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Characterization and dielectric behavior of a new dielectric ceramics $Ca(Mg_{1/3}Nb_{2/3})O_3$–$(Ca_{0.8}Sr_{0.2})TiO_3$ at microwave frequencies

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ABSTRACT

The crystal structures, phase compositions and the microwave dielectric properties of the $(1-x)Ca(Mg_{1/3}Nb_{2/3})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ perovskite-based composites prepared by the conventional solid state route have been investigated. The formation of solid solution is confirmed by the XRD patterns. A rapid grain growth is observed at temperatures higher than 1470 °C, which would lead to a decrease in the density and $Q \times f$ of the ceramics. The temperature coefficient of resonant frequency increases with increasing $(Ca_{0.8}Sr_{0.2})TiO_3$ content and tunes through near zero at $x = 0.3$. Specimen using $0.7Ca(Mg_{1/3}Nb_{2/3})O_3$–$0.3(Ca_{0.8}Sr_{0.2})TiO_3$ possesses an excellent combination of microwave dielectric properties: $\varepsilon_r \sim 43.75$, $Q \times f \sim 45{,}200$ GHz (where $f = 6.3$ GHz is the resonant frequency) and $\tau_f \sim -4.2$ ppm/°C. It is proposed as a suitable candidate material for small-sized GPS patch antennas.

1. Introduction

Miniaturization of patch antennas for volume efficiency in global positioning system (GPS) has become a primary issue in these few years. In particular, materials with dielectric constant in the 40s can reduce the antenna size from 25 mm × 25 mm to 18 mm × 18 mm or even to 15 mm × 15 mm. Several research efforts have recently been dedicated toward the development of such dielectric materials [1–5]. In addition, a high $Q \times f$ is also required [6,7] to simultaneously retain a small return loss and achieve a wide bandwidth of the GPS antennas for practical applications.

Several complex perovskites ceramics $A(B_{1/3}{}^{2+}B_{2/3}{}^{5+})O_3$ (where A = Ca, Ba; B^{2+} = Mg, Zn; B^{5+} = Nb, Ta) have been reported due to their excellent microwave dielectric properties [5,8–11]. Among these compounds, $Ca(Mg_{1/3}Nb_{2/3})O_3$ has an 1:2 ordered monoclinic structure, via the chemical ordering of B-site cations and structural ordering and disordering had been widely discussed. In addition, it also possesses a high dielectric constant ($\varepsilon_r \sim 28$), a high quality factor ($Q \times f$ value ~58,000 GHz at 7 GHz) and a negative τ_f value (−48 ppm/°C) [11], and has found wide applications as the dielectrics in resonators, filters and antennas for communication. In order to compensate the τ_f of the $Ca(Mg_{1/3}Nb_{2/3})O_3$, $CaTiO_3$ was added to form the $0.4CaTiO_3$–$0.6Ca(Mg_{1/3}Nb_{2/3})O_3$ solid solution with an $\varepsilon_r \sim 48$, a $Q \times f$ value ~32,500 GHz and a τ_f value ~−2 ppm/°C [5]. However, its $Q \times f$ still needs to be promoted before putting it to a practical application as GPS antennas.

In stead of $CaTiO_3$, $(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics ($\varepsilon_r \sim 181$, $Q \times f$ ~8300 GHz, $\tau_f \sim 991$ ppm/°C [12]), having a much higher $Q \times f$ than that of $CaTiO_3$, was chosen as a τ_f compensator for $Ca(Mg_{1/3}Nb_{2/3})O_3$. Consequently, not only compensation for the τ_f can be made by employing the solid solutions of $Ca(Mg_{1/3}Nb_{2/3})O_3$–$(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics, it also shows a more than 40% promotion in the $Q \times f$. In addition, the X-ray diffraction (XRD) patterning and scanning electron microscopy (SEM) analysis were also employed to study the crystal structures and microstructures of the ceramics. The correlation between the microstructure and the $Q \times f$ value was also investigated.

2. Experimental procedure

Mixed oxide powders of $(1-x)Ca(Mg_{1/3}Nb_{2/3})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ ($x = 0.1$–0.9) were prepared from $CaCO_3$, $SrCO_3$, MgO, Nb_2O_5 and TiO_2 with purity higher than 99.9% by conventional mixed-oxide method. The powders were separately prepared according to the desired stoichiometry $Ca(Mg_{1/3}Nb_{2/3})O_3$ and $(Ca_{0.8}Sr_{0.2})TiO_3$, and ground in distilled water for 24 h in a ball mill with agate balls. The prepared powders were dried and calcined at 1100 °C for 4 h in air. The calcined powders were mixed according to the molar fraction $(1-x)Ca(Mg_{1/3}Nb_{2/3})O_3$–$x(Ca_{0.8}Sr_{0.2})TiO_3$ and re-milled for 24 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder (PVA 500, Showa, Japan) was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under the pressure of 200 MPa. These pellets were sintered at temperatures of 1350–1500 °C for 4 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα ($\lambda = 0.15406$ nm) radiation with a Siemens D5000 diffractometer operated at 40 kV and 40 mA. The microstructures were evaluated for thermal-etched surfaces by scanning electron microscopy (SEM; Philips XL-40FEG, Eindhoven, the Netherlands). The apparent densities of the sintered pellets were measured by the

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Table 1
Microwave dielectric properties of $(1-x)Ca(Mg_{1/3}Nb_{2/3})O_3-x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramic system sintered at 1440 °C for 4 h.

x-Value	Apparent density (g/cm^3)	ε_r	$Q\times f$	τ_f (ppm/°C)
0.9	3.58	97.84	9,600	611.9
0.7	3.84	71.15	14,600	293.8
0.5	4.11	54.81	31,000	64.4
0.3	4.28	43.75	45,200	−4.2
0.1	4.36	33.51	52,700	−31.3

Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method [13,14]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. For temperature coefficient of resonant frequency (τ_f), the technique is the same as that of quality factor measurement. The test cavity is placed over a thermostat and the temperature range used is from 20 to 80 °C.

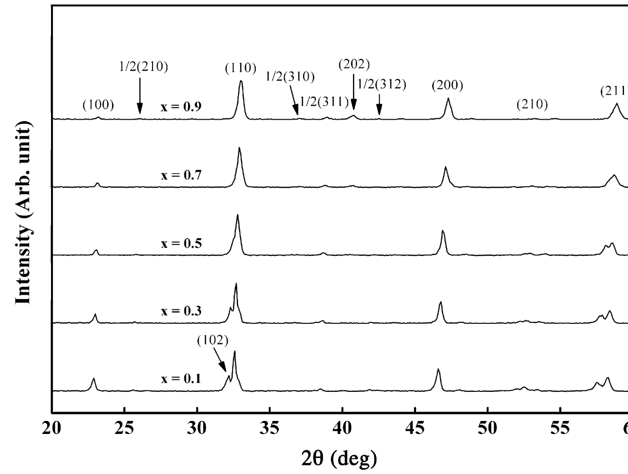

Fig. 1. X-ray diffraction patterns of $(1-x)Ca(Mg_{1/3}Nb_{2/3})O_3-x(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics sintered at 1440 °C for 4 h.

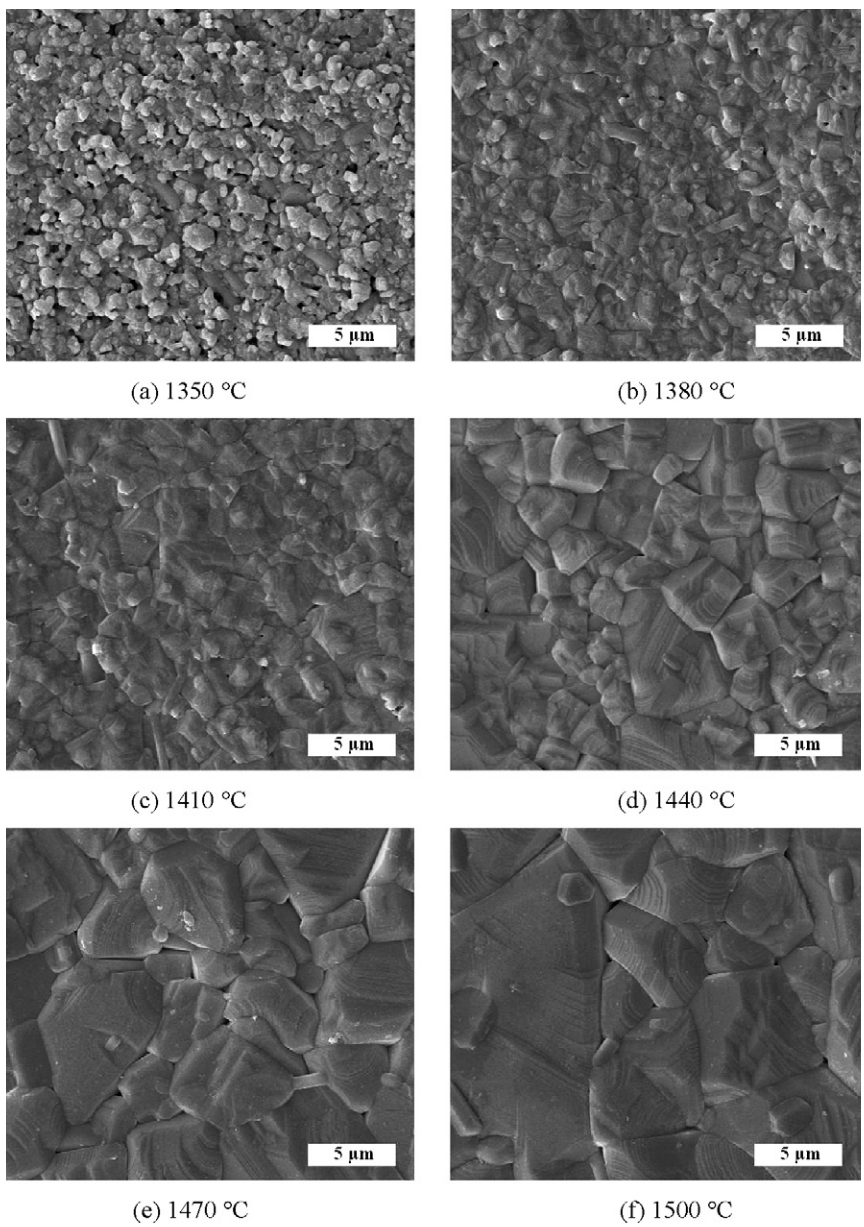

Fig. 2. SEM photographs of $0.7Ca(Mg_{1/3}Nb_{2/3})O_3-0.3(Ca_{0.8}Sr_{0.2})TiO_3$ ceramics sintered at (a) 1350 °C; (b) 1380 °C; (c) 1410 °C; (d) 1440 °C; (e) 1470 °C; (f) 1500 °C for 4 h.