J Electroceram (2006) 16:313–319
DOI 10.1007/s10832-006-9871-7

Conducting perovskite $LaNi_{0.6}Co_{0.4}O_3$ ceramics with glass additions

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Abstract $LaNi_{0.6}Co_{0.4}O_3$ (LNC) is a perovskite-type conducting ceramic oxide, which is an ideal electrode layer for perovskite ferroelectric and piezoelectric thin and thick film devices, owing to its unique crystal structure that can facilitate film growth and improve fatigue behavior. When used for thick films, however, one of the drawbacks is its high sintering temperature of above 1200°C, which can lead to severe inter-diffusion. In an attempt to reduce the sintering temperature of LNC without substantially deteriorating the electrical properties, we have investigated the effects of doping LNC with an appropriate glass addition. LNC powder was synthesized through a solid state reaction process. Varying amounts of glass compositions were then introduced, in order to study their effects on densification, microstructure and electrical properties of LNC. The glass compositions exhibited a strong effect on the sintering behaviors and microstructure, where the density after sintering was improved with increasing amount of glass addition. While the electrical conductivity was adversely affected by an increasing amount of glass addition, the composition with optimal glass addition showed a lowered sintering temperature of 950°C, and at the same time maintained a high conductivity of 117 S cm^{-1}.

Keywords Conductive oxide · Perovskite · Electrode · Glass addition · Sintering

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1 Introduction

In thick film fabrication for micro-electromechanical systems (MEMS) and solid fuel cells (SOFC) applications, the electrode materials must be able to remain electrically conductive and compatible with piezoelectric lead zirconate titanate (PZT) and electrolytes like yttria stabilized zirconia (YSZ) at high processing temperatures [1–3]. In recent years, conducting ceramics like RuO_2, $SrRuO_3$, IrO_2, and $YBa_2Cu_3O_7$ are considered as promising electrode materials, in replacement of Pt, Au, and Ag/Pd alloys, to solve problems associated with these metal electrodes, such as inter-diffusion and high cost [4–6].

$LaNi_{0.6}Co_{0.4}O_3$ (LNC) is a perovskite-type conducting ceramic oxide, which has a rhombohedral crystal structure that can facilitate film growth and improve fatigue behavior. It has a conductivity of 10^3 S cm^{-1} at room temperature, which arises from the interaction between atomic orbitals of the cations and oxygen atoms [7–9]. Unlike $LaNiO_3$, which is also conductive but decomposes at temperature above 860°C, LNC is stable at temperatures above 1000°C due to the stabilization effect from Co [7, 10, 11]. However, the drawback of using LNC in thick film applications is its high sintering temperature above 1200°C, which could lead to severe inter-diffusion and affect its mechanical and electrical properties [12]. The concept of liquid phase sintering to facilitate the sintering process of LNC could be adopted to achieve a low sintering temperature while maintaining a high conductivity for LNC in thick film applications. Glass, which could soften into a liquid medium at its melting point, is a cheap and effective sintering aid in liquid phase sintering. Single oxides and glass additives have successfully lowered the sintering temperatures of some conductive metal thick films like silver [13], copper [14] and tungsten [15]. Although there are some reports on LNC as a thick film electrode in SOFC [7, 12] and

Table 1 Composition and properties of the selected glass used in this work

Glass Cat. No.	Composition	Transformation point (°C)	Softening point (°C)	Density (g cm^{-1})	Particle size (μm)
ASF-1311	Bi_2O_3-SiO_2-ZnO-Al_2O_3	450	550	4.1	3.3

for capacitors [16], and as a thin film electrode for ferroelectric and piezoelectric films [17], few mentioned the lowering of sintering temperature of LNC through liquid-phase sintering.

In this paper, the effects of glass additions on the electrical properties and sinterability of LNC ceramics were investigated, where the feasibility of applying LNC with glass additions in thick film processing was considered.

2 Experimental procedure

Bulk ceramic $LaNi_{0.6}Co_{0.4}O_3$(LNC) was prepared using the starting materials of $La(OH)_3$, NiO and Co_3O_4, which were mixed together and calcined at 1100°C for 8 h in air to form the single phase of LNC. The resulting calcined powder was mixed with different amounts of a commercially available glass powder provided by Asahi Glass Co. Ltd., Japan (see Table 1). Using polyvinyl alcohol as the binder, the mixed powders were hydraulically pressed into pellets of 1 cm in diameter, and were debinded. Subsequently, the pellets were sintered in a temperature range of 800° to 1000°C for 0.5 hour each in air. For comparison, LNC without glass addition was pressed into pellets and fired in the same temperature range for 0.5 hour each in air. The sintered bulk samples were measured for density by the Archimedes' Principle. Linear shrinkage was measured using a micro-screw gauge. X-ray diffraction analysis, XRD (D8-ADVANCE), was carried out to determine the phase structure of the sintered pellets. The grain morphologies of the fractured surfaces were observed using field-emission scanning electron microscopy, FESEM (JSM-6700F). Electrical conductivity was measured using a four-point probe system (MCP-T360).

3 Results and discussion

3.1 Phase analysis

Figure 1 shows the XRD patterns of $LaNi_{0.6}Co_{0.4}O_3$(LNC) ceramic samples with different glass amount sintered at 1000°C for 0.5 h. A single perovskite phase with a rhombohedral structure depicted by the double peaks was detected for pure LNC (JCPDS File card No. 32-0296). When 3 to

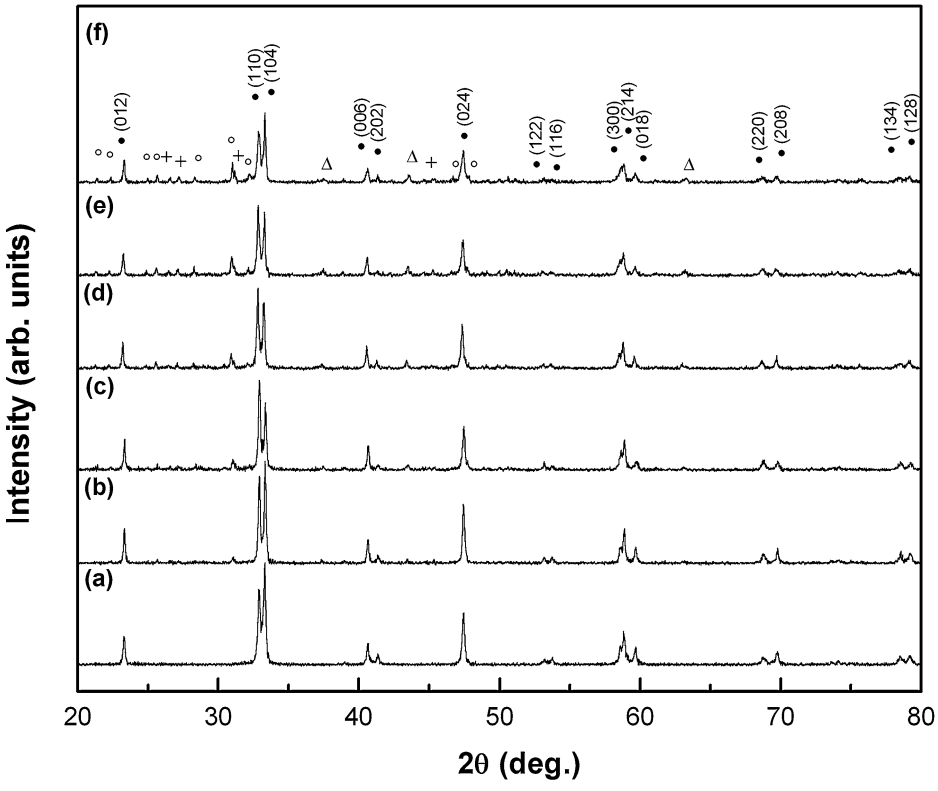

Fig. 1 X-ray diffraction patterns of the LNC ceramic samples containing (a) 0 wt%, (b) 3 wt%, (c) 6 wt%, (d) 10 wt%, (e) 15 wt%, and (f) 20 wt% glass, sintered at 1000°C for 0.5 h, respectively (•: $LaNi_{0.6}Co_{0.4}O_3$; o:$La_{9.33}Si_6O_{26}$; + : $BiLa_2O_{4.5}$; Δ: NiO)

20 wt% glass added, secondary phases, in addition to the primary perovskite phase, were observed. Overlapping of some peaks made the identification of minor secondary phases difficult. Nevertheless, the main secondary phases were found to be $La_{9.33}Si_6O_{26}$ (JCPDS File Card No. 49-0443) and $BiLa_2O_{4.5}$ (JCPDS File Card No. 47-0474). Smaller peaks belonging to NiO (JCPDS File Card No. 44-1159) were also observed in all compositions with glass additions. The peaks of the secondary phases become sharper with increasing amount of glass content, suggest that the amount of secondary phases became more significant. It is most likely that increasing the amount of glass could cause a degree of decomposition of the pure LNC phase into these secondary phases when LNC reacts with the glass composition.

3.2 Sintering characteristics

The density of LNC ceramic samples with different amounts of glass additions sintered at various temperatures is shown in Fig. 2. The theoretical density would be greatly affected by the composition since the density of the glass used is lower than pure LNC. To give a more accurate representation of the relative density of LNC with glass additions, theoretical densities, D_{theo}, of the samples with various glass amounts were calculated according to the rule of mixing:

$$D_{\text{theo}} = \frac{(W_1 + W_2)}{W_1/D_1 + W_2/D_2} \tag{1}$$

where W_1 and W_2 are the weights of pure LNC and glass in the composition, respectively; D_1 and D_2 are the densities of pure LNC and glass, respectively. From Fig. 2, it was observed that pure LNC had a low density in the temperature range of 800° to 1000°C. Its relative density increased slightly with a rise in the sintering temperature. The relative density of pure LNC when sintered at 1000°C is 87.3%. On the other hand, when pure LNC is added with glass, the relative density improved. The relative density of LNC with 3 wt% glass sintered at 1000°C is 92.2%, which is higher than the relative density of pure LNC fired at the same temperature. This indicates that adding glass can lower the sintering temperature of LNC ceramics by liquid phase sintering as the glass has a lower melting point.

The amount of glass addition also has a significant impact on the sinterability of LNC. Relative density increases when the amount of glass addition increases. The relative density of LNC with 20 wt% glass sintered at 1000°C reaches a maximum value of 98.3%. Relative density also increases with a rise in sintering temperature. At a sintering temperature of 800°C, the density of LNC with 10 wt% glass remained below 90%. However, its density rose greatly from 79% at 850° to 96.5% at 950°C, and increased slightly to 97.4% at 1000°C. This relative density is comparable to 98.8%, obtained from pure LNC sintered at 1200°C for 2 h. Therefore, the addition of glass could reduce the sintering temperature of LNC to as low as 950°C, and also reduce the sintering time.

Figure 3 plots the relationship between the linear shrinkage and sintering temperature of LNC with different amounts of glass. It was observed that pure LNC hardly shrink at low sintering temperatures, but when added with 3 wt% glass, the linear shrinkage increases significantly from 0.04% to 11%. The linear shrinkage further improved with the addition of 20 wt% glass, which indicates that shrinkage increases with the addition of glass to LNC. The linear

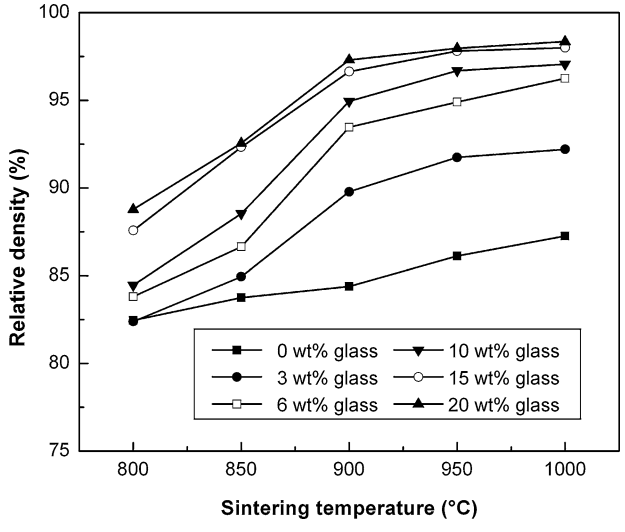

Fig. 2 Relative density of the LNC ceramic samples with different amount of glass addition against sintering temperature

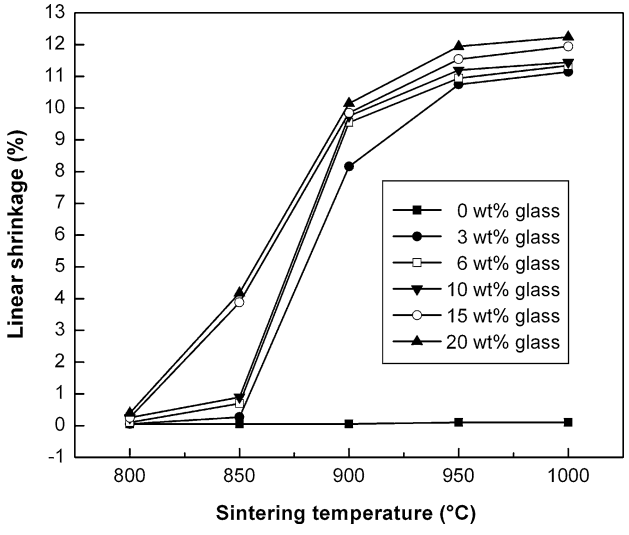

Fig. 3 Linear shrinkage of the LNC ceramic samples with different amount of glass addition against sintering temperature

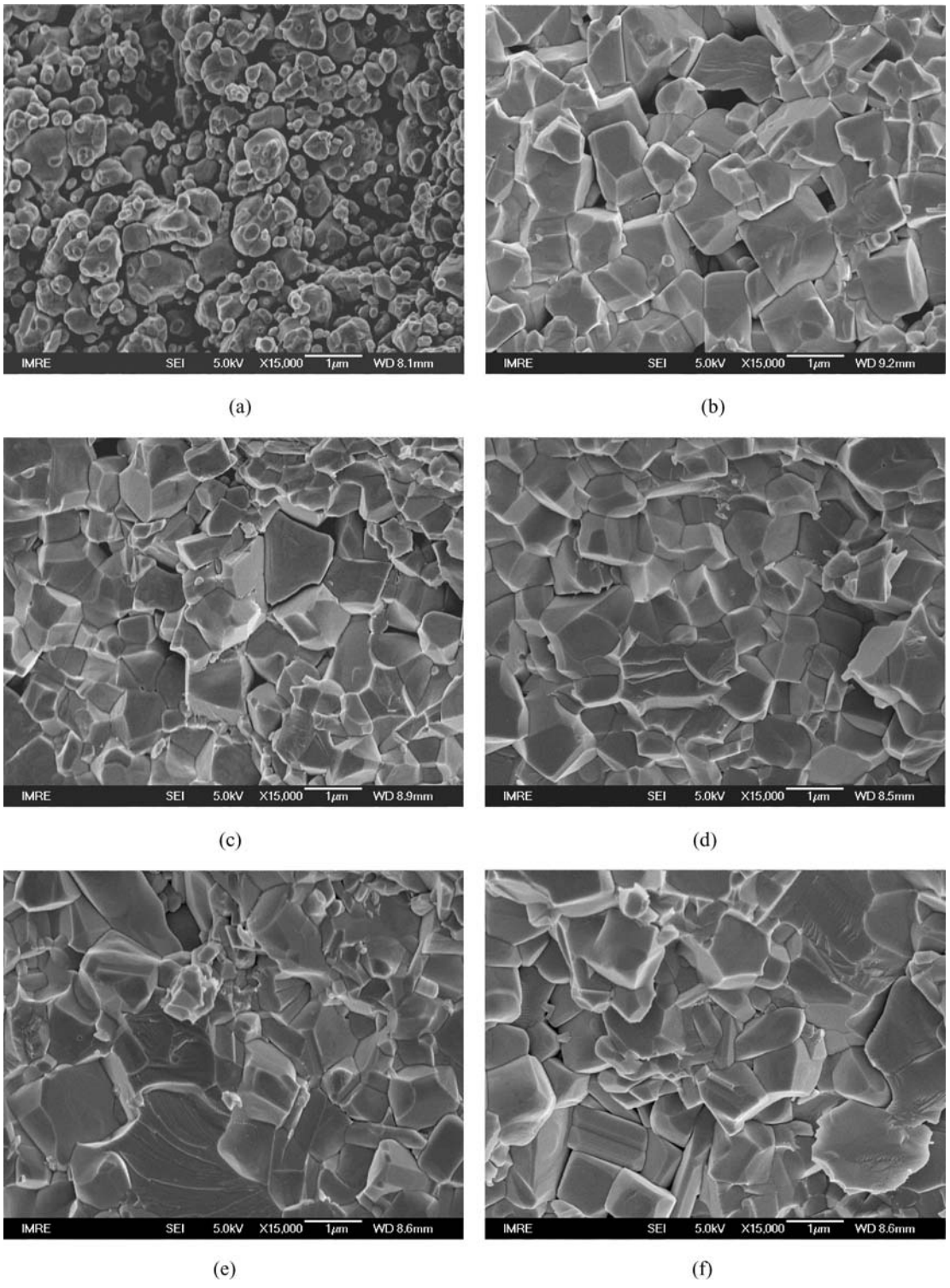

Fig. 4 SEM images of the LNC ceramic samples containing (a) 0 wt%, (b) 3 wt%, (c) 6 wt%, (d) 10 wt%, (e) 15 wt%, and (f) 20 wt% glass, sintered at 1000°C for 0.5 h, respectively

shrinkage of LNC with 10 wt% glass sintered at temperatures of 800°C and 850°C remained low at 0.25% but increased remarkably to 11.0% at 950°C, and 11.4% at 1000°C. This indicates that the glass promotes densification of LNC at 950°C. These results, supported by the densification results discussed previously, again indicate that glass additions could effectively lower the sintering temperature of LNC.

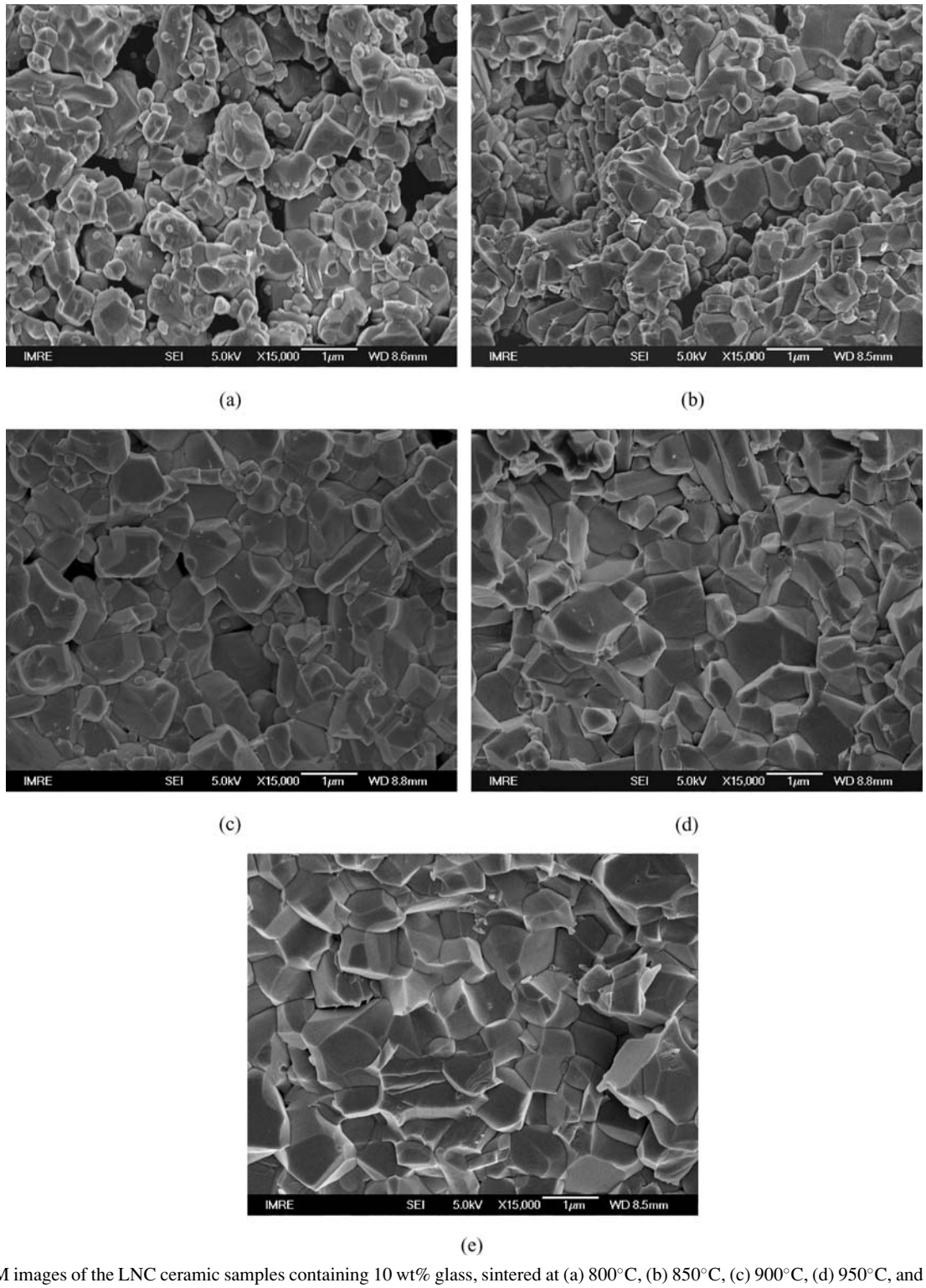

Fig. 5 SEM images of the LNC ceramic samples containing 10 wt% glass, sintered at (a) 800°C, (b) 850°C, (c) 900°C, (d) 950°C, and (e) 1000°C, for 0.5 h, respectively

3.3 Morphology

The morphological evolution of the LNC ceramic samples with glass additions is illustrated in Fig. 4. When pure LNC was sintered at 1000°C, the fractured surface was porous (Fig. 4(a)), indicating that sintering is not achieved. When LNC was added with 3 wt% glass, there is a significant morphological change (Fig. 4(b)). The specimen showed

well-connected grains, although there are a few pores between them. This indicates that the wettability of the selected glass compositions in LNC ceramic is good. With 6 wt% glass addition, the pores became smaller (Fig. 4(c)) and disappeared subsequently to give dense morphologies when more than 10 wt% glass was added (Fig. 4(e) and (f)). It was also observed that the grain size became bigger with increasing amount of glass. In the liquid phase sintering, densification occurs with the enhanced rearrangement of particles through the liquid glass and eventually removes pores from the body [18]. The liquid glass also helps facilitates mass transport and diffusion which cause grain growth. The glass additives are believed to be accumulated at the grain boundaries. The amount of glass addition was also found to affect the grain boundary properties of LNC. As can be observed from Fig. 4, the morphologies of LNC with 3–10 wt% glass showed an inter-granular fracture, indicating that the grain boundaries are mechanically weaker than the grains. However, with the addition of 15–20 wt% glass, a mixture of inter-granular and trans-granular fracture was revealed, indicating that the grain boundaries and grains have approximately the same strength. The effect of sintering temperature on the microstructure of LNC with 10 wt% glass is presented in the SEM micrographs of LNC shown in Fig. 5. The LNC with 10 wt% glass sintered at 800°C and 850°C revealed a very porous microstructure (Fig. 5(a) and (b)), which accounts for the low relative density. With increasing sintering temperature, porosity level decreased and grain growth apparently increased (Fig. 5(c)–(e)).

3.4 Electrical conductivity

Figure 6 presents the conductivity of LNC ceramic samples with different amount of glass additions when sintered at differing sintering temperatures. The conductivity of pure LNC sintered at 1000°C was measured to be 435 S cm^{-1}. It was found that this conductivity could also be achieved by adding 3 wt% glass sintered at 1000°C, which gives a conductivity of 367 S cm^{-1}. The conductivity remained fairly constant at 251 S cm^{-1} with 6 wt% glass and decreased slightly to 117 S cm^{-1} with 10 wt% glass. This implies that low glass additions could also maintain an acceptable conductivity with higher density at a lowered sintering temperature. However, the conductivity decreased dramatically to 0.94 Scm^{-1} when the amount of glass increased to 20 wt%. The low conductivity was attributed to the significant amount of non conductive secondary phases formed at the grain boundaries with larger amount of glass additions. The conductivity of LNC with glass addition could also be affected by the sintering temperature. It was observed that conductivity of LNC with 10 wt% glass showed a significant increase from 850° to 950°C and remained fairly constant from 950° to 1000°C, owing to a dense microstructure. Conductive paths become clearer as the conductive particles are brought closer to each other at higher annealing temperatures, thus conductivity improves. The electrical properties are also consistent with the dense morphologies shown in the SEM micrographs and the densification results shown in Figs. 2 and 5.

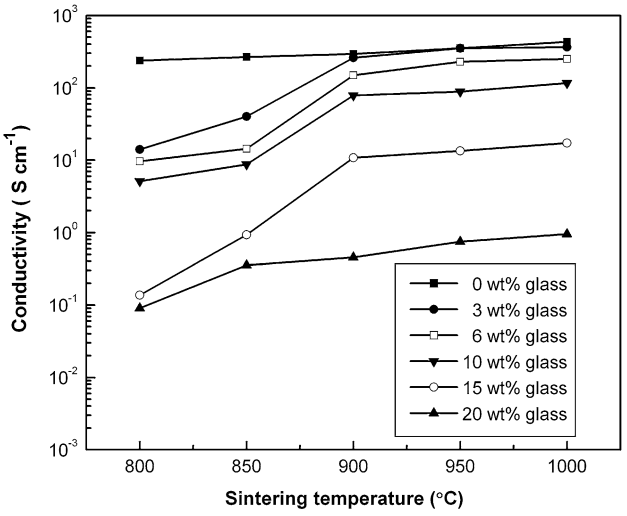

Fig. 6 Electrical conductivity of the LNC ceramic samples with different amount of glass addition sintered at various sintering temperatures

4 Conclusions

Varying amounts of Bi_2O_3-SiO_2-ZnO-Al_2O_3 glass additions were introduced in LNC to improve the relative density at a lowered sintering temperature of 950°C. While the ceramic became denser with an increasing amount of glass additions, substantial grain growth was observed with glass addition. However, the increased amount of glass addition has an adverse effect on the conductivity due to the increased amount of secondary phases present. The compositions with 6–10 wt% of glass could significantly improve the densification of LNC ceramics while maintaining a fairly high electrical conductivity of ∼117 S cm^{-1}.

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