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Ultra-Low Loss Dielectric Properties of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ Microwave Ceramics

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***Abstract*—**Microwave dielectric ceramic materials of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ for x = 0.01, 0.03, 0.05, 0.07 and 0.09 were prepared and sintered at 1250–1400 ºC. The microstructure and microwave dielectric properties of the ceramic materials were examined and measured. The observations shows that the content of Ni^{2+} ions has little effect on the crystal structure, dielectric constant, temperature coefficient of resonant frequency (τ_f) and sintering temperatures of the ceramics. However, the quality values ($Q\times f$) are greatly improved due to the addition of Ni^{2+} ions. The present study showed that the ceramic material prepared for x = 0.05 and sintered at 1325ºC had the best $Q\times f$ value of 392,000 GHz, about 23% improvement compared with that of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$.

***Keywords*—**$(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$, microwave dielectric ceramics, high quality factor, high frequency wireless communication.

I. Introduction

FOR the past decades, the frequency bands for wireless communications have increased from GSM 900 MHz for 2G cellular networks, 1.7 – 2.7 GHz for 3G or 4G mobile telecommunications, to 10.70 - 48.2 GHz for broadband radio access for multimedia services [1]. Ceramic materials have been used to fabricate dielectric resonators or substrates for microwave components for their low dielectric loss and stability both on physical and chemical properties. However, to meet the trend of high frequency communications, higher quality factor (Q) or ultra-low dielectric loss of microwave dielectric ceramics are needed to develop. For example, $MgTiO_3$- and Mg_2TiO_4-based ceramics have been developed for communication and radar systems at microwave frequencies. $MgTiO_3$ sintered at 1150 ºC had the microwave properties of dielectric constant (ε_r) of 17.5, $Q\times f$ of 170,000 GHz, and coefficient of the resonant frequency (τ_f) of -50 ppm/ºC [2], while Mg_2TiO_4 sintered at 1450ºC had ε_r= 14, $Q\times f$ = 150,000 GHz and τ_f = -50 ppm/ºC[3]. Experiments showed that $Q\times f$ of Mg_2TiO_4 can be increased with additive oxides while the composite materials based on $MgTiO_3$always display much lower Q values. For instance, $Q\times f$ for $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ sintered at 1390ºC and $(Mg_{0.95}Zn_{0.05})_2TiO_4$ sintered at 1330ºC were 318,000 GHz and 275,000 GHz [4], [5], while $Q\times f$ for $(Mg_{0.95}Zn_{0.05})TiO_3$ sintered at 1300 ºC was 264,000 GHz [6].

In this work, $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics were proposed to synthesize. NiO was added to modify the structure and microwave properties of $Mg_2(Ti_{0.95}Sn_{0.05})O_4$. Ni^{2+} is supposed to substitute Mg^{2+} because its radius is 0.72 Å, close to 0.69 Å, the radius of Mg^{2+}. Microstructure would be identified by using X-ray diffraction (XRD) and effects of varied x and sintering temperatures on the microwave properties of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics would be investigated and discussed.

II. Experimental Procedure

$(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ powders were prepared by using the solid state reaction method. High-purity oxides of MgO, NiO, TiO_2 and SnO_2 were used as the starting materials. MgO powders were first baked at 800°C for 6 h to remove moisture content and carbonates. Then the starting materials were weighed stoichiometrically and mixed with DI water. The mixtures were baked at 130°C for 24 h and calcined at 1100°C for 4 h to synthesize the compounds of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$. The calcined powders were combined with organic binder polyvinyl alcohol and pressed into bulk disks using a uniaxial press. The binder in the bulk disks evaporated when heated at 650°C for 2 h. $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ grains then grew as sintered at 1250-1400 °C for 4 h. The calcined powder and bulk disks were examined by using X-ray diffraction (XRD, SIEMENS D5000) with Cu Kα radiation (at 40 KV and 40 mA). The microstructure of the ceramics was observed by using a scanning electron microscope (SEM, JEOL JSM−7001).

The bulk densities of the ceramic disks were measured by using the Archimedes method. Microwave dielectric properties, such as dielectric constant and unloaded Q, were measured at 6–12 GHz by using the post-resonant method, as suggested by Hakki and Coleman [7]. The temperature coefficient of resonant frequency **(τ_f)** was measured in the temperature range of 20 to 80°C. The HP8757D network analyzer and the HP8350B sweep oscillator were used for the microwave measurement.

III. Results and Discussion

Fig. 1 shows the X-ray powder diffraction patterns of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x= 0.01 ~ 0.09) ceramics sintered at 1325°C. There are two crystal phases in the observation. The main phase is $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ which is of cubic structure with the space group Fd-3m(227), same as that of Mg_2TiO_4, according to ICDD-PDF#00-025-1157. The other,

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which is the secondary phase, is $(Mg_{1-x}Ni_x)(Ti_{0.95}Sn_{0.05})O_3$ which is of a cubic spinel structure with space group Fd-3m, according to ICDD-PDF#00-006-0494. The results show that the variation of x has little effect on the two crystal phase and their relative proportions.

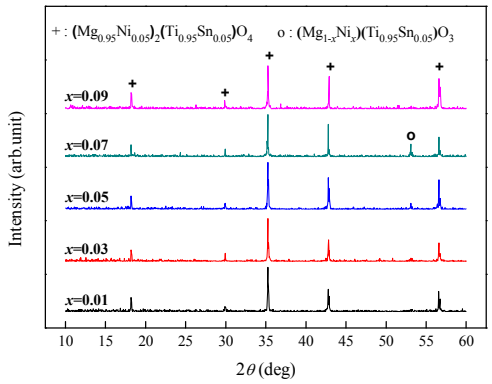

Fig. 1 X-ray diffraction patterns of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x= 0.01 - 0.09) ceramics sintered at 1325 °C

Fig. 2 displays the XRD of $(Mg_{0.95}Ni_{0.05})_2(Ti_{0.95}Sn_{0.05})O_4$ sintered at various temperatures. The result shows that the appearance of the two crystal phases almost keep the same in the interest range of sintering temperatures.

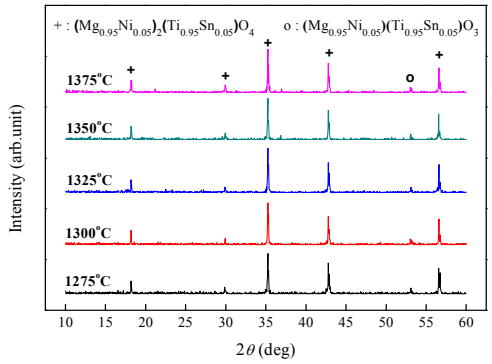

Fig. 2 X-ray diffraction patterns of $(Mg_{0.95}Ni_{0.05})_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics sintered at various sintering temperatures.

Fig. 3 is the SEM photographs of $(Mg_{0.95}Ni_{0.05})_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics sintered at various temperatures. Obviously, the grain size increases with increasing sintering temperatures till 1325ºC which indicates the most suitable sintering temperature. Beyond the temperature, such as 1350ºC, over-grown grains are observed. In addition, energy dispersive X-ray spectrometry (EDS) was employed on a grain of $(Mg_{0.95}Ni_{0.05})_2(Ti_{0.95}Sn_{0.05})O_4$. The analysis produced a ratio of 28.23:1.48 for the atom % of Mg and Ni which corresponded exactly stoichiometric value of 0.05 for Ni, indicating the complete substitution of Ni^{2+} for Mg^{2+} ions in the main phase.

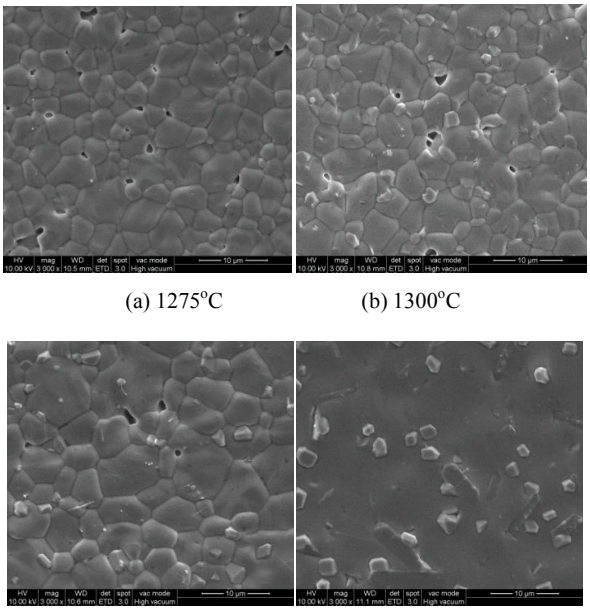

Fig. 3 SEM photographs of$(Mg_{0.95}Ni_{0.05})_2(Ti_{0.95}Sn_{0.05})O_4$ceramics sintered at (a) 1275, (b) 1300, (c)1325 (d) 1350 ºC, respectively

Fig. 4 is the measured apparent densities of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x= 0.01 - 0.09) ceramics sintered at various sintering temperatures. The result shows that 1325 ºC is the best sintering temperature for all values of x, consistence with the SEM observation of Fig. 3. And the density for x = 0.05 is higher than those for other x's overall. The highest apparent density was 3.57 g/cm^3, which corresponded to relative density of 96.83%.

Fig. 5 is the measured relative permittivity (ε_r) of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ (x = 0.01 ~ 0.09) ceramics sintered at different temperatures. The variation of ε_r versus x and sintering temperature is similar to the observation of density in Fig. 4, indicating the more the densification of the ceramic, the higher the value of ε_r. In fact, ε_r is around 14 for all x values and sintering temperatures. Therefore, the introduction of Ni and Sn does not alter the permittivity of the Mg_2TiO_4-based ceramics.

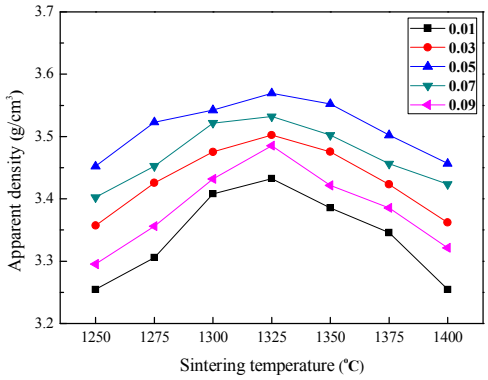

Fig. 4 Apparent densities of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$(x = 0.01 - 0.09) ceramics sintered at various sintering temperatures

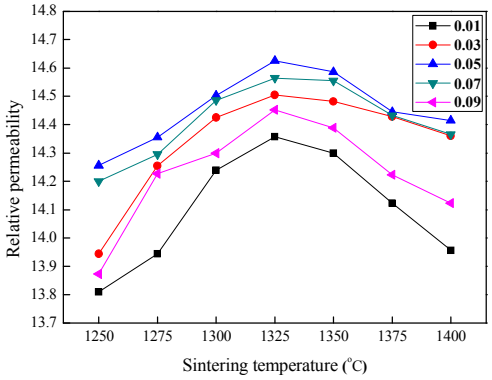

Fig. 5 Relative permittivity of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$($x$= 0.01 - 0.09) ceramics sintered at different temperatures

Fig. 6 shows the $Q\times f$ values of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics sintered at various temperatures as a functions of the x value. Similar to Fig. 5, the variation of $Q\times f$ also follows that of density. The maximum $Q\times f$ value is 392,000GHz for $(Mg_{0.95}Ni_{0.05})_2(Ti_{0.95}Sn_{0.05})O_4$ sintered at 1325°C, which is about 23% improvement compared to the value of 32,5000 GHz for $Mg_2(Ti_{0.95}Sn_{0.05})O_4$. The high Q values is generally related to the high cation ordering degree [8] which might be enhanced by the introduction of Ni^{2+} ions in $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$.

Fig. 7 is the measured τ_f values of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics with varied sintered temperatures and x. The result shows that τ_f varies in the range of -48.1 and-51.95 ppm/ºC. In other words, τ_f is about -50 ppm/ºC, almost the same as that of either Mg_2TiO_4 or $Mg_2(Ti_{0.95}Sn_{0.05})O_4$. Therefore, the addition of Ni^{2+} content has no effect on the modification of τ_f. Further adjustment of τ_f may be done by mixing positive τ_f value of ceramic material such as $CaTiO_3$ if a near-zero value of τ_f is anticipated in the future.

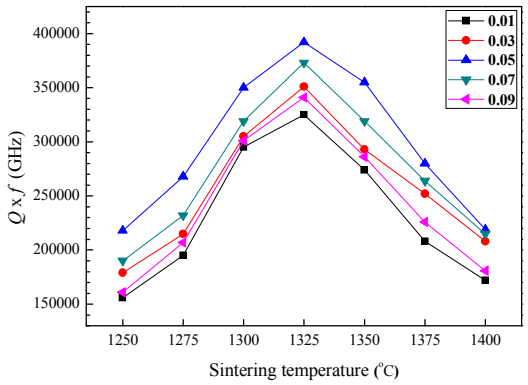

Fig. 6 $Q\times f$ values of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$(x = 0.01 ~ 0.09) ceramics system sintered at different temperatures

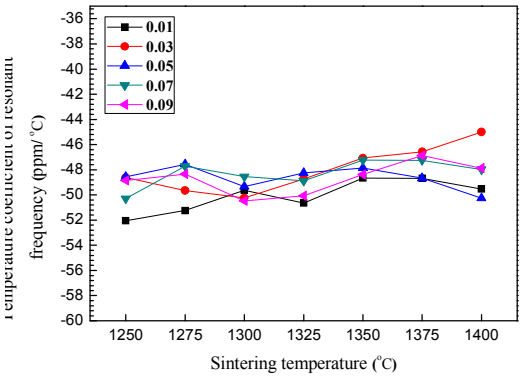

Fig. 7 Temperature coefficient of resonant frequency values of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$($x$= 0.01 ~ 0.09) ceramics sintered at different temperatures

IV. Conclusion

The microstructure and microwave dielectric properties of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics were investigated in this work. The experimental results show that Ni^{2+} ions can well substitute Mg^{2+} ions for small x. The best sintering temperature is 1325 ºC, lower than that of Mg_2TiO_4 or $Mg_2(Ti_{0.95}Sn_{0.05})O_4$. The addition of Ni does not alter the crystal structure, relative permittivity and temperature coefficient of resonant frequency significantly. However, the $Q\times f$ value is greatly improved to 392,000GHz for x = 0.05, i.e., $(Mg_{0.95}Ni_{0.05})_2(Ti_{0.95}Sn_{0.05})O_4$, which makes them being promising materials for the applications of high-frequency wireless communication services. For further improvement, other ceramic materials with positive τ_f are needed to adjust the τ_f of $(Mg_{1-x}Ni_x)_2(Ti_{0.95}Sn_{0.05})O_4$ ceramics in the future.

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