HIGH-Q CERAMICS WITH A NEAR-ZERO TEMPERATURE COEFFICIENT AT MICROWAVE FREQUENCIES

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With the rise of the 5G era, there is growing interest in microwave dielectric ceramics. These ceramics serve not only as insulating substrates in microwave circuits but also as essential materials for various microwave communication technologies such as dielectric resonators, filters, oscillators, phase shifters, and capacitors. Consequently, microwave components play a crucial role in the miniaturization, integration, and cost reduction of modern communication devices. For 5G technology, dielectric materials exhibiting high dielectric constant, high Q_f value, near-zero temperature coefficient of resonance frequency, and low sintering temperature are highly desirable.

Materials based on calcium titanate exhibit a high Q-factor (Q_f = 10700 GHz) and possess a positive temperature coefficient of the resonant frequency. Conversely, ceramics composed of $Ln(Mg_{0.5}Ti_{0.5})O_3$ with a perovskite structure have a Q_f value ranging around 40,000 and display a significantly negative τ_f value (approximately -70 × 10−6/°C). By combining calcium titanate materials with $Ln(Mg_{0.5}Ti_{0.5})O_3$ ceramics, it becomes feasible to create microwave dielectric ceramics with moderate values of ε, high Q_f, and τ_f values approaching zero. So far, there is limited existing literature data on the production of ceramics through the amalgamation of materials possessing positive and negative τ_f. This study employed high-temperature sintering to fabricate $(Ca_{2/3x}La_{1/3x}Nd_y)(Mg_{0.5y}Ti_{0.5y+x})O_3$ ceramics and conducted a comprehensive examination of the impact of the sintering process and component ratios on their microstructure and microwave dielectric properties.

The $(Ca_{2/3x}La_{1/3x}Nd_y)(Mg_{0.5y}Ti_{0.5y+x})O_3$ ceramics were synthesized using the solid-state reaction method. The raw materials, including high-purity $CaCO_3$, La_2O_3, Nd_2O_3, MgO, and TiO_2 powders, were mixed using a ball mill for 8 hours. The mixture was then dried for 24 hours, ground, sieved, and subjected to individual calcination processes (at 1200 °C for 3 hours). Subsequently, the calcined powders were mixed using a ball mill for 8 hours, dried for 24 hours, and sieved. A polyvinyl alcohol solution (PVA) was added as a binder, and the mixed powders were pressed into cylindrical specimens with a diameter of 10 mm and a thickness of 4 mm. These specimens were then sintered in air (1600 °C, 30 minutes). The samples were crushed, ground, and subjected to phase analysis using X-ray diffraction (XRD). The microstructures of the samples were observed using a scanning electron microscope (SEM). To measure the dielectric properties, polished cylindrical specimens of ceramics were placed in a metal cavity of a vector network analyzer. The dielectric constant (ε), quality factor (Q), and temperature coefficient of resonant frequency (τ_f) were measured at 25 °C.

The density initially increased with increasing sintering temperature but started to decrease after reaching a certain point, indicating the occurrence of oversintering. The data clearly show that ρ increases with increasing x, reaching a maximum value of 5.4. This can be attributed to the higher density of $Ln(Mg_{0.5}Ti_{0.5})O_3$ ceramic compared to $CaTiO_3$-based

ceramic. The diffraction peaks show significant overlap, indicating the presence of a perovskite structure without any secondary phase (Fig.1).

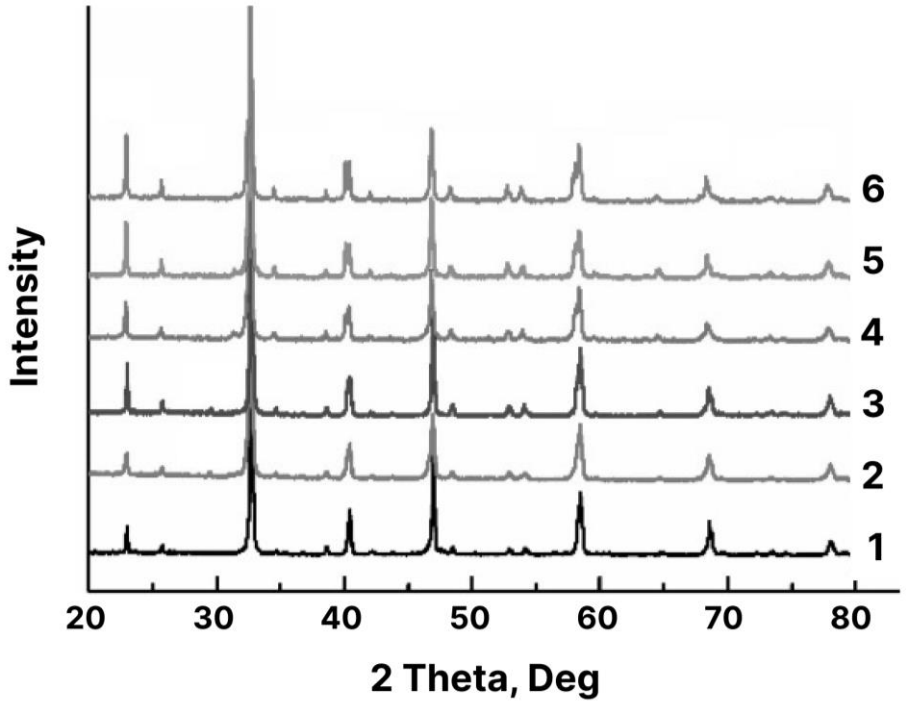

Fig. 1. XRD spectra for $(Ca_{2/3x}La_{1/3x}Nd_y)(Mg_{0.5y}Ti_{0.5y+x})O_3$ where x=0.3 (1), 0.35 (2), 0.4 (3), 0.45 (4), 0.5 (5), 0.55 (6).

However, superlattice diffraction peaks are observed at x = 0.40. Main diffraction peaks of $(Ca_{2/3x}La_{1/3x}Nd_y)(Mg_{0.5y}Ti_{0.5y+x})O_3$ ceramics shift towards lower angles as x increases. This shift suggests an increase in the lattice constant of the perovskite structure. The lattice constant and unit cell volume gradually increase with increasing x, consistent with the XRD analysis. This trend is influenced by two factors: the decreasing vacancy concentration in the A-site and the increasing Mg^{2+} content ($r(Mg^{2+}) > r(Ti^{4+})$) in the B-site.

For $x \leq 0.5$, the grain size ranges from 20 to 40 μm and shows relatively uniform distribution with minimal changes as the x content increases. As x increases, ε gradually decreases from 50 to 35 due to the lower dielectric constant of Ln(Mg0.5Ti0.5)O3 compared to CaTiO3. The Qf initially increases from 14000 GHz (x = 0.30) to 16000 GHz (x =0.6). The results indicate that τε is primarily influenced by the tilt of the BO6 octahedron. Increasing tilt of the BO6 octahedron leads to a positive change in τε. The tilt degree of the BO6 octahedron can be described by the tolerance factor: a greater difference between the t value and 1 indicates a higher tilt degree. There is a regular pattern between τε and t: when $t < 0.965$, a decrease in t leads to a positive change in τε. In the case of (Ca0.61xLa0.26xNdy)(Mg0.5yTi0.5y+x)O3 ceramics, a decrease in the t value results in an increased tilt degree of the BO6 octahedron. Consequently, τε increases, and τf decreases in the negative direction.

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