Improved microwave dielectric properties of \((\text{Mg}_{1-(x+y)}\text{Ca}_x\text{La}_y)(\text{Ti}_{1-y}\text{Al}_y)\text{O}_3\) ceramics

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Phase-singular solids of the composition, \((\text{Mg}_{1-(x+y)}\text{Ca}_x\text{La}_y)(\text{Ti}_{1-y}\text{Al}_y)\text{O}_3\) \((x=0\) to 0.88; \(y=0.05\) to 0.35) having the cubic perovskite-type structure were prepared by the substitution of \(\text{La}^{3+}\) and \(\text{Al}^{3+}\) in equivalent quantities which brought about complete miscibility between \(\text{MgTiO}_3\) and \(\text{CaTiO}_3\). These ceramics showed relative permittivities of 16.5 to 50 (at 6 GHz) with increasing Ca content, high \(Q\) values of 10 000 to 30 000 and retained near-zero temperature coefficients in permittivity at optimum \(y\) values. Their dielectric characteristics are better accountable in terms of the positional disorder rather than the tolerance factor of perovskite structure.

Empirical approaches only prevail for the development of microwave materials with high dielectric constants because of the apparent conflicts in the basic requirements, i.e., atomic polarization mechanism necessary for high relative dielectric constants \((\varepsilon_r)\) rarely gives rise to low dielectric losses \((\tan \delta=1/Q)\) and near-zero temperature coefficient in permittivity (TCK). From the application point of view, these three parameters are correlatable to the size, frequency selectivity, and temperature stability, respectively, of the devices such as dielectric resonators, filters, and antenna substrates used in microwave communication systems.\(^3\) (\(\text{Mg}_{1-x}\text{Ca}_x\))\(\text{TiO}_3\) ceramics are well known temperature compensating-type dielectrics, often marketed as mixed phases of magnesium titanate with \(\varepsilon_r\sim16.5\), \(Q\sim30\) 000 and TCK=+100 ppm K\(^{-1}\), and calcium titanate with \(\varepsilon_r\sim165\), \(Q\sim600\), and TCK=−1800 ppm K\(^{-1}\) (all values at 6 GHz), so that the temperature coefficient of resonance frequency, \(\tau_f\), is near zero \((\tau_f=−1/2\) TCK, \(\alpha\) where \(\alpha\) is the thermal expansion coefficient).\(^2\) The dielectric properties of these ceramics are influenced by the materials processing parameters which, in turn, affect the phase content and microstructure, including porosity as well as lattice defects such as vacancies and dislocations.\(^3\)\(^,\)\(^4\) Often, the TCK values tend to be negative with slight increase in Ca-rich phase content. Presently, we find that the complex dependence of dielectric properties of MCT ceramics on the processing conditions can be eliminated by bringing about complete miscibility between MgTiO\(_3\) having the 6:6 ilmenite-type structure and CaTiO\(_3\) with 12:6 perovskite-type lattice. The miscibility is made possible by the simultaneous substitution of Al\(^{3+}\) at the Ti\(^{4+}\) sites and equivalent amounts of La\(^{3+}\) at \((\text{Ca}/\text{Mg})\) sites. The anion and cation defects are mutually annihilated to yield phase-singular solids. The resulting ceramics have the unusual combination of higher dielectric constants \((\varepsilon_r=16\) to 50 in 2–8 GHz range) with quality factors \((Q)>10\) 000 and near-zero TCK values.

\((\text{Mg}_{1-x}\text{Ca}_x)\text{TiO}_3\) with \(x\) ranging from 0.05 to 0.75 was prepared by mixing appropriate amounts of magnesium hydroxy carbonate (99.99%), calcium carbonate (99.98%), and TiO\(_2\) (99.96%) by planetary milling (Fritsch, Germany) for 6–8 h in an acetone medium. The most undesirable impurities were alkali elements which enhanced the dielectric losses and were kept below 1 ppm level in the starting chemicals. The powders were calcined initially at 1100–1150 °C for 5–6 h followed by subsequent milling for 1 h using sapphire or agate balls and containers and recalcined at 1200–1250 °C for 4 h. Initially we used Al\(^{3+}\) by way of \(\gamma\)-Al\(_2\)O\(_3\) to bring about miscibility in \((\text{Mg}_{1-x}\text{Ca}_x)\text{TiO}_3\) with \(x<0.2\). The phase singularity could not be achieved at higher Ca contents \((x\) values) for which different amounts of La\(_2\)O\(_3\) and \(\gamma\)-Al\(_2\)O\(_3\) in 1:1 mole ratio were added and calcined at 1250 °C for 6 h. The granulated powders were cold pressed into disks. The green disks were sintered in the temperature range of 1380–1450 °C (4 h). Ceramic samples of >99% theoretical density were obtained after sintering. The bulk densities were determined by the pycnometric method. X-ray powder diffraction studies were carried out using Philips PW 1050/70/76 (Netherlands)
unit having the nickel filtered Cu Kα source and with polycrystalline silicon as internal standard. The microstructures of the polished and thermally etched specimens were examined with S-360 Cambridge scanning electron microscope. The grain size of the samples was found to vary between 2 to 5 μm with no discernible porosity. Electrodes were deposited by silver paint (Dupont) fired on at 800 °C which gave good ohmic contacts. The complex permittivities $\varepsilon_r$ were evaluated from the measured reflection coefficient at different specimen temperatures using a network analyzer (Agilent 8722Es) in the frequency range of 2 – 10 GHz. The dielectric constants and the unloaded $Q$ values were calculated by the Hakki–Coleman dielectric resonator method modified by Kobayashi and Katch.

Figure 1 shows the x-ray diffraction (XRD) patterns of MgTiO$_3$ (space group: R $\bar{3}$), CaTiO$_3$ (Pnma), and of (Mg$_{0.5}$Ca$_{0.5}$)TiO$_3$ as the example for the mixed-phase ceramics containing Mg-rich ilmenite-type phase and Ca-rich perovskite phase. Miscibility was limited to $x < 0.15$ with the incorporation of Al$^{3+}$ for the compositions of the type [(Mg$_{1-x}$Ca$_x$)TiO$_3$]$_{1-y}$Al$_2$O$_3$, where $y < 0.10$. On increasing the alumina content, magnesium aluminum titanate, Mg$_3$Al$_2$Ti$_9$O$_{25}$, is formed as the minor phase. Miscibility between MgTiO$_3$ and CaTiO$_3$ could be extended to a wider range of $x$ values when aliovalent substituents La$^{3+}$ and Al$^{3+}$ in combination were incorporated, wherein the general composition of the phase-singular solids can be represented as Mg$_{1-x}$La$_x$Ti$_{1-y}$Al$_y$O$_3$ ceramics. Figure 1(d) shows that for $x=0.45$, 10 at.% each of La$^{3+}$ and Al$^{3+}$, i.e., $y=0.1$, are inadequate to bring about the miscibility, whereas, with $y=0.2$, single-phased ceramics are realized [Fig. 1(e)]. Further, for higher $x$ values, miscibility could be achieved only with increased La+Al content as exemplified by (Mg$_{0.15}$Ca$_{0.85}$)Ti$_{1-y}$Al$_y$O$_3$ [Fig. 1(f)]. XRD of the single-phase solids can be indexed on the basis of the space group Pnma with lattice parameters of $a=3.87$ Å in Fig. 1(e) and $a=3.85$ Å in Fig. 1(f). Transformation of ilmenite to cubic perovskite structure is complex involving changes in the rotation angles of BO$_6$ frame work. The octahedral tilting also brings about severe changes for AO$_{12}$ polyhedron. At higher contents of Ca ($x > 0.70$), the solids have orthorhombic perovskite structure approaching that of CaTiO$_3$ (space group: Pbnm).

The presence of Ca-rich perovskite phase even in small quantities significantly renders the TCK negative (Fig. 2). Incorporation of Al$^{3+}$ has limited success in retaining low TCK. Fig. 2 (inset) shows that TCK dips tremendously to negative values within a narrow range of composition. Although the $\varepsilon_r$ for the alumina (only) added samples increased from 16.5 to 26 (6 GHz) with Ca content ($x$), the $Q$ values

![FIG. 2. Variation in TCK for the solid solution, Mg$_{1-x}$Ca$_x$TiO$_3$, with respect to mole fraction of CaTiO$_3$. Inset shows the effect of alumina addition on TCK.](image)

![FIG. 3. Variation in dielectric constant as a function of temperature (frequency of 6 GHz) for samples with 0–75 at.% calcium.](image)

![FIG. 4. Variation in TCK with varying $y$ values ($x=LaO_{0.15}$=AlO$_{0.15}$) in (Mg$_{1-x-y}$Ca$_{x}$La$_{y}$)[Ti$_{1-x-y}$Al$_y$]O$_3$ ceramics.](image)
were relatively low (2000–3500). Further, the $\varepsilon_r$ showed variations with sintering temperature as well as post-sinter annealing, the origin of which has been attributed to the multiphase contents from XRD studies.

Figure 3 shows the relative permittivities of polycrystalline ceramics (Mg$_{1-(r+y)}$Ca$_r$La$_y$)(Ti$_{1-x}$Al$_x$)O$_3$ which increase from 16.5 to nearly 50 with Ca content ($x$) when measured at 6 GHz; the high $Q$ values of 10 000 to 30 000 are retained by these ceramics. Figure 3 also indicates that the variation in $\varepsilon_r$ is nearly flat over a wider range of temperature, −40 to 100 °C. Further, the $\varepsilon_r$ are found to be independent of frequency even at lower ranges when measured with a commercial impedance analyzer (HP 4284A) at the applied field of ~3 V/cm at 20 Hz to 1 MHz. For example, the $\varepsilon_r$ of 47.2 remained nearly unchanged for (Mg$_{0.19}$Ca$_{0.56}$La$_{0.25}$)(Ti$_{0.75}$Al$_{0.25}$)O$_3$ ceramics over the range of 20 Hz to 10 GHz, rendering these materials suitable for microwave frequency applications. The $\varepsilon_r$ at lower-frequency ranges is higher if the alkali metal ion impurities are present in the ceramics. Figure 4 shows that the TCK diminishes with increasing $y$ values, (La+Al), in (Mg$_{1-(r+y)}$Ca$_r$La$_y$)(Ti$_{1-x}$Al$_x$)O$_3$ for a given Ca content ($x$). TCK reaches near-zero values at the optimal “$y$”, above which the TCK remains nearly invariant and positive. The optimal $y$-value shifts to higher side with increasing Ca content. Substitution of Al$^{3+}$ itself (without La$^{3+}$) is sufficient at lower Ca compositions ($x<0.15$) to bring about near-zero TCK (Fig. 2, inset). These results indicate that $\tau_f$ of the microwave devices fabricated out of these ceramics can be fine-tuned compositionally. Additional merit of these ceramics is that the dielectric characteristics are changed only marginally with the processing conditions including the postsinter annealing for extended periods of 6–8 h at $T_{\text{anneal}} < T_{\text{sinter}}$.

The dielectric characteristics of these ceramics can be explained on the following way: The anion vacancies formed due to the substitution of aliovalent Al$^{3+}$ in MCT, for reasons of electroneutrality render the solid unstable above certain concentration leading to phase separation and generation of secondary phases. This is avoided by the simultaneous equivalent substitutions of La$^{3+}$=1.18 Å at [Ca$^{2+}$=1.18 Å,Mg$^{2+}$=0.89 Å] (A) sites and Al$^{3+}$=0.53 Å at Ti$^{4+}$=0.605 Å (B) sites so that the vacancies formed in equivalence at the cation, as well as the anion sublattices are mutually annihilated. This will lead to positional disorder of A cations which arise from the dual occupancy of Mg on A sites as well as B sites due to ionic radii reasons (Mg$^{2+}$=0.89 Å,Mg$^{2+}$=0.72 Å). The positional disorder is not dependent on the processing conditions and will explain the negligible influence of the process parameters on the dielectric characteristics. Favorable changes in $\varepsilon_r$, $Q$, and TCK in the disordered dielectric systems, particularly cation disorder, as an apparent generic characteristics are proposed by Cava.$^1$ In contrast, the empirical correlation between TCK and the crystal structure by way of tolerance factor ($t$) in perovskite as attempted by Reaney et al.$^6$ is found inapplicable in the present case since “$t$” lies between 0.74$t >0.89$. A near-zero TCK within this range of tolerance factor indicates that TCK is influenced by the presence of octahedral tilting, the occurrence of distortion of the unit cell and the prevalence of A-cation positional disorder particularly Mg$^{2+}$: There may be short-range atomic ordering that may narrow the frequency width of phonon vibrations in the microwave frequencies which otherwise is contributory to the dielectric losses.

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