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The effect of composition on Ba-Nd-Sm-Ti-O microwave dielectric materials for LTCC application

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Abstract

Effect of composition of $BaO{\cdot}(R_2O_3)_y{\cdot}(TiO_2)_z{\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)$ materials, $R = Nd_{(1-x)}Sm_{(x)}$, BRT, on the materials characteristics and microwave dielectric properties of the samples was systematically examined. The Ti/Ba ratio (z value) shows the most significant effect on the microwave dielectric properties of the materials. The $Q \times f$-value is small for $z \leqq 3.82$ materials, and showing maximum value for $z = 4.32$ samples, then decrease for $z = 4.52$ composition, which is possibly due to the presence of secondary phase for $z = 3.82$ and 4.52 materials. Diffusion couple experiments shows that the interaction diffusion zone between glass and BRT ceramic is not pronounced, so that Ba-B-Si glass and BRT could be a good low temperature co-firable ceramic system is inferable.

Keywords: $BaO\text{-}Nd_2O_3\text{-}TiO_2$ series; Dielectric properties; Low temperature co-firable ceramic (LTCC) composites

1. Introduction

$BaO\text{-}Nd_2O_3\text{-}TiO_2$ series materials possess marvellous microwave dielectric properties, such as high dielectric constant and high quality factor, and were extensively investigated for the applications in microwave devices [1–6]. Processing of $BaO\text{-}Nd_2O_3\text{-}TiO_2$ series materials is, however, extremely difficult due to complicated interaction between the constituents. Kolar et al., [1] incorporated $2Bi_2O_3{\cdot}3TiO_2$, which possess positive coefficient of resonance frequency ($\tau_f = 650\,ppm\,^\circ C^{-1}$), with $BaNd_2Ti_4O_{12}$, which possess negative τ_f ($-120\,ppm\,^\circ C^{-1}$), to achieve low τ_f composite materials. Durand [2] and Kawashima [3] improved the microwave properties of $Bi_2O_3\text{-}BaO\text{-}Nd_2O_3\text{-}TiO_2$ materials by adding $BaSm_2Ti_5O_{14}$ into the materials, as soild solution [3]. Laffez [4] proposed the complicated formula $Ba_{6-x}(Sm_{1-y}Nd_y)_{8+2x/3}Ti_{18}O_{54}$ and Satheesh [5] assumed the formula $BaNd_{2(1-x)}Sm_{2x}Ti_5O_{14}$ for these series of materials. The trend by which the composition influences the microwave dielectric properties of the materials is quite controversial. In this paper, the Ti/Ba ratio and the Nd/Sm ratio in $BaO{\cdot}(R_2O_3)_{1.08}{\cdot}(TiO_2)_z{\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)$ where $R = Nd_{(1-x)}Sm_{(x)}$ were systematically examined to understand the mechanism that the composition influence the microwave dielectric properties of the materials. The interaction between BRT and glass was also examined for the possibility of using these materials as LTCC materials.

2. Experimental

The $BaO{\cdot}(R_2O_3)_{1.08}{\cdot}(TiO_2)_z{\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)$ materials with $R = Nd_{(1-x)}Sm_{(x)}$, designated as $(BRT)_{114}$ were prepared by conventional mixed oxide process. High purity oxides, $BaCO_3$ (Kali, 99.8%), TiO_2 (rutile, Bayor, 99.7%), $Nd_2(CO_3)_3$ (Treibache or Rhodia, 99%), and Sm_2O_3 (Rhodia, 99.5%), with the nominal composition $BaO{\cdot}(R_2O_3)_{1.08}{\cdot}(TiO_2)_z{\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)$ where $R = Nd_{(1-x)}Sm_{(x)}$ was mixed and then calcined at 1170 °C for 2 h, followed by pulverization, pressing and then sintering at 1330 °C for 2 h. In the first series of $(BRT)_{114}$ materials, the Nd/Sm ratio is controlled at $x = 0.3$ in $R = Nd_{(1-x)}Sm_{(x)}$ and the Ti/Ba ratio is controlled at $z = 4.0$, 4.5 and 4.7, which are designated as $(BRT)_I$, $(BRT)_{II}$ and $(BRT)_{III}$, respectively. In the second series of $(BRT)_{114}$ materials, $z = 4.5$ and $Nd/Sm = 5.67\text{-}2.33$, which corresponding to $x = 0.15$–0.30 in $Nd_{(1-x)}Sm_{(x)}$ The density of the sintered $(BRT)_{114}$ materials was measured by Archimedes method. The crystal structure and microstructure of the samples were examined using X-ray diffractmeter (XRD, Simens D5000) and scanning electron microscopy (Hitach, 2500-s). The microwave dielectric properties of the

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materials were measured by a cavity method using H.P. 8722A network analyzer. Besides the interaction between BRT and Ba-B-Si glases were investigated using diffusion couple method.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the BaO-Re_2O_3-TiO_2-Bi_2O_3 materials, designated as $(BRT)_{114}$, is shown as Fig. 1 to indicate that those materials with $z = 4.32$ and 4.52 possess the same structure, different from that of $z = 3.82$. The density of the materials increases with the TiO_2-content. Fig. 2a. So does the microwave dielectric constant of the $(BRT)_{114}$ materials. Fig. 2b. While the dielectric constant of the $(BRT)_{114}$ materials correlates with TiO_2-content intimately, the quality factor of the samples varies with the TiO_2 content in a quite different trend. Fig. 2c indicates that for $(BRT)_{114}$ with $R = Nd_{(1-x)}Sm_{(x)}$ and $x = 0.2$ the quality factor $(Q \times f)$ is small with value 5240 GHz when $z = 3.82$, $(BRT)_{I}$, and reach its maximum 7440 at $z = 4.32$, $(BRT)_{II}$, but the $Q \times f$-value decreases abruptly to $Q \times f = 6410$ for higher TiO_2-content materials at ($z = 4.52$, $(BRT)_{III}$.

Apparently, the increase in $Q \times f$-value for $z = 4.32$ materials can be ascribed to the higher density for these sample. But why $Q \times f$-value for $z = 4.52$ materials decreases abruptly for z exceed 4.52, even with higher density. To understand the mechanism for the abrupt decrease in $Q \times f$-value for high TiO_2-content samples, the microstructure for the surface and interior of the (BRT) samples were examined. Fig. 3 shows that grains of these BRT-series materials are of rod-geometry about 1–2 μm in diameter and 7–12 μm in length. The size of grains increases with TiO_2-content of the materials. The aspect ratio (α = length per diameter) of the rod-shaped grains also increases with z value.

SEM microstructure for polished and thermally etched surface shown in Fig. 4a–c reveals that the $(BRT)_{114}$ materials contain rod-shaped grains. As Ti/Ba ratio increased to 4.7 some elongated $(BRT)_{115}$ grains were distributed in the $(BRT)_{114}$ matrix. (Fig. 4c) Voids are observed for all the three samples, which are easily formed for the materials containing rod-shaped grains with large aspect ratio. The unique feature of the $(BRT)_{III}$ materials, as compared with the $(BRT)_{I}$ and $(BRT)_{II}$ materials, is that in additional to the grains with short-blunt-rod shaped (aspect ratio ∼ 4:1), there appears numerous grains with long-thin-rod shape (aspect

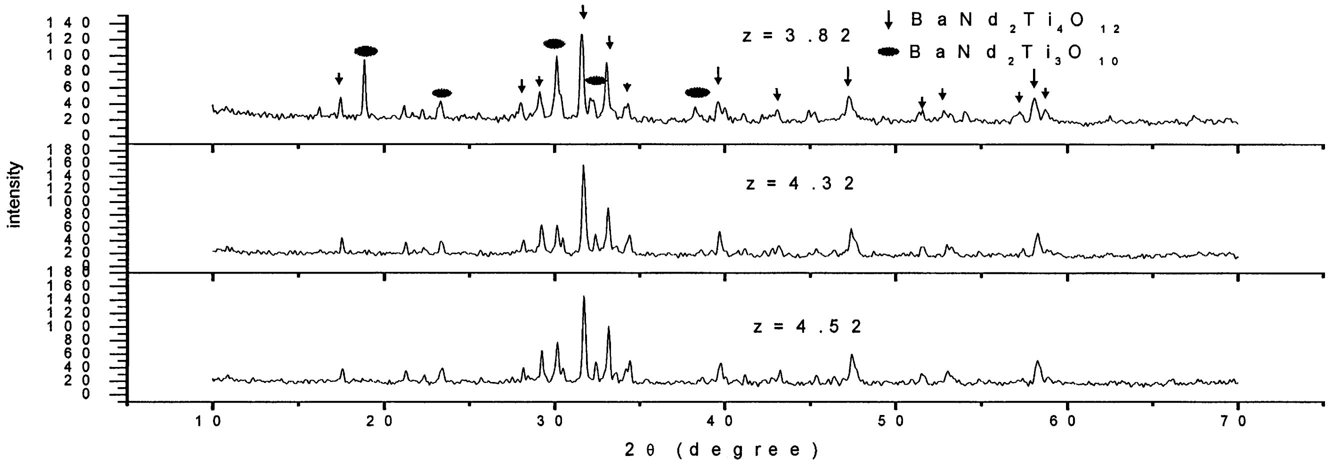

Fig. 1. X-ray diffraction patterns of $BaO\cdot(Nd_{1-x}Sm_x)_{1.08}\cdot(TiO_2)_z\cdot0.06(2Bi_2O_3\cdot3TiO_2)$ material which z = Ti/Ba = (a) 3.82, (b) 4.32 or (c) 4.52 and $x = 0.2$.

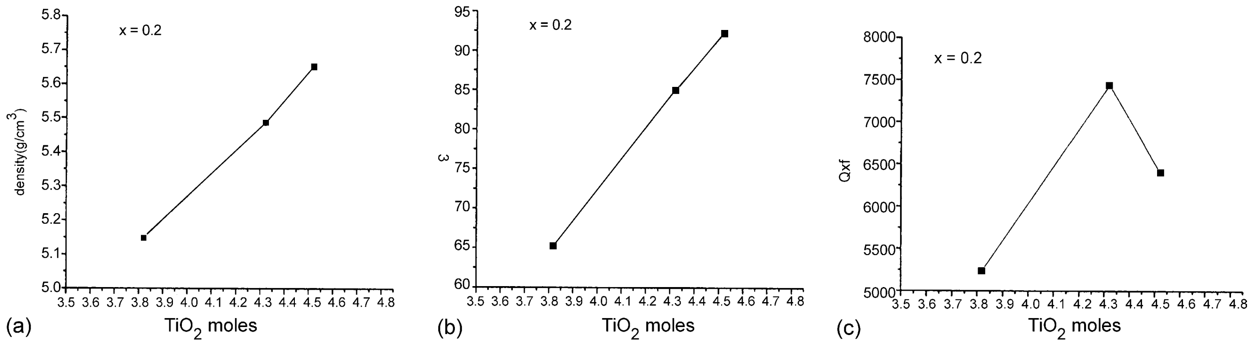

Fig. 2. (a) Density, (b) dielectric constant and (c) quality factor of $BaO\cdot(Nd_{1-x}Sm_x)_{1.08}\cdot(TiO_3)_z\cdot0.06(2Bi_2O_3\cdot3TiO_2)$ materials with z = Ti/Ba = 3.82, 4.32 or 4.52.

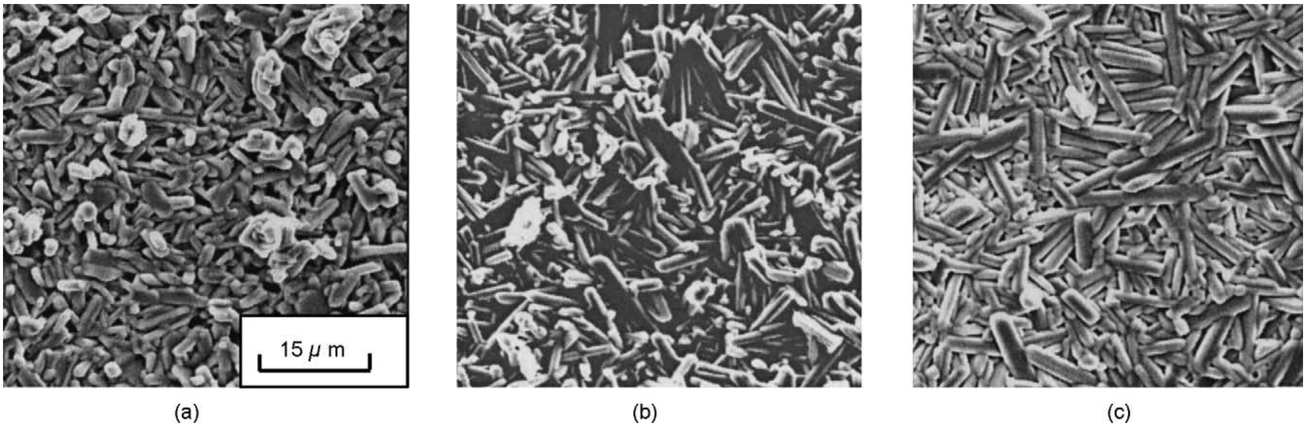

Fig. 3. SEM microstructure of the as-sintered surface of BaO·$(Nd_{1-x}Sm_x)_{1.08}$·$(TiO_3)_z$·0.06($2Bi_2O_3$·$3TiO_2$) materials with $z = Ti/Ba =$ (a) 3.82, (b) 4.32 or (c) 4.52 and $x = 0.2$.

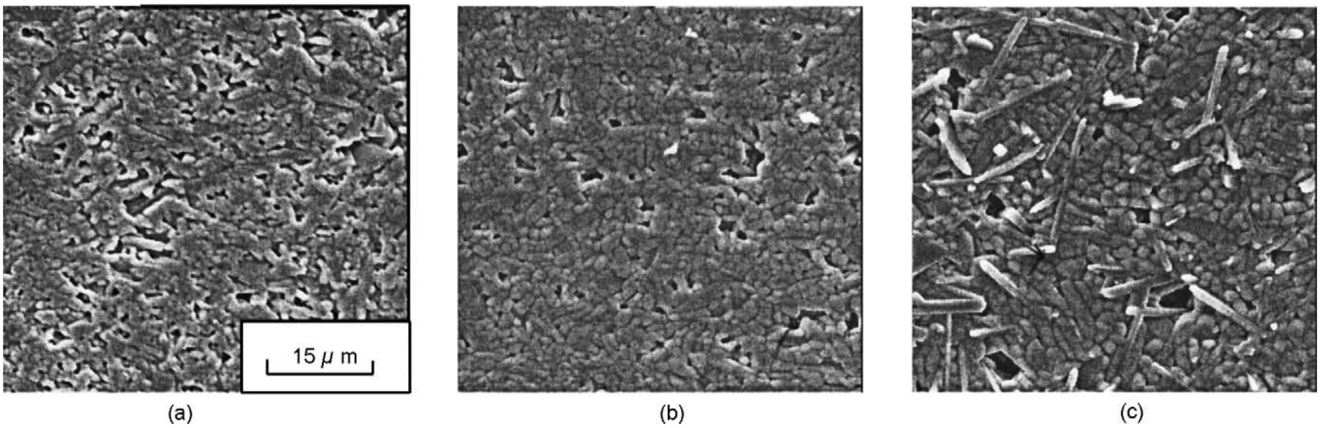

Fig. 4. SEM microstructure of the BaO·$(Nd_{1-x}Sm_x)_{1.08}$·$(TiO_3)_z$·0.06($2Bi_2O_3$·$3TiO_2$) materials with $z = Ti/Ba =$ (a) 3.82, (b) 4.32 or (c) 4.52, $x = 0.2$ after polishing and thermal etching.

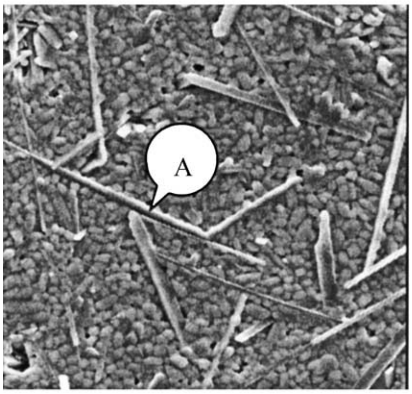

Table1. The comparison of EDS analysis between matrix and point A.

	TiKα	BaLα	NdLα
Matrix	53.76*	16.83	18.34
A	61.76	19.54	9.99
	SmLα	BiMα	
Matrix	9.81	1.63	
A	7.53	1.16	

*atomic percent

Fig. 5. The EDS analysis of the $(BRT)_{114}$ samples with $z = 4.52$, indicating that the long-thin-rod shaped grains are secondary phase, enriched in Ti-species and deficit in Sm- and Nd-species.

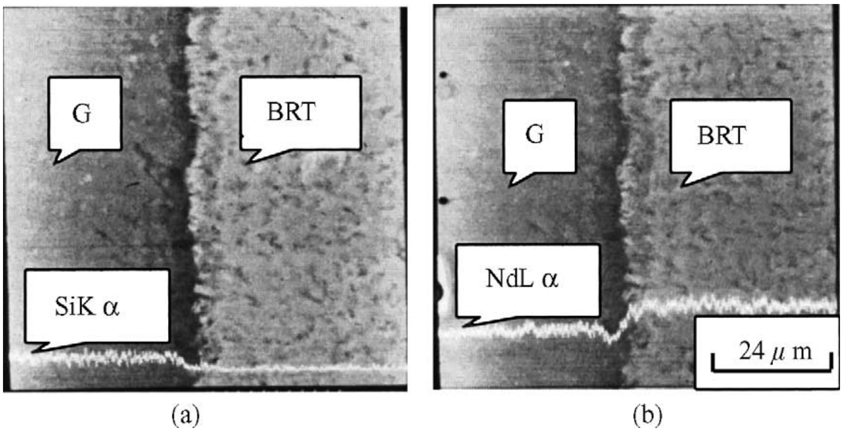

Fig. 6. Line scan of (a) SiKα and (b) NdLα over the surface of diffusion couple composed of Ba-B-Si glass and BRT ceramic material.

ratio ∼ 10:1). EDS analysis indicates that the long-thin-rod shaped grains are secondary phase enriched in Ti-species and deficit in Sm- and Nd-species (Fig. 5), (Table 1). It is believed that the presence of these high aspect ratio rod-shaped grains is the main factor for the quality factor of the $(BRT)_{114}$ materials decreasing. Whereas the nature of these unique grains is not quite understood yet.

Generally, the microwave dielectric materials were mixed with low melting temperature *glass* for synthesising low temperature co-firable ceramic (LTCC) composites, which *are* important materials for the development of microwave *multilayer* ceramic devices. The interaction between glass and dielectric materials is of concern, since such an interaction may impose deleterious effect on the repeatability in microwave characteristic of the sintered composites, or even completely degrades the dielectric properties of the dielectrics. To examine the suitability of $(BRT)_{114}$ materials for using as LTCC materials, a diffusion couple experiment was performed to investigate the inter-diffusion between the glass and microwave dielectrics.

The BaO-B_2O_3-SiO_2, BBS, glass with molar ratio of 27:18:55 is chosen, since the BBS glass possess highest Q-factor in microwave regime, among the MO-B_2O_3-SiO_2 and MO-Al_2O_3-B_2O_3-SiO_2 (M = Mg, Ca, Sr or Ba) glass materials. Fig. 6 reveals that there exists clear boundary between BBS glass (labelled as G) and $(BRT)_{114}$ material. Line scan of Si and Nd signals acrossing the glass-to-BRT boundary indicates the inter-diffusion is minimal. Restated, the BBS and $(BRT)_{114}$ composites (with 50 wt.%), which can be densified to more than 97% T.D. by sintering at 900 °C for 2 h, could be a good LTCC materials for multilayer microwave devices.

Table 1
The comparison of EDS analysis between matrix and point A

	α				
	TiK	BaL	NdL	SmL	BiM
Matrix	53.76[a]	16.83	18.34	9.81	1.63
A	61.76	19.54	9.99	7.53	1.16

[a] Values are in atomic percent.

4. Conclusion

Effect of composition of $BaO\cdot(R_2O_3)_y\cdot(TiO_2)_z\cdot0.06(2Bi_2O_3\cdot3TiO_2)$, with $R = Nd_{(1-x)}Sm_{(x)}$, on the materials characteristics and microwave dielectric properties of the samples was systematically examined. Both the density (D) and dielectric constant (ε) of the materials increase with the Ti/Ba ratio and Nd/Sm ratio monotonously, revealing the close relationship between these characteristics. However, the quality factor ($Q \times f$) of the materials varies with the Ti/Ba and Nd/Sm ratios in slightly different trends. The $Q \times f$-value is small for $Ti/Ba \leqq 3.82$ materials and increases to its maximun for $Ti/Ba = 4.32$ samples, then decrease abruptly for $Ti/Ba = 4.52$ samples. Such a phenomenon is more closely related to the microstructures rather than the density of materials. Excess TiO_2 can induce long- and -thin rod-shaped grains of large aspect ratio ($\alpha \geqq 10$). The results of diffusion couple experimental indicates that BRT and Ba-B-Si are insoluble to each other. However, an inter-diffusion zone was observed at the interface, which is good for LTCC application.

Acknowledgements

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