

# Improvement in the microwave dielectric properties of SrCa<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ceramics by Ba substitution

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**Abstract.** Microwave dielectric ceramics in the Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> (0 ≤ x ≤ 0.75) composition series were fabricated via a solid-state mixed oxide route. All the compositions formed single phase in Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> (0 ≤ x ≤ 0.75) solid solutions within the detection limit of in-house X-ray diffraction (XRD). The sintered microstructure of these ceramics comprised densely packed elongated and plate-like grains. The dielectric properties varied linearly with x. Relative permittivity ( $\epsilon_r$ ) increased from 47.2 to 54.5, unloaded quality factor multiplying the resonant frequency ( $Q_u f_0$ ) decreased from 11,984 to 9345 GHz and temperature coefficient of resonant frequency ( $\tau_f$ ) increased from -78.6 to 20 ppm/°C with an increase in x from 0 to 0.75. In the present study,  $\epsilon_r \approx 51.6$ ,  $Q_u f_0 \approx 10,160$  GHz (5.37 GHz) and  $\tau_f \approx -13.5$  ppm/°C were achieved for Sr<sub>0.5</sub>Ba<sub>0.5</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> (x = 0.5) ceramics.

**Keywords.** XRD; processing; phase; ceramics.

## 1. Introduction

Ceramics are extensively studied due to their unique microwave dielectric properties which make them potential candidate materials for manufacture of compact and low-cost dielectric resonators for wireless telecommunication devices (Reaney and Idles 2006). Ideal materials for commercial applications such as dielectric resonators (DRs) require a high relative permittivity ( $\epsilon_r > 24$ ), near-zero temperature coefficient of resonant frequency ( $\tau_f < \pm 20$  ppm/°C), and a high unloaded quality factor, generally reported as a product with the frequency  $f_0$  at which it is measured at microwave frequencies ( $Q_u f_0 > 10,000$  GHz) (Sebastian 2008). The inverse relationship of  $\epsilon_r$  with the component size (1) implies that  $\epsilon_r$  must be high enough to reduce the size of the relevant circuit and, hence, device (Manan and Iqbal 2012)

$$\lambda_d \propto 1/(\epsilon_r)^{1/2}. \quad (1)$$

Here  $\lambda_d$  is given by  $\lambda_d = \lambda_0/(\epsilon_r)^{1/2}$ , where  $\lambda_d$  and  $\lambda_0$  are the wavelengths of microwaves in a dielectric medium and free space, respectively.

Several ceramic materials have been commercialized and are used in the manufacture of DRs for mobile phone handsets and base stations; however, search for new materials with ultra-low loss (i.e. high  $Q_u f_0$ ),  $\tau_f \approx 0$  ppm/°C

and high  $\epsilon_r$  (> 50) continues (Reaney and Idles 2006; Freer and Azough 2008).

Dielectric ceramics with general formula  $A_n B_n O_{3n+2}$  have been investigated for practical applications as DRs (Jawahar *et al* 2002; Zhao *et al* 2006; Chen and Tsai 2008; Iqbal *et al* 2011; Manan and Iqbal 2011, 2012). Recently  $\epsilon_r \sim 47.2$ ,  $Q_u f_0 \approx 11,994$  GHz and  $\tau_f \approx -78$  ppm/°C was reported for SrCa<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> sintered at 1475 °C (Manan and Reaney 2012); however, the high negative  $\tau_f$  precluded its use in microwave applications. A couple of previous studies (Takata and Kageyama 1989; Sreemoolanadhan *et al* 1995) reported that most of the Ba-containing complex perovskites have positive  $\tau_f$ , while Sr-containing compounds have negative  $\tau_f$ . Thus, partial substitution of Ba for Sr in SrCa<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ceramics may be used to tune  $\tau_f$  through zero with little compromise on  $Q_u f_0$ ; therefore, in the present study, Ba was partially substituted for Sr in SrCa<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ceramics to adjust its  $\tau_f$  to near zero for possible microwave applications.

## 2. Experimental

Ceramics in the Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> (0 ≤ x ≤ 0.75) composition series were fabricated using a solid-state mixed oxide route. SrCO<sub>3</sub> (Aldrich, 99+%) and CaCO<sub>3</sub> (Aldrich, 99+%) were dried at  $\approx 185$  °C, while Nb<sub>2</sub>O<sub>5</sub> (Aldrich, 99.95%) and TiO<sub>2</sub> (Anatase, Aldrich, 99+%) were dried at  $\approx 900$  °C for 5 h to remove moisture prior to weighing in order to ensure the correct initial stoichiometry

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of the compounds. The dried carbonates and oxides were weighed in stoichiometric ratios and wet ball-milled for 24 h in disposable polyethylene mill jars, using Y-toughened ZrO<sub>2</sub> balls as grinding medium and 2-isopropanol as lubricant to make freely flowing slurries. The slurries were dried in an oven at  $\approx 95$  °C overnight. The resulting powders were sieved and calcined in air at 1300 °C for 6 h at a heating/cooling rate of 5 °C/min. The calcined powders were ground in a mortar and pestle for  $\approx 45$  min to dissociate agglomerates (if any). The powders were pressed into 4–5 mm thick and 10 mm diameter pellets at 80 MPa. The green pellets were placed on platinum foils and sintered in air at 1350–1500 °C for 4 h at a heating/cooling rate of 5 °C/min. Phase analysis of sintered crushed pellets was carried out using a Philips X-ray diffractometer operating at 30 kV and 40 mA at a scan speed of 1 °/min from  $2\theta = 10$ – $70^\circ$  with a step size of 0.02°. A STOE PSD X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.540598$  Å) was used for the measurement of lattice parameters. Bulk densities of the sintered pellets were measured using the Archimedes method. The theoretical densities of the compounds were calculated using (2)

$$\rho_{\text{th}} = ZM/VA_{\text{g}}, \quad (2)$$

where  $Z$  is the formula unit,  $M$  the molecular weight,  $V$  the volume of the unit cell and  $A_{\text{g}}$  the Avogadro number ( $6.022 \times 10^{23}$  atoms/mole).

Dense-sintered pellets were cut and finely polished before thermal etching for 30 min at temperatures  $\approx 10\%$  less than their corresponding sintering temperatures, at a heating/cooling rate of 5 °C/min. The etched surfaces of all the samples were gold-coated to avoid charging under the electron beam in the scanning electron microscope (SEM). A JEOL 6400 SEM operating at 20 kV was used for microstructural examination.

Microwave dielectric properties were measured using a R3767CH Agilent network analyser using cavity method proposed by Krupka *et al* (1998). The cylindrical pellets were placed on a low-loss quartz single crystal at the centre of an Au-coated brass cavity away from the walls of the cavity.  $\tau_{\text{r}}$  was measured by noting the temperature variation of the TE<sub>01 $\delta$</sub>  resonance at temperatures ranging from 20 to 80 °C using (3)

$$\tau_{\text{r}} = (f_2 - f_1)/f_1\Delta T, \quad (3)$$

where  $f_1$  and  $f_2$  are the resonant frequencies at 20 and 80 °C, respectively, and  $\Delta T$  the difference between the initial and final temperatures.

### 3. Results and discussion

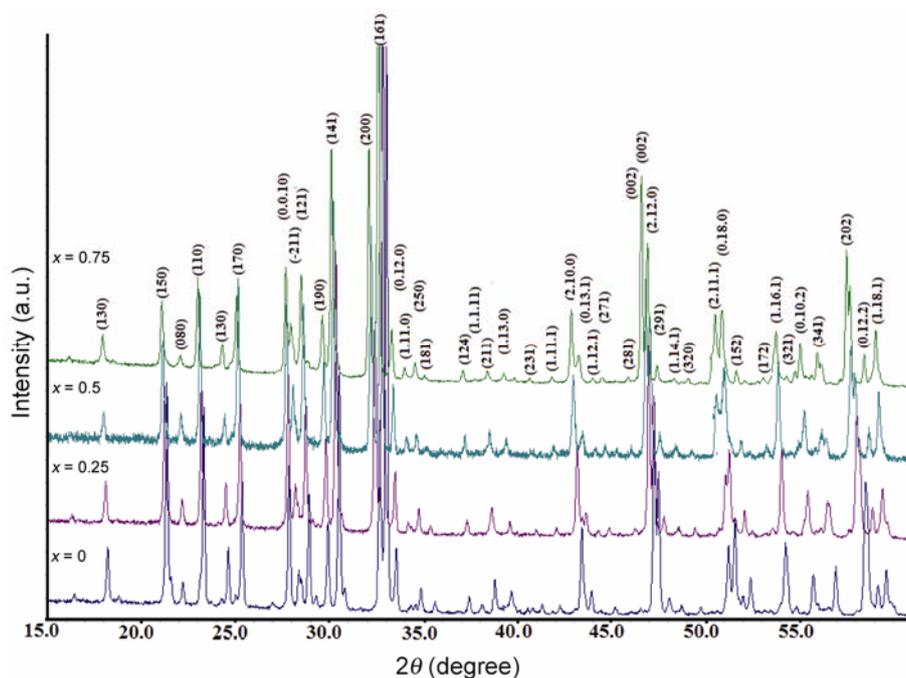
XRD patterns recorded from the optimally sintered (table 1) pulverized pellets of Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) ceramics are shown in figure 1. The reflections from all the compositions were identical and could be indexed according to the orthorhombic ( $Pnmm$ ) Sr<sub>5</sub>Nb<sub>4</sub>TiO<sub>17</sub> unit cell (PDF# 87-1170). There was no evidence of any second phase formation within the in-house XRD detection limit, which demonstrated the phase purity of all the sintered ceramics in the Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) composition series. The incorporation of large (1.61 Å) Ba ion for the relatively smaller (1.44 Å) Sr ion (Shannon 1976) at A-site of the Sr<sub>5</sub>Nb<sub>4</sub>TiO<sub>17</sub> unit cell resulted in an increase in the inter-planar spacings ( $d$ -values) and, hence, the volume of the unit cell. As expected, an appropriate shift was observed in the XRD peaks positions towards relatively larger  $d$ -values or lower  $2\theta$  angles with an increase in Ba<sup>2+</sup> concentration. The lattice parameters of the new Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) compounds were refined using least squares method and are given in table 1. Theoretical densities ( $\rho_{\text{th}}$ ) calculated from the XRD data also increased from 4.53 to 4.59 g/cm<sup>3</sup> with an increase in  $x$  from 0 to 0.75 due to the relatively higher ‘molecular weight to unit cell volume ratio’ ( $M_{\text{w}}/V$ ) for the compositions with  $x > 0$ . All the compounds in the Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) composition series sintered to  $> 95\%$  of the relevant theoretical density. The observed variation in the relative density ( $\rho_{\text{r}}$ ) of Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) ceramics as a function of sintering temperature is shown in figure 2. Consistent with a previous study (Sreemoolanadhan *et al* 1995), the optimum sintering temperatures of the Ba<sup>2+</sup>-substituted compositions were observed to be  $\approx 75$  °C lower than that of their Sr<sup>2+</sup> counterparts.

Figure 3 shows the secondary electron SEM images of thermally etched Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) samples. The sintered microstructure of all the ceramics in the Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) composition series comprised densely packed elongated and plate-like

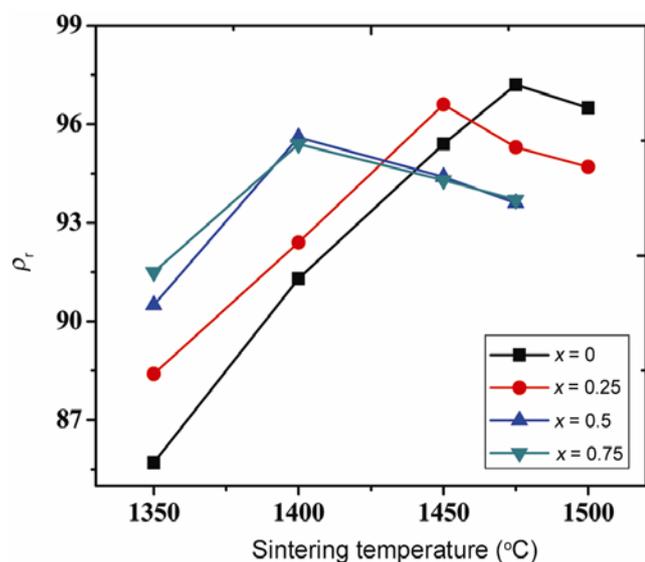
**Table 1.** Preparation conditions, lattice parameters, relative densities and microwave dielectric properties of Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) ceramics.

Composition (x)	S.T. (°C)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\rho_{\text{r}}$	$\epsilon_{\text{r}}$	$Q_{\text{u}}f_0$ (GHz)	$\tau_{\text{r}}$ (ppm/°C)
0	1475	5.536 (5)	32.150(7)	3.870(8)	97.6	47.2	11994	-78.6
0.25	1450	5.547(8)	32.188(6)	3.876(4)	96.6	49.3	10854	-40.3
0.5	1400	5.560 (10)	32.229 (7)	3.881 (9)	95.6	51.6	10160	-13.6
0.75	1400	5.585(9)	32.263 (6)	3.893(5)	95.4	54.2	9345	20.5

S.T., Sintering temperature and  $\rho_{\text{r}}$ , relative density.



**Figure 1.** XRD patterns from optimally sintered pulverized pellets of Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) ceramics, showing single-phase formation for all the investigated compositions.

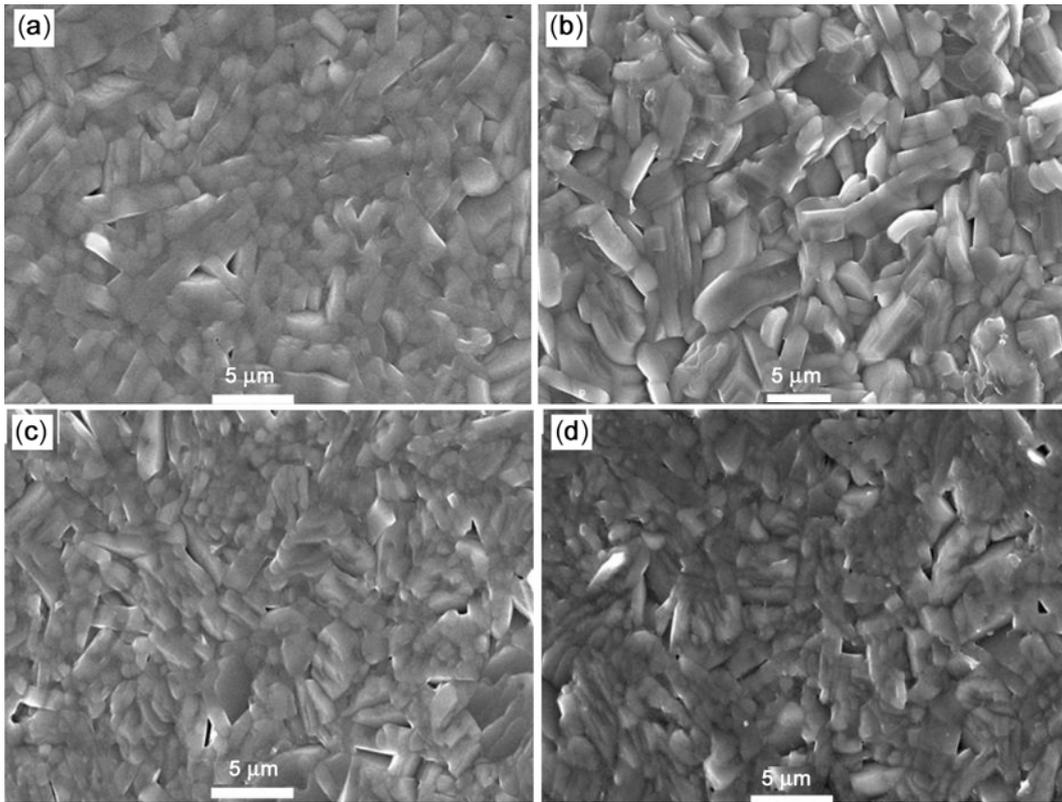


**Figure 2.** Variation of  $\rho_r$  with sintering temperature for ceramics in the Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) composition series.

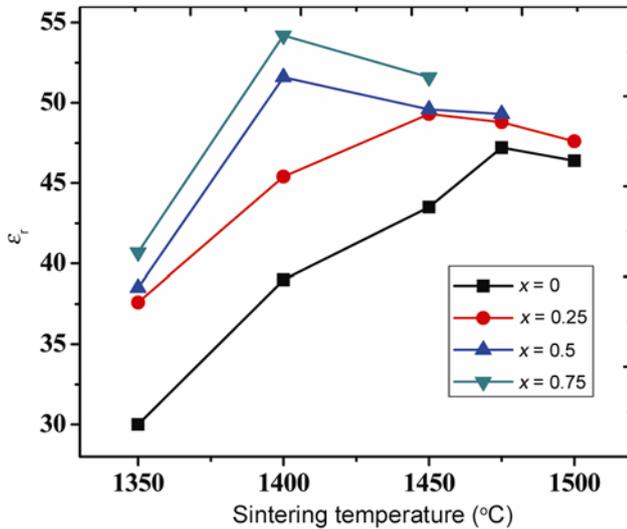
grains. The visibly homogeneous microstructure with no pores or voids appeared consistent with the calculated high relative density ( $\rho_{rel} > 95\%$ ) for the investigated ceramics.

The variation in microwave dielectric properties of Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) ceramics as a function of

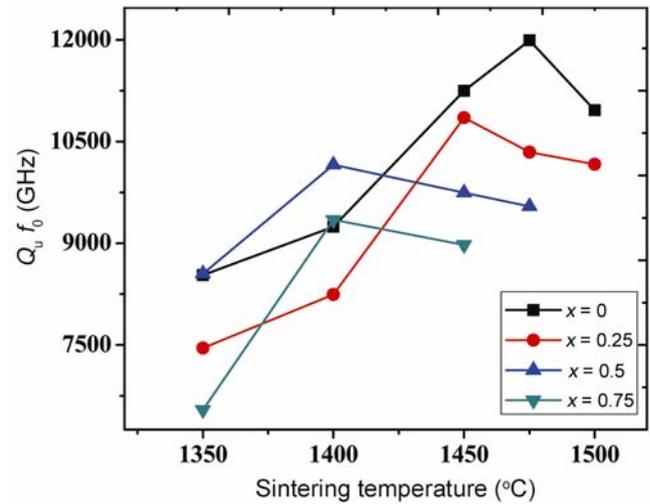
sintering temperature and Ba content is shown in figures 4 and 5, respectively. In general,  $\epsilon_r$  and  $Q_u f_0$  increase with an increase in the density of single-phase ceramics, which explains the observed increase in  $\epsilon_r$  and  $Q_u f_0$  with sintering temperature; however, when the apparent density began to fall,  $\epsilon_r$  and  $Q_u f_0$  also decreased with further increase in sintering temperature. To better understand the effect of Ba content on the microwave dielectric properties, the optimally sintered samples with  $\rho_{rel} > 95\%$  were selected, so that the effect of Ba substitution could be investigated. For optimally sintered Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $0 \leq x \leq 0.75$ ) ceramics,  $\epsilon_r$  linearly increased from 47.2 to 54, with an increase in Ba concentration from 0 to 0.75 (figure 6a). The observed increase in  $\epsilon_r$  may be due to the greater ionic dielectric polarizability of Ba<sup>2+</sup> ( $6.1 \text{ \AA}^3$ ) than that of Sr<sup>2+</sup> ( $4.24 \text{ \AA}^3$ ) (Shannon 1993). Alternatively,  $\epsilon_r$  may also increase with an increase in dipole moments and, hence, electric polarization as a result of unit cell enlargement due to Ba substitution for Sr (Sreemoolanadhan *et al* 1995). The observed monotonous increase in  $\epsilon_r$  as a function of Ba suggested the absence of any substitution-driven structural phase transitions in Sr<sub>1-x</sub>Ba<sub>x</sub>Ca<sub>4</sub>Nb<sub>4</sub>TiO<sub>17</sub>; however, an increase in atomic mass at the A-site increased the anharmonicity in the potential energy of the mean separation between ions which may affect the loss factor. The heavy Ba<sup>2+</sup> substituted for relatively lighter Sr<sup>2+</sup> may decrease the RF response of the ionic polarization, thereby increasing  $\tan \delta$  and this may be a possible reason for the observed



**Figure 3.** Secondary electron SEM images of optimally sintered  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $0 \leq x \leq 0.75$ ) ceramics: (a)  $x = 0$ , (b)  $x = 0.25$ , (c)  $x = 0.5$  and (d)  $x = 0.75$ , showing elongated and plate-like grain morphologies for all the investigated compositions.



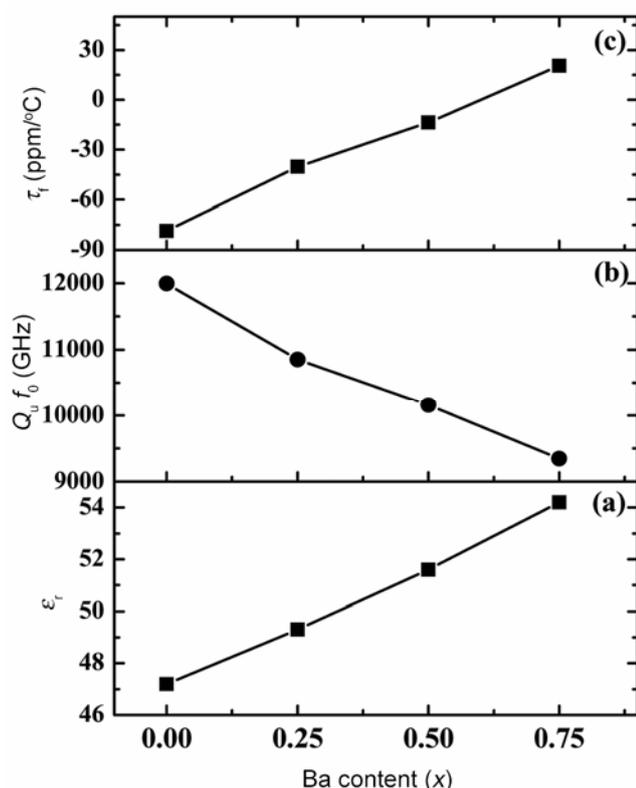
**Figure 4.** Variation of  $\epsilon_r$  of  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $0 \leq x \leq 0.75$ ) ceramics as a function of sintering temperature.



**Figure 5.** Variation of  $Q_u f_0$  of  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $0 \leq x \leq 0.75$ ) ceramics as a function of sintering temperature.

decrease in  $Q_u f_0$  with an increase in  $\text{Ba}^{2+}$  concentration (figure 6b). An increase in the ionic size difference at the A-site of the perovskite structure is known to increase the lattice strain, which affects  $Q_u f_0$  adversely (Iqbal *et al*

2011). The difference in the ion size between Ba and Ca is more than that of Sr and Ca at the A-site of the perovskite unit cell and, thus, Ba substitution in  $\text{SrCa}_4\text{Nb}_4\text{TiO}_{17}$  ceramics may cause an increase in the lattice strain which might decrease the  $Q_u f_0$  value as well.



**Figure 6.** Variation of (a)  $\epsilon_r$ , (b)  $Q_u f_0$  and (c)  $\tau_f$  of  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $0 \leq x \leq 0.75$ ) ceramics as a function of Ba concentration ( $x$ ).

The observed increase in  $\tau_f$  with increasing Ba concentration in the present study may be due to the resulting increase in the lattice constants.  $\tau_f$  is related to  $\tau_\epsilon$  (temperature coefficient of  $\epsilon_r$ ) and  $\alpha_L$  (coefficient of thermal expansion) by the relation given in (4)

$$\tau_f = -\tau_\epsilon/2 - \alpha_L. \quad (4)$$

In the present study,  $\tau_f$  of the optimally sintered samples was observed to increase from  $-78.6$  to  $20$  ppm/°C with an increase in Ba content from 0 to 0.75 (figure 6c). A relationship has been established between  $\tau_\epsilon$  and tolerance factor ( $\tau$ ) for complex perovskites and has been reported that the onset of structural phase transition was the major factor that influenced  $\tau_\epsilon$ ; however, no structural phase transitions were observed in the present study (Reaney *et al* 1994). Harrop (1969) investigated the relationship between  $\tau_c$  and  $\tau_f$  and reported a linear relationship between  $\epsilon_r$  and  $\tau_c$  and, therefore, also between  $\tau_f$  and  $\epsilon_r$ , which may probably explain the observed increase in  $\tau_f$ .

The microwave dielectric properties of  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $0 \leq x \leq 0.75$ ) ceramics, their sintering temperatures, relative densities and lattice constants are given in table 1. The best combination of microwave dielectric properties, i.e.  $\epsilon_r \approx 51.6$ ,  $Q_u f_0 \approx 10,160$  GHz

and  $\tau_f \approx -13.6$  ppm/°C, achieved in the present study, was for the  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $x = 0.5$ ) composition sintered at  $1400$  °C for 4 h.

#### 4. Conclusions

Single-phase >95% dense  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $0 \leq x \leq 0.75$ ) ceramics were fabricated via a solid-state sintering route. The optimum microwave dielectric properties, i.e.  $\epsilon_r \approx 51.6$ ,  $Q_u f_0 \approx 10,160$  GHz ( $5.37$  GHz) and  $\tau_f \approx -13.5$  ppm/°C, were achieved for  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $x = 0.5$ ) ceramics. An analysis of the present results indicates that  $\tau_f \approx 0$  ppm/°C,  $\tau_f \approx 53$  and  $Q_u f_0 \approx 10,000$  GHz could be achieved for ceramics in the  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  composition series at  $x = 0.6$ . The materials in the  $\text{Sr}_{1-x}\text{Ba}_x\text{Ca}_4\text{Nb}_4\text{TiO}_{17}$  ( $0 \leq x \leq 0.75$ ) solid solution may find application as cores in dielectrically loaded antenna.

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