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Microwave dielectric properties of glass-ceramic composites for low temperature co-firable ceramics

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Abstract

Ba–B–Si glass was added to Ba–Nd–Sm–Bi–Ti–O (BRT_{114}) microwave dielectric material for LTCC applications. Conventional one-step processing method for preparing glass-BRT_{114} composite materials yields low dielectric constant, since the glass was easy to react with BRT_{114} and forms a low dielectric constant phase, $Ba_3B_6Si_2O_{16}$. A large proportion of pores appeared. The nature of glass, whether it is sol-gel derived or fused, shows marked influence on the microstructure and microwave dielectric properties of the composites. A two-step process containing precoating the BRT_{114} powders with a thin layer of glass, followed by conventional samples preparation process, tremendously improved the densification behaviour of the material. The formation of pores and interactions between glass and BRT_{114} was greatly suppressed such that materials with high dielectric constant ($\varepsilon_r = 40$) were achieved by sintering 9 wt.% glass-containing composite at 950 °C for 2.5 h.

Keywords: Glass ceramics; Microwave ceramics; BRT_{114}; LTCC materials

1. Introduction

Low temperature co-firable ceramics (LTCC) possessing good microwave dielectric properties have been widely investigated due to the necessity for miniaturization of devices in order to reduce the size of wireless communication system.[1–3] However, the microwave dielectric materials possessing high quality factor and large dielectric constant usually require very high sintering temperature and long soaking time to achieve high enough density. On the other hand, using Ag material as conducting materials for transmission lines and ground planes is needed in order to minimize the microwave absorption loss. Reduction of the sintering temperature of the microwave materials to a level cofirable with Ag-electrode materials is thus called for. Generally, low softening temperature glass materials were mixed with the ceramic materials to reduce the firing temperature.[4–9] However, network formers contained in the glass materials may absorb the microwave power profoundly in high frequency regime, degrading the quality factor of the materials.[10] In this article, the microwave dielectric properties of the glass materials and the effect of processing parameters on the characteristics of the glass-to-ceramic composites were investigated. We show that a two-step processing method is able to raise the density of glass-BRT_{114} composites and to increase the dielectric constant of composite to a high value of 40.

2. Experimental

The glass-BRT_{114} specimens were prepared by conventional mixed oxide process. The glass component, which consists of $BaO:B_2O_3:SiO_2$ in the ratio of 42:45:13 wt.% with Ts = 619 °C, were prepared by either hydrolysis of alkoxide mixture (designated as sol-gel glass) or direct fusion process (designated as fused glass). The BRT_{114} was a commercial microwave dielectric (MBRT-90B, Fujititan).

In the one-step process, the sol-gel (or fused) glass of 9–40 wt.% was mixed directly with BRT114 powders, followed by pelletization, and then sintering at 850–950 °C for 2.5 h. For the two-step process, the BRT114 powders were mixed with a small proportion of either sol-gel glass or fused glass (~5.5 wt.%) and were calcined at 700 °C for 1 h. The glass coated BRT_{114} powders were then mixed with fused glass (4.5–34.5

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wt.%), which consists of $BaO:B_2O_3:SiO_2$ in the ratio of 51:45:4 wt.% with Ts = 609 °C, and processed by the same sample preparation conditions of the one-step process.

The crystal structure and microstructure of the sintered samples were examined by using X-ray diffraction (Siemens 5000D) and scanning electron microscopy (Hitachi-2500S), respectively. The microwave properties, dielectrics constant ε_r and quality factor $Q\times f$ of the sintered samples were measured by cavity method, using a HP-8722ES network analyzer.

3. Results and discussion

3.1. One-step processed materials

The SEM micrographs shown in Figs. 1 and 2 illustrate, respectively, the compositional dependence of microstructure with different amount of glass for the glass-BRT_{114} composites incorporated with the sol-gel glass or fused glass ($BaO:B_2O_3:SiO_2$ in the ratio of 51:45:4 wt.%). All the samples possess a large proportion of porosity, indicating that both the sol-gel glass and fused glass could not wet the BRT_{114} powders good enough and, therefore, could not effectively densify the ceramics.

The sol-gel glass derived materials contain pores with smaller size than the fused glass derived ones. The implication of this phenomenon is that the sol-gel glass powders, which are finer in size (~0.5 μm), mix more uniformly with the BRT_{114}-powders than the fused-glass powders, which are around 1.5. Moreover, the fused glass is more reactive such that large agglomerates were resulted prior to the interaction of the glass powders with the BRT_{114} materials. Bridging phenomenon occurred during firing process, resulting in large pores. Bridging phenomenon that occurred in sol-gel glass derived materials is not as serious as that observed in fused glass. Increasing the glass-content from 9 to 23 wt.% only slightly increases the density of the samples, which can also be ascribed to the agglomeration and bridging phenomenon occurred prior to densification of the composite materials. Moreover, Fig. 3(a) and (b), the *X*-ray diffraction patterns for sol-gel glass derived and fused glass derived BRT_{114} composites, respectively show that both kinds of glass material interact with the BRT_{114} powders markedly at firing temperatures, forming $Ba_3B_6Si_2O_{16}$ phase.

That the fused glass can react with BRT_{114} powders more readily than the sol-gel glass is further demonstrated by the compositional dependence of the microwave properties for composite materials [Fig. 4(a) and (b)]. Fig. 4(a) shows that the dielectric constant (ε_r) and quality factor ($Q\times f$) of the sol-gel glass-derived materials fluctuate profoundly with the concentration of glass added, whereas Fig. 4(b) reveals that both the ε_r and $Q\times f$-values vary with the glass-content in a more consisted trend for the fused glass derived materials. The dielectric constant decreases monotonously from about $\varepsilon_r = 15$ to 17 for 9 wt.% glass containing composites to

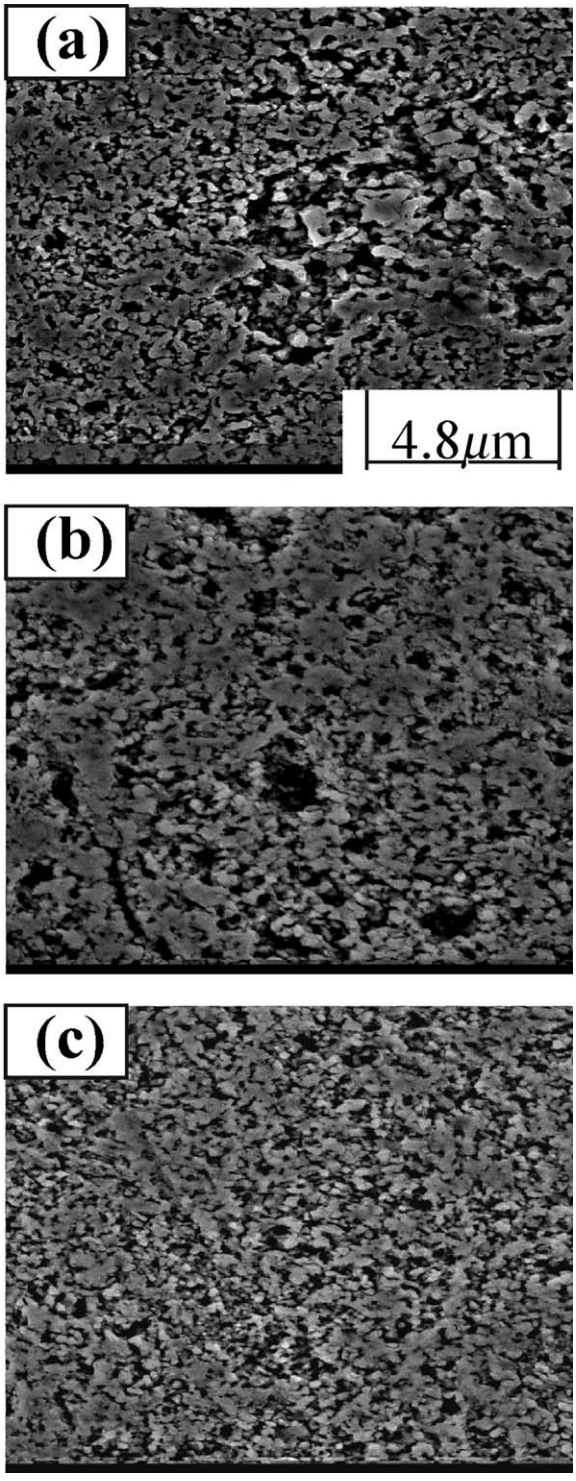

Fig. 1. SEM micrographs of polished and thermal-etched surface for the glass-BRT_{114} composite materials containing sol-gel derived glass of (a) 9 wt.%, (b) 16.7 wt.%, and (c) 23 wt.%, which were sintered at 950 °C for 2.5 h.

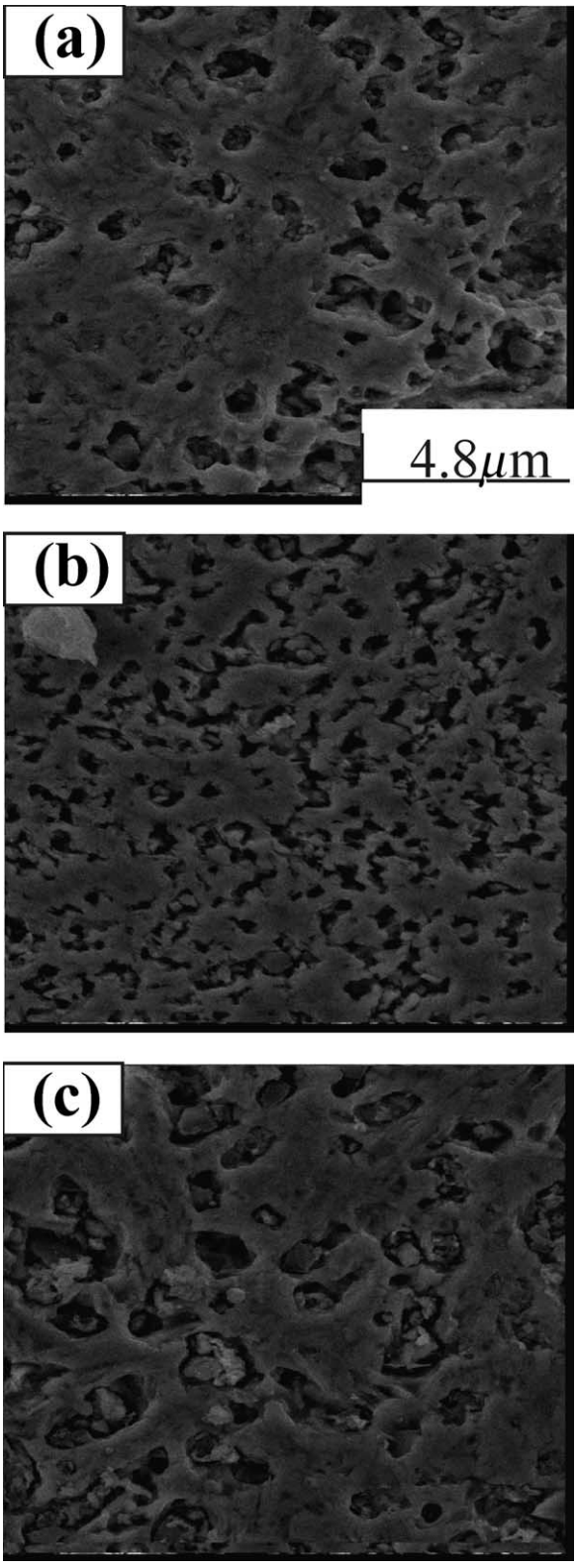

Fig. 2. SEM micrographs of polished and thermal-etched surface for the glass-BRT_{114} composite materials containing fused glass of (a) 9 wt.%, (b) 16.7 wt.%, and (c) 23 wt.%, which were sintered at 950 °C for 2.5 h.

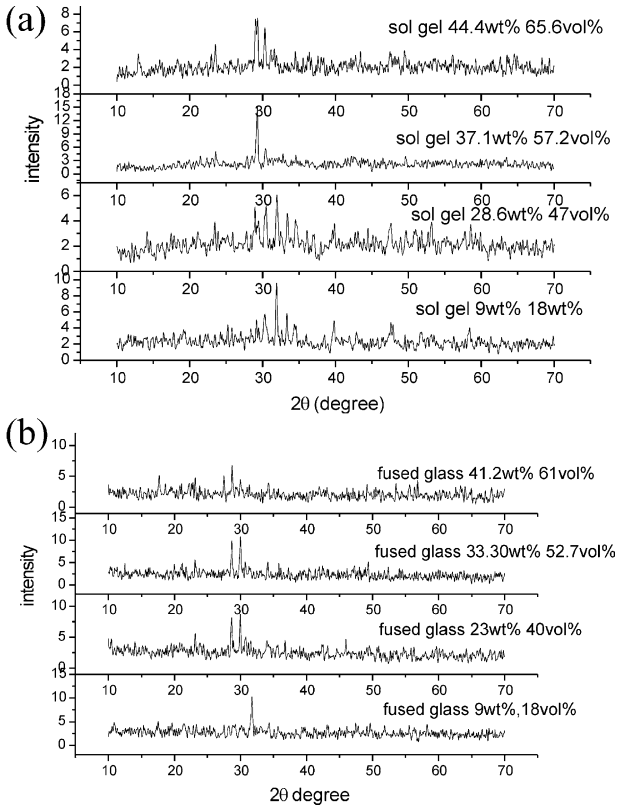

Fig. 3. X-ray diffraction patterns for the glass-BRT_{114} composite sintered at 950 °C for 2.5 h (a) sol-gel derived glass and (b) fused glass.

about $\varepsilon_r = 12.5$ for 23 wt.% glass containing samples. The quality factor ($Q \times f$) increases with proportion of glass added, reaching a maximum value, around 9000, for samples containing 23 wt.% glass and decrease again for further increase in glass content. The dielectric constant (ε_r) and quality factor ($Q \times f$) not only for the fused glass derived materials not only are of higher value, but also vary with the proportion of the glass more consistently, as compared with those for sol-gel glass derived ones.

3.2. Two-step processed materials

The above results imply that the prime factor, resulting in high porosity and poor microwave dielectric properties for the one-step processed glass-BRT_{114} composites, is that the glass can not wet the BRT_{114} powders very well. The possible process to improve the wetting of the glass with BRT_{114} materials is to precoat the BRT_{114} materials with a thin layer of glass composition, prior to the mixing with large proportion of glass.

Figs. 5(a) and 6(a) respectively show the tremendous improvement in densification behaviour for the glass-BRT_{114} composites due to the two-step process. For the specimens containing 9 wt.% fused BaBSiO glass, which were sintered at 950 °C for 2.5 h, very little pores were

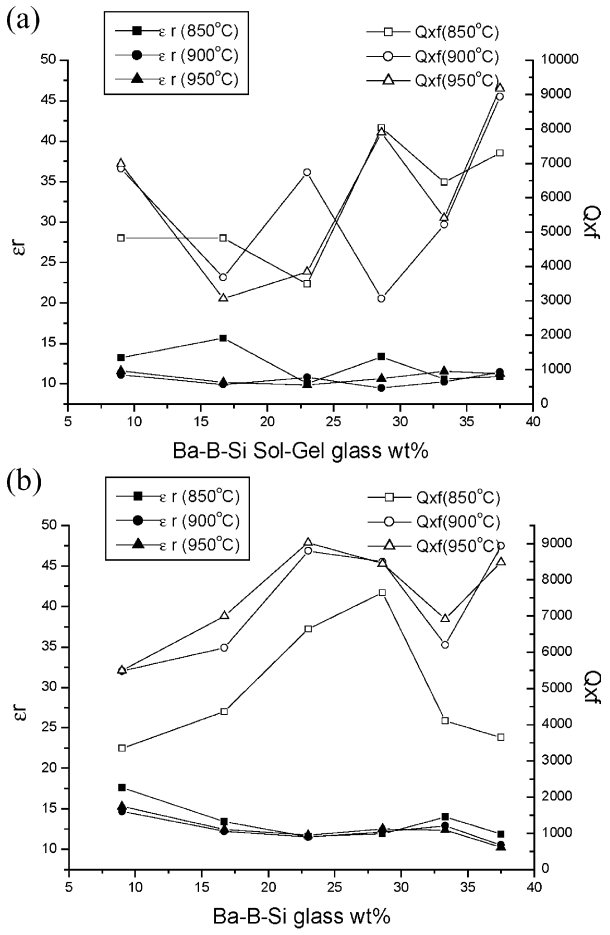

Fig. 4. Microwave dielectric properties (ε_r and $Q\times f$) for the glass-BRT_{114} composite sintered at 850–950 °C for 2.5 h (a) sol-gel derived glass and (b) fused glass.

observed. Whether the precoating layer was a sol-gel glass or fused glass seems to have no influence. Apparently, the pronounced improvement achieved in the two-step process can be ascribed to the increase in wetting ability of glasses with the BRT_{114} powders due to the presence of the thin glass coating. That the nature of coating layers does not influence the densification behavior is understandable, as the high temperature calcination (700 °C) after coating will react completely the glass layer with the BRT_{114} powders, regardless of the precoating materials.

Even for the two-step processed composites, the pores appear again when the materials contain a larger proportion of glasses, which are shown in Fig. 5(b) and (c) for sol-gel glass coated materials and Fig. 6(b) and (c) for fused glass coated materials. Presumably, an excess of glass results in agglomeration and bridging phenomenon, hindering the densification process. Lowering the firing temperature also markedly increases the porosity, which is presumed to be due to insufficient wetting ability between the glasses and glass-coated BRT_{114} powders. X-ray diffraction analysis (Fig. 7) indicates that interaction between glass and BRT_{114} powders is

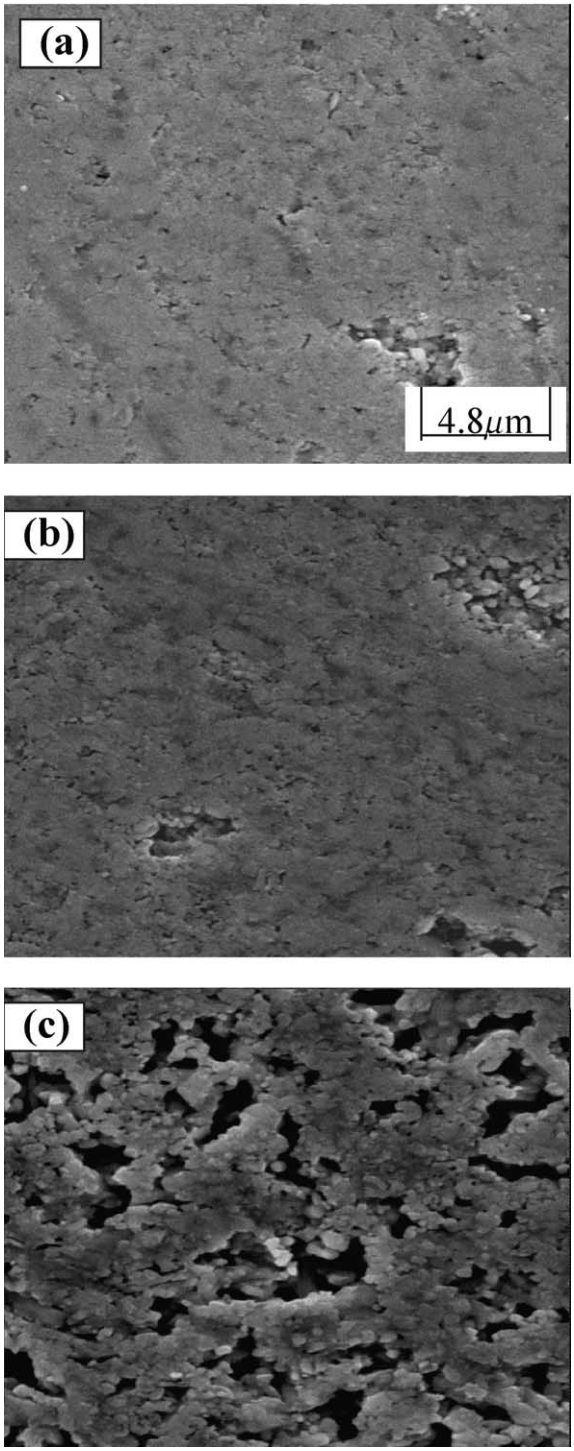

Fig. 5. SEM micrographs for two-step processed glass-BRT_{114} composite materials, which were precoated with a thin layer of sol-gel glass and then mixed with (a) 9 wt.%, (b) 16.7 wt.%, and (c) 23 wt.% fused glass, followed by sintering at 950 °C for 2.5 h.

significantly suppressed for the materials prepared by two-step process. Fig. 8(a) and (b) show the ε_r and $Q\times f$-properties of these materials, which were, respectively, precoated with a thin layer of the sol-gel glass and fused glass, followed by mixing with the fused glass and the other sample preparation process. For a specimen con-

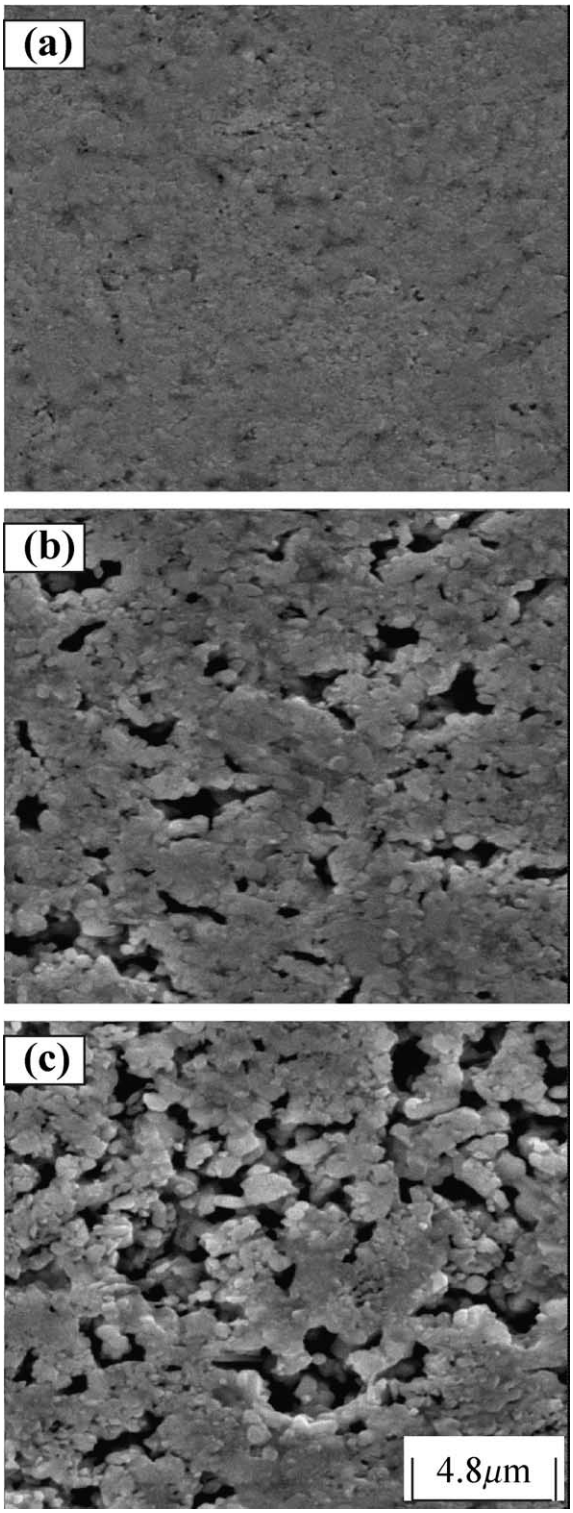

Fig. 6. SEM micrographs for two-step processed glass-BRT_{114} composite materials, which were precoated with a thin layer of fused glass and then mixed with (a) 9 wt.%, (b) 16.7 wt.%, and (c) 23 wt.% fused glass, followed by sintering at 950 °C for 2.5 h.

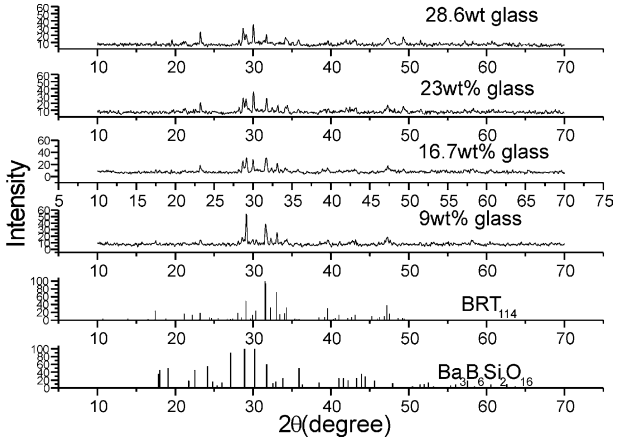

Fig. 7. X-ray diffraction patterns for two-step processed glass-BRT_{114}composites, which were precoated with a thin layer of fused glass and then mixed with 9–23 wt.% fused glass, followed by sintering at 950 °C for 2.5 h.

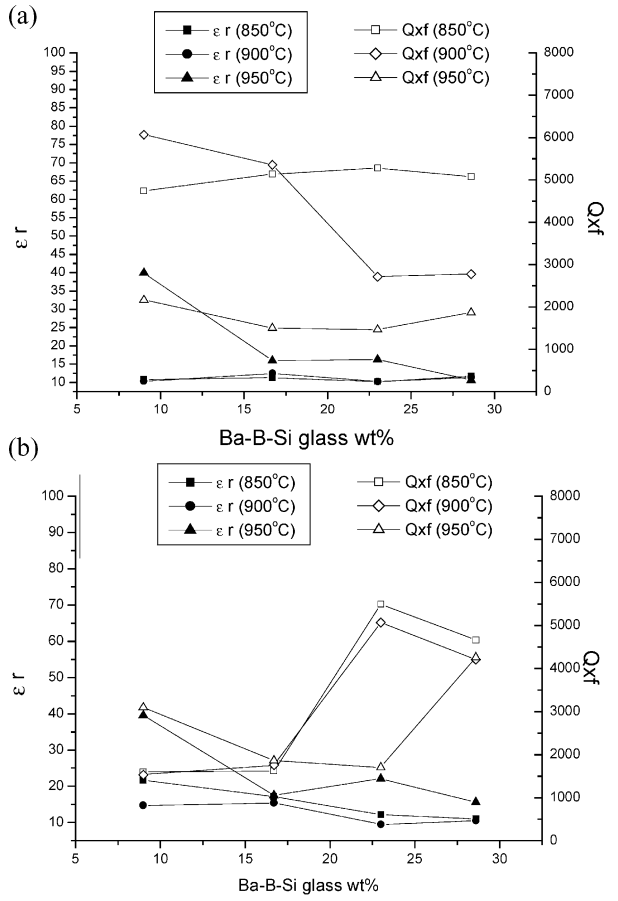

Fig. 8. Microwave dielectric properties for two-step processed glass-BRT_{114} composites, which were precoated with a thin layer of (a) sol-gel glass and (b) fused glass, and then were mixed with 9–23 wt.% of fused glass, followed by sintering at 850–950 °C for 2 h.

taining 9 wt.% glass, the dielectric constant was still low for 850 or 900 °C-fired samples, but increased markedly, to $\varepsilon_r = 40$, for 950 °C-fired samples. The same phenomenon was observed, no mater the precoating layer is sol-gel or fused glass. The dielectric constant decreases pronouncedly as the proportion of fused glass increased, which is apparently due to the presence of secondary phases that are rich in Bi_2O_3.

The quality factor ($Q \times f$) of the two-step processed materials is, however, markedly lower, as compared with the $Q \times f$ value for the one-step process materials. The probable explanation for such a phenomenon is that the porous materials contain air as secondary phase, which is known to possess much higher Q-value than the glass-BRT_{114} materials. Therefore, the $Q \times f$-value for the materials of lower porosity will have inferior quality factor, as compared with the porous materials.

4. Conclusions

The characteristics of the glass-BRT_{114} composite materials were systematically investigated. For one-step processed composites, a large proportion of pores appear, which results in low dielectric constant for the materials, but the Q is large. The nature of glass, whether it is sol-gel derived or fused, shows a marked influence on the microstructure and microwave dielectric properties of the composite materials. Pores are large and interconnected, inferring the occurrence of bridging phenomenon which, in turn, can be ascribed to the agglomeration of glass powders during firing process. A two-step process, which precoats the BRT_{114} powders with a thin layer of glass, tremendously improves the densification behaviour for the materials. The formation of pores were almost completely suppressed such that materials with high dielectric constant ($\varepsilon_r = 40$) were achieved by sintering the 9 wt.% glass containing composite material at 950 °C for 2.5 h. The $Q \times f$-value was, however, decreased significantly.

Acknowledgements

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