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Microwave dielectric properties of LTCC materials consisting of glass–$Ba_2Ti_9O_{20}$ composites

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Abstract

Interaction between $Ba_2Ti_9O_{20}$ microwave dielectric ceramics and BaBSiO glass materials was systematically investigated. $BaTi(BO_3)_2$ intermediate phase was induced and its proportion increased with firing temperature. Fortunately, the formed $BaTi(BO_3)_2$ phase does not result in marked degradation on the microwave dielectric properties of the $Ba_2Ti_9O_{20}$–BaBSiO composite materials. Good microwave dielectric properties (K = 13.2, $Q \times F = 1150$) were obtained by firing the $Ba_2Ti_9O_{20}$–BaBSiO (50:50 vol.%) materials at 900 °C for 30 min. Precoating a thin layer of $BaTi(BO_3)_2$ materials on the $Ba_2Ti_9O_{20}$ powders prior to processing of the ceramic tapes can markedly suppress the interaction between the $Ba_2Ti_9O_{20}$ and BaBSiO glass, significantly improving the consistency of the microwave dielectric properties for the low temperature cofirable ceramic (LTCC) materials.

Keywords: BaBSiO glass; $Ba_2Ti_9O_{20}$; LTCC; Microwave ceramics; Dielectric properties

1. Introduction

Low temperature co-firable ceramics (LTCC) possessing good microwave dielectric properties have recently been widely investigated, due to the necessity for miniaturization of microwave devices to reduce the size of wireless communication system.[1–3] However, the microwave dielectric materials, which possess high quality factor and large dielectric constant, usually need very high sintering temperature and long soaking time to achieve high enough density. On the other hand, using the Ag material as conducting materials for transmission lines and ground planes is needed in order to minimize the microwave absorption loss. Reduction on the sintering temperature for the microwave material to a level cofirable with Ag-electrode materials is thus called for, which can be achieved by mixing the low softening temperature glass materials with the ceramic materials.[4–10]

In this paper, the interaction of the glass materials with the $Ba_2Ti_9O_{20}$ microwave dielectric materials and the effect of processing parameters on the characteristics of the glass-to-ceramic composites were investigated.

2. Experiments

Pure $Ba_2Ti_9O_{20}$ materials were first prepared by mixed-oxide process. BaO and TiO_2, with a molar ratio of $Ba_2Ti_9O_{20}$ nominal composition, and 2 mol% SnO_2 as additives, were mixed and then calcined at 1150 °C (2 h). Thus obtained powders were then pulverized down to about 0.5 μm size by a dynomill. The glass powders of the composition $BaO:B_2O_3:SiO_2 = 42:45:13$ (BaBSiO) was then mixed with $Ba_2Ti_9O_{20}$ in 50-to-50 vol.%, followed by pelletization and then sintering at 800–900 °C for 1 h. The sintered density was measured using Achimedes' method. The crystal structure and the microstructure of the sintered $Ba_2Ti_9O_{20}$ and $Ba_2Ti_9O_{20}$–glass composite materials were examined by X-ray diffraction analysis (XRD, Rigaku D/max-IIB) and scanning electron microscopy (SEM, Jeol JSM-840A), respectively. The microwave dielectric properties for the pellets were measured using H.P.8722A network analyzer in a resonant cavity,[11–13] whereas those for the tapes were measured using a Split-Post test fixture.[14]

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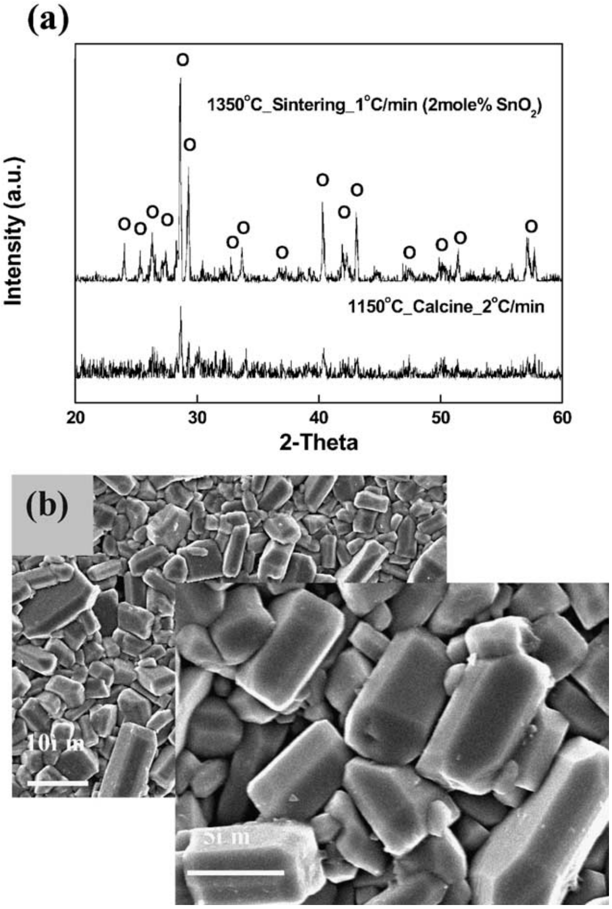

Fig. 1. (a) X-ray diffraction patterns of 1150 °C (12 h) calcined and 1350 °C (4 h) sintered $Ba_2Ti_9O_{20}$(2 vol.%SnO_2) ceramics materials, and (b) SEM microstructure of the sintered materials.

3. Results and discussion

XRD in Fig. 1a reveals that the mixed-oxide process can efficiently transform the $BaCO_3$–TiO_2 (2mol%SnO_2) mixture into Hollandite structure by calcining the materials at 1150 °C (6 h), although the $BaTi_4O_9$ (or $BaTi_5O_{11}$) phase usually formed preferentially when they were calcined at lower temperature. The samples pelletized from thus obtained powders maintained the same Hollandite structure without inducting the secondary phase when sintering at 1350 °C for 4 h (Fig. 1a). The $Ba_2Ti_9O_{20}$ materials thus prepared are of very high sintered density (97.7%T.D.), containing rod-shaped grains, ~5 to 7 μm (Fig. 1b), and possess very good microwave dielectric properties ($K = 37$, $Q \times F = 27{,}500$).

Diffusion couples made of sintered $Ba_2Ti_9O_{20}$ materials and BaBSiO–glass powders was then examined for the purpose of understanding the interdiffusional behavior between the two materials. Fig. 2a–c, the SEM cross-sectional micrographs of the diffusion couples, clearly show that very little interdiffusion occurs when the diffusion-couples were heat treated at 800 °C. The

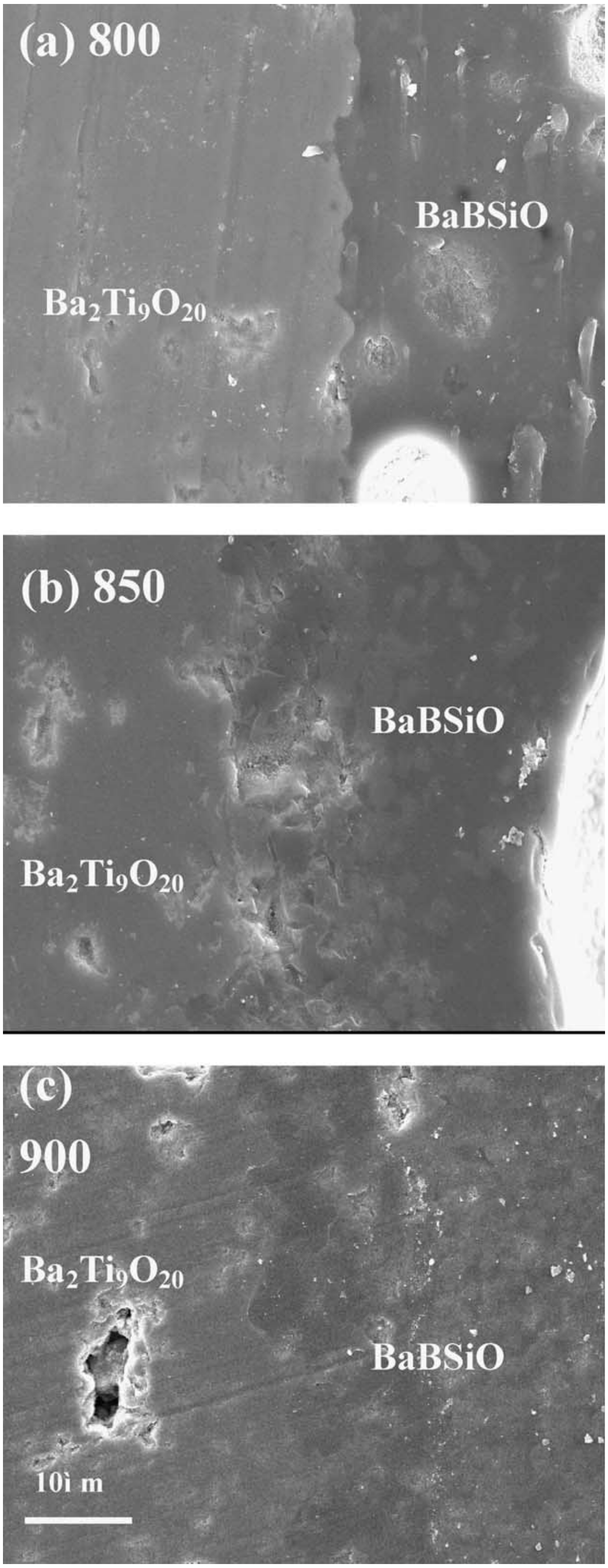

Fig. 2. Cross-sectional SEM micrographs for the $Ba_2Ti_9O_{20}$ ceramics–BaBSiO glass diffusion couples, which were heat treated at (a) 800 °C, (b) 850 °C, (c) 900 °C for 1 h.

interdiffusion started at 850 °C, becoming very pronounced when heat-treated at 900 °C. X-ray diffraction analysis showing in Fig. 3 reveals that the interdiffusional zone is mainly the $BaTi(BO_3)_2$ phase.

Similar interaction is expected for the $Ba_2Ti_9O_{20}$ powders and the BaBSiO–glass, which were the main constitutents in the ceramics–glass composite tapes. Therefore, how does the presence of such an intermediate $BaTi(BO_3)_2$ phase influence the microwave dielectric properties of the composite materials is of great concern. The $BaTi(BO_3)_2$ materials, were thus prepared separately by mixed oxide method to study their microwave dielectric properties. Fig. 4a and b show, respectively, the X-ray diffraction patterns and SEM micrographs of thus obtained $BaTi(BO_3)_2$ materials. These figures indicate that the $BaTi(BO_3)_2$ phase can be formed by calcining the $BaCO_3$–TiO_2–H_3BO_3 mixture, of nominated molar ratio, at 800 °C (1 h) and high density $BaTi(BO_3)_2$ ceramic materials can be obtained by sintering the samples at 1000 °C (2 h). Thus obtained $BaTi(BO_3)_2$ ceramics possess quite good microwave dielectric properties ($K = 11.5$ and $Q \times F = 23{,}000$). Therefore, the presence of $BaTi(BO_3)_2$ due to interaction between the $BaTi_9O_{20}$ materials and BaBSiO glass–ceramics is expected to have little effect or the microwave dielectric properties of the composite materials.

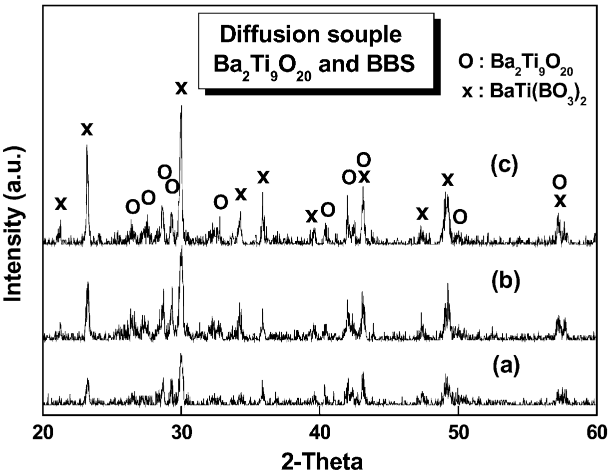

Fig. 3. X-ray diffraction patterns for the $Ba_2Ti_9O_{20}$ ceramics–BaBSiO glass diffusion couples, which were heat treated at (a) 800 °C, (b) 850 °C, (c) 900 °C for 1 h.

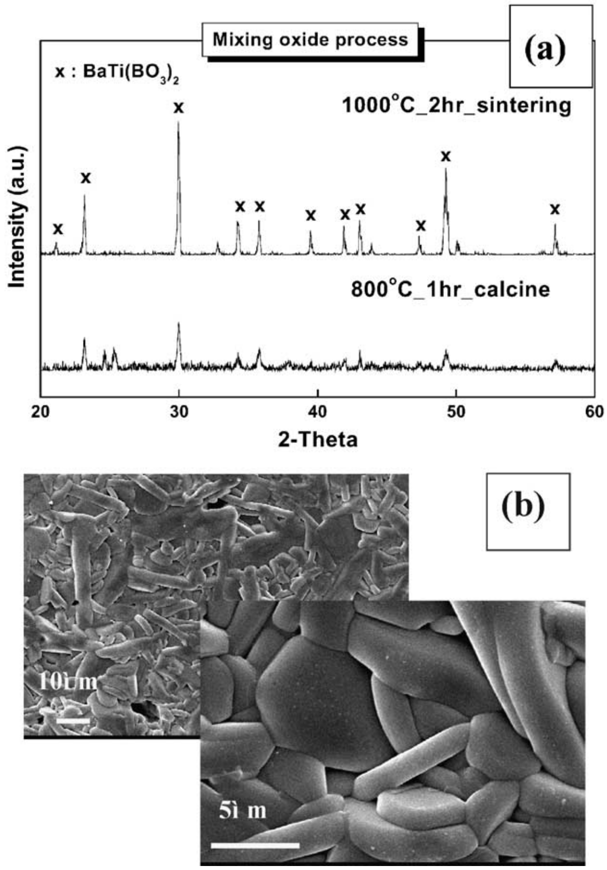

Fig. 4. (a) X-ray diffraction patterns for the 800 °C (1 h) calcined and 1000 °C (2 h) sintered $BaTi(BO_3)_2$ materials prepared by mixed-oxide method; (b) SEM micrographs the $BaTi(BO_3)_2$ ceramics.

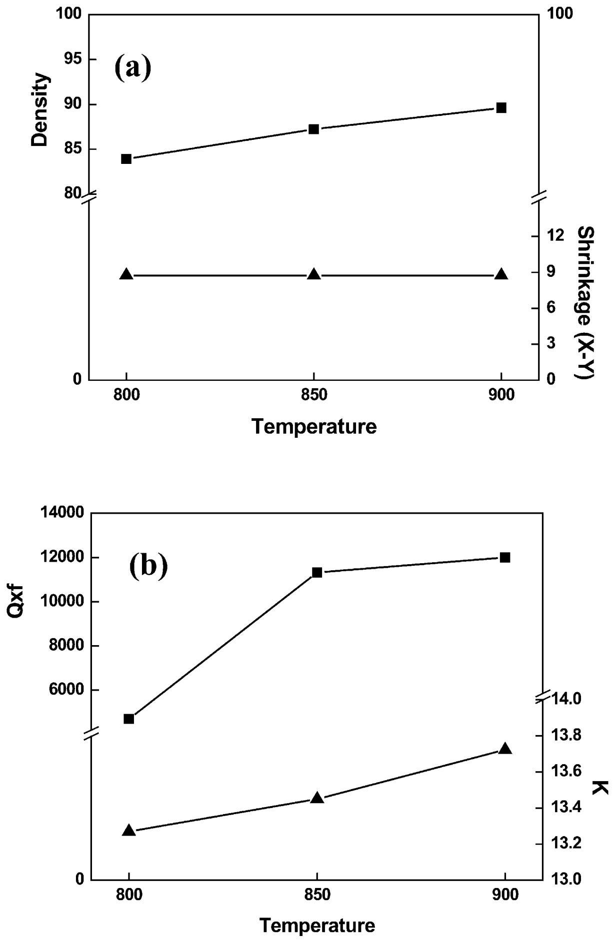

Fig. 5. Variation of (a) sintered density and shrinkage induced by sintering process and (b) dielectric constant; K and quality factor, Q, for $Ba_2Ti_9O_{20}$ ceramics–BaBSiO glass (50:50 vol.%) composite tapes with the firing temperature.

The glass–ceramics composite tape materials, containing 50 vol.%$Ba_2Ti_9O_{20}$ dielectric ceramics, were than prepared via the conventional Doctor-blade process. Fig. 5a shows that the density of the composite tape materials increases moderately (D $\cong$ 84.5–86%T.D.) and the shrinkage of the tape materials ($\cong$ 8.8%) changes insignificantly with the firing temperature. Fig. 5b indicates that the dielectric constant of the materials also increases with the sintering temperature, viz. $K = 13.2$–13.5, which is presumable due to the increase in the density of the materials. However, this figure also show that Q-factor is low ($Q = 450$ at 9 GHz) for 800 °C-fired tapes and increases abruptly (Q-1050 at 9 GHz) for 850 °C and 900 °C-fired ones.

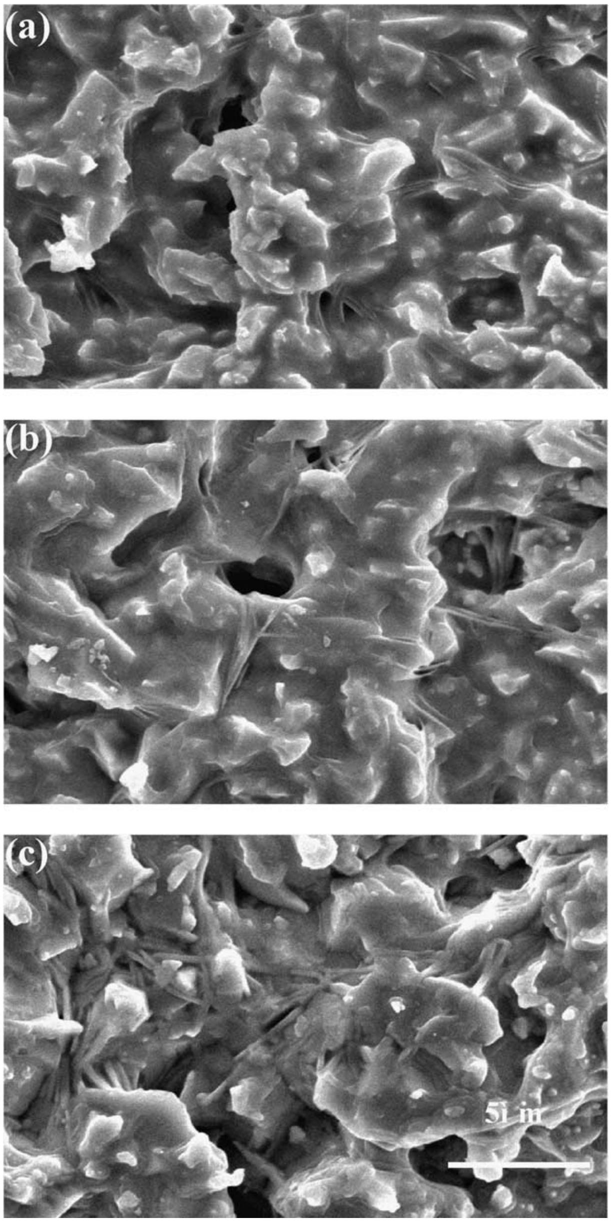

Fig. 6. Variation of SEM micrographs for $Ba_2Ti_9O_{20}$ ceramics–BaBSiO glass (50:50 vol.%) composite tapes with the firing temperature: (a) 800 °C; (b) 850 °C; (c) 900 °C (1 h).

SEM micrographs shown in Fig. 6a to c indicate that the microstructure varies insignificantly with the densification temperature. Detailed analysis reveals the presence of thin plate-like precipitates for the composite tapes fired at 850 °C and higher temperature (Fig. 6b and c). X-ray diffusion analysis shown in Fig. 7(b) and (c) indicates the presence of $BaTi(BO_3)_2$ phase for the high temperature sintered composites. These results imply that the plate-like precipitates are the $BaTi(BO_3)_2$ phase and are formed by the interaction between the $Ba_2Ti_9O_{20}$ ceramics and BaBSiO glass, a phenomenon similar with the diffusion couple experiment. Markedly increase in Q-factor of the composite tape materials fired at high temperature ($\geq$850 °C) is thus attributed to the conversion of low quality-factor glass materials into high-Q $BaTi(BO_3)_2$ crystalline phase.

Although the $BaTi(BO_3)_2$ crystalline phase formed due to the interaction between of the $Ba_2Ti_9O_{20}$ ceramics and the BaBSiO glass materials posses high microwave Q-factor and will not markedly degrade the microwave properties of composite tape materials, the continuous change of the dielectric constant of the composite tapes with processing temperature is undesirable in the design and fabrication of devices. Therefore, minimization on the interdiffusional process between the $Ba_2Ti_9O_{20}$ ceramics and BaBSiO glass materials is called for. Our approach to this end is to precoat a thin layer of either $BaTi(BO_3)_2$ or TiO_2 films by sol-gel process onto the $Ba_2Ti_9O_{20}$ powders, so as to hinder the interdiffusion between the dielectrics and the glass. Effect of BaBSiO precoating layer is also examined to facilitate the comparison on the efficiency of the precoating on suppression the interdifusion between the $Ba_2Ti_9O_{20}$ and BaBSiO glass materials. The sol-gel process includes mixing the powders with the sol-gel solution containing the desired constituents, followed by calcining the coated powders at 900 °C to form intermediate compound surrounding the $Ba_2Ti_9O_{20}$ powder.

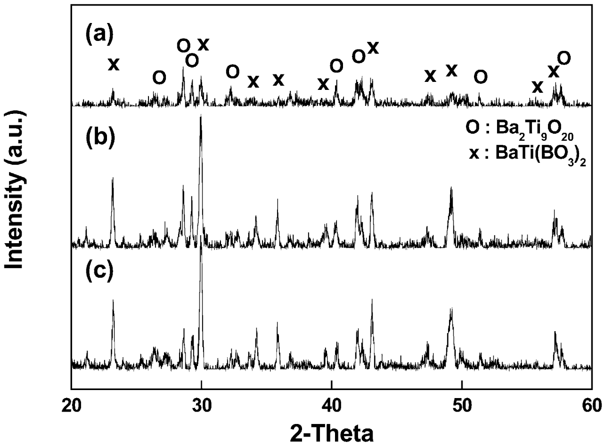

Fig. 7. Variation of X-ray diffraction patterns for $Ba_2Ti_9O_{20}$ ceramics–BaBSiO glass (50:50 vol.%) composite tapes with the firing temperature: (a) 800°C; (b) 850°C; (c) 900°C (1 h).

Table 1
Variation of the microwave dielectric properties of the $Ba_2Ti_9O_{20}$–BaBSiO glass composites LTCC materials with the firing temperature (the $Ba_2Ti_9O_{20}$ powders were either non-coated or precoated with a thin layer of BaBSiO, $BaTi(BO_3)_2$ or TiO_2 by sol-gel process prior to synthesizing the LTCC tapes)

Firing Temp. (°C)		Microwave properties			
		Uncoated	BaBSiO	$BaTi(BO_3)_2$	TiO_2
800	K	13.2	7.28	8.4	9.2
	Q	450	790	600	580
890	K	13.3	7.6	8.4	9.2
	Q	1150	920	800	700
900	K	13.4	8.1	8.2	9.2
	Q	1150	1240	1220	1100

Thus obtained $Ba_2Ti_9O_{20}$ powder were then mixed with BaBSiO glass (50:50 vol.%), followed by the tape fabrication processes.

X-ray diffraction examinations indicate that precoating a thin crystalline $BaTi(BO_3)_2$ layer markedly reduces the proportion of interdiffusional phase (not shown). Table 1 reveals that the dielectric constant (K) of $BaTi(BO_3)_2$ coated materials are less sensitive to the processing parameters, as compared with those for the BaBSiO-coated ones, in which the K-value varies markedly with with firing temperature. TiO_2-coating also effectively stabilizes the dielectric constant (K) of the composite tape against firing temperature. Meanwhile, this table indicates that Q-factor of the composite tapes increases monotonously with the firing temperature, which is presumably due to the increase in fired density for the composite tapes rather than the formation of $BaTi(BO_3)_2$ phase.

The $BaTi(BO_3)_2$ phase formed by the interaction of $Ba_2Ti_9O_{20}$ materials with the BaBSiO glass possesses quite good microwave properties. Whether can this material be used for the preparation of ceramics–glass composites is also of great interest. Unfortunately, the experiments indicate that the $BaTi(BO_3)_2$ materials directly in contact with the BaBSiO glass interact with the glass rigorously, forming $Ba_3B_6Si_2O_{16}$ phase, which posses low dielectric constant and high dielectric loss. Therefore, the $Ba_2Ti_9O_{20}$–BaBSiO glass composite material is still the better choice, even though the interdiffusion between the two materials is pronounced.

4. Conclusion

Diffusion couple experiments and the ceramics–glass composite materials processing were performed to study the interaction between $Ba_2Ti_9O_{20}$ microwave dielectric ceramics and BaBSiO glass materials. $BaTi(BO_3)_2$ intermediate phase was induced and its proportion increased with firing temperature. Fortunately, thus formed $BaTi(BO_3)_2$ phase does not result in marked degradation on the microwave dielectric properties of the $Ba_2Ti_9O_{20}$–BaBSiO composite materials. The low temperature cofirable ceramics (LTCC), possessing good microwave dielectric properties ($K = 13.2$, $Q \times F = 1150$), were obtained by firing the $Ba_2Ti_9O_{20}$–BaBSiO (50:50 vol.%) materials at 900 °C for 30 min. Moreover, the variation of the microwave dielectric properties of the LTCC materials with the processing parameters is significantly suppressed by using a thin layer of $BaTi(BO_3)_2$ materials as precoating on the $Ba_2Ti_9O_{20}$ powders prior to the tape processing.

Acknowledgements

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References

1. Chon, S. B., *IEEE Trans. on MTT*, 1968, **MTT-16**, 218.
2. Wakine, K., *Ferroelectrics*, 1989, **91**, 69.
3. Wilcox, D. L. Sr., Huang, R. F. and Dai, S. X., *Ceramic Trans.*, 1999, **97**, 201.
4. Takada, T. *et al.*, Effect of glass addition on BaO–TiO_2–WO_3 microwave ceramics. *J. Am. Ceram. Soc.*, 1994, **77**(7), 1909.
5. Takada, T. *et al.*, *J. Am. Ceram. Soc.*, 1994, **77**(9), 2485.
6. Lewis, M. H. Chapman and Hall, 1989.
7. Jantunen, H., Rautioaho, R., Uusimäki, A. and Leppävuori, S., *J. Eur. Ceram. Soc.*, 2000, **20**, 2331.
8. Yang, C. F. and Lo, S. H., *J. Mater. Sci. Letter*, 1998, **17**, 1029.
9. Wu, J. M. and Huang, H. L., *J. Materials Research*, 1998, **15**, 222.
10. Navias, L. and Green, R. L., *J. Am. Ceram. Soc.*, 1946, **29**(10), 267.
11. Hakk, B. W. and Coleman, P. D., *IRE. Trans. Microwave Theory and Tech.*, 1960, **MTT-8**, 402.
12. Courtney, W. E., *IEEE. Trans. Microwave Theory and Tech.*, 1970, **MTT-18**, 476.
13. Kobayashi, Y. and Katohy, M., *IEEE Trans. Microwave Theory and Tech.*, 1985, **MTT-33**, 586.
14. Krupka, J., Derzakowski, K., Riddle, B. and Baker-Jarvis, J., *Meas. Sci. Technol.*, 1998, **9**, 1751–1756.