Effect of glass additions on the sintering behaviors and electrical microwave properties of $BaO–Nd_2O_3–Sm_2O_3–TiO_2$ ceramics

LI-CHUN CHANG, BI-SHIOU CHIOU
Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, 1001 Ta Hsueh Road, Hsiunchu, 300, Taiwan
E-mail: bschiou@mail.nctu.edu.tw

WEN-HSI LEE
Phycomp Taiwan Ltd., 16, West 3rd Street, N.E.P.Z., Kaohsiung, 811, Taiwan

The effect of Al_2O_3-doped silica glass (AS-glass) addition on the structure and dielectric properties of the $BaO–Nd_2O_3–Sm_2O_3–TiO_2$ (BNST) microwave materials was investigated. This BNST material has a dielectric constant (k) of 80 and a quality factor $(Q \times f)$ of 6000 GHz when sintered at 1350 °C for 2 h. Both the microstructure and the microwave dielectric characteristics were determined as a function of the sintering temperature and glass content. A $Q \times f$ as high as 8700 GHz was achieved in ceramics added with 20 wt % glass, however, the k value drops to 30. The high $Q \times f$ value is attributed to the improved densification of the dielectric when glass is added. Results of X-ray diffraction experiments indicate that glass addition enhances the growth in the longitudinal direction of the columnar crystal and a preferred (0 0 2) orientation. The presence of columnar structure plays an important role in the improvement of the microwave dielectric properties.

1. Introduction

Recently, mobile radio communication networks have been greatly expanded by portable and automobile telephones. In order to reduce the size of microwave devices in communication systems, the dielectric components must be miniaturized [1]. High dielectric constant (k), high quality factor $(Q \times f)$ and low temperature coefficient of resonant frequency (τ_f) make ceramic dielectrics attractive substitutes for copper invar waveguide cavities in microwave-circuit applications. Many dielectric systems have been investigated for microwave applications; among them is the $BaO–Ln_2O_3–TiO_2$ (Ln = Nd, Sm, and La) ternary system, which received special attention because of its high dielectric constant [2, 3].

In producing miniaturized devices, multilayer structures with low sintering temperature are needed to cofire with low-loss conductors such as silver and gold. Chemical processing, glass additions, and smaller particle sizes of the starting materials are generally advantageous to lower the firing temperatures. Previous studies on the $BaO–Ln_2O_3–TiO_2$ system used the general formula $Ba_{6-x}(Nd, Sm)_{8+2x/3}Ti_{18}O_{54}$ (hereafter referred to as BNST). In the work of Wu and Chen [3] Bi_2O_3 and $Bi_4Ti_3O_{12}$ were introduced into BNST to adjust the temperature coefficient of the dielectric constant. Laffez *et al*. [4] used WO_3 and MnO_2 as the dopant and sintered BNST at 1450 °C in oxygen, to improve the dielectric constant and decrease the dielectric losses. Xu *et al*. [5] synthesized the ceramic powders by the modified Pechini method for reducing the sintering temperature. Liquid-phase sintering using glass additives is the most effective and least expensive. When glass is used as the sintering agent in microwave ceramics, the dielectric loss is a major concern; at least three types of dielectric losses for glasses were observed. One is resonance-type vibration losses at very high frequencies, the second is migration losses caused by the movement of mobile ions, and the third is deformation losses by defects or deformation of the basic silicon oxide network [6]. Some of the alumina-silicate-based glass, such as cordierite ($2MgO–2Al_2O_3–5SiO_2$) and celsian ($BaO–Al_2O_3–SiO_2$), show low loss factors in the microwave region [7]. The $BaO–Nd_2O_3–4TiO_2$ dielectrics with low softening glass ($B_2O_3–_2O_3–SiO_2–ZnO$) additions could achieve intermediate dielectric constant ranging from 20 to 70 [8, 9]. The purpose of this work was to study the effects of low-loss glass addition on the sintering behavior and microwave properties of BNST dielectrics. A BNST-based microwave dielectric, designated as K80, and an Al_2O_3-doped silica glass, designated as AS-glass, are employed in this study. Both K80 and AS-glass are proprietary. K80 powder supplied by Phycomp Inc. was used as the host material. This host

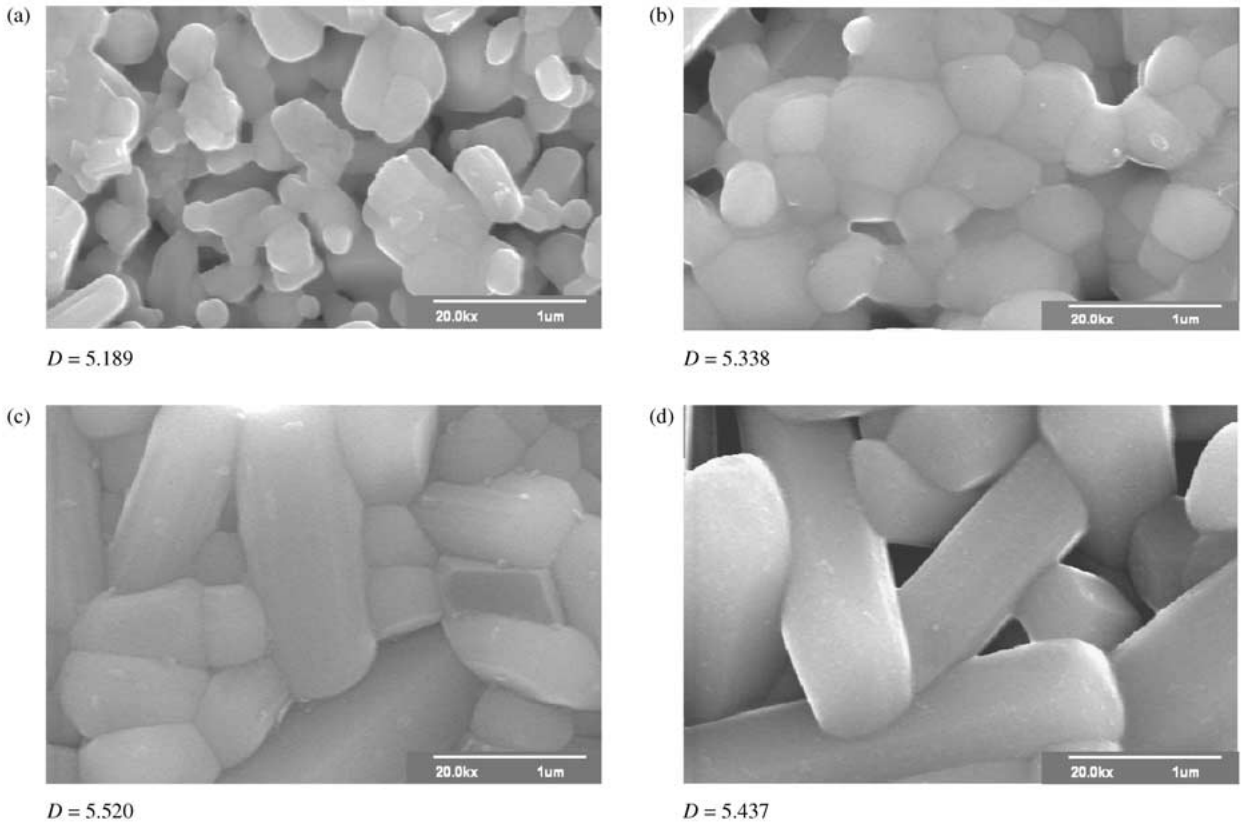

Figure 1 Surface micrographs and density D ($g\,cm^{-3}$) of K80 ceramics sintered at (a) 1150 °C, (b) 1250 °C, (c) 1350 °C, and (d) 1450 °C for 2 h in air.

material, sintered at 1350 °C for 2 h in air, was found to possess the following properties: k (8 GHz) = 80, $Q \times f = 6000$ GHz, density = 5.60 $g\,cm^{-3}$ [10].

2. Experimental procedures

K80 powders were mixed with AS-glass powder, then milled for 12 h, hydrated and granulated by mixing with 3 wt % polyvinyl alcohol solution. Pellets of 10 mm diameter and either 5.2 mm or 1.2 mm thickness were pressed using uniaxial pressing at a pressure of 750 $kg\,cm^{-2}$. After debinding, these pellets were sintered in the temperature range of 1050–1250 °C for 2 h in air.

The X-ray diffraction (XRD, MAC science MXP18) spectra were collected by using CuK_α ($\lambda = 0.15406$ nm) radiation with 30 kV and 20 mA in the 2θ range of 20–60°. The microstructural observations and composition analyses of sintered samples were performed by scanning electron microscopy (SEM, Hitachi S4000) and an electron probe microanalyzer (EPMA, Joel JXA-8800M), respectively. The bulk densities of the sintered specimens were measured by the Archimedes' method. The density of glass powder was measured by CNS 8834-K0015 (methods of test for density and relative density of chemical products).

The dielectric characteristics were measured by an impedance/gain-phase analyzer (Hewlett Packard, HP4194) in the frequency range of 100 Hz–15 MHz. Silver paste was used for the electrodes. The dielectric constant (k) and the quality factor ($Q \times f$) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method which was modified and improved by Courtney [11]. The $Q \times f$ factor was used for evaluating the loss quality, where f is the resonant frequency.

3. Results and discussion

The sintered bulk density of K80 increases from 4.880 to 5.520 $g\,cm^{-3}$ as the sintering temperature is increased from 1050 to 1350 °C. However, further raising the sintering temperature to 1450 °C reduces the bulk density to 5.437 $g\,cm^{-3}$. As shown in the SEM micrographs, Fig. 1, pores are observed in the sintered bulk even at a sintering temperature of 1250 °C. The sample sintered at 1350 °C for 2 h reveals a pore-free structure and indicates homogeneous columnar crystals. The one sintered at 1450 °C exhibits a preferred direction of grain growth, which formed a columnar feature accompanying voids. The abnormal grain is over 5 μm in length and 0.35 μm in diameter. The columnar grain is also reported in the work of Laffez *et al*. [4]. The theoretical density and dielectric constant of K80 are 5.60 $g\,cm^{-3}$ and 80, respectively [10]. Thus, the most densified K80 in this study achieves 98.6% of the theoretical density, which is sintered at 1350 °C and corresponds to a dielectric constant of 79.8 and a $Q \times f$ of 6000 GHz at 8 GHz.

Fig. 2 reveals that the densities of undoped and AS-glass doped K80 increase steadily with sintering temperature. Since the density of AS-glass is only 2.46 $g\,cm^{-3}$, the density of the glass-doped ceramics is decreased as the amount of glass is increased, if the

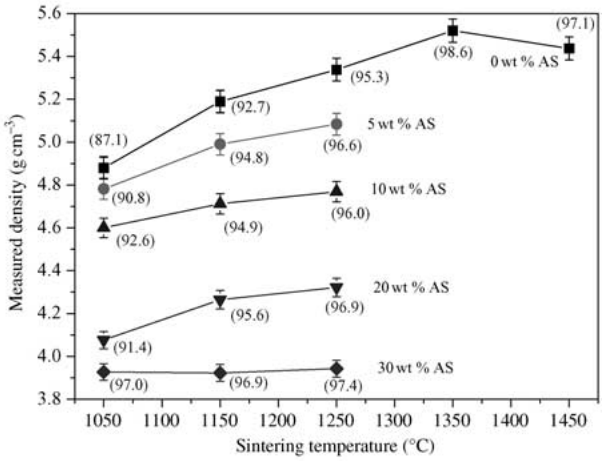

Figure 2 Density as a function of sintering temperature for K80 added with various wt % of AS-glass. Sintering time: 2 h in air. Data in the parentheses are $D_{\text{measured}}/D_{\text{calculated with mixing rule}}$.

mixing rule applies. According to the rule of mixing, the density of K80-AS ceramics is:

$$D_{\text{cal}} = (W_1 + W_2)/(W_1/D_1 + W_2/D_2) \qquad (1)$$

where W_1 and W_2 are the weight per cent of the K80 dielectric and AS-glass in the mixtures, respectively; D_1 and D_2 are the densities of the K80 and AS-glass, respectively. The calculated densities are 5.266, 4.970, 4.468, and 4.057 g cm^{-3} for 5, 10, 20, and 30 wt % AS-added K80 ceramics, respectively. The measured densities of the samples sintered at 1250 °C for 2 h were 95.3%, 96.5%, 96.0%, 96.7%, and 97.2% of the estimated densities for 0, 5, 10, 20, and 30 wt % glass-added K80, respectively. This implies that AS-glass enhances the densification of K80 and reduces the sintering temperature of the dielectric. In this study, even just 5 wt % glass dopant results in the formation of columnar structure at 1150 °C and an increased density of 94.8% as compared to that of the undoped ones (92.7%). For the sample doped with 30 wt % glass, the sintering temperature can be decreased to 1050 °C to produce a density of 97.0%. As mentioned in the classic liquid-phase sintering mechanism, rearrangement, solution-reprecipitation, and final-stage sintering are the three stage of densification [12]. In this study, 30 wt % AS-glass occupy 49 vol %. With such a high liquid level, the densification can be achieved via rearrangement upon liquid formation. On the other hand, for those samples doped with lower glass contents, the solid skeleton inhibits densification. Thus the sintering temperature needs to be raised to 1250 °C for full densification.

Fig. 1 indicates that the microstructure of the K80 ceramics varies significantly with the sintering temperature. Nearly equi-axis fine crystals were observed in the K80 ceramics sintered below 1350 °C for 2 h in air, but the K80 with 5 wt % AS-glass ceramics sintered at 1150 °C for 2 h in air reveals homogeneous columnar crystals as Fig. 3(a) shows. For K80 with 5 wt % to 20 wt % glass contents sintered at 1250 °C, shown in Fig. 3(b)–(d); exaggeratedly grown columnar crystals with a number of voids are observed. Chen *et al*. [13], argued that the liquid phase increased gradually at temperatures above the eutectic point, and this caused a large increase in nucleation rate (N) but a slight increase in nuclei growth rate (G) for $BaO \cdot Nd_2O_3 \cdot 5TiO_2$ system. Consequently, a homogeneous columnar structure with low aspect ratio is obtained at the sintering temperature of 1370 °C due to the recrystallization. In this study, the columnar structure is observed for specimens sintered at 1150 °C due to the introduction of the glass. Besides, it is found that the AS-glass enhances the growth in the longitudinal direction of the columnar grain significantly, but only slightly in the radial direction. The length (l) to diameter (d) ratio of the columnar grain, l/d, increases with the glass content and sintering temperature, as

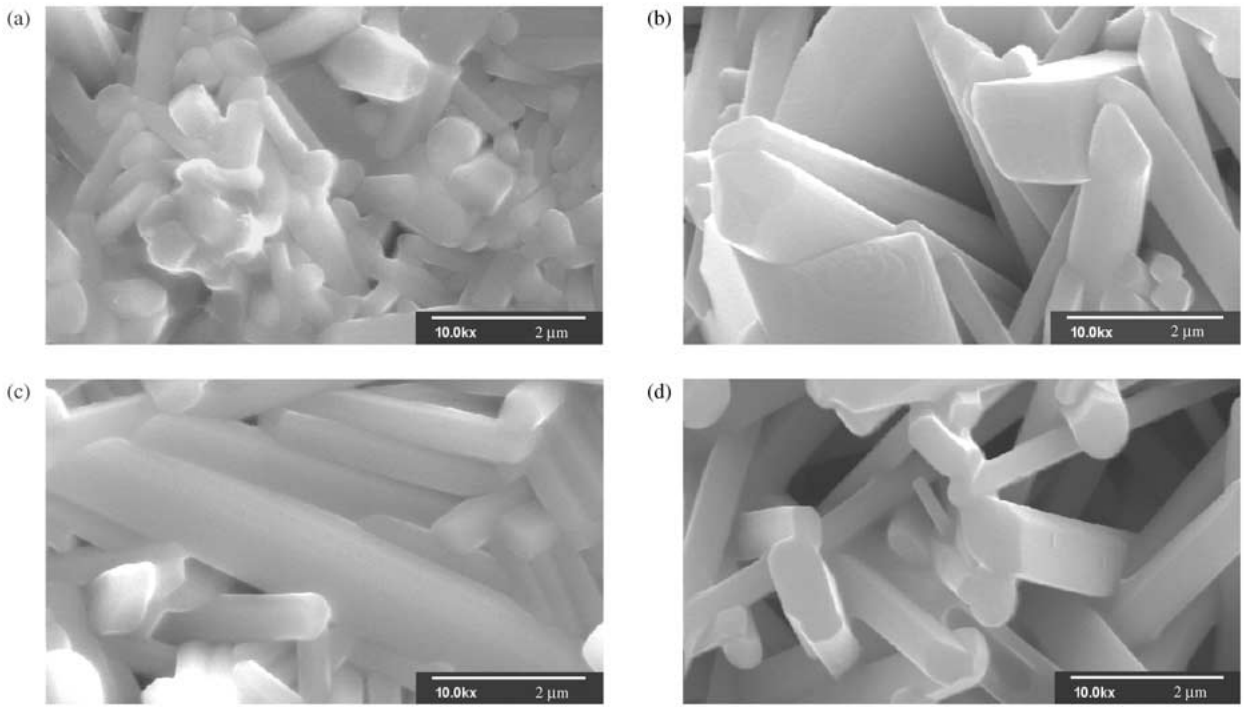

Figure 3 Surface micrographs of K80 ceramics sintered for 2 h in air at (a) 1150 °C with 5 wt %, and 1250 °C with (b) 5 wt %, (c) 10 wt %, (d) 20 wt % AS-glass addition.

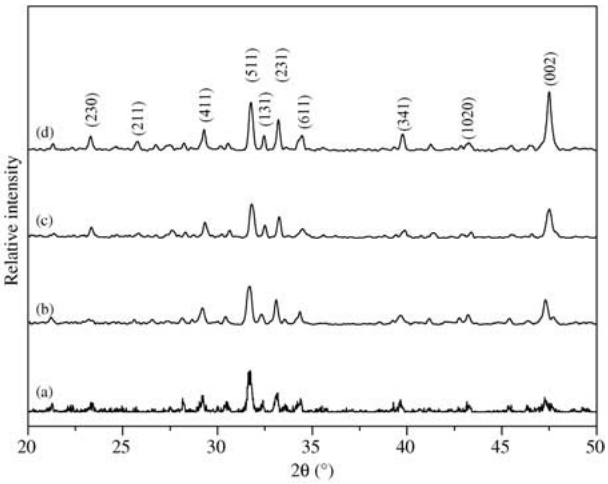

Figure 4 XRD patterns for (a), (b), (c), and (d) for 0 wt %, 5 wt %, 10 wt %, and 20 wt % AS-glass addition and sintered at 1250 °C for 2 h in air (B: $Ba(Nd, Sm)_2Ti_4O_{12}$).

TABLE I Sintering conditions and measured data of the samples in Fig. 3

SEM of Fig. 3	(a)	(b)	(c)	(d)
Amount of AS (wt %)	5	5	10	20
Sintering temp. (°C)	1150	1250	1250	1250
Grain shape	Columnar	Columnar	Columnar	Columnar
l, d (μm)[a]	1.86, 0.45	5.25, 0.44	11.76, 0.53	13.19, 0.58
l/d	4.13	11.93	22.19	22.74
D_m and D_m/D_{cal} (%)[b]	4.99, 94.8	5.08, 96.6	4.77, 96.0	4.32, 96.9

[a] l and d: length and diameter of columnar grain.
[b] D_m: measured density; D_{cal}: calculated density.

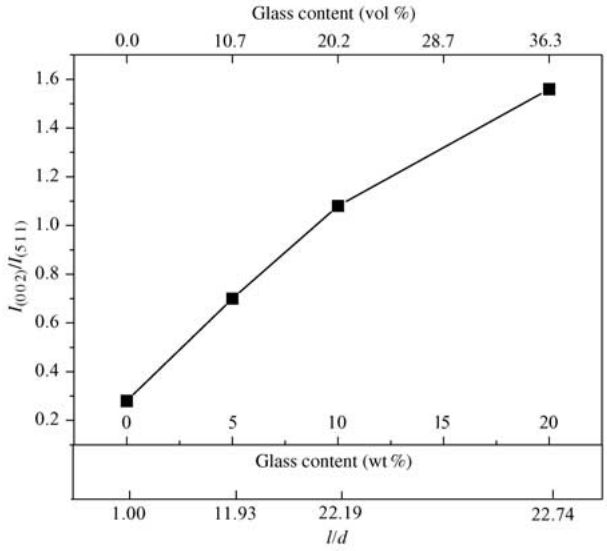

Figure 5 Intensity ratios $I_{(002)}/I_{(511)}$ as a function of glass content and l/d ratio. l and d are the length and diameter of the grains of sintered specimens of K80-AS ceramics sintered at 1250 °C for 2 h in air.

summarized in Table I. The l/d ratios for the samples with 5 wt % glass sintered at 1150 and 1250 °C are 4.13 and 11.93, respectively. As the glass content is increased to 20 wt %, the l/d ratio is increased to 22.74.

The X-ray diffraction patterns of sintered K80 without additive denote the phase of $Ba(Nd, Sm)_2Ti_4O_{12}$ as shown in Fig. 4(a), which indicates that the (5 1 1) peak is the main diffraction peak, while for the glass-doped K80, the intensity of the (0 0 2) peak increases with increasing

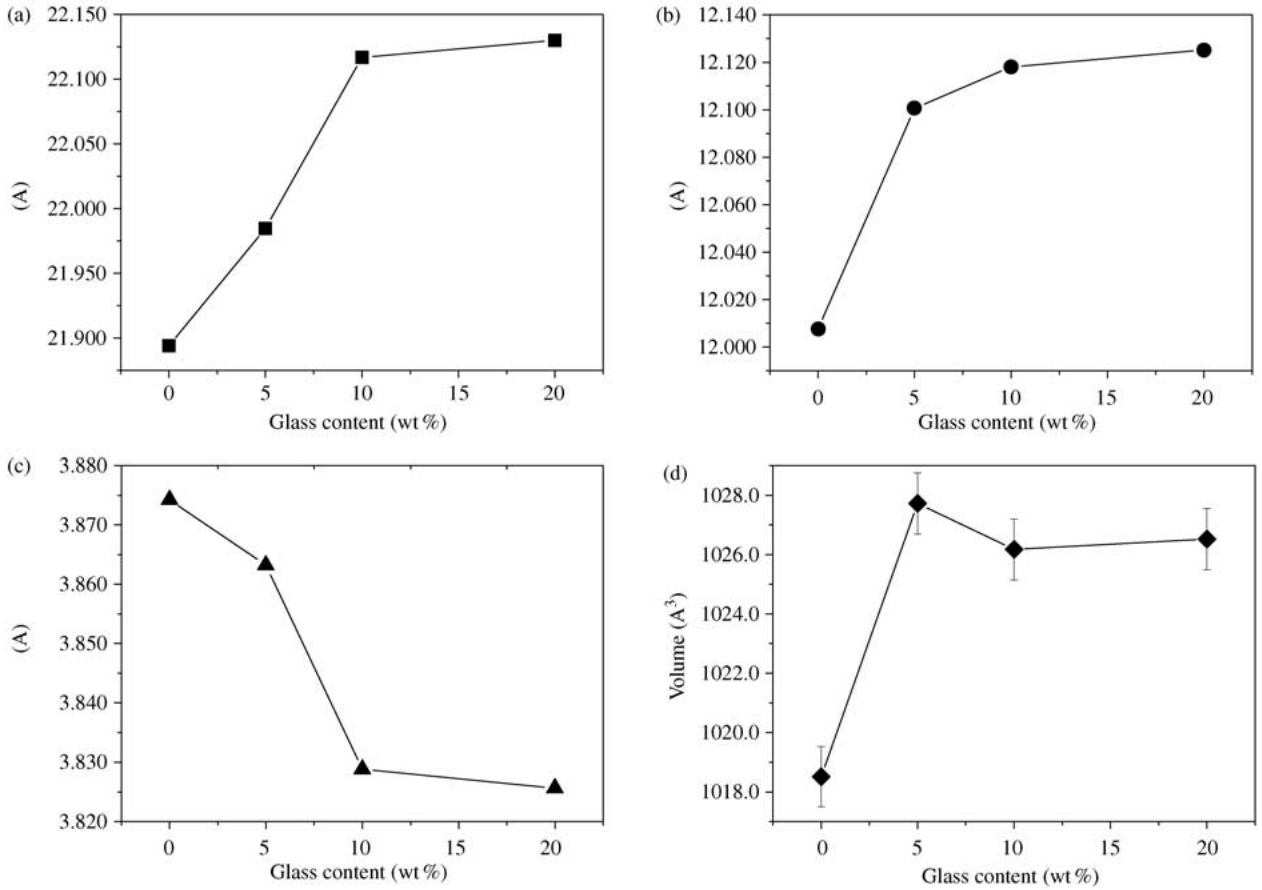

Figure 6 The lattice parameter (a) a, (b) b, (c) c, and (d) the unit cell volume of K80 ceramics as a function of AS-glass contents, the samples sintered at 1250 °C for 2 h in air.

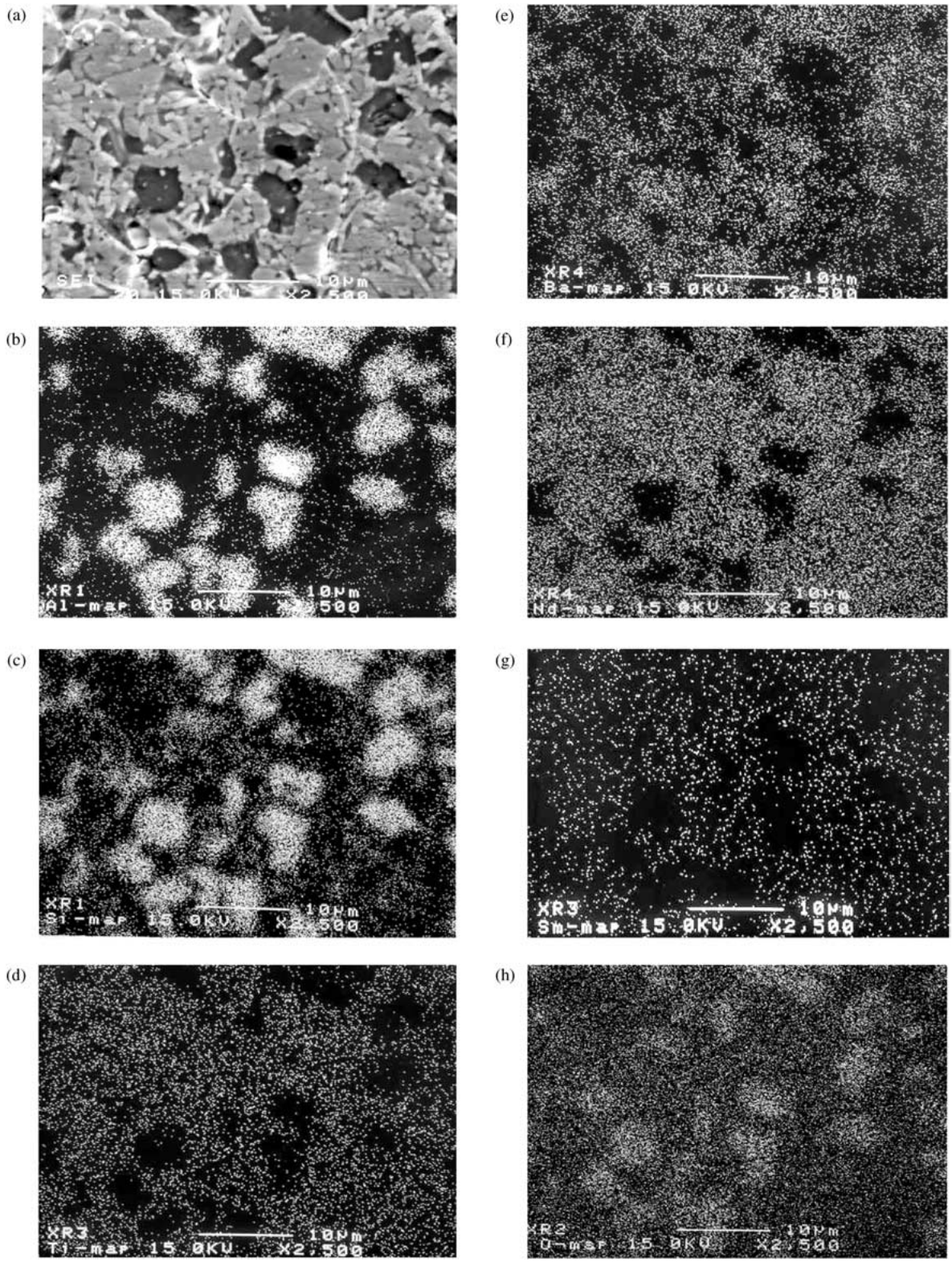

Figure 7 EPMA micrographs of K80 ceramics with 20 wt % glass addition and sintered at 1250 °C for 2 h in air, (a) SEI, (b) Al, (c) Si, (d) Ti, (e) Ba, (f) Nd, (g) Sm, and (h) O mapping.

glass content, as exhibited in Fig. 4(b)–(d). The peak intensity ratio of $I_{(0\,0\,2)}/I_{(5\,1\,1)}$ increases from 0.70 to 1.56 as the AS amount is increased from 5 to 20 wt %, as shown in Fig. 5, as compared to 0.27 of undoped K80. Also pointed out in Fig. 5 is the aspect dimension of grains. This implies that the preferred orientation (0 0 2) is generated from abnormal grain growth. Fig. 6 shows the lattice parameters as a function of AS-glass content. The lattice parameters a and b increase while c decreases with increasing amount of AS-glass. The unit cell volume increases initially and then remains constant with glass addition. A typical microstructure, exhibited in Fig. 7, shows that the glass-doped samples are an inhomogeneous mixture of BNST and AS-glass. Interdiffusion of ingredients is evident since the mapping of Si and Ba are found both in BNST and glass domains, as shown in Fig. 7(c) and (e), respectively.

Dielectric constant (k) and $Q \times f$ values of K80 ceramics as functions of sintering temperature are shown in Fig. 8. Both the dielectric constant and $Q \times f$ values

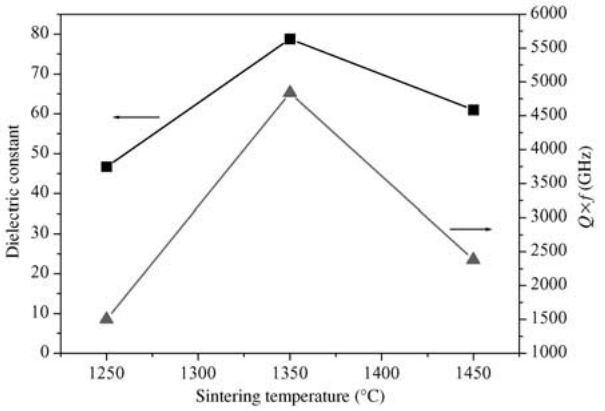

Figure 8 Microwave dielectric properties of K80 ceramics as function of sintering temperature.

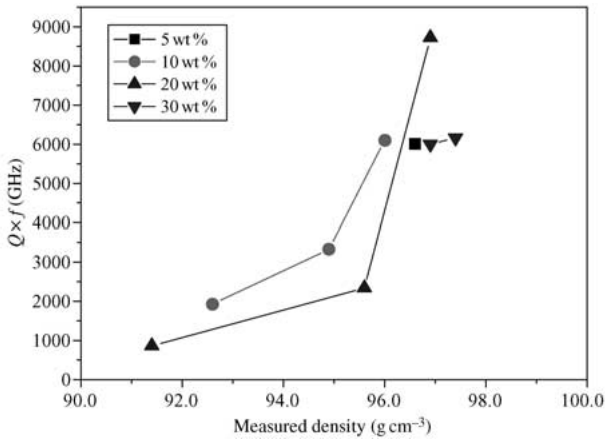

Figure 9 Dependence of $Q \times f$ on density of K80 sintered with AS-glass.

increase initially and then decrease with increasing sintering temperature. The dielectric properties showed a close correlation with density, the curve in accordance with the trend of that of the measured density in Fig. 2. For the K80 sintered with AS-glass, $Q \times f$ increases with density, similar to that of K80 dielectrics. An abrupt rise in $Q \times f$ is observed when the sintered density exceeds 96% of the theoretical density, as suggested in Fig. 9. In other words, the $Q \times f$ value increases with increasing AS-glass content, since the density increases with glass content. The specimen with 20 wt % glass exhibits the highest $Q \times f$ value ($\sim$ 8700 GHz) and a moderate k ($\sim$ 30), among all the compositions studied. The AS-glass is shown to be effective in both the densification and in enhancing the quality factor of BNST ceramics when added appropriately. However, the role of the glass in achieving the columnar microstructure is very complicated and is the subject of further investigation.

4. Conclusions

In this study, the effects of Al_2O_3-doped silica (AS) glass on the properties of BNST dielectric are investigated. It is found that BNST ceramics is achieved by the addition of AS-glass. A densification of 96.0% of theoretical densities is obtained for glass-doped specimens sintered at 1250 °C and below. Addition of glass also influences the microstructure evolution of the dielectric. For glass-free samples, nearly equi-axed fine grains are observed when sintered at 1250 °C and below, and a columnar structure is obtained when the sintering temperature exceeds 1350 °C. However, exaggerated columnar grains grow at 1150 °C for specimens doped with glass. For samples with 20 wt % glass, a columnar structure with grain length 22 times longer than the grain diameter is obtained. X-ray diffraction patterns show significant (0 0 2) preferred orientation. For K80 dielectrics with 20 wt % glass sintered at 1250 °C, $Q \times f$ was more than 8700 at 8 GHz, which was higher than that of K80 sintered at 1350 °C ($Q \times f = 6000$ GHz at 8 GHz), but the dielectric constant is 30 as compared to 80 of K80.

Acknowledgment

This work is supported by Phycomp Taiwan Ltd. under contract No. C90195.

References

1. H. LIANG, A. SUTONO, J. LASKAR and W. R. SMITH, *IEEE MTT-S International Microwave Symposium Digest* **4** (1999) 1901.
2. D. KOLAR, S. GABERSCEK, Z. STADLER and D. SUVOROV, *Ferroelectrics* **27** (1980) 269.
3. Y. J. WU and X. M. CHEN, *J. Am. Ceram. Soc.* **83** (2000) 1837.
4. P. LAFFEZ, G. DESGARDIN and B. RAVEAU, *J. Mater. Sci.* **30** (1995) 267.
5. Y. XU, X. M. CHEN and Y. J. WU, *J. Am. Ceram. Soc.* **83** (2000) 2893.
6. J. O. ISRAD, *Int. Conf. Comp. Mater. Electron. Eng.*, IEEE Paper (1961) 3636.
7. T. TAKADA, S. F. WANG, S. YOSHIKAWA, S. J. JANG and R. E. NEWNHAM, *J. Am. Ceram. Soc.* **77** (1994) 1909.
8. O. DERNOVSEK, A. NAEINI, G. PREU, W. WERSING, M. EBERSTEIN and W. A. SCHILLER, *J. Euro. Ceram. Soc.* **21** (2001) 1693.
9. H. S. NALWA, ''Handbook of Low and High Dielectric Constant Materials and their Applications'', Vol. 1 (Academic Press, 1999) p. 431.
10. Phycomp Taiwan Ltd. internal research center K80 data sheet.
11. B. W. HAKKI and P. D. COLEMAN, *IRE Trans. Microw. Theory Tech.* **8** (1960) 402.
12. R. M. GERMAN, ''Sintering Theory and Practice'' (John Wiley & Sons, Inc., 1996) p. 228.
13. X. M. CHEN, Y. SUZUKI and N. SATO, *J. Mater. Sci.: Mater. Electron.* **6** (1995) 10.

Received 13 December 2002
and accepted 7 June 2003