Synthesis and microwave dielectric properties of Ca substituted SrLa$_{4}$Ti$_{4.93}$Zr$_{0.07}$O$_{17}$ ceramics

ABDUL MANAN$^{1,*}$ and IBRAHIM QAZI$^2$

$^1$Department of Physics, University of Science and Technology, Bannu, 28100 KPK, Pakistan
$^2$Department of Materials Science and Engineering, Institute of Space Technology, Islamabad 44000, Pakistan

MS received 15 February 2013; revised 18 April 2013

Abstract. Microwave dielectric ceramics in Sr$_{1-x}$Ca$_x$La$_4$Ti$_{4.93}$Zr$_{0.07}$O$_{17}$ (0 ≤ x ≤ 0.5) composition series were processed via a solid-state mixture route. X-ray diffraction revealed single phase ceramics. Ca substitutions for Sr tuned $\tau$ towards zero with increased $Q_{f o}$ values. In the present study, $\varepsilon_r$ ~ 55, $Q_{f o}$ ~ 11960 GHz and $\tau$ ~ 5-2 ppm/°C were achieved for the composition with $x$ = 0-3.

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 ($\tau$ ~ 0 ppm/°C), and a high unloaded quality factor, generally reported as a product with the frequency ($f_o$) at which it is measured ($Q_{f o}$ = 30,000 GHz) (Reaney and Idles 2006). For certain applications, e.g. antennas, the values of $\tau$ and $Q_{f o}$ can be compromised to ±10 ppm/°C and > 10,000 GHz (Sebastian 2008).

Layered perovskites with general formula, A$_n$B$_2$O$_{3n+2}$ ($n = 5$), 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$_4$Ti$_3$O$_{17}$ was reported to have $\varepsilon_r$ ~ 39-1, $Q_{f o}$ ~ 14200 GHz and $\tau$ ~ 58 ppm/°C (Demsar et al. 2008). However, in another study, $\varepsilon_r$ ~ 61, $Q_{f o}$ ~ 9969 GHz and $\tau$ ~ 117 ppm/°C was reported for SrLa$_4$Ti$_3$O$_{17}$ (Iqbal and Manan 2012a, b). This difference in the microwave dielectric properties of SrLa$_4$Ti$_3$O$_{17}$ 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 $\tau$ precluded its application at microwave frequencies. Nd substitutions for La in SrLa$_4$Ti$_3$O$_{17}$ tuned $\tau$ towards 0 ppm/°C with $\varepsilon_r$ > 50 but at the cost of decreasing $Q_{f o}$ respectively (Manan and Iqbal 2012). In another study, partial substitution of Zr for Ti in SrLa$_4$Ti$_3$O$_{17}$ (SrLa$_4$Ti$_{4.93}$Zr$_{0.07}$O$_{17}$) decreased $\tau$ to 72 ppm/°C with slight increase in $Q_{f o}$, from 9969 to 10,046 GHz (Iqbal and Manan 2012a). The high positive $\tau$ of SrLa$_4$Ti$_{4.93}$Zr$_{0.07}$O$_{17}$ also precluded its application at microwave frequencies. In a previous study, Ca substitution for Sr tuned $\tau$ of Sr$_5$Nb$_2$Ti$_3$O$_{17}$ towards zero along with increase in $Q_{f o}$ value (Manan et al 2011). Therefore, aim of the present study was to investigate the microwave dielectric properties of Sr$_{1-x}$Ca$_x$La$_4$Ti$_{4.93}$Zr$_{0.07}$O$_{17}$ solid solution and assess their suitability as temperature stable microwave ceramics.

2. Experimental

Sr$_{1-x}$Ca$_x$La$_4$Ti$_{4.93}$Zr$_{0.07}$O$_{17}$ (0 ≤ x ≤ 0.5) 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$_2$O$_3$ (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 isopropanol as liquid. The slurries were dried in a drying chamber at ~185 °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
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 2θ = 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 2θ = 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 Sr1–xCa4LaTi4.93Zr0.07O17. 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) was measured in the range 20–70 °C using (1).

\[ \tau = \frac{(f_2 - f_1)}{f_1(T_2 - T_1)} \]

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 (\( \rho_r \)) of Sr1–xCa4La4Ti4.93Zr0.07O17 (0 ≤ x ≤ 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 (Sreeenoolanadhan 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 Sr1–xCa4La4Ti4.93Zr0.07O17 (0 ≤ x ≤ 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 SrLa4Ti4O17 (PDF#27-1059). There was no evidence of any secondary phase in each composition within the in-house XRD detection limits.