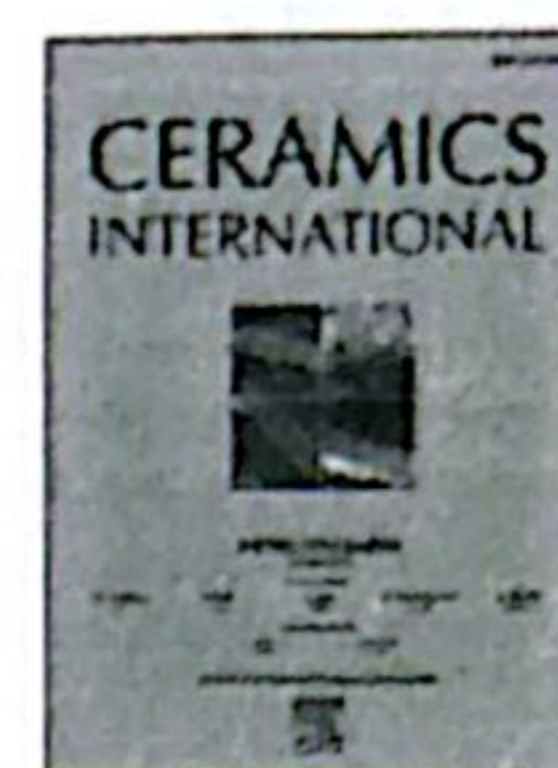




CuO-doped borosilicate glass fluxes for dense, low-resistivity copper films

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ABSTRACT

To meet the increasing demand for multilayer ceramic capacitors (MLCCs) with higher capacitance, miniaturization, and greater reliability, advanced copper electrode materials combining high conductivity and mechanical stability are required. In this study, a CuO-doped R_2O -BaO- B_2O_3 - SiO_2 glass system was developed as an inorganic flux for conductive copper pastes. Its performance was evaluated on alumina substrates and MLCC terminations. The effects on the glass network structure and properties were investigated by varying the CuO/BaO substitution ratio (0–16 mol %). Results reveal that CuO doping improves wettability, lowers sintering and hemispherical temperatures (enabling low-temperature co-firing at $\approx 820^\circ\text{C}$), enhances electrical performance, and strengthens interfacial adhesion. The 12 mol % CuO composition yields optimally densified and uniform copper films, demonstrating that tailored glass formulations can enable high-performance copper electrodes at reduced processing temperatures.

1. Introduction

Multilayer ceramic capacitors (MLCCs) and alumina (Al_2O_3)-based devices are key components in modern electronics, widely employed in communications, automotive systems, mobile devices, and RF modules [1–6]. As electronic technologies advance toward miniaturization, higher integration, and improved reliability, stricter demands are imposed on internal electrode materials [1–4,7]. Copper has emerged as a promising alternative to noble-metal electrodes (e.g., Pd-Ag) due to its high electrical conductivity and low cost [8–13]. However, its practical application is limited by oxidation at elevated temperatures, high sintering temperatures, and poor interfacial compatibility with ceramic substrates during co-firing, leading to degraded performance and reliability [9,11]. A widely adopted strategy to mitigate these issues is the incorporation of an appropriate amount of glass phase into copper pastes. Glass improves wettability, reduces sintering temperatures, and enhances interfacial adhesion, thus promoting performance and reliability [14–16]. The glass-binder fraction is typically 5–12 wt % in thick-film Cu pastes [6,13]. Despite its low content, the glass phase promotes spreading on Cu particles and Al_2O_3 substrates, fills surface imperfections, and forms a compliant viscous layer that accommodates sintering shrinkage and thermal mismatch, thereby suppressing defects such as pores, cracks, and delamination [9,10,17,18]. Among various

glass systems, borate glasses are attractive candidates due to their low melting temperature, environmental compatibility, and low dielectric constant; however, their limited thermal and chemical stability and modest ionic conductivity still constrain further performance optimization [19,20].

To enhance the performance of borate glasses, modification of glass network structures through metal oxide incorporation has been widely explored. Among various modifiers, CuO is considered particularly effective due to its high field strength and distinctive coordination characteristics, which can significantly alter glass network connectivity. Previous studies have shown that CuO addition promotes non-bridging oxygen formation and increases free volume, thereby lowering melting and softening temperatures while improving glass flowability and wettability. However, studies on CuO-doped borosilicate glasses have mainly focused on optical, radiation-shielding, or glaze-related applications, whereas their role as inorganic fluxes in conductive copper pastes—especially under identical paste-processing and co-firing conditions—remains insufficiently understood [21–27]. In particular, the intrinsic correlations among glass network evolution, wettability and flow behavior, sintering-assisting effects, and the resulting electrical performance and interfacial bonding of copper electrodes have not been systematically elucidated. Moreover, it is still unclear whether CuO acts merely as a conventional network modifier similar to alkaline-earth

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Table 1
Chemical compositions of the glass samples (mol %).

No.	SiO ₂	B ₂ O ₃	R ₂ O (Na ₂ O + K ₂ O)	BaO	CuO
G1	35	35	5	25	0
G2	35	35	5	21	4
G3	35	35	5	17	8
G4	35	35	5	15	10
G5	35	35	5	13	12
G6	35	35	5	9	16

oxides (e.g., BaO), or whether it exerts a distinct influence on glass–copper interfacial reactions, local oxygen partial pressure regulation, and overall co-firing compatibility.

In response to the aforementioned issues, a series of CuO-doped borosilicate glasses with the composition $5R_2O-(25-x)BaO-35B_2O_3-35SiO_2-xCuO$ ($x = 0, 4, 8, 10, 12, 16$ mol %) were developed to systematically examine the influence of CuO on glass structure, thermal and chemical stability, and wettability. The aim was to correlate these structural and thermophysical variations with co-firing performance under identical copper-paste processing conditions. The results demonstrate that incorporation of Cu^{2+} ions modifies the glass network by increasing the non-bridging oxygen content, which reduces the sintering temperature of the copper paste to 820 °C and enhances the wettability of the glass toward copper particles, thereby improving sintering uniformity and densification. At 10 mol % CuO, the minimum contact angle between the glass and substrate reached 36.9°, while the copper paste achieved its lowest sintering temperature of 820 °C. Further increasing the CuO content to 12 mol % yielded the lowest resistivity of 6.96 mΩ/□ for the conductive copper thick film. These findings highlight the critical role of CuO in tailoring the structure of borosilicate glasses and regulating liquid-phase sintering behavior, thereby establishing an effective composition window for low-temperature co-firing and high-performance copper electrodes.

2. Experimental procedure

2.1. Preparation of glass powder

A series of glasses (G1–G6) based on the $Na_2O-K_2O-BaO-B_2O_3-SiO_2$ system were prepared by partially substituting BaO with CuO as a

dopant. Using high-purity (>99.0 %) raw materials (Table S1 in the Supporting Information), the compositions were designed according to formula $5R_2O-(25-x)BaO-35B_2O_3-35SiO_2-xCuO$ where x ranges from 0 to 16 mol % (see Table 1). The detailed synthesis procedure for the glass powders is provided in the Supporting Information.

2.2. Characterization

To probe the structural evolution of the borate and silicate networks, Fourier transform infrared (FTIR) spectroscopy was conducted via the KBr pellet method. The spectra were recorded from 400 to 4000 cm^{-1} . The plot is focused on the 400–2000 cm^{-1} region, as it contains the principal vibrations related to $[BO_4]$ and $[BO_3]$ units.

Raman spectroscopy ($\lambda = 532$ nm, 400–1600 cm^{-1}) was used to complement the FTIR analysis and resolve overlapping borate modes. The wavenumber axis was calibrated to the Si standard at 520.7 cm^{-1} . Spectra were processed with a unified linear baseline, and constrained deconvolution employed Gaussian-Lorentzian (GL) profiles with uniform FWHM across comparable sub-bands. Peak centers were anchored to canonical borate assignments— $[BO_3] \approx 1450$ cm^{-1} and $[BO_4] \approx 1350$ cm^{-1} —allowing only minor sample-to-sample shifts; fitted sub-band areas were normalized to the total area for inter-sample comparison. From these fits, the tetrahedral-boron fraction (N_4) was estimated, and the intensity ratio between the bending region ($\approx 300\text{--}600$ cm^{-1} , Q^n) and the stretching region ($\approx 900\text{--}1200/1300$ cm^{-1} , Q^n) was used as an auxiliary index of network polymerization and non-bridging-oxygen formation.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the B 1s, O 1s, and Cu 2p core levels. All spectra were charge-referenced to the C 1s peak at 284.8 eV. After Shirley background subtraction, they were fitted with Gaussian-Lorentzian (GL) profiles, constraining the FWHM to be uniform for chemically similar components. The B 1s spectra were deconvoluted to quantify the $[BO_4]/[BO_3]$ ratio. The O 1s spectra were fitted to distinguish bridging oxygen (BO) from non-bridging oxygen (NBO), and the NBO/BO area ratio was used to assess network connectivity. The copper valence state was evaluated by analyzing the Cu 2p_{3/2} main peak, its shake-up satellites, and the Cu LMM Auger line. The modified Auger parameter (Wagner parameter) was utilized to differentiate between Cu^{2+} and Cu^+ species.

X-ray diffraction (XRD) was used to evaluate crystallization under

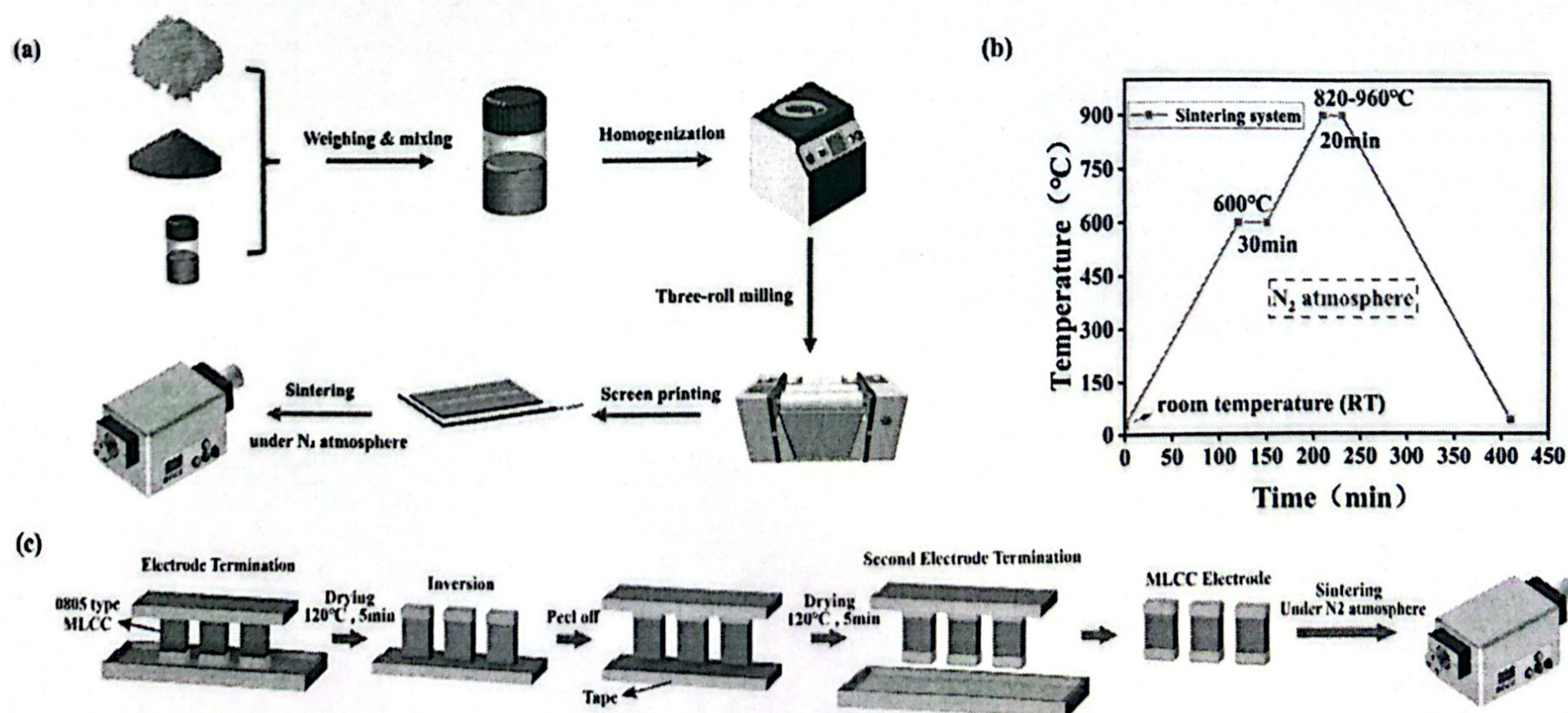


Fig. 1. (A) Preparation flowchart of conductive copper paste; (b) Temperature profile for copper paste sintering; (c) Process flow of copper paste encapsulation at both terminals of the MLCC.

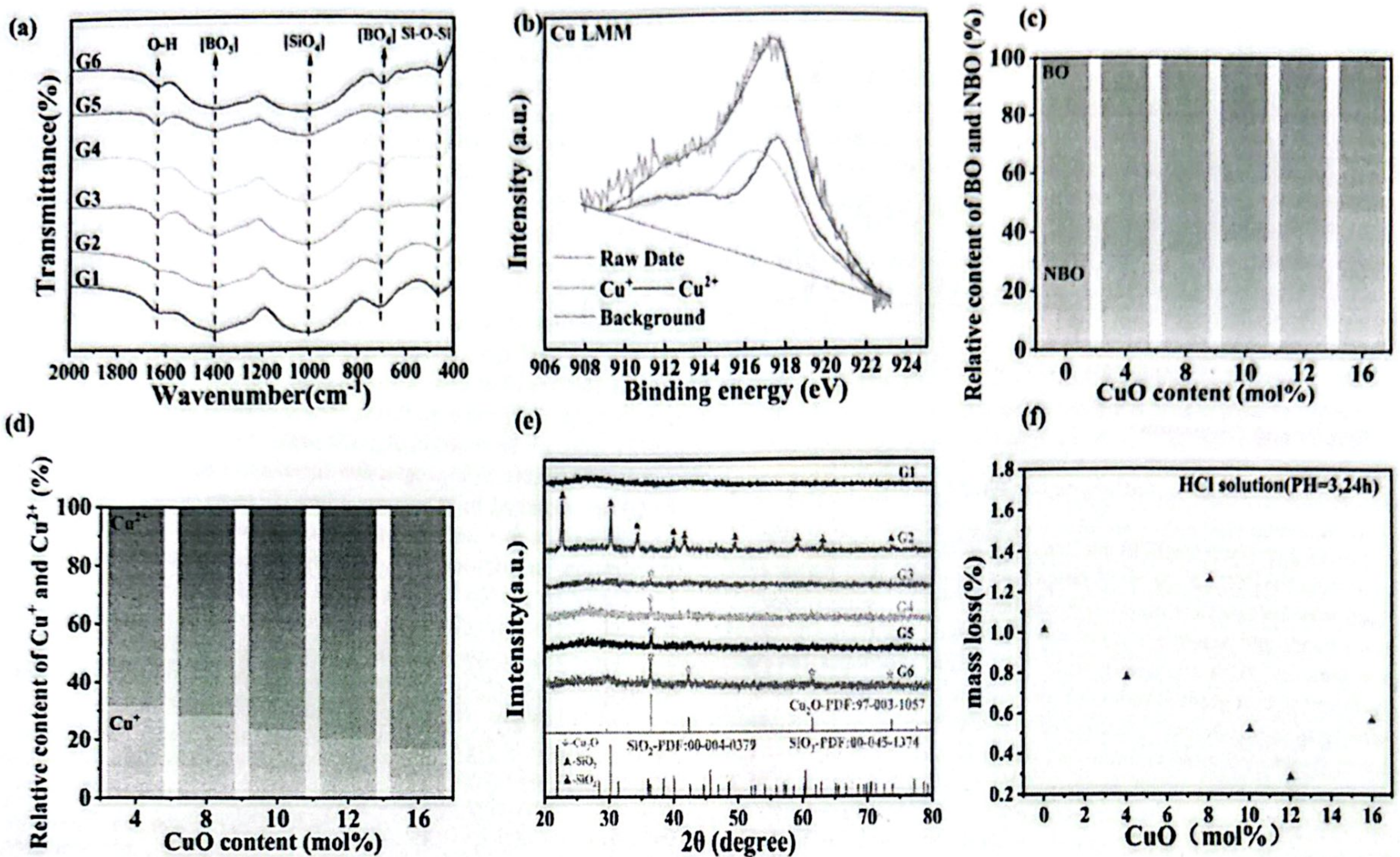


Fig. 2. (A) FTIR spectra of G1-G6 (recorded 400~4000 cm^{-1} ; plotted 400~2000 cm^{-1} , where the network-related bands are concentrated); (b) Cu LMM Auger spectrum; (c) Variation of NBO/BO ratio as a function of CuO content; (d) Variation of $\text{Cu}^+/\text{Cu}^{2+}$ ratio as a function of CuO content; (e) XRD patterns of glass samples G1-G6 fired under the same schedule as Cu paste co-firing; (f) acid-leaching weight loss.

the same co-firing schedule applied to the copper paste. Glass powders were heat-treated following the thermal profile in Fig. 1(b) and then measured by XRD. Diffractograms were compared against ICDD PDF database entries; the appearance of discrete reflections above the amorphous halo was taken as evidence of crystalline phase formation and used for phase assignment.

The thermal properties of the glass were investigated using a Differential Scanning Calorimeter (DSC). The testing parameters were set as follows: a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and a temperature range of 25~1000 $^{\circ}\text{C}$. From the DSC curve analysis, the glass transition temperature (T_g), crystallization onset temperature (T_p), and thermal stability parameter ΔT ($\Delta T = T_p - T_g$) were obtained. These parameters were used to evaluate the thermal stability and crystallization resistance of the glass.

The sintering behavior of the glass powder and its wettability characteristics on the substrate were studied using a Heating Microscope (HM, EM301-M16). Cylindrical specimens (2 mm diameter) were prepared by pressing approximately 0.1 g of powder at 0.5 MPa. These specimens were heated to 1000 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ while monitoring the process in real time. Key parameters such as the sphere temperature (ST), hemisphere temperature (HT), and wettability angle were recorded to assess sintering performance and interfacial bonding.

To evaluate the chemical stability in an acidic environment, cylindrical specimens (approximately 0.2 g each) were pressed from glass powder and sintered at 820 $^{\circ}\text{C}$ for 20 min. The sintered samples were then immersed in a hydrochloric acid solution (pH 3.0) at 55 $^{\circ}\text{C}$ for 24 h. Subsequently, they were rinsed three times with ethanol and dried at 100 $^{\circ}\text{C}$ for 10 h. Corrosion resistance was assessed based on the mass change before and after immersion, with the mass loss rate (WL) calculated by Eq. (1):

$$WL = \frac{W_0 - W_1}{W_0} \times 100\% \tag{1}$$

where W_0 and W_1 are the masses before and after immersion, respectively.

Together, these multi-faceted characterization methods provided a comprehensive understanding of the structural characteristics and property evolution of the CuO-doped glasses.

2.3. Preparation of MLCC copper paste

Paste Composition & Preparation: The conductive copper paste comprised 35 wt% spherical Cu powder (1 μm), 35 wt% flake Cu powder (1 μm), 20 wt% organic vehicle (ethyl cellulose/ α -terpineol), and 10 wt % flake-like base glass powder (prepared per the optimized process). The procedure for paste preparation and conductive copper thick-film formation is schematically illustrated in Fig. 1(a). The constituents were first weighed and placed into a sealed plastic container. A non-contact homogenizer was employed for cyclic pre-dispersion to achieve preliminary solid-liquid mixing. The pre-mixed paste was subsequently finely ground using a three-roll mill. After five rolling cycles, a uniformly dispersed paste with a fineness below 10 μm was obtained. The viscosity of this paste, as measured by a Brookfield-DV2T viscometer at 25 $^{\circ}\text{C}$ and 10 rpm, was in the range of 69~99 kCP.

Thick-Film Fabrication & Sintering: The paste was screen-printed onto alumina substrates. The films were dried (140 $^{\circ}\text{C}$, 10 min) and sintered in N_2 (80 mL/min) using the profile in Fig. 1(b). This profile involved heating at 5 $^{\circ}\text{C}/\text{min}$ to 600 $^{\circ}\text{C}$ (10 min hold) for organic removal, followed by a ramp to 820 $^{\circ}\text{C}$ (20 min hold) for metal particle sintering, and furnace cooling.

MLCC Application & Characterization: The same paste and protocol were used to form terminal electrodes on 0805 MLCCs (Fig. 1(c)). Electrode sheet resistance was averaged from five four-point probe measurements (Model RT-70V, SZT-C). Cross-sections (prepared as in Fig. 4(a)) were analyzed by SEM and EDS to examine the Cu/ceramic

Table 2
FTIR peak assignments for the R_2O -BaO- B_2O_3 - SiO_2 -CuO glass samples.

Absorption bands (cm ⁻¹)	Vibration types
440–450	Characteristic vibration of Si-O-Si [28,37,38]
702–714	Stretching motion of [BO ₄] [37]
1000–1005	Stretching vibrations of Si-O and Si-O-Si in the [SiO ₄] tetrahedron [39]
1383–1394	Stretching vibration of B-O-B in the [BO ₃] triangle [40]
1636	Bending vibration of OH in water [28,40]

interface microstructure and glass phase distribution.

3. Results and discussion

3.1. Structural analysis of CuO-doped borosilicate glasses

Fig. 2(a) presents the FTIR spectra of R_2O -BaO- B_2O_3 - SiO_2 -CuO glass samples in the 400–2000 cm⁻¹ range, used to assess how partial substitution of BaO by CuO modifies the network. Table 2 summarizes the major bands and assignments. All samples exhibit the typical borosilicate features. With increasing CuO, the diffuse envelopes broaden, consistent with a gradual reduction in network polymerization [28]. A weak band at ~1636 cm⁻¹, attributed to H-O-H bending of physisorbed water, shows negligible variation across the series, indicating a similar trace moisture level in all samples. The 1383–1394 cm⁻¹ band is assigned to [BO₃]-related B-O stretching, while the 702–714 cm⁻¹ band corresponds to [BO₄]-related vibrations. As the CuO content increases, the [BO₃] band intensifies whereas the [BO₄] band weakens, indicating a trend toward [BO₄] → [BO₃] conversion in the borate sub-network. A band near ~1000 cm⁻¹ is assigned to the non-bridging O stretch in [SiO₄]; the 440–450 cm⁻¹ feature corresponds to Si-O-Si vibrations. Across the composition window, only minor changes are observed in these silicate-related bands, suggesting a comparatively stable silicate

backbone.

For copper-valence analysis, we combined Cu LMM Auger (Fig. 2(b)) with Cu 2p XPS (Fig. S2(a–e)). Because Cu⁺ and Cu⁰ can overlap in the Cu 2p region, the LMM spectra were analyzed concurrently; the absence of a Cu⁰ fingerprint in LMM, together with pronounced Cu 2p shake-up satellites and the modified Auger (Wagner) parameter, indicates that copper is predominantly Cu²⁺ with a minor Cu⁺ fraction [29]. Under this valence distribution, Cu behaves as a network-modifying cation, and its local coordination is dominated by Jahn-Teller-distorted CuO₆ octahedra [28,30,31].

Fig. 2(c) and (d) present statistical summaries of the NBO/BO ratio and the Cu⁺/Cu²⁺ ratio as a function of CuO content, respectively. The relative fractions of BO, NBO, and different copper valence states were derived from XPS peak-area fitting. The corresponding O 1s deconvolution results are provided in Fig. S3. As shown in Fig. 2(c), increasing CuO content leads to a progressive increase in non-bridging oxygen (NBO) accompanied by a corresponding decrease in bridging oxygen (BO), indicating that CuO incorporation promotes glass-network depolymerization. In addition, Fig. 2(d) shows that copper remains predominantly in the Cu²⁺ state, while the relative fraction of Cu⁺ gradually decreases with increasing CuO content. These trends suggest that CuO incorporation promotes network depolymerization primarily through the action of Cu²⁺ as a network-modifying cation, leading to the cleavage of bridging oxygen bonds and the formation of non-bridging oxygens. Notably, while these XPS results clearly reveal the compositional trends and network-modifying role of CuO, they reflect the glass surface chemistry after processing, and the long-term stability of the Cu valence states and NBO/BO distribution under prolonged service or aging conditions remains to be investigated in future work.

Fig. 3 summarizes the Raman constrained deconvolutions (sub-band areas normalized to the total), with peak positions and assignments listed in Table S2 [31–33]. The fraction of tetrahedral boron is defined as

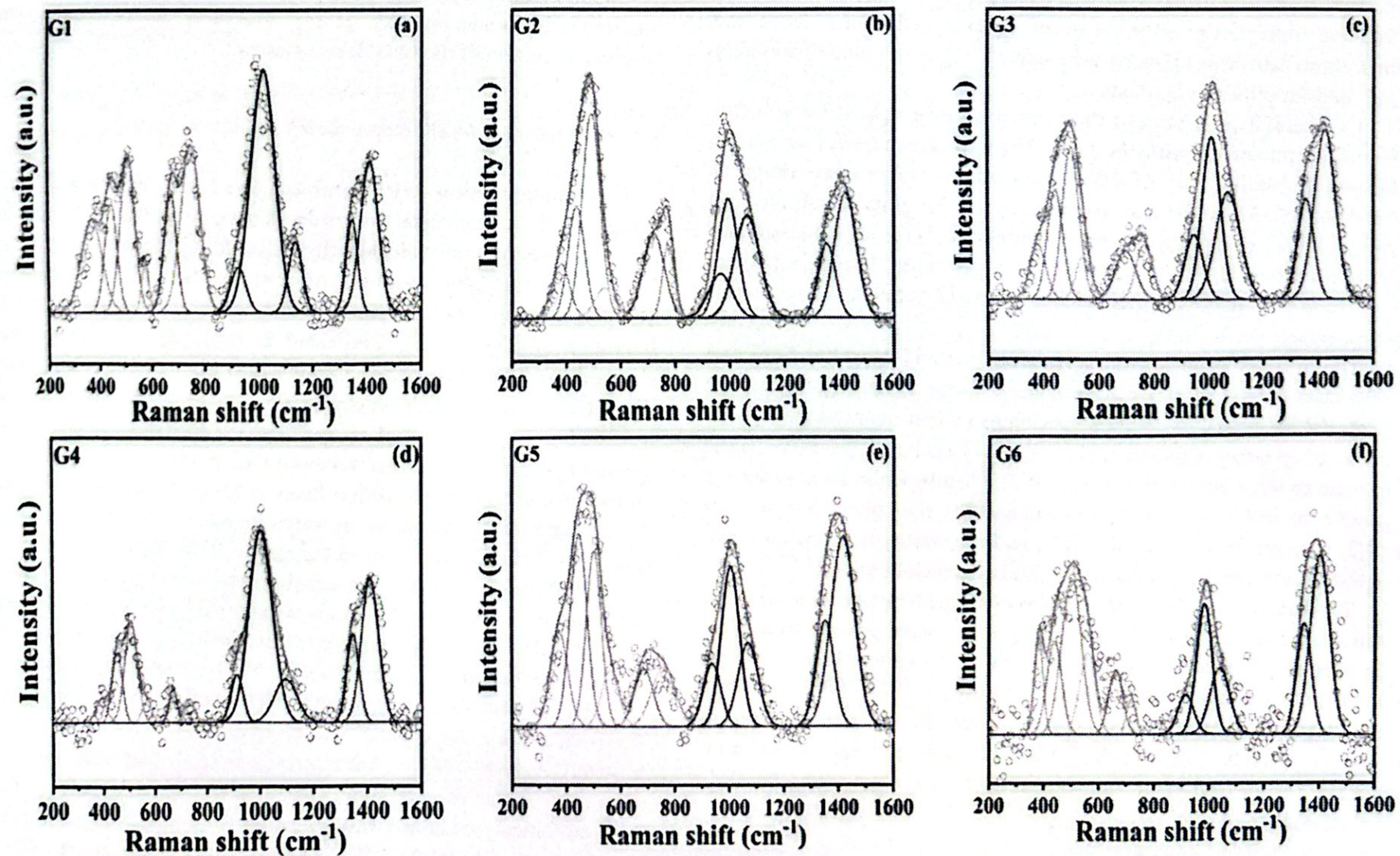


Fig. 3. Raman band deconvolution of glasses G1-G6.

Table 3

Thermal parameters of the glass series: T_g , T_p , ΔT , spheroidization (ST) and hemispherical (HT).

No.	T_g (°C)	T_p (°C)	ΔT (°C)	ST (°C)	HT (°C)
G1	604	665	61	>1000	>1000
G2	570	692	122	894	960
G3	558	678	120	819	826
G4	557	683	126	811	817
G5	560	689	129	819	846
G6	543	702	159	911	926

$$N_4 = \frac{A_{[BO_4]}}{A_{[BO_3]} + A_{[BO_4]}} \quad (2)$$

where $A_{[BO_4]}$ and $A_{[BO_3]}$ are the summed fitted areas of the $\sim 1350\text{ cm}^{-1}$ and $\sim 1450\text{ cm}^{-1}$ band groups, respectively. As an auxiliary depolymerization index, we use

$$R_{Q/Q} = \frac{A_{300-600}}{A_{900-1200/1300}} \quad (3)$$

the integrated-area ratio between the bending ($\sim 300\text{--}600\text{ cm}^{-1}$, Q^m) and stretching ($\sim 900\text{--}1200/1300\text{ cm}^{-1}$, Q^n) regions [31,34]. With increasing CuO, N_4 decreases from 0.32 to 0.26, and $R_{Q/Q}$ drops from 1.23 to 0.36. Meanwhile, the high-polymerization Q3 band red-shifts and the Q2/Q1 bands move to lower wavenumbers, indicating a transition toward lower-polymerized silicate units with NBO enrichment [34]. These trends are consistent with the findings from FTIR and XPS. In particular, Fig. S4 presents the B 1s XPS deconvolutions, showing a decrease in $[BO_4]$ units accompanied by a corresponding increase in $[BO_3]$, which is consistent with the structural evolution inferred from the Raman analysis.

Although both BaO and CuO act as network modifiers, their structural roles are distinct. Ba^{2+} —with a larger ionic radius, lower field strength, and predominantly ionic bonding—primarily serves as a charge compensator and can stabilize $[BO_4]^-$ units at low modifier contents [35]. By contrast, Cu^{2+} —with a smaller radius, higher field strength, and a tendency toward partially covalent Cu–O coordination—more effectively competes for coordination sites, weakens B–O–B and Si–O–Si bridges, generates non-bridging oxygens (NBOs), and thereby depolymerizes the network [36]. Therefore, even when CuO increases at the expense of an equimolar amount of BaO, the characteristic depolymerizing action of Cu^{2+} destabilizes $[BO_4]$ and drives its conversion to $[BO_3]$. The correlated variations in O 1s, B 1s, and Raman metrics support this interpretation, indicating that the transformation is not simply due to BaO reduction but arises from the intrinsic network-modifying behavior of Cu.

In summary, with increasing CuO content, the borate subnetwork undergoes a $[BO_4] \rightarrow [BO_3]$ transformation accompanied by NBO enrichment, leading to a more relaxed glass network, whereas the silicate backbone remains structurally intact.

3.2. Glass performance and phase stability: wettability, thermal behavior, and chemical durability

Figure S5 shows a representative DSC thermogram of G1, which illustrates how the glass transition temperature (T_g , tangent method) and the crystallization onset temperature (T_p , onset method) are determined. The T_g and T_p values for G1–G6 were extracted using the same procedure and are summarized in Table 3. With increasing CuO content, T_g decreases overall—with a slight rebound at 12 mol %—whereas T_p exhibits a modest overall increase; consequently, the interval $\Delta T = T_p - T_g$ widens. This behavior is attributed to gradual substitution of Cu^{2+} for Ba^{2+} in the glass network, which increases non-bridging oxygens (NBOs), relaxes the network, and thus lowers T_g while enhancing resistance to crystallization. These thermal trends are consistent with

the IR results indicating network relaxation and an increased NBO content.

Figure S6 shows the hot-stage evolution of G1–G6. Upon heating, the compacts first contract, then expand slightly, and finally soften and flow. The thermal parameters are listed in Table 3, and we use the hemispherical temperature (HT) as the softening-related metric. As the CuO content increases from 0 to 10 mol % (G1→G4), HT drops from $>1000\text{ °C}$ to 817 °C , indicating facilitated softening and higher melt fluidity. When CuO is further increased to 16 mol % (G6), HT rises to 926 °C , the melt flowability decreases, and the contact angle increases. Consistently, the glass-substrate contact angle decreases up to 10 mol % CuO and then increases at higher CuO—i.e., wettability improves at moderate CuO but deteriorates when CuO is excessive.

Fig. 2(e) shows the XRD patterns of the G1–G6 glass samples heat-treated under the same co-firing schedule used for the Cu paste. G1 exhibits only a broad amorphous halo; G2 shows diffraction peaks at $2\theta \approx 23\text{--}27^\circ$ and $\approx 36\text{--}45^\circ$, corresponding to SiO_2 crystalline polymorphs; G3–G6 display weak to moderate reflections matching Cu_2O , with no characteristic CuO peaks detected. These results indicate that with increasing CuO content, the redox equilibrium tends to favor Cu_2O + glass coexistence rather than precipitation of crystalline CuO, while SiO_2 crystallization is suppressed at medium-high CuO levels.

Mechanistically, the appearance of a small amount of Cu_2O is consistent with the equilibrium $Cu_2O + \frac{1}{2}O_2 \rightleftharpoons 2CuO$ suggesting that Cu_2O/CuO acts as an oxygen-buffering pair that fine-tunes the local oxygen partial pressure $p(O_2)$ during co-firing: shifting toward CuO under higher $p(O_2)$ (consuming oxygen) and toward Cu_2O under lower $p(O_2)$ (releasing oxygen) [41]. This buffering behavior reduces the driving force for further oxidation of metallic copper and facilitates burnout of organic components during the co-firing process. In contrast, the low-doped sample (G2) exhibits SiO_2 crystallization, which increases viscosity and may induce thermal-expansion mismatch, thereby hindering co-shrinkage with the Cu paste [42]. Consistent with the subsequent electrical-performance analysis, a distinct composition/process window is observed: when the CuO content is $\geq 8\text{ mol %}$ (G3–G6), discernible Cu_2O reflections appear; at $<8\text{ mol %}$ (G1–G2), Cu_2O reflections are absent and SiO_2 crystallization is more readily induced.

Fig. 2(f) presents the percentage mass loss (wt %) of G1–G6 after 24 h of immersion in pH 3.0 HCl at 55 °C . The mass loss of all glass samples is less than 1.5 %, indicating good acid durability under pH 3 HCl; this suggests tolerance to acidic processing steps, although specific plating chemistries warrant separate evaluation. The sample with 12 mol % CuO exhibits the lowest mass loss and demonstrates the best acid corrosion resistance.

Borate glasses are generally more susceptible to acid attack; however, in the present system, the comparatively high field strength of Cu^{2+} and its partially covalent Cu–O coordination can improve the local chemical environment, enhance bond stability, and reduce the effective density of weakly bonded sites prone to proton attack, thereby lowering the dissolution rate and yielding a more stable surface morphology at the macroscopic level [18,23].

Overall, moderate CuO levels ($\approx 8\text{--}12\text{ mol %}$) simultaneously lower HT and contact angle, suppress SiO_2 crystallization, and provide a beneficial Cu_2O -based oxygen-buffer effect during co-firing, whereas excessive CuO ($\geq 16\text{ mol %}$) increases melt viscosity, impairs wettability, and undermines uniform densification.

3.3. Microstructural and electrical performance of the CuO-modified copper paste

Fig. 4(a1–a6) shows the surface microstructures of copper films formed from copper pastes based on glasses with varying CuO-for-BaO substitution levels (mol %), sintered at their respective optimal temperatures, along with the corresponding trends in sheet resistance. Experimental results demonstrate that the CuO content significantly affects both the sintering densification and electrical conductivity of the

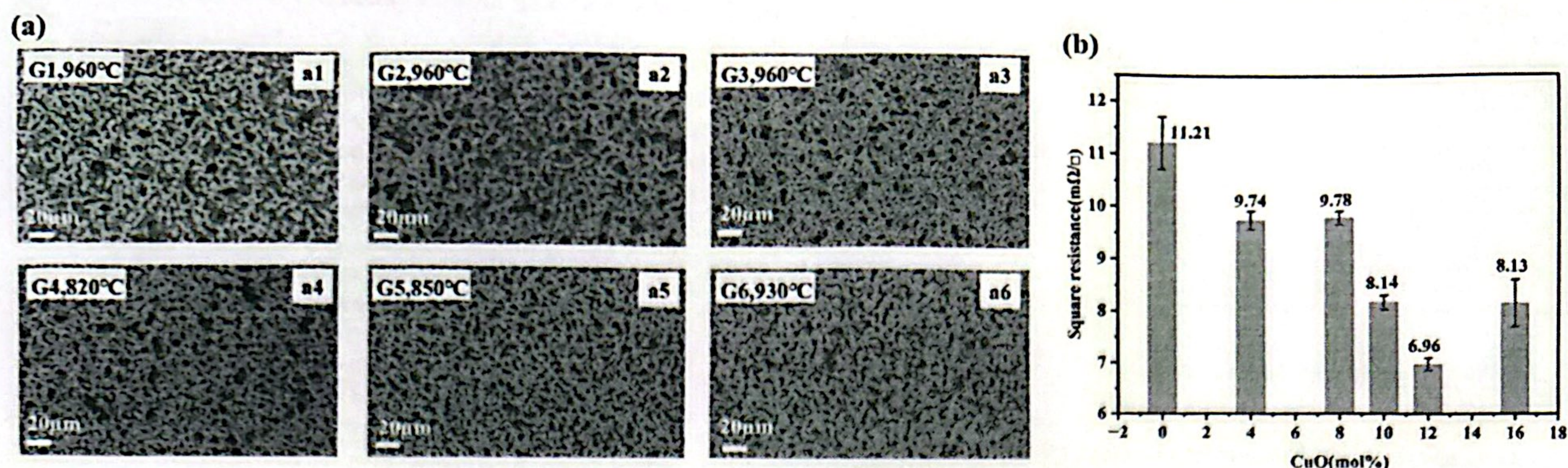


Fig. 4. ((a) Surface microstructures of Cu films prepared with different glasses sintered at their respective optimal temperatures (a1) G1, 960 °C; (a2) G2, 960 °C; (a3) G3, 820 °C; (a4) G4, 820 °C; (a5) G5, 850 °C; (a6) G6, 930 °C; (b) Variation of sheet resistance of copper thick films as a function of CuO content in the glass.

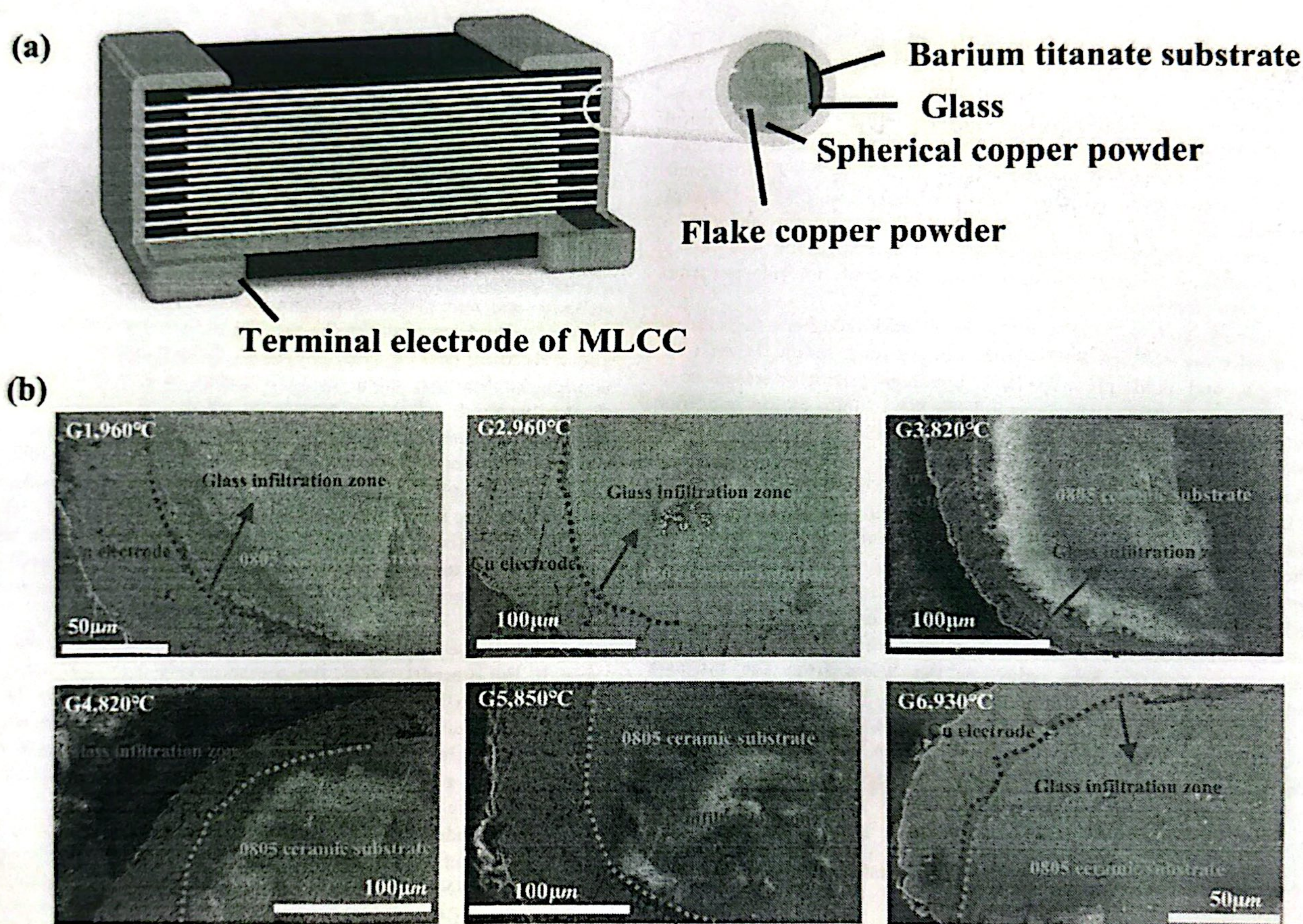


Fig. 5. (A) Schematic cross-sectional view of the MLCC terminal electrode. (b) Cross-sectional SEM images of the interfaces between sintered Cu electrodes and 0805 ceramic substrates for G1-G6 samples after terminal electrode fabrication.

copper paste. The sheet resistance of the conductive copper films as a function of CuO content in the glass is presented in Fig. 4(b). When the CuO content is 12 mol %, the copper film exhibits the best sintering quality and electrical performance, with a minimum sheet resistance of 6.96 mΩ/□.

Fig. 4(a1-a6) illustrates the variations in sintering densification and pore distribution of copper films as a function of CuO content. When the

CuO content is low (G1 and G2), even at a high sintering temperature of 960 °C, the copper films still exhibit a high density of small pores, with insufficient interparticle bonding and moderate sintering densification. This phenomenon may be attributed to inadequate wettability of the glass melt, which fails to effectively promote the rearrangement and bonding of copper powder particles. As the CuO content increases gradually (G3-G5), the pore distribution becomes more uniform, and the

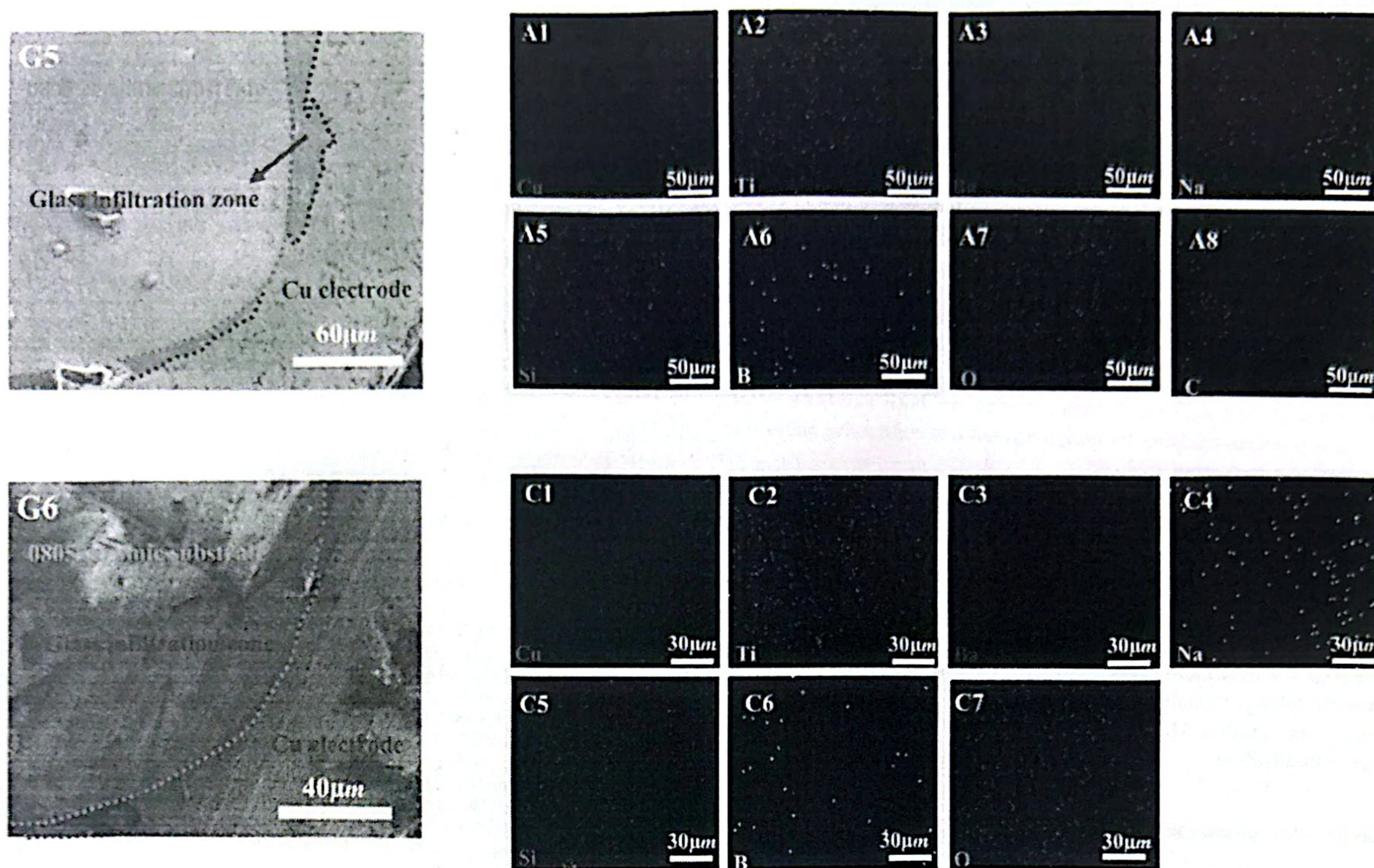


Fig. 6. Cross-sectional SEM and corresponding EDS elemental mapping images of the interfaces between sintered Cu electrodes and 0805 ceramic substrates for samples G5 and G6.

interparticle bonding appears more continuous and better connected at lower sintering temperatures (820–850 °C) consistent with the reduced contact angle and enhanced glass spreading. This indicates enhanced flowability and wettability of the glass melt, enabling more pronounced sintering connectivity of the copper powder. Notably, the sample with 12 mol % CuO (G5) exhibits the densest microstructure, with the fewest pores and tightly bonded particles, demonstrating pronounced glass-assisted connectivity under the tested condition. However, when the CuO content further increases to 16 mol % (G6), although a certain degree of densification is achieved, some regions show inhomogeneous sintering or larger pores. This may result from excessive CuO increasing the glass viscosity and reducing its flowability, thereby hindering the uniform rearrangement and packing of copper powder particles.

Fig. 5(b) shows SEM cross-sectional images of the interface between copper electrodes formed from glasses with different CuO doping levels and 0805-type ceramic substrates. The glass penetration zones indicated by dashed lines clearly reveal the regulatory role of CuO content on glass wettability and interfacial penetration behavior. When the CuO content in the glass is low (G1–G2; $x = 0\text{--}4$ mol %), a narrow, discontinuous penetration layer with a sharp glass-ceramic boundary is observed, indicating limited spreading under the present co-firing conditions. As the in-glass CuO content increases to 8–12 mol % (G3–G5), the penetration depth increases and becomes continuous; the glass infiltrates surface micropores and develops a more continuous interface with a diffuse transition zone in line with the lower contact angle observed for this composition range. However, at 16 mol % CuO (G6), the penetration depth decreases and the interfacial morphology becomes irregular, suggesting inhibited glass infiltration. Taken together, a more continuous penetration layer and a lower contact angle are indicative of improved interfacial bonding in the 10–12 mol % CuO range.

Fig. 6 further presents EDS elemental mapping of the interface

between G5 and G6 samples. The analysis confirms that Cu remains confined to the electrode layer without diffusing into the ceramic body, indicating that interfacial bonding is dominated by the glass phase. In G5, glass components (Si, B, Na) deeply penetrate the ceramic, creating a broad, composite interlayer with Ti and Ba that promotes strong adhesion. In contrast, a reduced distribution and penetration of glass components were observed in G6, indicating that higher CuO content limits glass spreading and inhibits the formation of a continuous bonding layer.

In summary, the in-glass CuO content primarily governs film densification, electrical conductivity, and bond strength during sintering. At an optimal range of CuO levels ($\approx 10\text{--}12$ mol %), the glass melt shows improved wettability and flowability, thereby promoting dense sintering of the copper particles and facilitates deeper, more continuous penetration into the ceramic substrate. This process results in a structurally dense and strongly bonded interface. Among the compositions tested, 12 mol % CuO achieved the highest film densification and the lowest sheet resistance ($\approx 6.96 \text{ m}\Omega/\square$), demonstrating effective sintering assistance and superior electrical performance.

A process-effective composition window of 10–12 mol % CuO has been established based on an integrated analysis of structural, thermal, microstructural, and electrical data. Compositions within this window are characterized by low softening temperatures, effective wettability (minimum contact angle $\approx 36.9^\circ$ at 10 mol %), low sheet resistance ($\approx 6.96 \text{ m}\Omega/\square$ at 12 mol %), and high chemical stability (acid weight loss $< 1.5\%$), without crystallization or interfacial inhomogeneity. At lower CuO contents, inadequate melt flow compromises bonding, while higher contents increase viscosity and degrade wettability, impeding densification. Thus, this optimal window represents a critical balance between structural depolymerization, processing compatibility, and device performance.

4. Conclusion

The CuO-doped R_2O -BaO- B_2O_3 - SiO_2 glass system proved to be an effective inorganic flux for copper thick films, successfully validated on both alumina substrates and multilayer ceramic capacitors (MLCCs). The incorporation of CuO was found to modify the glass network, resulting in reduced sintering temperature, improved wettability (minimum contact angle 36.9°), and enhanced liquid-phase sintering. An optimal CuO range of 10–12 mol % was identified: 10 mol % achieved the lowest firing temperature, while 12 mol % produced the minimum sheet resistance ($\approx 6.96 \text{ m}\Omega/\square$) and highest densification. At higher contents, sintering homogeneity was compromised. It is concluded that CuO regulates melt flow and wettability, thereby stabilizing the co-firing environment. The successful demonstration on both substrate types provides practical guidance for designing lead-free conductive adhesives in electronic packaging applications.

CRediT authorship contribution statement

Jihong Wang: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Chunyu Chen:** Writing – review & editing, Visualization, Supervision, Data curation. **Shenrui Zhang:** Visualization, Formal analysis, Data curation. **Wenzhi Wang:** Visualization, Methodology. **Zhuoling Xu:** Investigation, Data curation. **Huidan Zeng:** Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2026.01.091>.

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