Structural and Dielectric Properties of the Mn-Doped $BaO-Nd_2O_3-4TiO_2$ System

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Abstract: *The effect of the Nd_2O_3 and TiO_2 ratios on the microstructure, dielectric properties and quality factor ($Q.f_r$) of the 1 wt% Mn-doped $BaO-Nd_2O_3-4TiO_2$ system were investigated. The samples sintered at various temperatures were analysed by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and a network analyser at 3 GHz. The grains of the Nd_2O_3 poor composition MBN0.5T4 were more spherical, whereas the grains of the excess Nd_2O_3 composition MBN1.5T4 were spherical and rod-like. The grains of the TiO_2 poor composition MBNT4 and the TiO_2 rich composition MBNT5 were more rod-like than spherical. The grain size increased with increasing sintering temperature. The $BaNd_2Ti_5O_{14}$ phase was observed for compositions based on a $BaO/Nd_2O_3 = 1$ ratio. The composition that deviated from the $BaO/Nd_2O_3 = 1$ ratio was composed of a major phase, $BaNd_2Ti_5O_{14}$, with some secondary phases, $Nd_2Ti_2O_7$ and $BaTi_4O_9$. The formation of the secondary phases affects the density, dielectric properties and quality factor of the Mn-doped $BaO-Nd_2O_3-4TiO_2$ system. The dielectric constant varies from 35–85 with different Nd_2O_3 and TiO_2 contents. Quality factor values of 4200 to 10500 (at 3 GHz) can be obtained by varying the Nd_2O_3 and TiO_2 contents.*

Keywords: Mn, dielectric properties, quality factor, $BaO-Nd_2O_3-4TiO_2$

Abstrak: *Kesan nisbah Nd_2O_3 and TiO_2 ke atas mikrostruktur, sifat dielektrik dan, faktor kualiti ($Q.f_r$) 1% berat Mn-dop $BaO-Nd_2O_3-4TiO_2$ telah dikaji. Sampel yang disinter pada pelbagai suhu dianalisa dengan menggunakan mikroskop elektron imbasan (FESEM), teknik pebelauan sinar-X (XRD) dan penganalisis rangkaian pada 3 GH_Z. Butiran bagi sistem MBN0.5T4 yang kekurangan Nd_2O_3 berbentuk sfera manakala butiran yang berlebihan kandungan Nd_2O_3 berbentuk rod. Saiz butiran pula didapati meningkat dengan suhu persekitaran. Fasa $BaNd_2Ti_5O_{14}$ terbentuk bagi sampel dengan nisbah $BaO/Nd_2O_3 = 1$. Selain daripada komposisi didapati sampel mengandungi fasa utama $BaNd_2Ti_5O_{14}$ bersama fasa sekunder $Nd_2Ti_2O_7$ dan $BaTi_4O_9$. Pembentukan Fasa sekunder mempengaruhi ketumpatan, sifat dielektrik dan faktor kualiti sistem Mn-dop $BaO-Nd_2O_3-4TiO_2$. Pemalar dielektrik berubah dari 35–85 dengan kandungan Nd_2O_3 dan TiO_2 yang berlainan. Faktor kualiti yang bernilai 4200 hingga 10500 (pada 3 GHz) boleh dicapai dengan mengubah kandungan Nd_2O_3 dan TiO_2.*

Kata kunci: Mn, sifat dielektrik, faktor kualiti, $BaO-Nd_2O_3-4TiO_2$

1. INTRODUCTION

Modern microwave telecommunication systems require ceramic dielectric resonators (DR) that exhibit a high quality factor ($Q \cong (\tan \delta)^{-1}$) and relative permittivity (ε_r) and a near-zero temperature coefficient of resonant frequency (τ_f).[1,2] Despite their technical importance and widespread use, only a very few ceramic materials are known that meet these stringent property requirements. In the early days, TiO_2 attracted substantial attention due to its high relative permittivity (ε_r~100) and high quality factor ($Q.f_r$ ~50000 at 3 GHz).[3] Subsequent development resulted in useful compounds in the BaO-TiO_2 system. One of the materials described as having practical applications as a DR was $BaTi_4O_9$, which has an ε_r~38 and $Q.f_r$ ~28160 at 11GHz.[4] These results provoked exploration of materials in several BaO-M_2O_3-TiO_2 systems, where M is a rare earth species. The first system to be investigated was BaO-Nd_2O_3-TiO_3. A later work by Kolar *et al.*[5] reported a compound with a molar ratio near BaO-Nd_2O_3.5TiO_2 that was identified as having practical microwave properties because it exhibited εr~77 and *Q.fr*~17600. It is generally accepted that the characteristics of BaO–Nd_2O_3–TiO_2 ceramics strongly depend on their crystal structure, stoichiometry, grain size, additives and phase composition.[6–9] Consequently, numerous approaches existed for modifying the characteristic of BaO-Nd_2O_3-TiO_2 including (1) doping with additives of SrO, PbO, Ta_2O_5 and other rare earth oxides[10–14] and (2) varying the composition. As for this work, we have attempted to vary the composition by changing the ratio of Nd_2O_3 and TiO_2 in 1 wt% Mn-doped BaO-Nd_2O_3-4TiO_3 system. The effects of compositional change upon the microstructure, dielectric properties and quality factor are reported in this study. Mn of 1 wt% was added to all the compositions in our experiment because, in our previous work, we acknowledged that Mn addition promotes densification of BaO-Nd_2O_3-4TiO_3 and enhances the quality factor of the system.[15]

2. EXPERIMENTAL

Samples were prepared by the conventional method using $BaCO_3$. TiO_2, MnO and Nd_2O_3 powders of high purity above 99.9% (Merck, Germany). The compositions investigated in this study are summarised in Table 1.

Table 1: Composition of the samples.

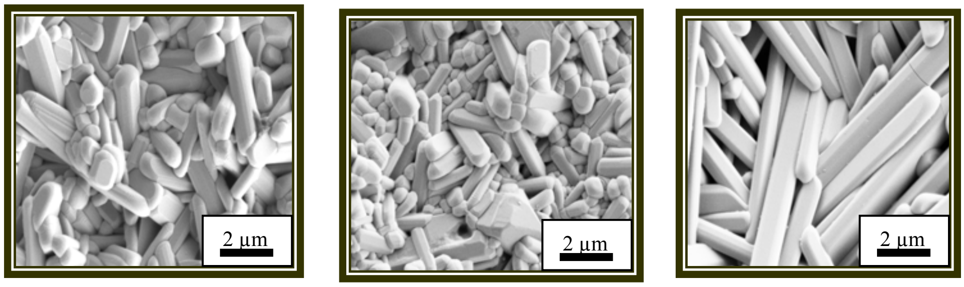
Sample	Composition
MBN0.5T4	$1BaO$-$0.5Nd_2O_3$-$4TiO_2$ with 1 wt% Mn
MBNT4	$1BaO$-$1Nd_2O_3$-$4TiO_2$ with 1 wt% Mn
MBN1.5T4	$1BaO$-$1.5Nd_2O_3$-$4TiO_2$ with 1 wt% Mn
MBNT5	$1BaO$-$1Nd_2O_3$-$5TiO_2$ with 1 wt% Mn

Mixing was carried out in a polyethylene bottle containing zirconia balls and deionised water. The mixture was calcined at 1150°C for 2 h, dried, crushed and then pressed with a cylindrical mould with a diameter of 16 mm under a pressure of 150 MPa to yield samples in pellet form. The specimens were sintered at various temperatures in the range of 1200°C to 1400°C for 2 h. The relative densities of the sintered samples were measured using a densitometer. Phase analysis was performed using a Bruker D8 powder diffractometer operating in reflection mode with Cu Kα radiation. Microstructure observation was conducted using a field emission scanning electron microscope (FESEM SUPRA 35VP ZEISS) operating at working distances down to 1 mm and an extended accelerating voltage range from 30 kV down to 100 V. Samples for ε_r and $Q.f_r$ measurements were prepared from sintered pellets by polishing both faces of the pellets with SiC paper (1000) followed by 0.1 μm Al_2O_3 paste. The ε_r and $Q.f_r$ were measured using a network analyser at 3 GHz.

3. RESULTS AND DISCUSSION

3.1 Microstructure

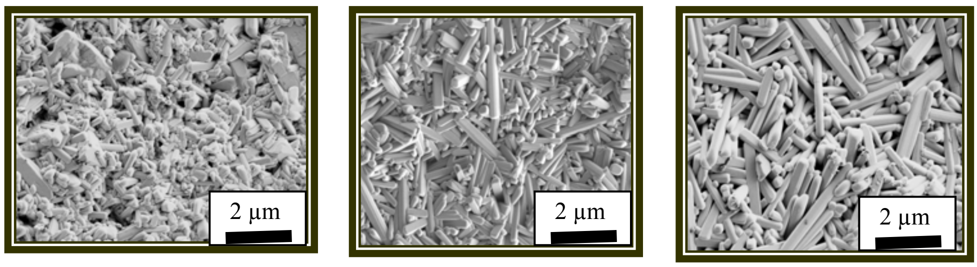
Figure 1 shows the microstructures of sintered MBNT4 at different sintering temperatures (1250°C, 1300°C and 1350°C). Both spherical and rod-shaped grains were observed in the sample sintered at 1250°C. The diameter of the spherical grains and rod-like grains are similar in the range of 0.5 to 0.8 μm. The lengths of the rod-like grains were of 2.0 to 2.5 μm. As the temperature was increased to 1300°C, the grains became slightly larger, with diameters of 1.0 to 1.2 μm. The lengths of the rod-like grains were approximately 2.0 to 4.0 μm. By increasing the sintering temperature to 1350°C, the spherical grains disappeared, and rod-like grains with diameters of 1.5 to 2.0 μm and lengths of 8.0 to 10.0 μm were observed. The change in the shape suggests that the grain growth occurs along orthorhombic a or b axes because these axes are longer than the c axis in the orthorhombic structure.



(a) (b) (c)

Figure 1: SEM micrographs of sintered MBNT4 at different sintering temperatures: (a) 1250^{o}C, (b) 1300^{o}C and (c) 1350^{o}C.

Figure 2 shows the microstructures of the sintered samples (1300^{o}C, 2 h) with different compositions. Both spherical and rod-like grains were observed in all the samples. The grains of the Nd_2O_3 poor composition MBN0.5T4 were mostly spherical with little rod-like structure. For the excess Nd_2O_3 composition MBN1.5T4, the grains were mostly rod-like with little spherical structure. The shapes of the grains in MBNT4 comprised both spherical and rod-like, whereas the grains in the excess TiO_2 composition, MBNT5, were mostly rod-like. The grain sizes in MBN0.5T4 and MBNT4 were relatively small compared to those of MBN1.5T4 and MBNT5. This result is in agreement with the results reported by Chen et al[11] and Fu et al.[16], in which they found that excess Nd_2O_3 and excess TiO_2 promote grain growth.



(a) (b) (c)

Figure 2: SEM micrographs of the sintered samples with different compositions: (a) MBN0.5T4, (b) MBN1.5T4 and (c) MBNT5.

3.2 XRD Results

The corresponding XRD patterns of the four different compositions are shown in Figure 3. The patterns for all the compositions fit well with the orthorhombic phase of standard $BaNd_2Ti_5O_{14}$, ICDD No 33–136. The lattice parameters of the XRD show a = 12.20 Å, b = 22.35 Å and c = 3.84 Å. However, detailed observation shows the presence of extra peaks in MBN0.5T4 and MBN1.5T4. The extra peaks in MBN0.5T4 and MBN1.5T4 were identified as $BaTi_4O_9$ and $Nd_2Ti_2O_7$, respectively. $Nd_2Ti_2O_7$ compounds may have formed because the excess Nd_2O_3 reacted with TiO_2, whereas $BaTi_4O_9$ compounds may have formed because the $BaTiO_3$ reacted with excess TiO_2. However, XRD peaks that correspond to MnO were not detected in any of the compositions, probably due to the small content of MnO in the samples.

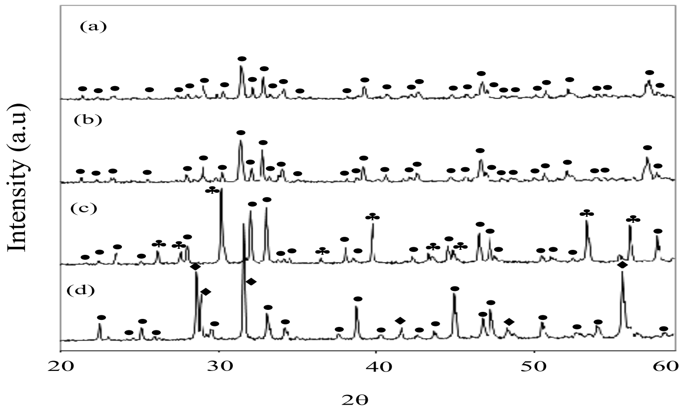


Figure 3: XRD patterns of the four different compositions: (a) MBNT5, (b) MBNT4, (c) MBN0.5T4 and (d) MBN1.5T4. [(●) $BaNd_2Ti_5O_{14}$, (♦) $Nd_2Ti_2O_7$, (♣)$BaTi_4O_9$]

3.3 Density

Various factors influence the microwave properties of dielectric materials, including the contents of individual crystalline, secondary phases and the degree of densification. Therefore, a series of experiments was performed to find the optimum densification of each sample. Figure 4 presents the densities of MBNT4, MBNT5, MBN0.5T4 and MBN1.5T4 sintered at various temperatures for 2 h.

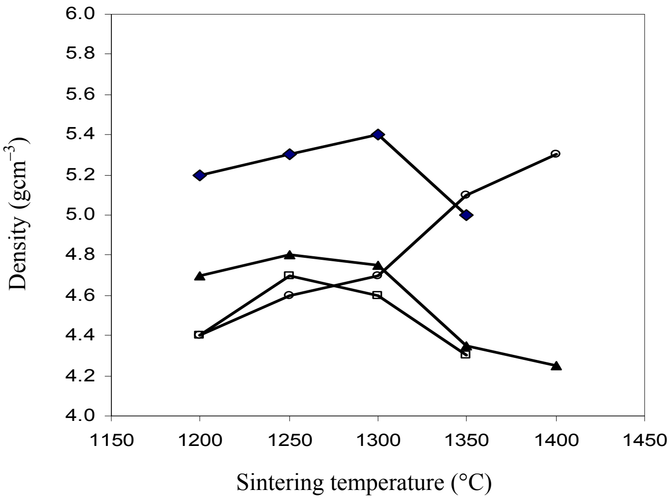


Figure 4: Densities of samples sintered at various temperature for 2 h. [(□) MBNT5, (♦) MBNT4, (▲) MBN0.5T4 and (O) MBN1.5T4].

The sintered density of MBNT5 was higher than MBNT4 at a given sintering temperature. This behaviour could be explained by considering the microstructure changes of MBNT5, which showed elongated grain and high porosity compared to MBNT4. MBNT5 showed a maximum density of 4.7 gcm^{-3} at 1250°C, whereas MBNT4 showed a maximum density of 5.4 gcm^{-3} at 1300°C. This result indicates that the excess TiO_2 in MBNT5 promotes densification at low temperature, and this might be due to the TiO_2 having a lower melting temperature than other oxides.[16] The density of the composition containing excess Nd_2O_3 (MBN1.5T4) increased gradually with sintering temperature and showed a maximum density of 5.3 gcm^{-3} at 1400°C, whereas the composition containing less Nd_2O_3 (MBN0.5T4) shows a maximum density (4.8 gcm^{-3}) at 1250°C, which declined as the sintering temperature increased. This result suggests that the composition containing more Nd_2O_3 requires high temperature for interdiffusion of the Nd_2O_3, which has a high melting temperature, into a chemically and crystallographically uniform structure to attain maximum density.[11]

3.4 Dielectric Properties

Figure 5 shows the changes in dielectric constant at 3 GHz as a function of sintering temperature with different compositions. The sample with composition MBNT4 showed the highest dielectric constant in the range of 75 to 85 with different sintering temperatures. The value of the dielectric constant decreased by 50% as the TiO_2 content increased (MBNT5). Furthermore, the results also demonstrate that the sintering temperature to achieve maximum dielectric value decreased as TiO_2 increased. For example, the maximum dielectric of MBNT4 was 85, and it was attained at 1300°C, whereas for MBNT5, the maximum dielectric constant, 60, was obtained at 1250°C. The trend of this result indicates that the dielectric constant is closely related to the density changes in Figure 4. This can be explained by considering the capacitance of a porous sample and a dense sample. For the porous sample, the total capacitance comprises the capacitance of the grain and air in the pores. It is well known that the capacitance of air is very much less than that of the grains.[17] Therefore, the less dense sample has a lower dielectric constant than the dense sample. The composition containing excess Nd_2O_3, MBNT1.5T4, has a dielectric constant below 55, and the maximum dielectric constant was obtained at 1400°C. The composition containing less Nd_2O_3, MBNT0.5T4, has a dielectric constant below 60, and the maximum dielectric constant was obtained at 1250°C and 1300°C. In summary, the dielectric constants for the samples with compositions deviating from a BaO/Nd_2O_3 = 1 ratio were relatively low, and this might be due to the presence of the secondary phase $Nd_2Ti_2O_7$ and $BaTi_4O_9$ compound.

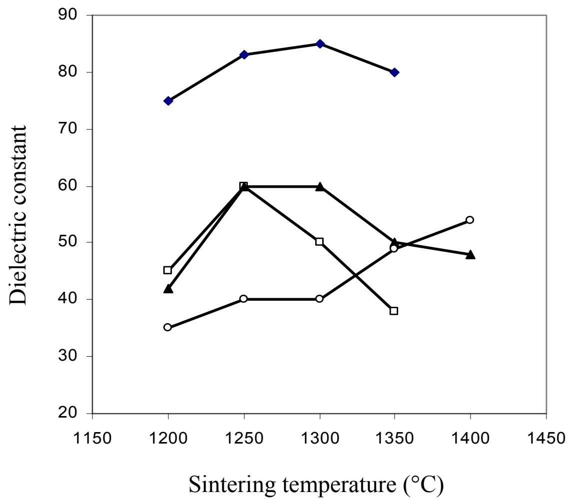


Figure 5: Dielectric of samples sintered at various temperature for 2 h. [(□) MBNTS, (♦) MBN0.5T4, (▲) MBN0.5T4, (O) MBN1.5T4]

3.5 Quality Factor *($Q.f_r$)*

The effect of sintering temperature on the $Q.f_r$ of Mn-doped BaO-Nd_2O_3-$4TiO_2$ is shown in Figure 6. As the proportion of TiO_2 increased in MBNT, the samples exhibited excellent $Q.f_r$ values. For example, the $Q.f_r$ of MBNT5 was in the range of 9000 to 10500, whereas for MBNT4, the $Q.f_r$ value was in the range of 7000–8500. The enhancement in the $Q.f_r$ value in MBNT5 is probably due to the fact that TiO_2 has a high $Q.f_r$ value. The composition containing less Nd_2O_3 showed a higher $Q.f_r$ value than the composition containing excess Nd_2O_3. This fact could be explained by the existence of the secondary phase $Nd_2Ti_2O_7$ in MBN1.5T4, which is known to have a low Q value, and $BaTi_4O_9$ compound in MBN0.5T4, which is known to have a high Q value.[18]

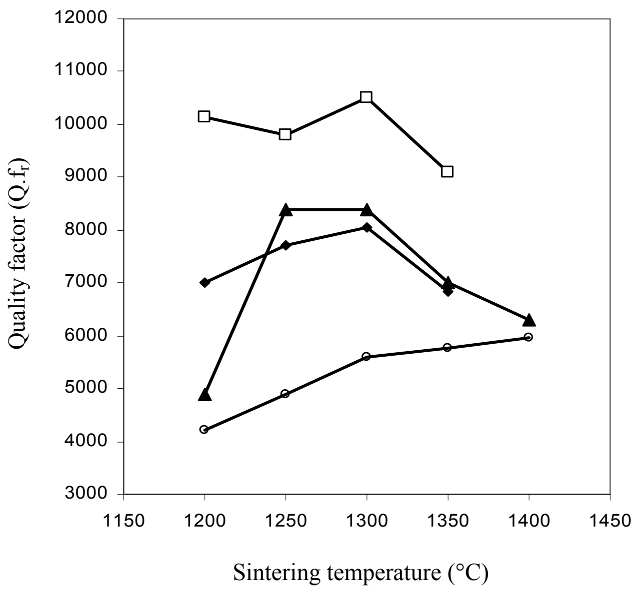


Figure 6: Quality factors of samples sintered at various temperatures for 2 h. [(□) MBNT5, (♦) MBNT4, (▲) MBNO. 5T4 and (O) MBN1.5T4.

4. CONCLUSION

The Nd_2O_3 and TiO_2 ratio control the density, dielectric constant, quality factor, phase and microstructure of 1 wt% Mn-doped BaO-Nd_2O_3-$4TiO_2$. The proportions of spherical and rod-like grains depend on the composition and sintering temperature. The pure phase was obtained for a BaO/Nd_2O_3 ratio = 1, and any deviation from this ratio causes the formation of secondary phases.

Excess Nd_2O_3 in the composition increased the sintering temperature for a maximum density, whereas excess TiO_2 decreased it. The dielectric constant was high for a BaO/Nd_2O_3 ratio = 1 and deteriorated when the ratio deviated from 1 due to secondary phase formation. The value of the quality factor decreased as Nd_2O_3 increased. In contrast, the quality factor value increased as TiO_2 increased.

5. ACKNOWLEDGEMENTS

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