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Structure and Microwave Dielectric Properties of $MgTiO_3$–$Na_{0.5}Nd_{0.5}TiO_3$ Ceramic Bodies

KEYWORDS: $MgTiO_3$, NdO_2, NaO, microwave, dielectric properties, X-ray diffraction

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ABSTRACT

The effect on the microwave dielectric properties of $MgTiO_3$ ceramics after addition of $Na_{0.5}Nd_{0.5}TiO_3$ (i.e. MT–NNT) was investigated. Increasing the proportion of $Na_{0.5}Nd_{0.5}TiO_3$ and raising the sintering temperature greatly affect the density of the material. The maximum density (~4.40 g/cm^3) was obtained with MT–NNT ceramic bodies sintered at 1300 °C for 4 h. The microwave dielectric properties, crystalline phases and microstructure development can be effectively controlled by varying the MT–NNT ratio. The best combination of microwave dielectric characteristics was obtained for MTNNT50 ceramics (1:1 MT–NNT ratio) sintered at 1300 °C for 4 h. It had dielectric constant $\varepsilon_r = 38$ and quality factor $Q \times f \sim 180{,}000$ GHzat 18 GHz. This is attributed to the high amount of $(Na_{0.5}Nd_{0.5})TiO_3$ (orthorhombic) crystalline phase present in the body.

1. Introduction

The microwave dielectric resonator properties of perovskite ceramics can be conveniently altered for various applications by forming new mixed phases of materials having different dielectric constants (ε_r) and a temperature coefficient of resonant frequency (τ_f) close to zero. Low-loss dielectric materials with high relative permittivity (ε_r) and low τ_f are useful for creating innovative devices in microwave communications. These materials are utilised in mobile telephone base stations, radar and global positioning systems. An advantage of using microwave dielectric resonators is that size reduction of microwave components is possible. The dielectric resonators are required to combine the following dielectric properties: high dielectric constant (between 20 and 100) to minimize the size of the resonator component, low dielectric loss (high quality value $Q = 1/\tan\delta$ should be above 35,000 GHz to enable the resonator to be highly selective to the target frequency), and a near-zero temperature coefficient of resonant frequency (τ_f) for frequency stability [1, 2]. Use of complex perovskite ceramics has recently been proposed for controlling these dielectric properties. It has been observed that mixing two or more compounds with negative and positive temperature coefficients is the most promising method for achieving a zero τ_f value [3, 4]. $MgTiO_3$ (MT) based ceramic materials combined with perovskite ceramics to improve dielectric properties are now gaining attention in the field of microwave dielectric resonators. Perovskite-structured magnesium titanate ($MgTiO_3$) is characterised by a high $Q \times f$ of 160,000 GHz (at 7 GHz), $\varepsilon_r = 17$, and $\tau_f = -50$ ppm/K [5]. Complex perovskite structures based on MT ceramics were studied by D. Abdel Aziz [6], who found that ceramic bodies containing $0.8MgTiO_3$ and $0.2CaTiO_3$, doped with ZnO and sintered at 1325 °C for 3 h exhibited a maximum quality factor ($Q \times f$) of 118,000 GHz at 11 GHz and relatively low $\varepsilon_r = 20$ due to reductions in lattice imperfection and dielectric loss. A near-zero τ_f of -4.9 ppm/K was obtained for $0.95MgTiO_3$–$0.05CaTiO_3$ ceramics with 0.25 mass-% ZnO sintered at 1250 °C for 4 h [3]. Complex perovskite in $0.96MgTiO_3$–$0.036SrTiO_3$ ceramic bodies also showed improved dielectric properties, with a high $Q \times f$ of 71,000 GHz at 9 GHz, $\varepsilon_r = 21$ and $\tau_f = -1.3$ ppm/K, which can be used for microwave frequency applications [7]. Cheng et al. [8] reported that $MgTiO_3$ (MT) combined with $Ca_{0.6}$ $La_{0.8/3}TiO_3$ (CLT) forms a two-phase system and leads to a near zero τ_f. With increasing CLT, the microwave $Q \times f$ decreased and ε_r increased.

The optimum result of $\varepsilon_r = 25.45$, $Q \times f \sim 82{,}500$ GHz (at 8.5 GHz) and $\tau_f \sim 0.5$ ppm/K was obtained with $0.85MgTiO_3$–$0.15Ca_{0.6}La_{0.8/3}TiO_3$ sintered at 1275 °C for 4 h. Replacing $MgTiO_3$ by $(Mg_{0.95}Zn_{0.05})TiO_3$ in the ceramic composition $0.93(Mg_{0.95}Zn_{0.05})TiO_3$–$0.07CaTiO_3$ yields better dielectric properties ($\varepsilon_r \sim 22.6$, $Q \times f \sim 93{,}200$ GHz and $\tau_f \sim 2.62$ ppm/K) [9]. Chunet et al. [10] concluded that the mixed complex perovskite ceramic containing $0.81Mg_{0.95}Ni_{0.05}TiO_3$ and $0.19Nd_{0.5}Na_{0.5}TiO_3$, fired at 1300 °C for 4 h, also exhibited excellent microwave dielectric properties: a dielectric constant of 25.61, $Q \times f$ of 69,100 GHz and a τ_f close to zero, with value –6 ppm/K.

In this paper, $(Na_{0.5}Nd_{0.5})TiO_3$ (NNT, with $\varepsilon_r \sim 98$, $Q \times f \sim 7200$ GHz and $\tau_f \sim 260$ ppm/K) [10] was added to $MgTiO_3$ in the ceramic system (1-x) $MgTiO_3$–$x(Na_{0.5}Nd_{0.5})TiO_3$ to achieve an ultra-high quality factor. The crystalline phases, microstructures and microwave dielectric properties of the resulting MT-NNT ceramic bodies were investigated.

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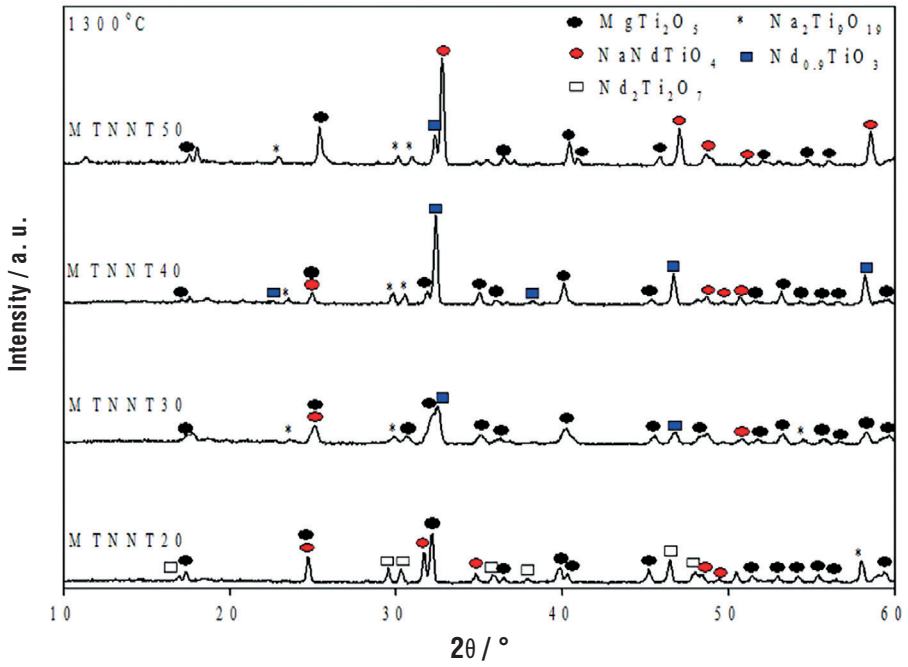

Fig. 1 • X-ray diffraction patterns of MT–NNT ceramics sintered at 1300 °C for 4 h

Table 1 · Main types and amount of crystalline phases and crystal structure detected in the MTNNT ceramic bodies sintered at 1300 °C for 4 h

Sample phase		MTNNT20	MTNNT30	MTNNT40	MTNNT50	Structure
$MgTiO_3$	Magnesium titanate	0.0	0.0	0.0	0.0	hexa
$MgTi_2O_5$	Karrooite	93.1	68.1	50.5	51.7	ortho
$Na_{0.5}Nd_{0.5}TiO_3$ or $NaNdTiO_4$	Sodium neodymium titanate	0.8	0.0	0.0	44.5	ortho
$Nd_2Ti_2O_7$ or $Nd_{0.9}TiO_3$	Neodymium titanate	5.1	23.7	49.5	0.0	mono
$Na_2Ti_9O_{19}$	Sodium nonatitanium oxide	1.0	8.2	0.0	3.8	mono

2. Experimental procedure

Samples of $MgTiO_3$ and $Nd_{0.5}Na_{0.5}TiO_3$ were individually synthesised by conventional solid-state methods from high purity MgO, $NaCO_3$, Nd_2O_3 and TiO_2 oxide powders (>99.9 %). The starting materials were mixed according to the stoichiometric proportions (1-x)$MgTiO_3$ and x($Na_{0.5}Nd_{0.5}$)TiO_3, for x = 0.2, 0.3, 0.4 and 0.5. The samples were denoted by MTNNT20, MTNNT30, MTNNT40 and MTNNT50, respectively. They were then ground using zirconia balls in distilled water for 24 h in a planetary mill and dried at 110 °C for 24 h. The mixed/milled powders were then calcined at 1100 °C for 4 h. A secondary milling of the calcinated powder in distilled water was performed for 6 h. The powder was then pressed into pellets 10 mm in diameter and 5 mm thick at a pressure of 100 kgf (force)/cm^2 using a hydraulic press. The pellets were sintered at maximum temperatures between 1200 and 1350 °C for 4 h. The controlled heating schedule involved increases of 5 K per minute up to 500 °C for a half hour period, followed by increases at the rate of 5 K per minute up to the sinter temperature. The final cooling rate was set at 5 K/min. The densities of sintered ceramics were measured using the Archimedes method. Structural analysis of samples using x-ray diffraction (XRD) analysis was performed in the range 2θ = 10°–90° on a Bruker D8 ADVANCE with CuKα radiation (λ = 1.5418 Å), Ni-filter and detector scan speed of 0.001°/s. Sintered bodies were polished and their microstructure was thermally etched for 90 min at 150 °C below the sintering temperature for examination by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDAX) using a JEOL JXA-840A Electron Probe Microanalyzer (Japan) equipped with an x-ray energy-dispersive spectrometer (Oxford INCAx-sight). The dielectric constant ε_r and quality factor Q×f were measured using a PNA-X 8720D Network Analyzer (10 MHz–50 GHz).

3. Results and discussion

3.1 Crystalline phases of MT–NNT bodies

The X-ray diffraction patterns of MTNNT20, MTNNT30, MTNNT40 and MTNNT50 ceramics sintered at 1300 °C for 4 h are shown in Fig. 1. The XRD patterns show three main crystalline phases in the different formulations: $MgTi_2O_5$ (orthorhombic MT_2), $Na_{0.5}Nd_{0.5}TiO_3$ or $NaNdTiO_4$ (orthorhombic NNT) and $Nd_{0.9}TiO_3$ (monoclinic NdT), in addition to trace amounts of two other phases: $Nd_2Ti_2O_7$ (monoclinic NT_2) and $Na_2Ti_9O_{19}$

Table 2 · Unit cell parameters a, b and c (Å) and volume V (Å3) of MT–NNT ceramics for various x values sintered at 1300 °C for 4 h

MTNNT20				MTNNT30			
a / Å	b / Å	c / Å	V / Å^3	a / Å	b / Å	c / Å	V / Å^3
3.936	9.839	10.324	399.886	3.741	9.786	10.022	366.929
2.542	2.542	80.457	519.737	0.708	0.708	112.049	56.148
7.743	5.547	26.409	1125.584	5.424	7.713	5.460	228.421
1.366	1.614	15.7689	33.905	13.406	3.702	20.329	924.961
MTNNT40				**MTNNT50**			
a / Å	b / Å	c / Å	V / Å^3	a / Å	b / Å	c / Å	V / Å^3
3.7417	9.791	10.030	367.446	3.736	9.784	10.032	366.741
3.801	3.801	2.257	32.605	5.466	7.700	5.444	229.112
5.4393	7.703	5.440	227.906	16.751	20.565	0.739	254.516
2.772	2.755	0.869	2.985	16.001	3.416	16.971	899.129

Table 3 · EDX data of the MT-NNT ceramic bodies for spectrums 2, 6, 8 and 11 (atom-%)

Atom-%					
Spectrum	Mg–K	Na–K	Nd– K	Ti–K	O–K
2	11.08	0.0	0.0	13.68	74.09
6	11.44	0.0	0.0	17.32	69.89
8	5.72	5.77	4.31	12.83	71.38
11	13.70	2.35	3.72	17.40	62.83

(monoclinic NT_9). The amount and degree of crystallization of these phases in the MT-NNT ceramic bodies depend on the composition (1-x) $MgTiO_3$–x($Na_{0.5}Nd_{0.5}TiO_3$), where x = 0.2–0.5. NNT was added in varying proportions to form hybrid MT-NNT phases and improve certain microwave dielectric properties. With increasing content of NNT in the system, the intensity of MT_2 reflection lines decreases gradually, benefiting the $Na_{0.5}Nd_{0.5}TiO_3$ and $Nd_{0.9}TiO_3$ solid solution phases detected in the sintered bodies. $MgTi_2O_5$ phase was identified, but $MgTiO_3$ phase completely disappeared from all mixed oxide samples sintered at 1300 °C. The added $Na_{0.5}Nd_{0.5}TiO_3$ seemed to enhance the formation of $MgTi_2O_5$ in MT–NNT ceramics through thermal decomposition of $MgTiO_3$. The distribution of crystalline phases detected in ceramic bodies calculated from the major peak intensities and the crystal structure is listed in Table 1. On the basis of refined crystallographic data, the unit cell parameters and volumes of the unit cells for phases present in the MT–NNT ceramics were calculated and listed in Table 2. Table 2 shows that with increasing $Na_{0.5}Nd_{0.5}TiO_3$ content, the crystal lattice of $MgTiO_3$ (i.e. $MgTi_2O_5$ in the table) had maximum volume at x = 0.2 and decreased thereafter. A similar result was reported by Tang et al. and Hui et al. [11, 12]. The $Na_{0.5}Nd_{0.5}TiO_3$ also caused a shift of XRD peak positions to higher diffraction angles, as shown in Fig. 1. This may be due to the presence of Mg^{2+} (0.072 nm) ions in proximity to Na^{2+} (0.098 nm) and Nd^{3+} (0.115 nm) ions, leading to generation of oxygen vacancies that contract and distort the unit cells of Table 2 [13].

3.2 Microstructural evolution and densification of MT–NNT ceramics

The SEM micrographs of MT–NNT ceramic bodies sintered at 1300 °C displayed in Fig. 2 show relative differences in densification and grain growth. Within the porous microstructure of the MTNNT20 and MTNNT30 compositions, small grains varying from 1 to 5 µm in size were observed (Fig. 2a, b). A significant increase in the grain sizes was observed for MT-NNT40 (Fig. 2c). However, x = 0.5 (MTNNT50) showed inhomogeneous grain growth (Fig. 2d). This suggests that increased amounts of NNT can induce grain growth in a sample and improve its microwave dielectric properties. Energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to examine representative grains of MT–NNT ceramics sintered at 1300 °C. The morphology of the MT–NNT ceramics reveals several types of grain structure. Table 3 lists EDX analysis data corresponding to marked locations on the SEM micrographs in Fig. 2 (labelled spectrum 6, 8, 10 and 11). The small cubic-shaped grains (spectrum 2) and elongated grains (spectrum 6) are associated with $MgTi_2O_5$. In the MTNNT40 and MTNNT50 images, MgO and TiO_3 appear as white cubic-shape grains (spectrum 8) and ($Na_{0.5}Nd_{0.5}$)TiO_3 as large dark grains (spectrum 11). As expected, the MT and NNT phases exhibit virtual solubility with each other because of the presence of Mg^{2+} (0.072 nm) between the Na^{2+} (0.098 nm) and Nd^{3+} (0.115 nm) ions.

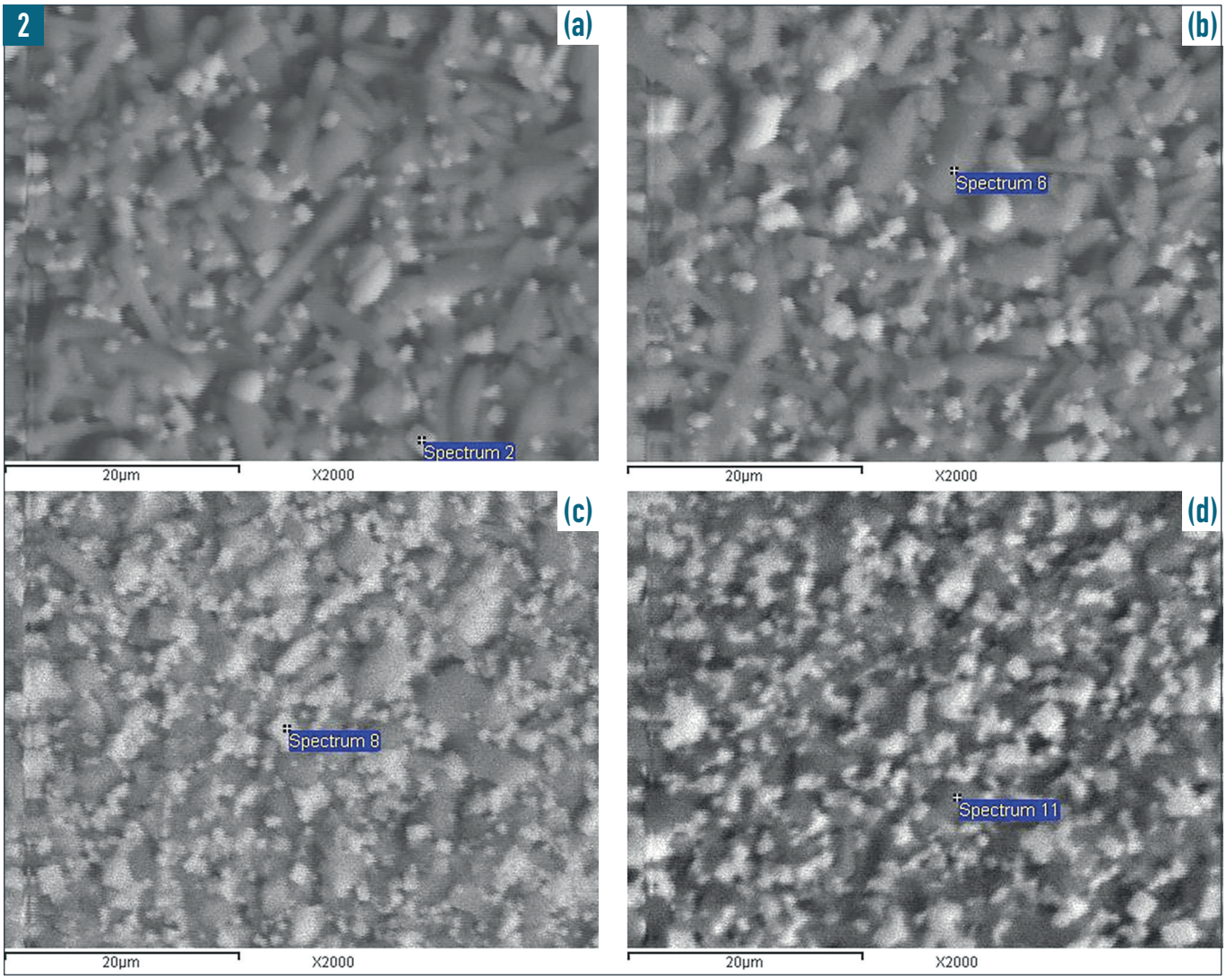

Fig. 2 • SEM of MT–NNT ceramics for various x values sintered at 1300 °C for 4 h

3.3 Physical properties

Figure 3 shows the bulk densities of the $(1-x)MgTiO_3–x(Na_{0.5}Nd_{0.5})TiO_3$ ceramics for x = 0.2, 0.3, 0.4 and 0.5 after sintering at different temperatures between 1200 and 1350 °C for 4 h. The densities increased with higher temperature and increasing amounts of NNT from 0.2 up to 0.5. This may be related to the composition of NNT, which possesses a higher density than MT (~5.24 g/cm^3 for NNT [10], ~3.86 g/cm^3 for MT [11]). Similar results obtained by Chun et al. [10] found that increasing the amount of $Nd_{0.5}Na_{0.5}TiO_3$ at the expense of $MgTiO_3$ in ceramic bodies also led to greater density. Moreover, the increase in bulk density of MT–NNT ceramics with higher sintering temperature is attributed to grain growth resulting in denser microstructure, as shown in Fig. 2. The maximum density of ~4.40 g/cm^3 was obtained for MTNNT50 ceramics sintered at 1300 °C.

3.4 Dielectric properties of MT–NNT ceramics

Fig. 4 shows the dielectric constant (ε_r) of MT–NNT ceramics as a function of x = 0.2, 0.3, 0.4 and 0.5 and sintering temperature (4 h). At microwave frequencies, ε_r is dependent on density, secondary phases and crystal structure [13]. The variation of dielectric constant was in general accord with the density change in Fig. 4. The ε_r value increased with increasing amount of NNT up to a value of 38 for x = 0.5 sintered at 1300 °C. This maximum may be explained by that body's higher amount of $(Na_{0.5}Nd_{0.5})TiO_3$ crystalline phase. The large difference in dielectric constant (ε_r) between $(Na_{0.5}Nd_{0.5})TiO_3$ (~98) and $MgTi_2O_5$ [14] is the reason for an increase in dielectric value.

Figure 4 also shows the Q×f values of the MT–NNT solid solutions sintered at different temperatures for 4 h. Many factors are believed to affect microwave dielectric loss and their effects can be divided into two categories, the intrinsic loss and the extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by the influence of secondary phases, oxygen vacancies, grain sizes and densification or porosity [15]. In the case of the results in Fig. 4, the Q×f values for different sintering temperatures are mainly affected by the density and grain size of the ceramic bodies. As densities increase, grain sizes also increase, but pore volume and grain boundary area decreases, thus reducing lattice imperfections and increasing Q×f. The Q×f values in Fig. 4 rise to a maximum at 1300 °C and then decrease as the densities level off with higher temperature in Fig. 3. Among the tested (1-x)MT–xNNT ceramic bodies, the highest Q×f value of 180,000 GHz (measured at 18 GHz) was obtained for MTNNT50 ceramics sintered at 1300 °C for 4 h.

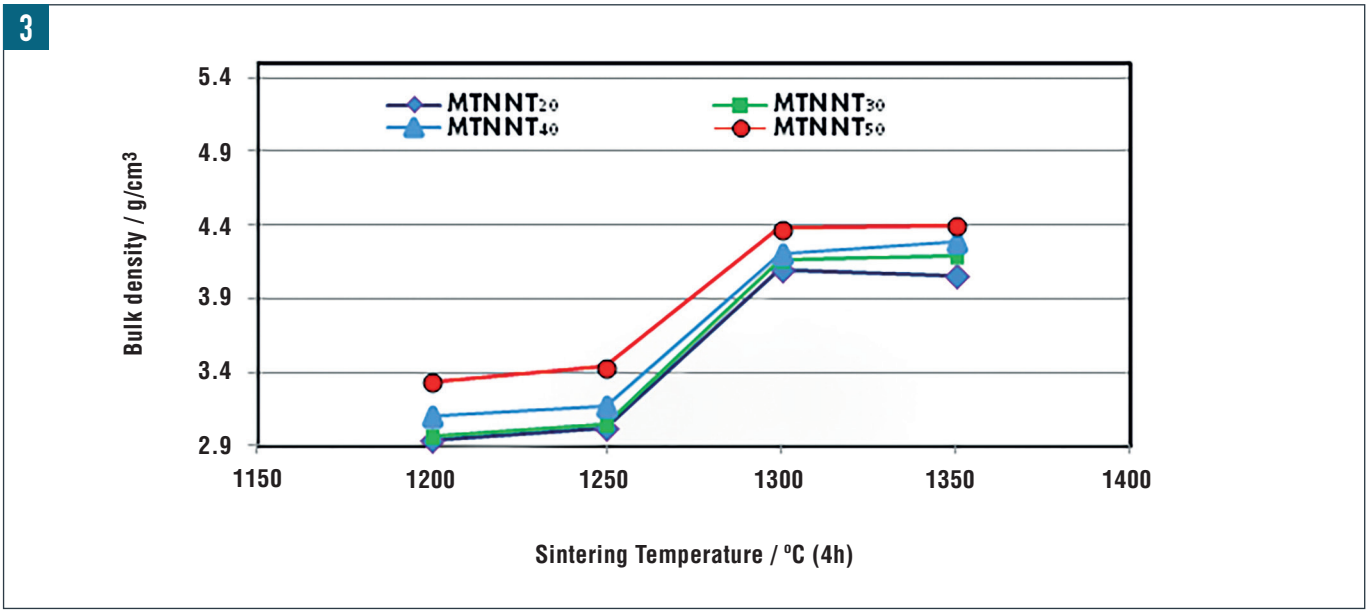

Fig. 3 • Densities of MT–NNT ceramics for various x values as a function of sintering temperature

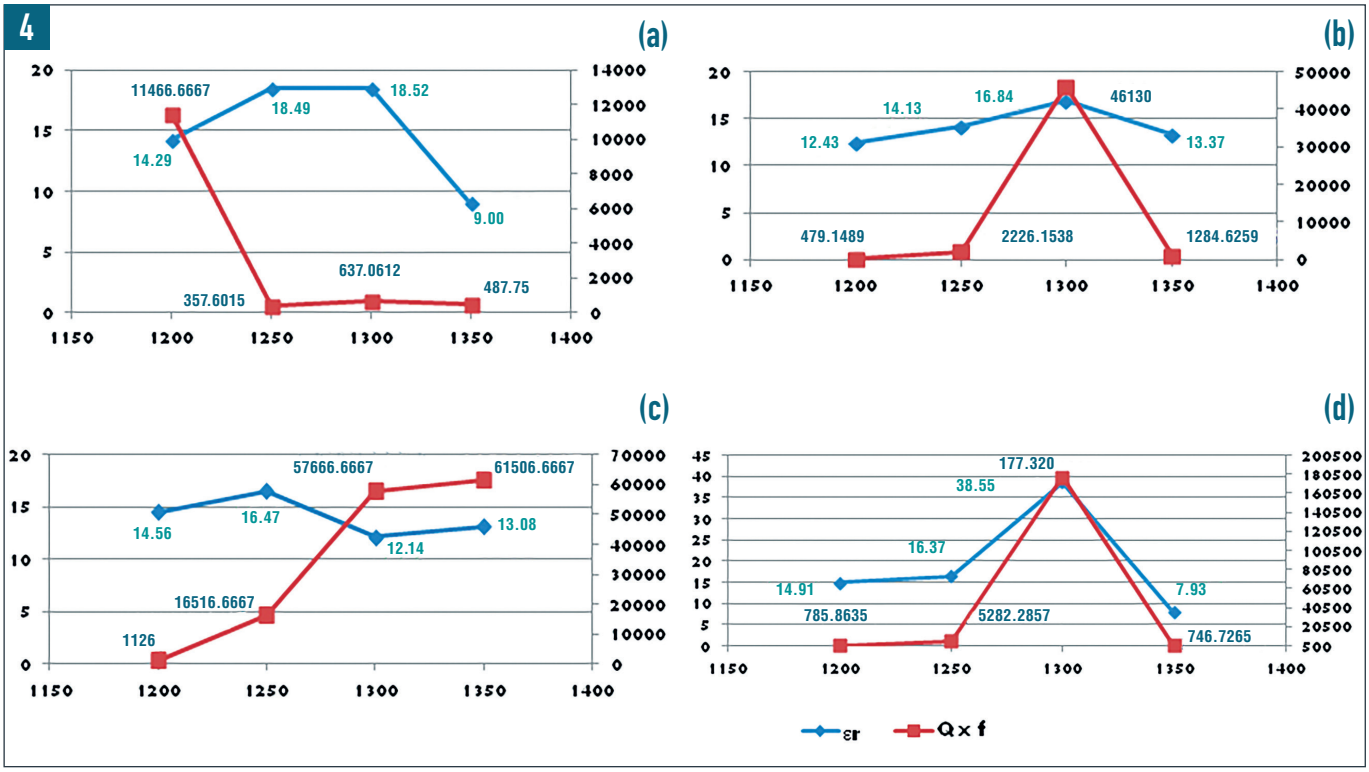

Fig. 4 • Q×f quality factor and ε_r dielectric constant of MT–NNT ceramic bodies for various x values as a function of sintering temperature (°C for 4 h)

4. Conclusions

- The results demonstrate that the $Na_{0.5}Nd_{0.5}TiO_3$ in (1-x)$MgTiO_3$–x($Na_{0.5}Nd_{0.5}TiO_3$) ceramic bodies sintered at 1300 °C for 4 h (where x is varied from 0.2 to 0.5) plays an important role in the development of crystalline phases. The main phases detected were $NaNdTiO_4$, $Nd_{0.9}TiO_3$ and $MgTi_2O_5$, in addition to trace amounts of $Nd_2Ti_2O_7$ and $NaTi_9O_{19}$.
- The amount of $Na_{0.5}Nd_{0.5}TiO_3$ and the sintering temperature greatly affect the density. The maximum density (~4.40 g/cm^3) was obtained with MTNNT50 ceramic bodies sintered at 1300 °C.
- The microwave dielectric properties of MT–NNT ceramics can be effectively controlled by varying the MT/NNT ratio and the development of crystalline phases and microstructure.

- The best combination of microwave dielectric characteristics, $\varepsilon_r = 38$ and quality factor ($Q \times f$) ~180 K at 18 GHz, was obtained with the MT-NNT50 ceramic (x = 0. 5) sintered at 1300 °C for 4 h.
- The MNT–NNT ceramic bodies, especially those with higher NNT content, are suitable for applications in microwave dielectric resonators and filters because of their excellent microwave dielectric properties.

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