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Microwave dielectric properties and sintering behaviors of $(Mg_{0.95}Ni_{0.05})TiO_3$–$CaTiO_3$ ceramic system

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ABSTRACT

The microwave dielectric properties and sintering behaviors of the new ceramic system $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$ ($x \leq 0.1$) prepared by conventional solid state route were investigated. The compositions with $x = 0.02$–0.1 resulted in the mixture of two main phases, $(Mg_{0.95}Ni_{0.05})TiO_3$ and $CaTiO_3$, and a second phase $(Mg_{0.95}Ni_{0.05})Ti_2O_5$, which was favorable at high temperatures. The two-phased system was confirmed by both XRD and EDS analysis. Zero τ_f can be achieved by appropriately adjusting the compositional ratio. Specimen with $x = 0.06$ possessed an excellent combination of microwave dielectric properties: $\varepsilon_r \sim 20.8$, $Q \times f \sim 79{,}200$ GHz and $\tau_f \sim 1.2$ ppm/°C. It is proposed as a candidate material for GPS patch antennas and ISM band filters.

1. Introduction

Regarding materials for microwave use, requirements for these candidates must satisfy three major criteria: a high dielectric constant for component size reduction, a low dielectric loss for high selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stable frequency stability. However, increasing the carrier frequencies from 900 MHz to 2.4, 5.2, 5.8 GHz or even to millimeter regime, would render materials with high dielectric constant a less of interest. Low dielectric loss, on the other hand, would play a more prominent role instead. For instance, low loss dielectrics with dielectric constants in the 20 s have become most popular materials used for today's GPS patch antennas, Wireless LAN and 5.8 GHz ISM band filters [1,2]. Still, zero τ_f remains as one of the primary requirements for high frequency materials and becomes more and more critical as the operating frequency going higher.

Two conventional approaches are usually employed in the development of excellent dielectric ceramics; one is to create a new material and the other one is to combine two or more materials to achieve characteristic compensation. The latter one, mixing two or more compositions with different dielectric properties, is more popular due to its simplicity. In other words, combining two compounds having negative and positive τ_f values to form a solid solution or mixed phases is the most convenient and promising way to achieve a zero τ_f [3,4].

The ilmenite-type structured $MgTiO_3$, belonging to the trigonal space group $R\bar{3}$, is one of the leading dielectric materials for microwave applications. At microwave frequency range, it exhibits a good quality factor $Q \times f \sim 160{,}000$ at 8 GHz, a dielectric constant $\varepsilon_r \sim 17$, and a temperature coefficient of resonant frequency $\tau_f \sim -50$ ppm/°C [5]. $MgTiO_3$-based ceramics has been widely applied as dielectric materials for resonators, filters and antennas for communication, radar, and global positioning systems operated at microwave frequencies. For instance, $0.95MgTiO_3$–$0.05CaTiO_3$ ceramic is well known as the material ($\varepsilon_r \sim 20$, $Q \times f \sim 56{,}000$ GHz and a zero τ_f [5]) for temperature compensating type capacitor, dielectric resonator and patch antenna. With partial replacement of Mg by Ni, $(Mg_{0.95}Ni_{0.05})TiO_3$ (hereafter referred to as MNT) ceramic with a ilmenite-type structure was reported to possess a better combination of dielectric properties ($\varepsilon_r \sim 17.2$, $Q \times f \sim 180{,}000$ GHz, $\tau_f \sim -45$ ppm/°C) [6]) in comparison with that of $MgTiO_3$. That makes it a good candidate as a dielectric material for microwave applications.

In this paper, $CaTiO_3$ (hereafter referred to as CT) was added to $(Mg_{0.95}Ni_{0.05})TiO_3$ to form a new ceramic system $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$xCaTiO_3$, which demonstrated an effective compensation in its τ_f value and a lower dielectric loss. The microwave dielectric properties were discussed based upon the obtained densification, X-ray diffraction patterns and the microstructures of the ceramics. The correlation between the microstructures and the $Q \times f$ value was also investigated.

2. Experimental procedure

Samples of $(Mg_{0.95}Ni_{0.05})TiO_3$ and $CaTiO_3$ were individually synthesized by conventional solid-state methods from high-purity oxide powders (>99.9%): MgO,

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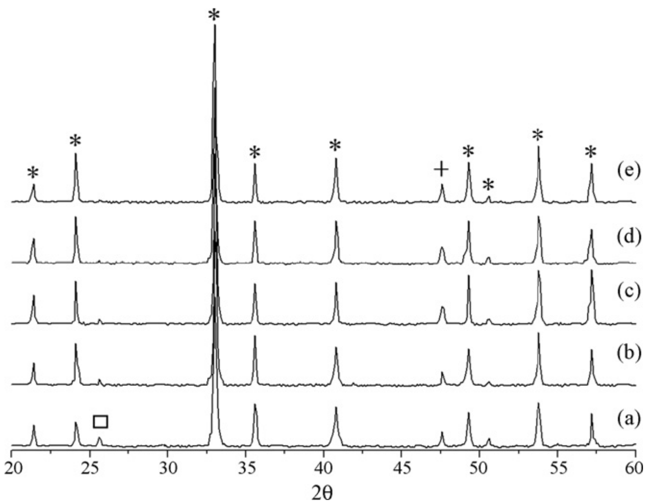

Fig. 1. X-ray diffraction patterns of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$x$$CaTiO_3$ ceramics as a function of the x value, sintered at 1300 °C/4 h, (a) $x=0.02$, (b) $x=0.04$, (c) $x=0.06$, (d) $x=0.08$ and (e) $x=0.1$. (*) Ilmenite, (+) perovskite, (□) $(Mg_{0.95}Ni_{0.05})Ti_2O_5$.

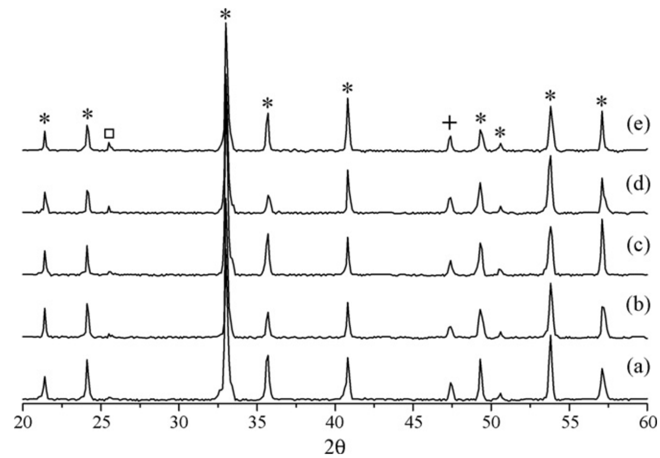

Fig. 2. X-ray diffraction patterns of $0.94(Mg_{0.95}Ni_{0.05})TiO_3$–$0.06CaTiO_3$ ceramics sintered at (a) 1250 °C, (b) 1275 °C, (c) 1300 °C, (d) 1325 °C, and (e) 1350 °C for 4 h.

NiO, $CaCO_3$, and TiO_2. The starting materials were mixed according to the stoichiometry: $(Mg_{0.9}Ni_{0.05})TiO_3$ and $CaTiO_3$. They were then ground in distilled water for 24 h in a ball mill with agate balls. Both mixtures were dried and calcined at 1100 °C for 4 h. The calcined reagents were mixed to the desired composition $(1-x)(Mg_{0.95}Ni_{0.05})$–$x$$CaTiO_3$ and ground into a fine powder for 24 h. The fine powder together with the organic binder were forced through a 100-mesh sieve and pressed into pellets of 11 mm in diameter and 5 mm in thickness. These pellets were sintered at temperatures of 1250–1350 °C for 4 h in air. Both the heating rate and the cooling rate were set at 10 °C/min.

The densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were analyzed using the X-ray powder diffraction method with Cu Kα radiation from 20° to 60° in 2θ. The scanning rate was 4° min^{-1}. The microstructure was observed with a scanning electron microscope (SEM). The dielectric constants and the unloaded Q values were measured using the Hakki–Coleman dielectric resonator method as modified and improved by Kobayashi–Katoh [7,8]. The apparatus consisted of parallel conducting brass plates and coaxial probes connected to an HP8757B network analyzer and an HP8350B sweep oscillator. The same technique was applied to measure the temperature coef-

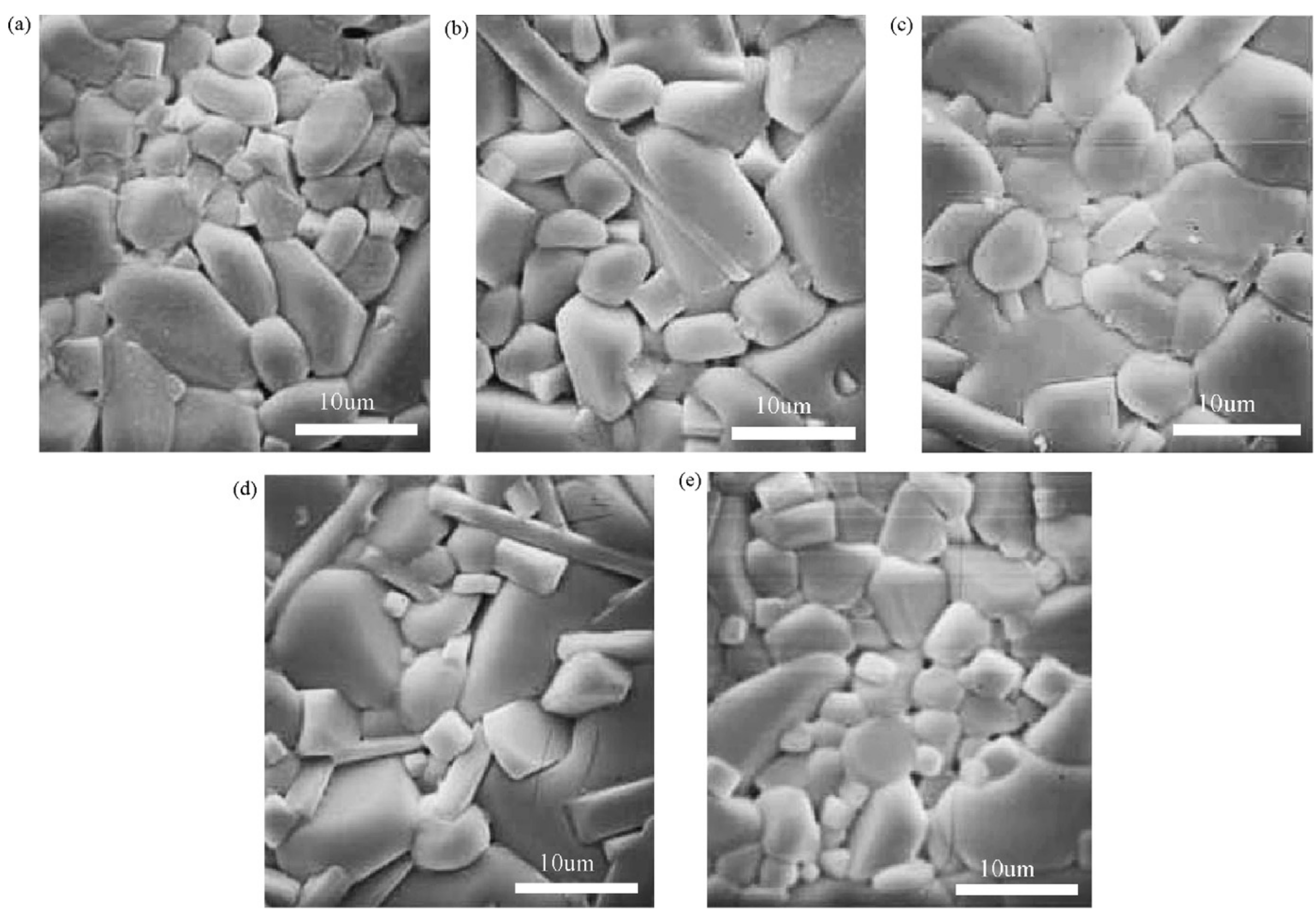

Fig. 3. SEM micrographs of $(1-x)(Mg_{0.95}Ni_{0.05})TiO_3$–$x$$CaTiO_3$ ceramics sintered at 1300 °C/4 h, (a) $x=0.02$, (b) $x=0.04$, (c) $x=0.06$, (d) $x=0.08$ and (e) $x=0.1$.