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Influence of TiO_2 additive on sintering temperature and microwave dielectric properties of $Mg_{0.90}Ni_{0.1}SiO_3$ ceramics

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ABSTRACT

(1-x)$Mg_{0.90}Ni_{0.1}SiO_3$-$x$$TiO_2$ ($x = 0, 0.01, 0.03, 0.05$) ceramics were successfully formed by the conventional solid-state methods and characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS), and their microstructure and microwave dielectric properties systematically investigated. It was observed that when TiO_2 content increased from 0 to 5 wt%, the Q_uf_o of the sample decreased from 118,702 GHz to 101,307 GHz and increases the τ_f value from −10 ppm/°C to +3.14 ppm/°C accompanied by a notable lowering in the sintering temperature (125 °C). A good combination of microwave dielectric properties ($\varepsilon_r \sim 8.29$, $Q_uf_o \sim 101{,}307$ GHz and $\tau_f \sim -2.98$ ppm/°C) were achieved for $Mg_{0.90}Ni_{0.1}SiO_3$ containing 3 wt% of TiO_2 sintered at 1300 °C for 9 h which make this material of possible interest for millimeter wave applications.

1. Introduction

During the last four decades, a lot of microwave dielectric ceramics were investigated to evaluate the significant role play in growing wireless communication systems, such as global positioning systems, cellular phones, direct broadcasting satellites and wireless local area networks. The available frequencies have been prolonged from microwave to millimeter-wave ranges, because large number of information can be passed with a high speed in later range. Wireless communication utilizing millimeter waves require a low dielectric constant ($\varepsilon_r < 10$) to minimize the cross-coupling with the conductors to reduce the time for electronic signal transmission. The lower power dissipation and increase the selectivity of signal frequency as due to the high Q_uf_o value, a near zero temperature coefficient of resonant frequency (τ_f) for the frequency stability under the working environment temperature [1]. Silicates have low ε_r due to having about 55% covalent bonding in silica tetrahedron (SiO_4) [2]. Hence, they are considered to be one of the good candidates for millimeter-wave dielectric ceramics [3–5]. Forsterite (Mg_2SiO_4) has been widely investigated for millimeter-wave applications due to low dielectric constant (about ε_r: 7.0) and high Q_uf_o value.

However, forsterite (Mg_2SiO_4) had largely negative temperature coefficient of resonant frequency (−61 ppm/°C) [6], which precluded its applications in microwave communication systems. Therefore, TiO_2 with high positive τ_f value (+450 ppm/°C) was added to Mg_2SiO_4, in order to improve the τ_f value near to zero. In the previous work Tsunooka et al. has been reported that Mg_2SiO_4-TiO_2 ceramics synthesized by conventional solid-state reaction were enhanced τ_f to 0 ppm/°C [6,7]. Though, Q_uf_o of the Mg_2SiO_4-TiO_2 ceramics decreased because of the other phases such as $MgTi_2O_5$ and $MgSiO_3$ by a chemical reaction between Mg_2SiO_4 and TiO_2 during sintering temperature. $MgSiO_3$ has been reported to have $\varepsilon_r \sim 6.5$, high $Q_uf_o \sim 120{,}000$ GHz and $\tau_f \sim -19$ ppm/°C [8]. Even the τ_f of $MgSiO_3$ required being process through zero. $MgSiO_3$ has also low sinterability. Recent research trend suggests that the least expensive and the easiest way to carry out, and it is commonly used to improve the sinterability and microwave dielectric properties of compounds by various A- or B-site ionic substitutions. It has been reported that substitution of cation with less ionic radii for ion with larger ionic radii boosted the microwave dielectric properties [9,10]. Substitution of Mg^{2+} by Ni^{2+} in the various compounds has improved the sinterability and significantly enhanced the Q_uf_o values [10,11,14].

Recently we succeeded in the synthesis of high purity monoclinic ($Mg_{0.90}Ni_{0.1}SiO_3$) ceramics with excellent properties $\varepsilon_r \sim 6.10$, $Q_uf_o \sim 118702$ GHz and $\tau_f \sim -10$ ppm/°C sintered at 1425 °C for 9 h [14]. Moreover, a great deal of emphasis has been put on the adjustment of the τ_f of a material. The most popu-

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Table 1
Elemental composition (in moles) calculated from semi-quantitative EDS data for spots A–D in Fig. 3(a and c).

Grain	Mg (wt.%)	Ni (wt.%)	Si (wt.%)	Ti (wt.%)	O (wt.%)
A	26.2	9.1	24.9	0	39.8
B	27.7	8.5	23.3	0	40.5
C	32.8	6.1	18.8	0	42.3
D	0	0	0	35.9	64.1

lar method of achieving stable τ_f is the mixing of materials, that have opposite values of τ_f. TiO_2 has been reported to have $\varepsilon_r \sim 100$, $Q_u f_o \sim 50{,}000$ GHz and $\tau_f \sim +450$ ppm/°C [13]. Therefore, TiO_2 was added to improve the τ_f value of $Mg_{0.90}Ni_{0.1}SiO_3$ ceramics near to zero.

2. Experimental procedure

($Mg_{0.90}Ni_{0.1}SiO_3$) ceramics was prepared through a solid-state reaction method using starting materials of high-purity, MgO (99.99%, Aladdin), SiO_2 (99.99%, Aladdin) and NiO (99.0%, Aladdin). The raw materials were weighted in stoichiometric ratios and mixed by ball milling with zirconia grinding media in ethanol for 24 h. The slurry was put in an oven at 100 °C to get dried powder. The dried powder was calcined at 1300 °C for 5 h at heating/cooling rate of 3 °C per min. The calcined powder was mixed with different amounts of TiO_2 (>99.0%) in the ratio of 0, 1, 3 and 5 weight percent, respectively. These mixtures were grinded through ball milling with zirconia grinding media in ethanol for 20 h. The slurries were put in an oven at 100 °C to get dried powders. These powders were mixed with 5 wt% of (PVA) as binders and were pressed into 12 mm diameter and 5–6 mm thick pellets at 220 MPa. The green body pellets were dried under vacuum (rotary evaporator SHZ-D III) for the removal of air and pores from the pellets and finally were subjected to cold isostatic pressing. The green compact discs of pure $Mg_{0.90}Ni_{0.1}SiO_3$ and TiO_2 assed $Mg_{0.90}Ni_{0.1}SiO_3$ samples were initially heated at 600 °C for 2 h to expel the binder and then sintered at 1260 °C to1320 °C respectively at heating/cooling rate 3 °C per min for 9 h in air. The bulk densities of all the sintered samples were measured via Archimedes method. The phase and microstructure of the sintered samples were examined by X-ray diffraction (XRD, Panalytical Expert PRO), and scanning electron microscopy (FESEM, EDS) measurements after thermal etching for 30 min, respectively. The dielectric constant, and $Q_u f_o$ values were measured by Hakki–Coleman dielectric resonator method using an Agilent 8722ET (50 MHz–40 GHz) Network Analyzer. The τ_f values were measured by noting the variation in the resonant frequency of TE_{011} resonant mode over the temperature range of 20 °C to 80 °C using (1).

$$\tau_f = f_2 - f_1 / f_1 (T_2 - T_1) \tag{1}$$

where f_1 and f_2 are the initial and final resonant frequencies at 25 °C and 85 °C, respectively.

3. Results and discussion

The XRD Patterns recorded for calcined and sintered samples of $Mg_{0.90}Ni_{0.1}SiO_3$ and TiO_2 added $Mg_{0.90}Ni_{0.1}SiO_3$ ceramics are shown in Fig. 1. The major peak in the XRD pattern of the calcined sample could be well indexed according to PDF #34-189 for Mg_2SiO_4 (Forsterite), labeled as "$*$", with slightly shifting in the peak position towards larger 2θ (Fig. 1a). The shifting might be due to the partial incorporation of smaller cation of Ni^{2+} (0.69 Å for CN = 6) at Mg^{2+} (0.72 Å for CN = 6) site in Mg_2SiO_4 resulting in a shrinkage of the unit cell of Mg_2SiO_4 [12]. Some extra peaks labeled as "∘" and "♦" were also detected in the XRD pattern that matched for SiO_2 (PDF#071-0785) and $MgSiO_3$ (PDF #013-0415), orthorhombic) respectively. This shows that at lower temperature (1300 °C), Ni based Mg_2SiO_4 do not react fully to SiO_2 to form the required $Mg_{0.90}Ni_{0.1}SiO_3$ phase.

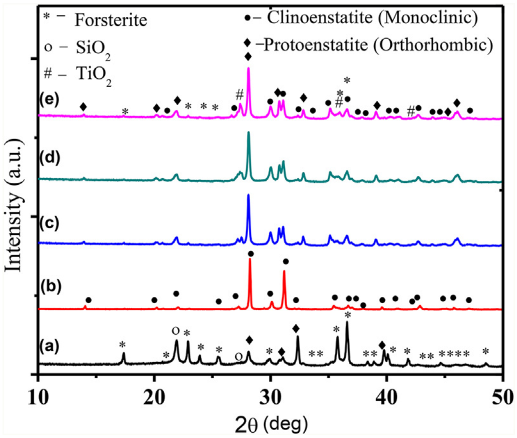

Fig. 1. X-ray diffraction patterns of $Mg_{0.90}Ni_{0.1}SiO_3$ ceramics (a) calcined at 1300 °C for 5 h, (b) 0 wt% sintered at 1425 °C for 9 h, (c) 1 wt%, (d) 3 wt% and (e) 5 wt% of TiO_2 addition sintered at 1300 °C for 9 h.

The d-values and XRD peak intensities of the sintered sample of the composition with $x = 0$ ($Mg_{0.90}Ni_{0.1}SiO_3$) matched PDF #75-1404 for $MgSiO_3$ (Clinoenstatite, system), labeled as "●", with slightly shifting of the peaks positions towards larger 2θ values because of the presence of smaller Ni^{2+} (0.69 Å) ions in place of larger Mg^{2+} (0.70 Å) ions (Fig. 1b). There was no evidence of any secondary phase, showing the formation of a single $Mg_{0.90}Ni_{0.1}SiO_3$ phase through complete reaction of Ni based Mg_2SiO_4 and SiO_2 phases at high temperature (1425 °C). $Mg_{0.90}Ni_{0.1}SiO_3$ phase crystallized in monoclinic crystal structure with space group $P2_1/c$.

The major peak in the XRD patterns of the compositions with $x \geq 0.01$ (Fig. 1(c–e)) matched PDF #75-1806 for $MgSiO_3$ (Protoenstatite, system), labeled as "♦", with slightly shifting of the peaks positions towards larger 2θ angles. The shifting is due to the incorporation of smaller cation of Ni^{2+} (0.69 Å) for Mg^{2+} (0.72 Å) [12], that results into decrease in the unit cell volume. Clinoenstatite ($Mg_{0.90}Ni_{0.1}SiO_3$) was also developed in all TiO_2 added compositions whose peaks are labeled as "•". Few very low intensity peaks labeled as "$*$" matched PDF#78-1370 for Mg_2SiO_4 (forsterite), were also observed as shown in Fig. 1(c–d). Similarly, peaks of TiO_2 (PDF #77-0443, Rutile system) labeled as "#" were also observed and the intensities of their peaks increased with increase in TiO_2 content (Fig. 1(c–d)) [13]. Besides this, the formation of precipitate (Mg_2SiO_4) like phase is favorable at temperature ≤1320 °C. The formation of precipitate like phase in composition with $0.01 \leq x \leq 0.05$ is due to the lower sintering temperature (≤1320 °C), however, for composition with $x = 0$ the precipitate like phase disappeared after being sintered at 1425 °C as illustrating in Fig. 1(b). Further, the same precipitate like phase is also observed in the raw powders after being calcined at temperature 1300 °C for 5 h (Fig. 1a). It indicates that the sintering temperature play dominate rule to control the precipitate like phase. Moreover, the addition of TiO_2 to the calcined powder of $Mg_{0.90}Ni_{0.1}SiO_3$ lowered the optimum sintering temperature from 1425 °C to 1300 °C and also promoted the reaction between Ni based Mg_2SiO_4 and SiO_2 phases to form Ni based $MgSiO_3$ (Protoenstatite and Clinoenstatite) phases at lower temperature (1300 °C). Protoenstatite is reported to exist at lower temperatures, therefore, our results consistent with previous study [8]. The bulk densities of (1-x)$Mg_{0.90}Ni_{0.1}SiO_3$-$x$$TiO_2$ ($0 \leq x \leq 0.05$)

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