          | 6.69                | 1.19                    | 0.75                   | 3.09                        |
| Ignition loss       | 1.28                         | 7.68                      | 1.96           | 2.16                | 6.87                    | 0.12                   | 0.01                        |

Table 2. Firing properties of raw materials at 1200 °C

| Raw materials         | Ignition loss (wt%) | Line shrinkage (%) | Water absorption (%) | Color after firing |
|-----------------------|---------------------|--------------------|----------------------|-------------------|
| Extra-white potash sand | 1.28                | 7.68               | 0.26                 | White             |
| Zhiji porcelain sand  | 3.14                | 5.12               | 1.96                 | White             |
| Ball clay             | 12.07               | 5.93               | 2.16                 | Luidity           |
| Composite clay        | 6.62                | 4.18               | 6.87                 | Gray              |
| Jiangning feldspar    | 1.19                | 8.24               | 0.12                 | Popcorn           |
| Sodium feldspar       | 1.18                | 8.29               | 0.10                 | Popcorn           |
| Lithium porcelain stone | 3.02                | 8.33               | 0.11                 | White             |

Table 3. Batch compositions and the corresponding chemical composition

| Samples | Al2O3/SiO2 molar ratio | Extra-white potash sand (wt%) | Zhiji porcelain sand (wt%) | Ball clay (wt%) | Composite clay (wt%) | Jiangning feldspar (wt%) | Sodium feldspar (wt%) | Lithium porcelain stone (wt%) |
|---------|-------------------------|------------------------------|---------------------------|----------------|---------------------|-------------------------|------------------------|-----------------------------|
| L      | 0.1357                  | 31                           | 6                         | 4              | 10                  | 24                      | 25                     | 0                           |
| B1     | 0.1407                  | 21                           | 6                         | 4              | 10                  | 24                      | 15                     | 20                          |
| B2     | 0.1434                  | 18                           | 6                         | 4              | 10                  | 24                      | 13                     | 25                          |
| B3     | 0.1453                  | 16                           | 6                         | 4              | 10                  | 24                      | 10                     | 30                          |
| B4     | 0.1476                  | 13                           | 6                         | 4              | 10                  | 24                      | 8                      | 35                          |

| SiO2 | Al2O3 | K2O | Na2O | CaO | MgO | Fe2O3 | Li2O |
|------|-------|-----|------|-----|-----|-------|------|
| 73.47 | 17.51 | 4.65 | 3.19 | 0.54 | 0.27 | 0.27  | 0    |
| 72.82 | 17.75 | 4.55 | 2.85 | 0.47 | 0.24 | 0.25  | 0.41 |
| 72.64 | 18.05 | 4.51 | 2.78 | 0.44 | 0.23 | 0.24  | 0.49 |
| 72.48 | 18.25 | 4.50 | 2.68 | 0.43 | 0.22 | 0.24  | 0.56 |
| 72.30 | 18.50 | 4.46 | 2.61 | 0.40 | 0.21 | 0.23  | 0.64 |
The bending strength of the samples was characterized via an electronic universal testing machine (DWD 3020). To evaluate the phase transformations, glassy and crystallization of the samples, the typical samples were collected in the 10–80° 2θ, 0.050°/s scan rate, 1 s per step performed by X-ray powder diffraction (XRD, PANalytical x’pert pro, Holland). The quantitative phase composition using the Gsas-Expgui software packages following the Rietveld method which considers the full profile.16,20 The samples were admixed with 10 wt% CaF₂ as internal standard (Xₐ). The method is based on the normalization equation \( \Sigma X_i / \Sigma (X_i + X_c) = 1 \), where \( X_i \) and \( X_c \) are the weight fractions of the crystalline components and the glassy phase, respectively. Thus the amount of the glassy phase can be estimated directly from the weight of the internal standard by: \( X_g = \frac{(100/90)(1 - (X_i/X_c)}{X_i} \) \( X_c \) is the added weight and \( X_c \) is the refined weight of the internal standard.21 Up to 40 independent variables were refined: phase fractions, zero point, 25–30 coefficients of the shifted Chebyschev function to fit the background, unit cell parameters, profile coefficients (one Gaussian, \( g_{\text{pp}} \), and one Lorentzian term, \( L_{\text{pp}} \)), the agreement indices, as defined in gxs, for the final least-squares cycles of all refinements are represented by \( R_{\text{wp}} \) (% expected r factor), \( R_{\text{wp}} \) (% weighted profile R-factor), \( X_2 \) (goodness of the fit) and \( R(F^2) \) (% residual factor). The refined patterns were found in the following ranges: 10.0% < \( R_{\text{wp}} < 13.5 \), 13.0% < \( R_{\text{wp}} \) < 15.0%, 3.5% < \( X_2 < 6.0 \), and 10.0% < \( R(F^2) \) < 13.0%. The experimental error is within 5% relative. The chemical composition of the glassy phase was calculated by subtracting from the bulk composition the contribution of each crystalline phase, assuming a stoichiometric composition for quartz and mullite. The mullite composition was calculated by means of Eq. (4) based on the empirical relationship between the length of the unit cell edge \( a \) and the \( Al_2O_3 \) content:22

\[
Al_2O_3 \text{ (mol.%) = 1443 (unit cell parameter a) - 1028.06 (4)}
\]

The microstructure of the fired samples was observed by a scanning electron microscope (SEM, JSM-6700F, Japan) equipped with an energy spectrometer (EDS, JSM-6700F, Japan) operating at an accelerating voltage of 5.0 or 15 kV (15 kV for EDS). The beginning melting temperature of feldspar was characterized by a melting temperature tester (SJY-130763, China).

The shrinkage sensitivity of the sample is calculated by the Eq. (5).

\[
\Omega = \frac{\Delta L_a / \Delta T}{100} \times 100 \%
\]

\( \Delta L_a \) and \( \Delta T \) - the shrinkage diameter (mm) of the sample and temperature range. \( \Omega \) - shrinkage sensitivity of the sample. The larger the \( \Omega \) value is, the greater the shrinkage change of the sample is within the same temperature range.

3. Results and discussion

3.1 Physical properties

Considering that the water absorption of the binary flux sample without \( Li_2O \) are too large (7.9–20.4%) at 1090–1140°C, the sintering properties of the samples with \( Li_2O \) equimolar replacement of \( K_2O \) and \( Na_2O \) contents are only compared as shown in Fig. 1. It can be seen that from Fig. 1, when lithium porcelain stone content is 20%, water absorption of the sample decreases, however, firing shrinkage and bulking density of the sample increase with firing temperature. When lithium porcelain stone content is equal or more than 30%, the firing shrinkage and bulking density of the sample increases and reaches a maximum value, and thus the water absorption decreases and reaches a minimum value. When lithium porcelain stone content is equal or more than 30%, the water absorption reduces to less than 0.5% and the bulking density is more than 2.3 g/cm³, suggesting that the sample is sintered at 1090°C. However, to further increasing the temperature to 1140°C, the water absorption of the samples increase, the bulking density and firing shrinkage of the samples decrease, which indicates that the blowing is occurring in the sample. Therefore, the sintering temperature range is broaden to 40°C (1090–1130°C). Further increasing lithium porcelain stone content to 35%, the firing temperature of the sample did not decrease and thus the sintering temperature range is still 40°C (1090–1130°C). It is obvious that suitable \( Li_2O \) content could decrease the firing temperature of the samples. To discuss and compare the sintering mechanism of the binary and ternary flux sample, effects of the temperature on the properties of the typical samples are discussed using 0 and 30% lithium porcelain stone prepared samples as follows.

Figure 2 shows two typical examples of Rietveld refinement of the binary flux and the ternary flux sample sintered at 1130 and 1090°C, respectively. The samples are composed of quartz (JCPDS files Nos. 46-1045) and a small amount of mullite phase (JCPDS files Nos. 02-0428). The amount of crystal phases (42% quartz and 7% mullite) in the ternary flux sample are higher than those of the binary flux sample (32% quartz and 3% mullite) through the quantitative XRD analysis. It indicates that the ternary flux sample could not dissolve more quartz phase, because the sintering temperature of the ternary flux sample decreases due to the formation of low eutectic phase at the earlier stage by introducing \( Li_2O \), which will be further verified by the following experiment results.

To explain the change in crystal structure at firing temperature, Fig. S1 shows XRD patterns of the binary and ternary flux samples at the different temperature used for this quantitative evaluation, respectively. Similar with Rietveld refinement of Fig. 2, the quantitative results of each mineral composition against temperature changes are listed in Fig. 3. The mineral components of the porcelain building ceramic samples undergo complex phase transformations during the thermal treatment involving: firstly, the breakdown of clay minerals leading to the formation of amorphous components which, starting from about 900 and 850°C for the binary and ternary samples, respectively, give rise to a viscous phase; secondly, abundant formation of glassy phase, starting approximately from
1050 and 960 °C set the firing shrinkage sensitivity temperature ($T_1$) in Table 4; thirdly, progressive dissolution of quartz in the glassy phase in absence of feldspars. Finished the binary and ternary samples-commonly fired at maximum temperature in the 1090–1130 and 1130–1160 °C range, respectively-contain essentially glassy phase associated with quartz and mullite. In the binary and ternary samples under investigation, the glassy phase ranges from 32 % to 77 wt% and the crystalline components are in the following ranges: quartz (30–50 wt%), mullite (0–9 wt%) and feldspars (0–24 wt%) (Fig. 3). These data differ from those of early porcelain stoneware batches:23),24) feldspars and the glassy phase occur in wider ranges while the amount of mullite is lower than previously expected because of the better reliability of full-profile interpretation of XRD patterns with respect to single peak RIR (Reference Intensity Ratio). The densification is basically driven by progressive melting of feldspars and to a minor extent of quartz. In the final stage of sintering, when the decreasing densification rate is contrasted by coarsening phenomena (i.e. over 1170 °C for binary samples and 1130 °C for the ternary samples), the phase composition seems to reach an equilibrium and the unique transformations are solution/precipitation of mullite and some dissolution of quartz in the liquid phase. Therefore, most feldspar is already melted before the glassy phase begins to flow, so starting densification, which goes on while feldspar fusion is accomplished and reactions involve to a certain extent quartz and mullite. The maximum densification is achieved: in the example of Fig. 4(a), the maximum firing shrinkage of the binary and ternary sample is 7.35 and 7.15 %, respectively, which corresponds to bulk density of about 2.36 and 2.37 g/cm³, and the water absorption of 0.09 and 0.08 %, respectively, which is accordance with the common value in porcelain building ceramics.18),23) Any further temperature increasing beyond maximum densification may induce overfiring effects, reducing bulk density and eventually leading to blowing.25) Above all, it can be observed that the sintering temperature of the ternary flux samples (1090–1130 °C) is lower than that of binary flux sample (1130–1160 °C), and thus the sintering temperature range is broadened from 30 to 40 °C [Fig. 4(a)]. The glassy content in the binary sample is higher than those in the ternary sample, however, the crystal contents in the binary sample are lower than those in the ternary sample (Figs. 2 and 3). Compared with Na₂O and K₂O, Li₂O has the strongest fusible effect due to its smallest Li-ion radius. In the firing process, Li₂O can form the low eutectic with other basic substances, and thus promote the pre-sintering of the sample. With the increase of the firing temperature, more liquid phase appears gradually and makes the glassy phase distribute evenly (Fig. 3),
therefore, the ternary samples is helpful for the suppression of the deformation, the detail discussion is as follows.

It can be seen from Fig. 5 that the bending strength of the ternary flux sample is higher than that of the binary flux sample. With the increase of the firing temperature, the bending strength of the samples firstly increases, reaches the maximum values at sintering temperature range and then decreases, which is consistent with the trend of the sintering properties of the samples. It can be attributed to the smaller glassy and higher crystalline contents in the ternary sample (Figs. 2 and 3).

Firing shrinkage sensitivity of the samples is as shown in Table 4. It can be seen that the firing shrinkage sensitivity of the binary flux sample is larger than that of the ternary flux sample indicating the ternary flux sample has a wide firing temperature range, which is favorable for industrial production. It is accordance with the trend of the glassy and crystalline results (Fig. 3).

**Figure 6** shows the SEM images of the binary flux and ternary flux samples at different temperature. The binary flux and ternary flux samples exhibit the loose bulk accumulation, and some small particles still adhere to the large particles, the space gap is large, indicating the binary flux and ternary flux samples are not sintered at 1110 and 1070 °C, respectively [Figs. 6(a) and 6(b)]. Figures 6(c) and 6(d) show the dense structure and a small amount of pores at 1130 and 1090 °C, respectively. Compared with binary flux sample, the ternary flux sample exhibits smaller pores and less glassy phase (Fig. 3). Further increasing firing temperature to 1170 and 1140 °C, respectively, more and larger pores appear in the samples [Figs. 6(e) and 6(f)].

It can be attributed that the sample gradually generates more liquid phases with the increase of the firing temperature (Fig. 3), the relative movement of the particles is rearranged, and thus the sample is densified. However, Fig. 6(d) exhibits relatively smaller pore and pore size, because a little liquid phase appears in advance, and then more liquid phase increases steeply with the increase of the temperature (Figs. 1 and 4), which can successfully infiltrate in the gap of the skeleton particles, and thus the sample turns denser. Moreover, the ternary flux sample has more crystals than those of the binary flux sample (Figs. 2 and 4), so that the firing shrinkage sensitivity and bending strength of the ternary flux sample improves (Table 4 and Fig. 5). Further increasing firing temperature, the over-

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**Table 4. Firing shrinkage sensitivity of the samples**

| Samples     | $T_1$ (°C) | $T_2$ (°C) | $\Delta T = T_2 - T_1$ (°C) | $L_1$ (%) | $L_2$ (%) | $\Delta L = L_2 - L_1$ (%) | $\Omega$ |
|-------------|------------|------------|-----------------------------|-----------|-----------|-----------------------------|--------|
| Binary fluxes | 1050       | 1130       | 80                          | 3.76      | 6.95      | 3.19                        | 3.98   |
| Ternary fluxes | 960        | 1090       | 130                         | 2.54      | 6.86      | 4.32                        | 3.32   |

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Fig. 2. The two typical examples of Rietveld refinement XRD patterns of the binary flux (a) and the ternary flux sample (b) sintered at 1130 and 1090 °C, respectively.

Fig. 3. Phase composition (weight percent) of the binary and ternary samples at different firing temperature based on XRD patterns in Fig. S1 used for Rietveld refinement similar with Fig. 2: E1–E5 and S1–S5 show the binary and ternary samples at different temperature.
firing phenomenon occurred (Fig. 4). It can be ascribed to that the liquid phase rapidly increase (Fig. 4) and the undischarged air hole is coated, so that the samples exhibit more and larger pore [Figs. 6(e) and 6(f)], and the bending strength of the sample decreased.

**Figure 7** shows SEM surface images of the typical samples prepared at different temperature. It can be seen that the surface of the ternary flux sample is more smooth than that of the binary flux samples. When the temperature is lower than 1090 °C, the binary sample is not dense due to a small amount of glass phase [Figs. 3 and 4(b)], however, the ternary sample is relatively dense due to lots of glass phase [Figs. 3 and 4(b)]. It indicates that lithium porcelain stone introduction can promote ahead the liquid phase appearance and thus be available for the mullite crystals growth (**Fig. 8**). The liquid phase tends to draw the particles and thus open porosity decreases, and closed porosity increases. Therefore, the ternary samples become denser with the increase of temperature during firing [Fig. 4(b)], which is accordance with the result of the properties e.g. water absorption and bending strength in Figs. 4 and 5.

**Figure 8** shows SEM fracture images of the typical binary and ternary sample at the temperature of 1090 and 1130 °C etched by immersion in 3% HF solution for 30 min, respectively. Some crystals, and undissolved quartz are obtained in the samples. Fig. S2 shows the corresponding EDS spectrum of some crystals (Red in square). It can be seen that the crystals consists of Al and Si elements, and the molar ratio of Al/Si is about 3:1, which is close to the stoichiometry of mullite (3Al2O3·2SiO2) phase. It is obvious that mullite crystals in the ternary sample exhibit longer size in length than those of the binary sample. It can be ascribed that feldspar diffuses into the decomposition of clay area, and react with to form mullite crystals. The elongated rod-shape mullite crystals in the ternary sample were more conducive to form from feldspar-clay relics, which is ascribed to the ahead appearance of the liquid phase and high SiO2 and Al2O3 due to the introduction of lithium porcelain stone [Table 3, **Figs. 8(a) and 8(b) and 10**]. Based on XRD results (Figs. 2 and 3), the glassy phase content (62%) in the binary flux sample is higher than (51%) of that in the ternary sample, therefore, much glassy liquid appears and thus liquid phase viscosity rapidly decreases, silica phase dissolves more into the glassy phase (Figs. 2 and 3), which is accordance with the previous literature. The closed pores and glassy phase increase in the binary sample during the firing process, and thus make the sample brittle and slab deformation (Fig. 3 and Table 4).

As is above the experimental results, it is obvious that the lithium porcelain stone play a key important role in the low sintering temperature and the growth of the mullite phase (Figs. 3, 5–8). To further explain the low temperature mechanism of lithium porcelain stone as a flux, the composition of the glassy phase in the binary and ternary samples at different firing temperature was characterized by EDS analysis. The average value was calculated by choosing 8 points at different glassy phase regions. The typical EDS spectrum shown in Fig. S3 reveals that the glass phase consists of Si, Al, K, Na and Ca elements for binary and ternary flux samples. **Figure 9** shows the glass phase composition and contents in the binary flux and ternary flux samples at the different firing temperature, respectively. It can be seen that the appeared temperature of the glassy phase (900 °C) in the binary flux sample is
Fig. 6. SEM images of fracture samples (a, c, e: binary flux, b, d, f: ternary flux).

Fig. 7. SEM surface images of the typical samples: (a, b: binary flux, c, d: ternary flux).
higher than that of the ternary flux sample (850 °C), due to a little amount of Na2O, K2O, CaO, MgO and Li2O contents in the glass phase, which is accordance with the eutectic point of “Li2O–K2O–Na2O–CaO–MgO” the phase diagram. Na2O + K2O contents in the ternary flux sample are less than those of the binary flux sample. However, the relatively low temperature of the appeared glass phase is not consistent with relatively high Al2O3 and SiO2 contents in the ternary flux sample. In our experiment, it can be theoretically explained that Li2O will enter the liquid phase earlier than Na2O and K2O, due to small Li ion radius and large electric field strength, the abilities of polarization oxygen ion and weakening the silicon oxygen bond is stronger than that of K and Na ions, which can improve the surface tension and crystallization ability (Fig. 3), and thus lower the firing temperature and melting temperature of the sample, which is verified by the frit experiment (Figs. 10 and 11). On the other hand, Al2O3 and SiO2 contents in the ternary flux sample at low sintering temperature are more than those in the binary flux sample (Table 3). It is well known that different Al/Si molar ratio, fluxing contents and purities have different melting point due to the formation of the liquid phase.11) Accordingly, the low beginning melting temperature of the ternary sample can be attributed to lithium porcelain stone fluxing agents. And Al2O3 and SiO2 contents in the sample containing lithium porcelain stone (Table 3) is relatively high which maybe produce a little of liquid phase gradually and prevents a lot of liquid from appearing suddenly once arriving at the lowest total melting point temperature, and thus reduce porcelain slab deformation and brittle, which is accordance with the glassy phase content (Figs. 2 and 3) and the firing shrinkage sensitivity of the ternary sample smaller than that of the binary sample (Table 4) and the improvement of the bending strength of the ternary flux sample (Fig. 5). Increasing the firing temperature, Na2O and K2O contents in glassy phase decrease, however, SiO2 and Al2O3 contents increase gradually. When the binary flux sample is between 1130 and 1160 °C, Na2O + K2O, SiO2 and Al2O3 contents are about 8.5, 70.9 and 17.1 %, respectively. For ternary flux samples, Na2O + K2O, SiO2 and Al2O3 contents are about 8.0, 71.9 and 17.8 % at 1090–1130 °C, respectively. Further increasing the firing temperature, compared to SiO2 and Al2O3 contents, more Na2O and K2O contents are dissolved due to lots of liquid phase formation. Combined with the quantitative XRD analysis and EDS results, it could be concluded that the ternary samples by introducing the lithium porcelain stone is helpful for the suppression of deformation and the bending strength (Table 3 and Fig. 5).

In order to infer lithium content in the glass phase due to too small lithium radius, which is not detected by EDS analysis, Li2O content in glass phase and the reaction temperature of the eutectic mixture are deduced by the simulated molten block experiment and the related phase diagram. The frit sample C1 was prepared using K2CO3, Na2CO3, Al(OH)3 and H2SiO3 as frit materials based on the glassy phase composition of the ternary flux sample at 850 °C by EDS analysis (Fig. 9). Because Li2O mol content is 1.2 % calculated by 30 wt % lithium porcelain stone in the ternary flux sample, Na2O + K2O contents are equivalently replaced by 0, 0.3, 0.6, 0.9 % and 1.2 mol % Li2O content, keeping Na2O and K2O molar ratio of 2:1, named as C1, C2, C3, C4, C5, respectively. The corresponding samples are melted at 1500 °C, and then ground into powder to make Φ 4 mm × 5 mm cylinder. Figure 10 is the
firing shrinkage curves of the frit samples prepared by different Li$_2$O content. It can be seen that the firing shrinkage of each frit sample keeps almost unchanged before 580 °C due to the volatilization of free water and a small amount of organic binder. When the firing temperature is between 580 and 750 °C, the firing shrinkage of the sample increases, which can be attributed that a certain amount of liquid phase appears in the sample and fills the particle gap, at the same time, the particles could migrate and transfer in the liquid phase by flow mass transferring mode, resulting in the increase of the contact surface of adjacent particles and thus the pore decreases with the increase of firing temperature. The firing shrinkage of the ternary flux samples are larger than the binary flux sample, which indicates the liquid phase appears earlier in the ternary flux samples than that of the binary flux samples. When the firing temperature is over 750 °C, the firing shrinkage of each frit sample decreases gradually, which indicates that the sample expands at this stage. It is due to the sample overfiring caused by too much liquid phase. It can be also seen that when the firing temperature is more than 600 °C, the firing shrinkage of the sample increases with Li$_2$O content at the same firing temperature (Fig. 10). When Li$_2$O content continues to increase (>0.9 %), the

Fig. 9. Different oxides contents in the glass phase for the binary and ternary flux samples at different firing temperature by EDS analysis (%).
firing shrinkage of the sample keeps almost unchanged (Fig. 10), indicating that more Li$_2$O content has little effect on the formation of the liquid phase temperature.

Melting point is the temperature of something turning to liquid from the solid phase, it is the main method to measure the fusing characteristics of the sample. The corner of the samples becomes round, which indicates the corresponding temperature is the initial melting point of the sample. The temperature shown in Fig. 11 corresponds to the initial melting temperature. The melting temperature of the frit sample without Li$_2$O content is 680 °C. The initial melting point of the frit samples decreases with the increase of Li$_2$O content (Fig. 11). It indicates that the addition of Li$_2$O is effective for lowering the sintering temperature, which is accordance with the experimental results (Figs. 4 and 10 and Table 4). It can be mainly due to the formation of the “K$_2$O–Na$_2$O–Li$_2$O” eutectic mixture and thus the liquid phase appears in the sample ahead of time. Based on the “K$_2$O–Na$_2$O–Al$_2$O$_3$–SiO$_2$” phase diagram, the lowest eutectic point of the sample is 1020 °C. According to “Na$_2$O–Al$_2$O$_3$–SiO$_2$” and “Li$_2$O–Na$_2$O–Al$_2$O$_3$–SiO$_2$” phase diagrams, the lowest eutectic point of the two phase diagrams are about 730 °C. Therefore, it can be concluded that the liquid phase formation temperature range of the ternary and binary flux sample should be between 730 and 1020 °C. It is well known that if the original sample is melted, the initial melting temperature of the frit sample will decrease. It is accepted that the initial melting point of the frit sample will decrease as low as tens to 200 °C. The initial melting temperature of the sample C1 without Li$_2$O content was higher than that of the sample C2, C3, C4 and C5 (0.3, 0.6, 0.9 and 1.2 %), respectively. The results show that the initial melting point of C4 (0.9 %, 630 °C) is 50 °C earlier than that of C1 (0 %, 630 °C), which is consistent with the liquid formation temperature of the experimental binary (900 °C) and ternary flux samples (850 °C), respectively. Therefore, based on the phase diagram, combined with the firing shrinkage and melting point analysis results, it can be concluded that Li$_2$O molar percentage in the ternary flux sample is more than 0.9 %, respectively.

4. Conclusions

When appropriate Li$_2$O contents (that is, lithium porcelain stone content was 30 %) replace partially K$_2$O and Na$_2$O content, the sintering temperature of “K$_2$O–Na$_2$O–Li$_2$O” ternary flux system was further reduced to 1090–1130 °C and thus the firing temperature range was broadened to 40 °C. XRD, SEM and EDS analysis show that there are more crystals, higher densification and bending strength in the ternary flux samples than those of binary flux samples. Na$_2$O, K$_2$O percentage content in glass phase decreased with the increase of temperature, however, Al$_2$O$_3$, SiO$_2$ percentage content increased gradually. Moreover, Al$_2$O$_3$ and SiO$_2$ contents in the ternary flux sample are more than those of binary flux sample at lower sintering temperature. It can be attributed that the liquid phase appeared in advance due to the “Li$_2$O–K$_2$O–Na$_2$O” eutectic formation. Thus, there is enough time to dissolve clay and quartz, that is, Al$_2$O$_3$, SiO$_2$ contents increase with the firing temperature, and thus the liquid phase content increases step by step, which makes the sample keep high liquid phase viscosity all the time. Accordingly, the sintering temperature of the sample further decrease and the...
sintering temperature range is broadened keeping the properties of the architecture ceramic unchanged.

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