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$(1-x)CaTiO_3$–$x(Li_{0.5}Nd_{0.5})TiO_3$ for ultra-small dielectrically loaded antennas

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Abstract Microwave (MW) dielectric ceramics based on the solid solution $(1-x)CaTiO_3$–$x(Li_{0.5}Nd_{0.5})TiO_3$ ($0.25 \leq x \leq 1.0$) were prepared by conventional solid-state synthesis using the mixed oxide route. Compositions closest to zero τ_f (+65 ppm/°C) were obtained at $x = 0.8$ where $\varepsilon_r = 110$ and the microwave quality factor, $Qf_0 \cong 2600$ GHz for samples sintered at 1300 °C. To reduce the sintering temperature and compensate for any Li_2O loss during fabrication, ≤0.5 wt% $0.5Li_2O$–$0.5B_2O_3$ was added as a sintering aid in the form of raw oxides (LBR) and also as a pre-reacted glass (LBG). 0.5 wt% LBR was the most effective, reducing the temperature to achieve optimum density by ~50 °C with no significant deterioration of microwave properties ($\varepsilon_r = 115$, $\tau_f = +65$ ppm/°C and $Qf_0 \cong 2500$ GHz). The high permittivity and relatively low sintering temperatures (1250 °C) are ideal for the development of low cost ultra-small dielectric loaded antenna, assuming the system can be tuned closer to zero by fractionally increasing x.

Introduction

Direct handset to satellite communication is becoming increasingly important in the telecommunications industry. Applications such as global positioning systems (GPS) and satellite radio are already prevalent but small handheld satellite phones which do not require a cellular network are becoming increasingly attractive in large countries where coverage via conventional mast technology is expensive and prone to disruption. To compete with conventional handset cellular phone technology, satellite phones must be comparable in size and aesthetically appealing to the customer. [1] The development of dielectrically loaded antennas (DLAs) in the last 10 years has enabled extensive miniaturisation of satellite-enabled handsets. However, in order to satisfy the consumer market, further miniaturisation is required. With DLAs, miniaturisation can be achieved by increasing the relative permittivity (ε_r) whilst still maintaining a low temperature coefficient of the resonant frequency (τ_f) and a microwave quality factor (Qf_0) high enough to maintain a stable circularly polarised field [1]. Within antenna design, the minimum requirements of τ_f and Qf_0, for a workable device are not clear since the microwave properties are dominated by the surface metallisation. In a recent review by Mirsaneh et al. [1], microstrip patch and quadrifilar helix (QH) antennas were compared and the potential of further miniaturisation discussed. The first generation of DLAs used materials such as $MgCaTiO_3$ and $(Zr,Sn)TiO_4$ originally developed for use as base station resonators [2]. Further miniaturisation was anticipated by the use of $BaNd_2Ti_4O_{15}$ compounds which are temperature stable with $\varepsilon_r \cong 80$ [3]. However, these authors did not speculate on materials which could potentially further miniaturise antennas. Here, we investigate a family of ceramics based on $(RE_{0.5}Li_{0.5})TiO_3$–$CaTiO_3$ solid solutions, to assess whether their base microwave properties could be used to reduce further the critical dimensions of dielectrically loaded antennas.

$(RE_{0.5}Li_{0.5})TiO_3$–$CaTiO_3$ (RE = rare earth)-based solid solutions were first studied as potential resonator ceramics

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by Ezaki and co-workers [4, 5] in the early 1990s with subsequent work focussing on the Nd and Sm analogues [6–9]. $CaTiO_3$ (CT) system has $\varepsilon_r = 160$ and $Qf_0 \sim 12000$ GHz [10] while the $Li_0RE_{0.5}TiO_3$ (LRET) system typically has $\varepsilon_r \sim 80$ and $Qf_0 \sim 6000$ GHz [6]. Each has a heavily distorted perovskite structure due to rotations of the O octahedra and tuning through zero occurs because the LRET and CT have −ve and +ve values of τ_f, respectively. A wide range of MW properties have been reported for this system which depends on RE ionic radius and processing conditions. However, temperature-stable ceramics are invariably described with $\varepsilon_r > 100$ but with Qf_0 too low for base station filter and resonator applications [4–9]. Consequently, recent papers have focussed on reducing sintering temperature by the addition of sintering aids with the aim of developing compositions suitable for low-temperature co-fired ceramic (LTCC) applications [11]. In the present study, the basic dielectric properties of the solid solution $(1 - x)CaTiO_3$–$x(Li_{0.5}Nd_{0.5})TiO_3$ $(0.25 \le x \le 1.0)$ are investigated to determine potential temperature stable compositions. Further studies have then been carried out to determine the effect of the addition of Li_2O-based sintering aids on the MW properties and to determine whether such compositions have potential for the fabrication of ceramic cores for dielectrically loaded antennas.

Experimental procedure

Ceramics in the solid solution series $(1 - x)CaTiO_3$–$x(Li_{0.5}Nd_{0.5})TiO_3$ (CTLNT100x) $(0.25 \le x \le 1)$ powder were prepared by a conventional solid-state reaction. Oxide powders (>99.5% purity) of $CaCO_3$, $LiCO_3$, Nd_2O_3 and TiO_2 were mixed and ball milled in appropriate stoichiometric ratios in polyethylene containers with propan-2-ol using Y-stabilised zirconia milling media for 24 h and then dried. The mixed/milled powders were then calcined at 1100 °C for 4 h. The calcined powders were then lightly hand ground in a pestle and mortar and sieved through a 200-mesh screen. Where appropriate, the calcined powders were mixed with either excess 0.25 or 0.5 wt% Li_2O–B_2O_3 in the raw oxide/carbonate (LBR) form or as a glass phase (LBG). The glass was prepared by melting Li_2CO_3 and B_2O_3 (>99.9% purity) treatment at 1000 °C for 1 h in a Pt crucible. The calcined samples were re-milled in propan-2-ol for 24 h. The milled samples were pressed into pellets with dimension of 10 mm in diameter and ~5 mm in thickness under a pressure of 200 MPa and then sintered at temperatures ranging from 1150 to 1350 °C for 3 h. Densities of sintered pellets were measured using the Archimedes method.

The crystalline phases of the calcined powder and sintered pellets were identified by X-ray powder diffraction (XRD) analysis using Cu-Ka radiation from 20° to 60° in 2θ. The microstructure of the polished, chemical and thermal etched surfaces was examined using scanning electron microscopy (SEM) (Model JEOL 6400). Microwave dielectric resonance measurements were performed using a network analyser (Model ADVANTEST R3767CH), in the frequency range of 40 MHz to 8 GHz.

Results and discussion

Initial investigations across the CTLNT100x solid solution revealed that CTLNT80 was single phase according to XRD (Fig. 1) and exhibited a dense microstructure composed of cuboid crystals when sintered at ~1300 °C (Fig. 2). This composition was closest to the zero τ_f (+65 ppm/°C) with $Qf_0 = 2600$ and $\varepsilon_r = 112$. Although this composition is promising for applications as dielectrically loaded antennas, repeated fabrication gave inconsistent results with variation in MW properties which could preclude their usage. It was postulated that loss of Li_2O played the major role in the variation of MW properties and consequently, the following details methods by which Li_2O loss can be compensated directly and sintering temperature reduced by utilising Li_2O-based sintering aids. In the first method, the raw materials, Li_2O and B_2O_3 were milled directly with pre-reacted powder prior to sintering (LBR). In the second method, the Li_2O and B_2O_3 were melted to form a glass, fritted and milled with the CTLNT80 powder prior to sintering (LBG).

Figure 3 shows the bulk density of CTLNT80 ceramic bodies as a function of sintering temperature for compositions which contain 0.25 and 0.5 wt% of LBR and LBG as sintering aids. In general, the addition of LBR and LBG, decreases the sintering temperature with optimum density obtained at 1250 °C for 0.5 wt% LBR.

Figure 1 also shows the XRD data of CTLNT80 ceramics with 0.25 and 0.5 wt% LBR/LBG and sintered at 1250 °C for 3 h. All ceramics could be indexed according to an orthorhombic perovskite structure (Pnma symmetry) $a = 5.44$, $b = 7.66$ and $c = 5.40$ and no second phase was detected.

Figure 4a, b shows the micrographs of thermally etched CTLNT80 ceramics with 0.25 wt% LBR and LBG sintered at 1250 °C. The ceramics exhibit microstructures consistent with near 100% density but the grain size is considerably reduced (~1–3 μm) with respect to ceramics sintered without LBR and LBG (50–100 μm).

Figure 5a–c shows the microwave dielectric properties of CTLNT80 ceramics with LBR and LBG, sintered at 1250 °C for 3 h. Consistent with an improved densification and reduced Li_2O loss, ε_r increases to ~115 with τ_f (+65 ppm/°C) and Qf_0 (~2500 GHz) remaining largely unchanged by adding LBG and LBR sintering aids.

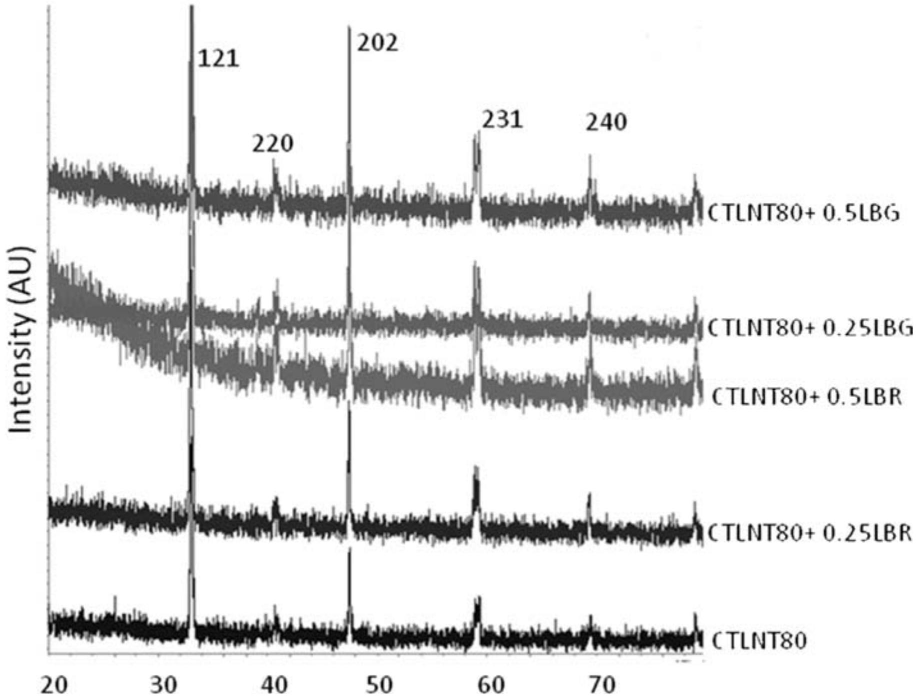

Fig. 1 XRD traces from samples in the CTLNT80 with LBR and LBG additions

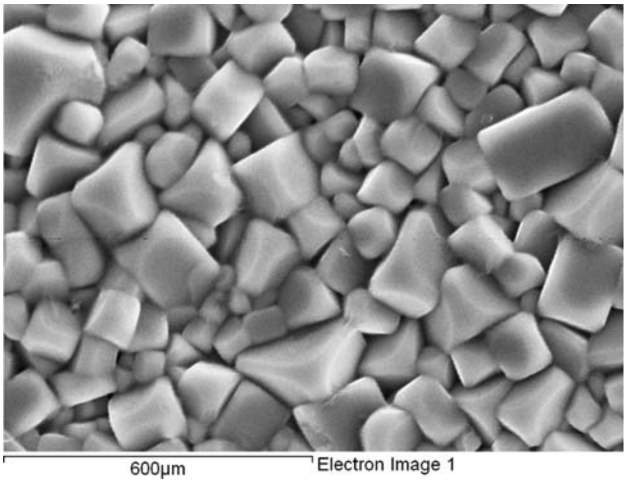

Fig. 2 SEM image showing a thermally etched surface of CTLNT80 sintered at 1300 °C

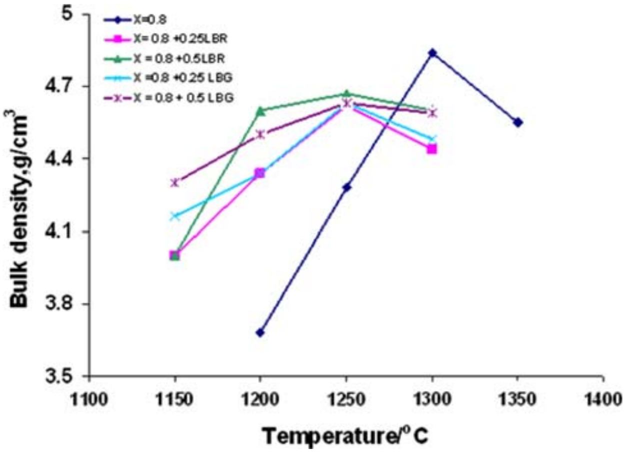

Fig. 3 Bulk density versus temperature for CTLNT80 with LBR and LBG additions

The current generation of DLAs use ceramic bodies with $\varepsilon_r \cong 80$ which for QH designs [10] gives an antenna ~7.5 mm diameter. The development of temperature-stable ceramics with higher ε_r (110–120) based on CTLNT would reduce further the ceramic core diameter, miniaturising the antenna to ~5.5 mm. The use of LBG and LBR sintering aids gives greater reliability to the ceramic fabrication and may hold the key to their commercial usage. The proof of concept has been demonstrated in this study but further work is required to fine tune the compositions and sintering temperatures to give optimum properties.

Conclusions

The effects of $Li_2O–B_2O_3$ (0.2 and 0.5 wt%) in the form of raw materials (LBR) and glass (LBG) sintering aids on the microwave dielectric properties of CTLNT80 were investigated. Both LBR and LBG reduced the grain size and increased the density of the ceramics. ε_r increased marginally consistent with an increase in density, whereas Qf_0 and τ_f remain largely unchanged. The use of LBR and LBG additions was particularly useful in improving the reproducibility of the data with similar results obtained from

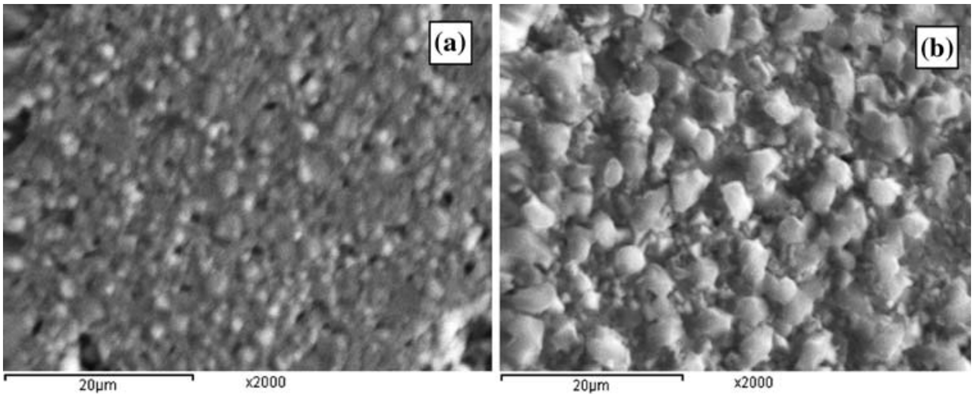

Fig. 4 SEM images of CTLNT80 sintered at 1250 °C with **a** 0.25 wt% LBR and **b** 0.25 wt% LBG

sample to sample. It is concluded therefore that compositions close to CTLNT80 with either LBR or LBG additions have potential for use as cores for ultra-small dielectrically loaded antennas.

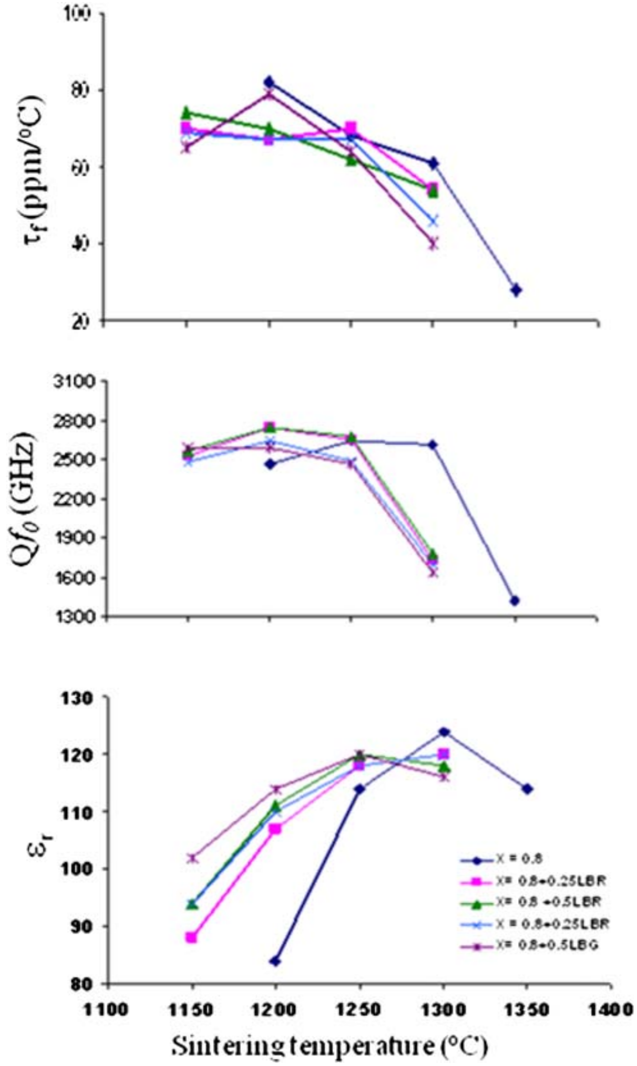

Fig. 5 τ_f, Qf_0 and ε_r, for CTLNT80 with LBR and LBG additions at different sintering temperatures

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