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# Structural determination and microwave properties of $(x)Re(Co_{1/2}Ti_{1/2})O_3–(1-x)CaTiO_3$ (Re = La and Nd) solid solutions

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**Abstract**

Solid solutions of $(x)Re(Co_{1/2}Ti_{1/2})O_3–(1-x)CaTiO_3$ (Re = La and Nd, abbreviated to *x*LCT and *x*NCT, respectively) where $x = 0$, 0.25, 0.5, 0.75 and 1 have been fabricated using solid state synthesis. Samples have been examined using X-ray diffraction (XRD), scanning electron microscopy, transmission electron microscopy (TEM) and their dielectric properties measured at microwave (MW) frequencies. Formation of single phase solid solutions were confirmed by XRD and the measured lattice parameters varied linearly from LCT ($a = 5.66$ Å, $b = 7.867$ Å and $c = 5.494$ Å) and NCT ($a = 5.636$ Å, $b = 7.914$ Å and $c = 5.461$ Å) to CT ($a = 5.596$ Å, $b = 7.731$ Å and $c = 5.424$ Å). XRD and TEM confirmed both in-phase and antiphase rotations of O-octahedra consistent with an $a^-a^-c^+$ tilt system across the entire solid solution series. Electron diffraction revealed that LCT and NCT have reflections associated with B-site cation ordering which is absent for $x \leq 0.75$. MW dielectric measurements showed that LCT and NCT were highly insulating with microwave quality factor ($Qf_0$) values of 39,000 and 34,000, respectively. Compositions anticipated to have a zero temperature coefficient of resonant frequency ($\tau_f$) are 0.48LCT-CT and 0.52NCT-CT with $\varepsilon_r = 45$ and $Qf_0 \sim 5000$ and $\varepsilon_r = 43$ and $Qf_0 \sim 4000$, respectively.


*Keywords:* La(Co,Ti)$O_3$; Dielectric properties; Microwave dielectrics; $CaTiO_3$

## 1. Introduction

Candidate materials for MW dielectric resonators suitable for 3G technology must satisfy three main criteria; high quality factor ($Q > 15{,}000$), permittivity, $\varepsilon_r > 25$ and a temperature coefficient of resonant frequency, $\tau_f = \pm 3$ ppm/°C. $Q$ is defined as the resonant frequency ($f_0$) divided by the bandwidth ($\Delta f_0$) at 3 dB below peak height, shown in Eq. (1):

$$Q = \frac{f_0}{\Delta f_0} \tag{1}$$

The $Q$ value ($Q = 1/\tan\delta$) is a measure of a resonating body's ability to resonate at a given frequency. A $Qf_0$ value is usually quoted which is a figure of merit to compare resonating bodies of different sizes and permittivities. $\varepsilon_r$ is related to $f_0$ and the volume, $V$, of the resonating disc as shown by Eq. (2).

$$f_0 \propto \frac{1}{V\sqrt{\varepsilon_r}} \tag{2}$$

The final parameter is the temperature coefficient of resonant frequency ($\tau_f$) which should be tunable through zero to stop drift of the resonant frequency with temperature and is given by Eq. (3).

$$\tau_f = -\left(\frac{1}{2}\tau_\varepsilon + \alpha_L\right) \tag{3}$$

where $\tau_\varepsilon$ is the temperature coefficient of relative permittivity and $\alpha_L$ the linear thermal expansion coefficient.

In 1994, a patent emerged from the Kyocera Corporation detailing a new zero $\tau_f$ material $0.65CaTiO_3–0.35NdAlO_3$ (0.65CT-NA).[1] This material replaced existing dielectric

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resonators such as Sn-doped zirconium titanate (ZTS) due to its superior properties, $\varepsilon_r = 45$ and $Qf_0 \sim 43{,}000$. Zero $\tau_f$ was achieved by producing a composition in a solid solution formed from positive (CT, $\varepsilon_r = 160$, $Qf_0 = 12{,}000$ GHz and $\tau_f = +850\ MK^{-1}$) and negative $\tau_f$ ($NdAlO_3$, $\varepsilon_r = 20$, $Qf = 50{,}000$ GHz and $\tau_f = -33\ MK^{-1}$) end members.[2] Since the emergence of this compound several researchers have attempted to form similar solid solutions with CT using different negative $\tau_f$ lanthanide based perovskite end members, e.g., $La(Mg_{1/2}Ti_{1/2})O_3$ (LMT, $\varepsilon_r = 27.6$, $Qf_0 = 70{,}000$ and $\tau_f = -81\ MK^{-1}$) and $Nd(Mg_{1/2}Ti_{1/2})O_3$ (NMT, $\varepsilon_r = 25.9$, $Qf \sim 60{,}000$ and $\tau_f = -47\ MK^{-1}$).[3]

At room temperature LMT and NMT have a distorted perovskite structure due the occurrence on cooling of a sequence of structural phase transitions, which involve rotations of the oxygen octahedral (Glazer tilt system, $a^-a^-c^+$).[4] In addition, X-ray and electron diffraction data have shown that LMT and NMT have 1:1 ordered B-site ions in a generic 'rock salt' arrangement which in combination with the $a^-a^-c^+$ tilt system results in a monoclinic $P2_1/n$ space group.[5] At room temperature, CT has the same tilt system, $a^-a^-c^+$, as LMT and NMT but clearly no B-site ordering is possible and the space group remains that defined uniquely by the oxygen octahedral tilt system, *Pbnm*. It has generally been observed that the addition of CT to the LMT and NMT end members destroys B-site ordering. In both CT-LMT and CT-NMT systems zero $\tau_f$ occurs at $x \sim 0.5$ which gives a reduction in $Qf_0$ values, from the LMT and NMT end members, due to the loss of B-site cation ordering.[6–8]

The substitution of $Co^{2+}$ for $Zn^{2+}$ in $Ba([Co_xZn_{1-x}]_{1/3}Nb_{2/3})O_3$ (BCZN) has been shown to tune $\tau_f$ close to zero. It has also been shown that co-doping with 10 at.% $Ga^{3+}/Ta^{5+}$ on the B-site results in a high $Qf_0$ (32,000 @ 2.8 GHz) composition, $0.9Ba([Co_{0.40}Zn_{0.60}]_{1/3}Nb_{2/3})O_3$–$0.1Ba(Ga_{1/2}Ta_{1/2})O_3$ (BCZN-BGT).[9] Co is a transition metal and as such has a variable oxidation state between 2 and 4. BCZN has an ordered $2\ Nb^{5+}$:$Co^{2+}$, B-site trigonal superlattice and, is therefore, stoichiometric.[10] However, very little is known about compounds where Co ions share the B-site with, e.g., $Ti^{4+}$, whose valence state may also vary depending on process conditions. Recently, $La(Co_{1/2}Ti_{1/2})O_3$ (LCT) has been fabricated to give a highly insulating material with $\varepsilon_r = 25$, $Qf_0 \sim 39{,}000$ and TCF = $-42\ MK^{-1}$.[11] These values suggest that LCT and possibly the sister compound $Nd(Co_{1/2}Ti_{1/2})O_3$ (NCT) may be suitable as end-members in solid solution with $CaTiO_3$. Therefore, it is the intention of this paper to investigate the microstructure and structure of ${}_xLCT\text{-}_{1-x}CT$ and ${}_xNCT\text{-}_{1-x}CT$ solid solutions and assess their suitability as temperature-stable MW dielectric ceramics.

## 2. Experimental

All solid solutions, general formulae ${}_xLa(Co_{1/2}Ti_{1/2})O_{3-(1-x)}CaTiO_3$ ($x$LCT) and ${}_xNd(Co_{1/2}Ti_{1/2})O_{3-(1-x)}CaTiO_3$ ($x$NCT), were synthesised using a conventional mixed oxide route with raw materials of $La_2O_3$, $Nd_2O_3$, $TiO_2$, $CoCO_3$ and $CaCO_3$ (Acros Organics, >99%). The starting reagents, weighed in the appropriate ratios, were balled milled for 16 h in propan-2-ol using $ZrO_2$ media. All pre-reacted powders had a mean particle diameter of 1 μm, Laser Coulter Analyser. The slurry was dried at 100 °C then calcined at 1350 °C for 6 h, $CaTiO_3$ was calcined at 1150 °C for 4 h. The calcined powders were re-milled for 16 h in propan-2-ol. The dried powders were pressed into 1 and 2 cm discs and sintered at 1550 °C for 6 h on $ZrO_2$ boards, $CaTiO_3$ was sintered at 1600 °C for 4 h. Densities were calculated using the Archimedes water method and all sintered discs had a density of >96% of theoretical.

An X-ray diffractometer (Model PW 1730/10 Philips, Holland) with Cu Kα source (λ = 1.540562 Å), operated at 50 kV and 30 mA, was used for the identification of phases in the calcined powders and sintered pellets. A step size of 0.02°, a scan rate of 2°/min and scan ranges of 10–70° were adopted. Samples for scanning electron microscopy (SEM) were obtained from fracture surfaces of the sintered pellets. Samples were then mounted on stainless steel stubs using silver dag and carbon coated. A JEOL JSM6400 SEM equipped with a LINK energy dispersive spectroscopy (EDS) detec-

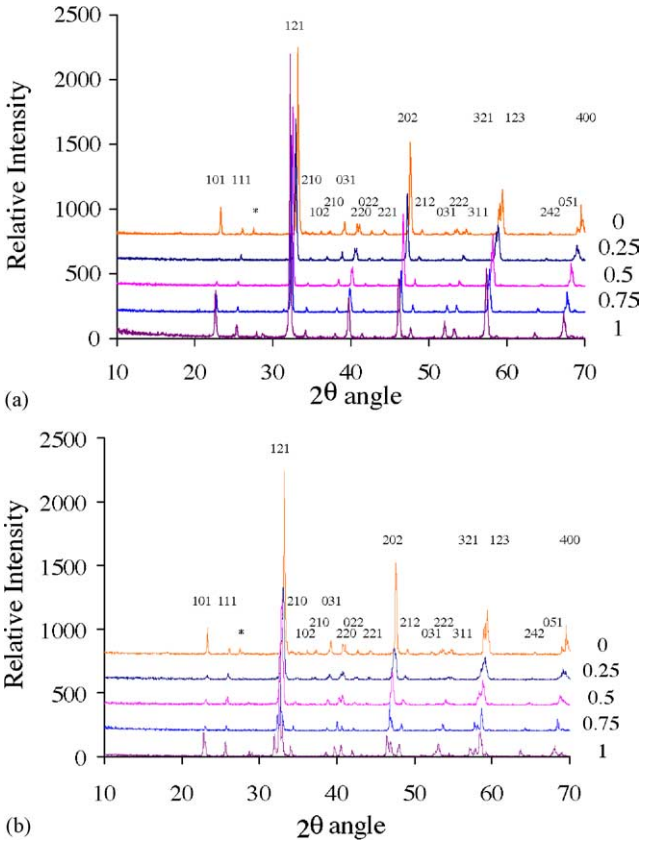


Fig. 1. XRD traces from the (a) $x$LCT and (b) $x$NCT solid solution series indexed using an orthorhombic setting.