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Synthesis and microwave dielectric properties of Ca substituted $SrLa_4Ti_{4.93}Zr_{0.07}O_{17}$ ceramics

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Abstract. Microwave dielectric ceramics in $Sr_{1-x}Ca_xLa_4Ti_{4.93}Zr_{0.07}O_{17}$ ($0 \le x \le 0.5$) composition series were processed via a solid-state sintering rout. X-ray diffraction revealed single phase ceramics. Ca substitutions for Sr tuned τ_f towards zero with increased $Q_u f_o$ values. In the present study, $\varepsilon_r \sim 55$, $Q_u f_o \sim 11960$ GHz and $\tau_f \sim 5{\cdot}2$ ppm/°C were achieved for the composition with $x = 0{\cdot}3$.

Keywords. Patch antenna; theoretical density; phase; ceramics.

1. Introduction

Extensive research has been carried out in the last three decades on dielectric ceramics due to their unique electrical properties which make them suitable candidates as dielectric resonators for microwave based wireless telecommunication industry by reducing the size and cost of filters and antennas in the circuit. Ideal materials for commercial applications as dielectric resonators (DRs) for base stations require high relative electric permittivity ($\varepsilon_r > 24$), near-zero temperature coefficient of resonant frequency ($\tau_f \sim 0$ ppm/°C), and a high unloaded quality factor, generally reported as a product with the frequency (f_o) at which it is measured ($Q_u f_o \approx 30{,}000$ GHz) (Reaney and Idles 2006). For certain applications, e.g. antennas, the values of τ_f and $Q_u f_o$ can be compromised to ± 10 ppm/°C and > 10,000 GHz (Sebastian 2008).

Layered perovskites with general formula, $A_nB_nO_{3n+2}$ ($n = 5$), have received much attention due to their high dielectric performance for applications in patch antenna (Chen and Tsai 2008; Chen and Zeng 2009; Wang *et al* 2010).

$SrLa_4Ti_5O_{17}$ was reported to have $\varepsilon_r \sim 39{\cdot}1$, $Q_u f_o \sim 14200$ GHz and $\tau_f \sim 58$ ppm/°C (Demsar *et al* 2008). However, in another study, $\varepsilon_r \sim 61$, $Q_u f_o \sim 9969$ GHz and $\tau_f \sim 117$ ppm/°C was reported for $SrLa_4Ti_5O_{17}$ (Iqbal and Manan 2012a, b). This difference in the microwave dielectric properties of $SrLa_4Ti_5O_{17}$ could be attributed to the different processing conditions employed in two separate studies milling for 0·5 h and sintering at 1580 °C for 20 h with relative density of 92% in the study carried out by Demsar *et al* (2008) and milling for 24 h and sintering at 1500 °C for 4 h with relative density of 94·5% in the study carried out by Iqbal and Manan (2012a, b). The high positive τ_f precluded its application at microwave frequencies. Nd substitutions for La in $SrLa_4Ti_5O_{17}$ tuned τ_f towards 0 ppm/°C with $\varepsilon_r > 50$ but at the cost of decreasing $Q_u f_o$ respectively (Manan and Iqbal 2012). In another study, partial substitution of Zr for Ti in $SrLa_4Ti_5O_{17}$ ($SrLa_4Ti_{4.93}Zr_{0.07}O_{17}$) decreased τ_f to 72 ppm/°C with slight increase in $Q_u f_o$ from 9969 to 10,046 GHz (Iqbal and Manan 2012a). The high positive τ_f of $SrLa_4Ti_{4.93}Zr_{0.07}O_{17}$ also precluded its application at microwave frequencies. In a previous study, Ca substitution for Sr tuned τ_f of $Sr_5Nb_4TiO_{17}$ towards zero along with increase in $Q_u f_o$ value (Manan *et al* 2011). Therefore, aim of the present study was to investigate the microwave dielectric properties of $Sr_{1-x}Ca_xLa_4Ti_{4.93}Zr_{0.07}O_{17}$ solid solution and assess their suitability as temperature stable microwave ceramics.

2. Experimental

$Sr_{1-x}Ca_xLa_4Ti_{4.93}Zr_{0.07}O_{17}$ ($0 \le x \le 0{\cdot}5$) ceramics were fabricated via solid-state mix oxide route. Laboratory reagent-grade $SrCO_3$ (Aldrich, 99 + %) and $CaCO_3$ (Aldrich, 99 + %) dried at ~ 185 °C and La_2O_3 (Aldrich, 99·95%), ZrO_2 (Aldrich, 99.95%), and TiO_2 (Aldrich, Anatase, 99 + %) were dried at 900 °C for 24 h to remove adsorbed moisture. The dried carbonates and oxides were weighted in stoichiometric ratios and were wet ball-milled for 24 h in the disposable polyethylene mill jars using Y-toughened ZrO_2 balls as grinding medium and isoprapanol as liquid. The slurries were dried in a drying oven at ~ 95 °C for 24 h. The powders were sieved and calcined at 1350 °C for 6 h at heating/cooling rates of 5 °C/min. The calcined powder samples were remilled for 4 h. the calcined powders were pressed into 4- to 5-mm

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thick and 10-mm in diameter at 100 MPa. The pellets were placed on platinum foil and sintered at 1450 to 1590 °C for 4 h at heating/cooling rates of 5 °C/min. The sintered samples were crushed into fine powders. Phase analyses of the pulverized sintered pellets were carried out using X-ray diffractometer (model D500) operating at 30 kV and 40 mA at 1°/min from $2\theta = 10$ to 70° with step size of 0·02°.

For lattice parameters measurement, XRD was performed using STOE PSD X-ray diffractometer with CuKα (λ = 1·540598 Å) operating at 30 kV and 40 mA at 1°/min from $2\theta = 10$ to 70° with step size of 0·01°. STOE WinXPOW software (version 1.06, STOE and Cie GmbH, Darmstadt, Germany) was used to determine and refine the lattice parameters for the new unit cell resulting from the substitution of Ca for Sr in $Sr_{1-x}Ca_xLaTi_{4·93}Zr_{0·07}O_{17}$. For microstructure examination, optimal dense pellets were cut into halves and were well-polished before thermal etching at temperature 10% less than their corresponding sintering temperature at heating and cooling rates of 5 °C/min. The thermally etched surfaces were gold coated to avoid charging in SEM. A JEOL 6400 SEM (JEOL, Japan) operating at 20 kV was used.

Microwave dielectric properties were measured using Agilent network analyser (R3767CH, Agilent, USA) via the cavity method. Cylindrical samples were placed at the centre of Au-coated cavity made of brass on low-loss quartz single crystal to avoid conduction loss from the walls of the cavity. The temperature coefficient of resonant frequency (τ_f) was measured in the range 20–70 °C using (1).

$$\tau_f = (f_2 - f_1)/[f_1(T_2 - T_1)], \quad (1)$$

where f_1 and f_2 are the initial and final resonant frequencies at 20 and 70 °C, respectively.

3. Results and discussion

The relative density (ρ_r) of $Sr_{1-x}Ca_xLa_4Ti_{4·93}Zr_{0·07}O_{17}$ ($0 \le x \le 0·5$) ceramics as a function of sintering temperature is shown in figure 1. Previous study revealed that substitution of an ion with lower ionic radius for an ion with larger ionic radius increases the sintering temperature (Sreemoolanadhan *et al* 1995). In the present study, the optimum sintering temperature is increased for about 40 °C with Ca substitution for Sr. All the ceramics were sintered more than 95% of their theoretical density.

XRD patterns recorded at room temperature for $Sr_{1-x}Ca_xLa_4Ti_{4·93}Zr_{0·07}O_{17}$ ($0 \le x \le 0·5$) ceramics sintered at their optimum sintering temperatures for 4 h are shown in figure 2. The d values and intensities corresponding to XRD peaks of the compositions with x = 0–0·5 matched with the one reported for $SrLa_4Ti_5O_{17}$ (PDF#27-1059). There was no evidence of any secondary phase in each composition within the in-house XRD detection limits. XRD peaks for the compositions with x = 0·1–0·5 shifted towards higher diffraction angles, i.e. smaller d values due to smaller ionic radius of Ca^{2+} (1·34 Å) than Sr^{2+} (1·44 Å) for 12-coordination (Shannon 1976). The unit cell parameters refined by the least squares method are observed to decrease with Ca concentration as given in table 1. The corresponding unit cell volume and theoretical density are observed to decrease for the investigated ceramics and also compared in table 1.

The secondary electron images (SEIs) from thermally etched and gold coated surfaces of optimally sintered $Sr_{1-x}Ca_xLa_4Ti_{4·93}Zr_{0·07}O_{17}$ ($0 \le x \le 0·5$) ceramics are shown in figure 3. Highly dense microstructure for each composition is observed and consisted with their relative density

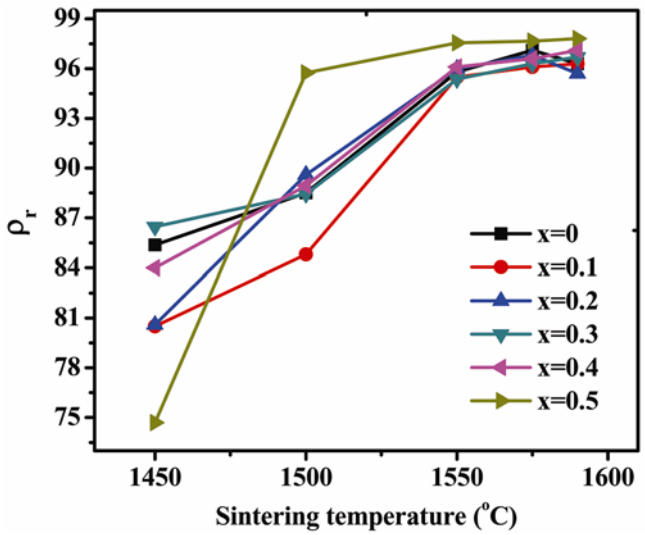

Figure 1. Variation in relative density (ρ_r) of $Sr_{1-x}Ca_xLa_4Ti_{4·93}Zr_{0·07}O_{17}$ ($0 \le x \le 0·5$) ceramics as a function of sintering temperature.

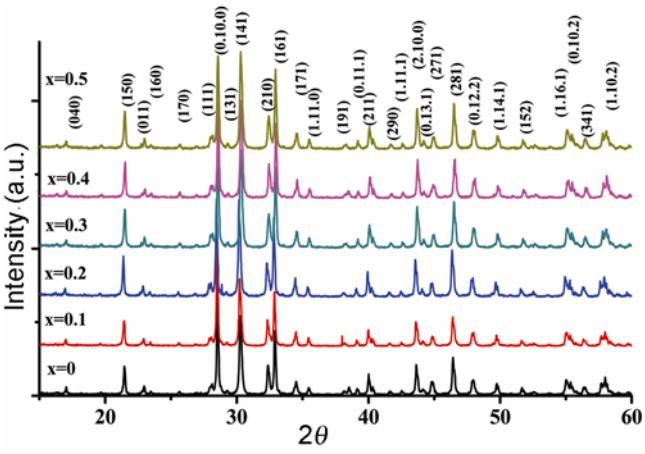

Figure 2. XRD patterns from $Sr_{1-x}Ca_xLa_4Ti_{4·93}Zr_{0·07}O_{17}$ ($0 \le x \le 0·5$) ceramics sintered at optimum sintering temperatures, showing formation of a single phase ceramics for each composition.

Table 1. Processing temperatures, apparent densities, theoretical and relative densities and microwave dielectric properties of $Sr_{1-x}Ca_xLa_4Ti_{4.93}Zr_{0.07}O_{17}$ ($0 \le x \le 0{\cdot}5$) ceramics.

(x)	S.T (°C)	a (Å)	b (Å)	c (Å)	V (Å^3)	ρ_{th} (g cm^{-3})	ρ_r	ε_r	$Q_u f_o$ (GHz)	τ_f (ppm/°C)
0	1575	5·551 (3)	31·316 (13)	3·9095 (18)	679·6	5·65	97·1	58·2	10800	73·5
0.1	1590	5·547 (3)	31·308 (6)	3·9063 (4)	678·3	5·64	96·3	57·1	11150	50·1
0.2	1575	5·540 (10)	31·301 (7)	3·9024 (9)	676·7	5·63	96·8	56·3	11500	25·2
0.3	1590	5·535 (12)	31·296 (8)	3·8997 (13)	675·5	5·62	96·7	55·0	11960	5·4
0.4	1590	5·529	31·293	3·8981	674·4	5·60	97·1	53·9	12345	–10·3
0.5	1590	5·526	31·289	3·8972	673·9	5·59	97·8	52·8	12750	–22·3

S.T, Sintering temperature, ρ_r, relative density.

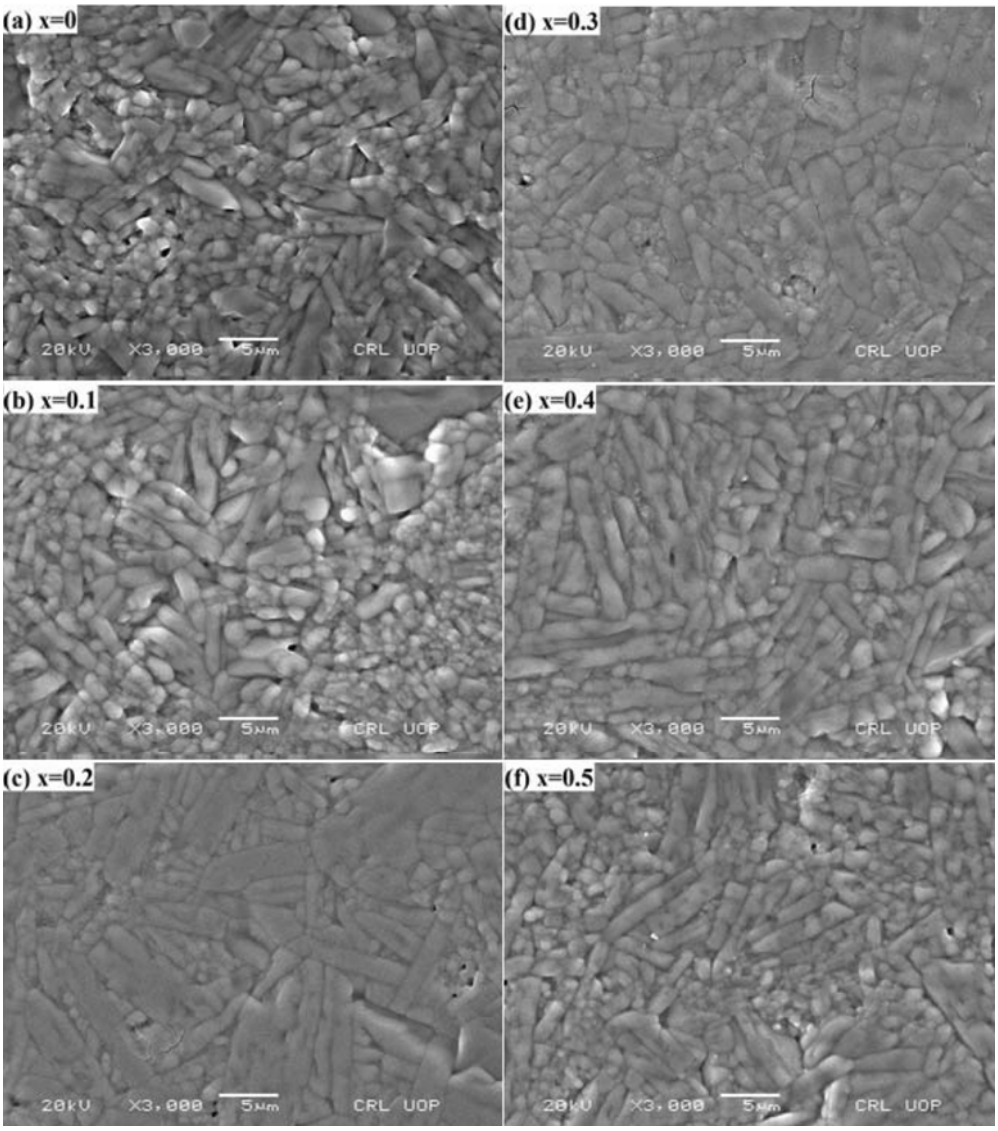

Figure 3. SEIs of $Sr_{1-x}Ca_xLa_4Ti_{4.93}Zr_{0.07}O_{17}$ ($0 \le x \le 0{\cdot}5$) ceramics showing highly dense microstructure for each composition.

data (figure 1). The typical elongated grain morphology of layered perovskites was observed for each composition.

The variation in ε_r and τ_f for $Sr_{1-x}Ca_xLa_4Ti_{4.93}Zr_{0.07}O_{17}$ ($0 \le x \le 0{\cdot}5$) ceramics sintered at their optimum sintering temperatures for 4 h in air as a function of Ca content is shown in figure 4. Both ε_r and τ_f are observed to decrease from 58 to 52 and 73·5 to –22·3 ppm/°C with increasing Ca^{2+} concentration from 0 to 0·5, respectively. The decrease in ε_r is presumably due to lower ionic polarizabilty of Ca^{2+} (3·16 Å^3) compared with Sr^{2+} (4·24 Å^3) (Shannon 1993). The monotonous decrease in ε_r suggests

that there are no structural phase transitions in the solid solution as a function of increasing x. It has been suggested that ε_r is directly proportional to 'τ_f' in the absence of structural phase transition as a function of x within the solid solution (Reaney and Idles 2006). Ca^{2+} has a smaller ionic radius than Sr^{2+} but substitution results in only a small decrease in the average cuboctahedral ion radius which principally contain La^{3+} ions. The tolerance factor of the perovskite-like blocks in the layered structured is low enough to induce rotations of the O-octahedra at high temperature and substitution of Ca for Sr has little impact on their type and magnitude. $Q_u f_o$ (GHz) value was increased from 10,800 to 12,750 GHz (figure 5) as Ca concentration was increased from 0 to

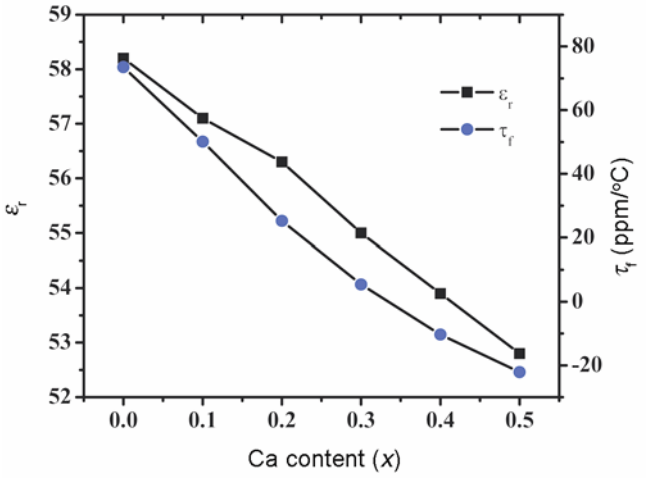

Figure 4. Variation in ε_r and ε_f with Ca content for $Sr_{1-x}Ca_xLa_4Ti_{4\cdot93}Zr_{0\cdot07}O_{17}$ ($0 \le x \le 0\cdot5$) ceramics, showing a decrease in both ε_r and τ_f with increasing x.

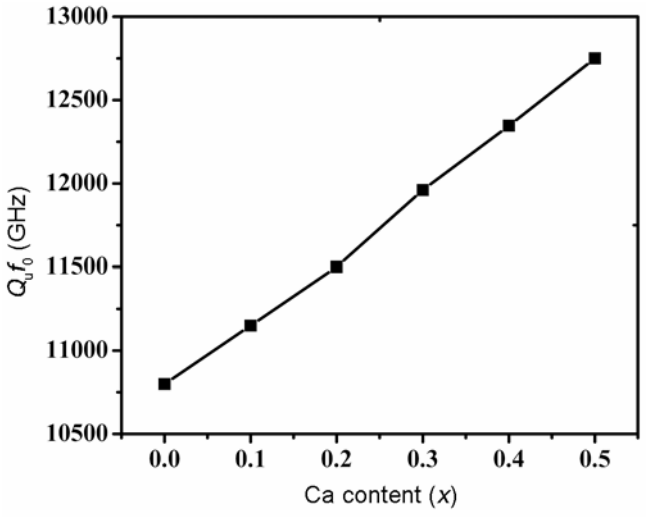

Figure 5. Variation in $Q_u f_o$ with Ca content (x) for $Sr_{1-x}Ca_xLa_4Ti_{4\cdot93}Zr_{0\cdot07}O_{17}$ ($0 \le x \le 0\cdot5$) ceramics, showing increase in $Q_u f_o$ value with increasing x.

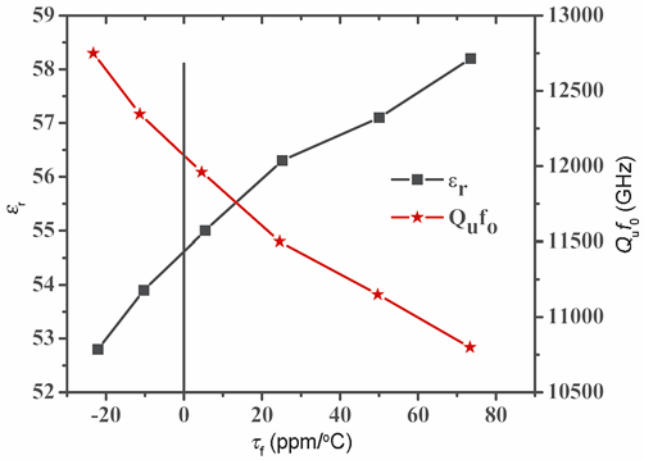

Figure 6. ε_r and $Q_u f_o$ vs τ_f for $Sr_{1-x}Ca_xLa_4Ti_{4\cdot93}Zr_{0\cdot07}O_{17}$ ($0 \le x \le 0\cdot5$) ceramics showing that $\tau_f \sim 0$ ppm/°C corresponds to $\varepsilon_r \sim 54\cdot5$ and $Q_u f_o \sim 12000$ GHz.

0·5. It is generally, reported that as atomic size difference at the A-site of the perovskite structure decreases, the lattice strain decreases which in turn decreases the loss of the material and vice versa (Fang *et al* 2008; Fang *et al* 2010). Since the size of Ca < Sr therefore, the substitutions of Ca for Sr decreased the size difference at the A-site and hence increased the $Q_u f_o$ value. The analysis of the present result indicates that $\tau_f \sim 0$ ppm/°C corresponds to $\varepsilon_r \sim 54\cdot5$ and $Q_u f_o \sim 12{,}000$ GHz as shown in figure 6.

4. Conclusions

Dielectric ceramics in $Sr_{1-x}Ca_xLa_4Ti_{4\cdot93}Zr_{0\cdot07}O_{17}$ ($0 \le x \le 0\cdot5$) series were prepared via conventional solid-state mix oxide route. XRD revealed the formation of a single phase ceramics for each composition sintered in air for 4 h in the temperature range 1450–1590 °C. The substitution of Ca for Sr tuned τ_f towards zero with increased $Q_u f_o$ value. $\varepsilon_r \sim 55$, $Q_u f_o \sim 11{,}960$ GHz and $\tau_f \sim 5$ ppm/°C were achieved for the composition with $x = 0\cdot3$ ($Sr_{0\cdot7}Ca_{0\cdot3}La_4Ti_{4\cdot93}Zr_{0\cdot07}O_{17}$) in the present study. $Q_u f_o$ is too low for use as dielectric resonator but ceramics in $Sr_{1-x}Ca_xLa_4Ti_{4\cdot93}Zr_{0\cdot07}O_{17}$ ($0 \le x \le 0\cdot5$) solid solution may find application as cores in dielectrically loaded antennas or patch antenna.

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