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Effects of La_2O_3 additions on properties of $Ba_{0.6}Sr_{0.4}TiO_3$–MgO ceramics for phase shifter applications

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Abstract

Influence of La_2O_3 additions on the microwave dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) mixed with magnesium oxide ($w = 60\%$) composites was investigated. With increasing quantities of lanthanum oxide x (wt%), the lattice constant of BST–MgO material decreases to a minimum at $x = 0.4$ and then increases up to a maximum at $x = 1.0$. The XRD patterns analysis reveal that the solubility of MgO in BST is influenced by the amount of La_2O_3 doping. SEM observations show that the BST grain sizes decrease with increasing amounts of La_2O_3. The dielectric properties of BST–MgO–La_2O_3 indicate that La_2O_3 additives shift the Curie point towards lower temperatures. Optimum doping amount of La_2O_3 can reduce the high frequency loss tangents of BST–MgO compound which also can ensure the moderate dielectric constant and tunability. Excessive doping of La_2O_3 tends to significantly lower dielectric constant and deteriorate tunability. When the doping amount of La_2O_3 is 0.2 wt%, BST–MgO composite has the following properties: dielectric constant = 94.05, $\tan\delta = 0.012$ (at 2.853 GHz) and the dielectric constant tunability = 16.26% (under electric field 3.57 kV/mm), which is suitable for ferroelectric phase shifter.

Keywords: $BaTiO_3$ and titanates; Dielectric property; Tunability

1. Introduction

Barium-strontium titanate, $Ba_{1-x}Sr_xTiO_3$ [BST, $0 \le x \le 1$] has been investigated with considerable interest as a new dielectric material for tunable microwave application.[1,2] The large electrical field dependent dielectric constant can be used for tunable devices, such as tunable oscillators, phase shifters and varactors.[3–5] In phase shifters, it is desirable to have a low permittivity for good impedance matching, a low dielectric loss to minimize the insertion losses of devices, and a high dielectric tunability, which is the change of permittivity with dc field, for less power driving and high speed of phase shift. Many studies have been done to reduce the dielectric constant and loss tangent. Mg-doped BST bulk ceramics were reported to possess low loss tangents, low dielectric constant and suitable tunability.[6–8] The effects of 0.5 mol.% of various rare earth oxide dopants on 40 wt% $Ba_{0.6}Sr_{0.4}TiO_3$, 60 wt% MgO (BSTM) had been studied.[9] It shows that the composite is tunable with very low loss insertion and can be used over a wide range of frequencies. The most interesting aspect is that La_2O_3 additions can improve the tunability from 9.23% to 14.70% at 2 kV/mm. In this paper, the effects of La_2O_3 additive on the dielectric properties of BSTM were further investigated. In addition, the X-ray diffraction (XRD) and the scanning electron microscopy (SEM) analysis were also employed to study the crystal structures and the microstructure of the ceramics.

2. Experimental procedure

Samples were prepared by the conventional solid-state reaction. High purity (above 99.9%) $BaCO_3$, $SrCO_3$, TiO_2, were weighed and mixed according to the composition $Ba_{0.6}Sr_{0.4}TiO_3$ using alcohol and zirconia milling media for 3 h. After drying, the mixtures were calcined in an alumina crucible at 1200 °C for 3 h in air. Then 60 wt% MgO and different amounts of La_2O_3 were added to the calcined BST. The materials were re-milled and then dried. The mixtures were re-calcined at 1200 °C for 3 h in air, then re-milled and dried. PVA binder was added and powders pressed at 100 MPa into disks of two different sizes. One was 15 mm in diameter and a thickness of 7–10 mm, the other

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was 20 mm in diameter and a thickness of 1.5 mm. The samples were sintered at 1550 °C for 2 h with a heating rate of 100 °C/h in air. The thin sintered samples were polished to 1 mm in thickness and electrodes printed using silver ink. The bulk samples densities were measured by Archimedes' method.

Microstructures of the sintered samples were examined by scanning electron microscope (SEM, JSM-5610LV). X-ray diffraction (XRD, RIGAKU D/MAX-IIIA, Japan) with Cu Kα radiation was used for phase identification. The low frequency dielectric properties were measured using a TH2613A capacitance meter coupled with a 3000 V dc power supplier. The microwave dielectric properties were measured using dielectric post resonator technique developed by Hakki and Coleman.[10]

3. Results and discussions

3.1. Microstructure

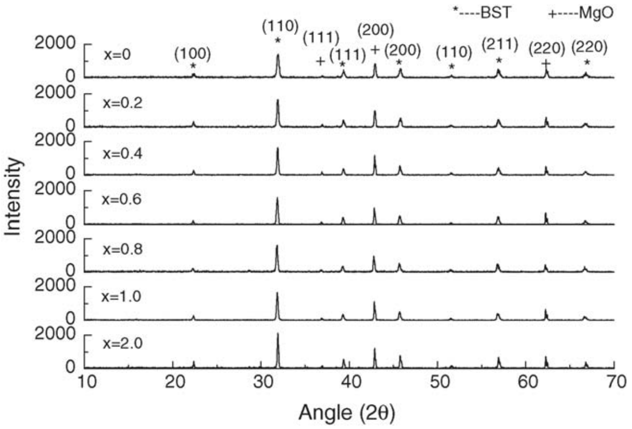

Fig. 2. XRD patterns of x wt% La_2O_3 doped BSTM.

The SEM micrographs of x wt% La_2O_3 doped BSTM ceramics sintered at 1550 °C are shown in Fig. 1. Two phases were observed in the SEM micrographs. The MgO resides in the grain boundary. The grain of BSTM decreased slightly by small additions of La_2O_3, as illustrated in Fig. 1a–e. Nevertheless, substantial grain growth suppression is observed for La_2O_3 concentrations larger than 2 wt%, as shown in Fig. 1f. XRD patterns of BSTM–x wt% La_2O_3 ($0 \leq x \leq 2.0$) ceramics are shown in Fig. 2. The XRD results clearly show that the main phases in all La_2O_3 doped samples are BST and MgO. Full width at half maximum of the most intense diffraction peaks increases with

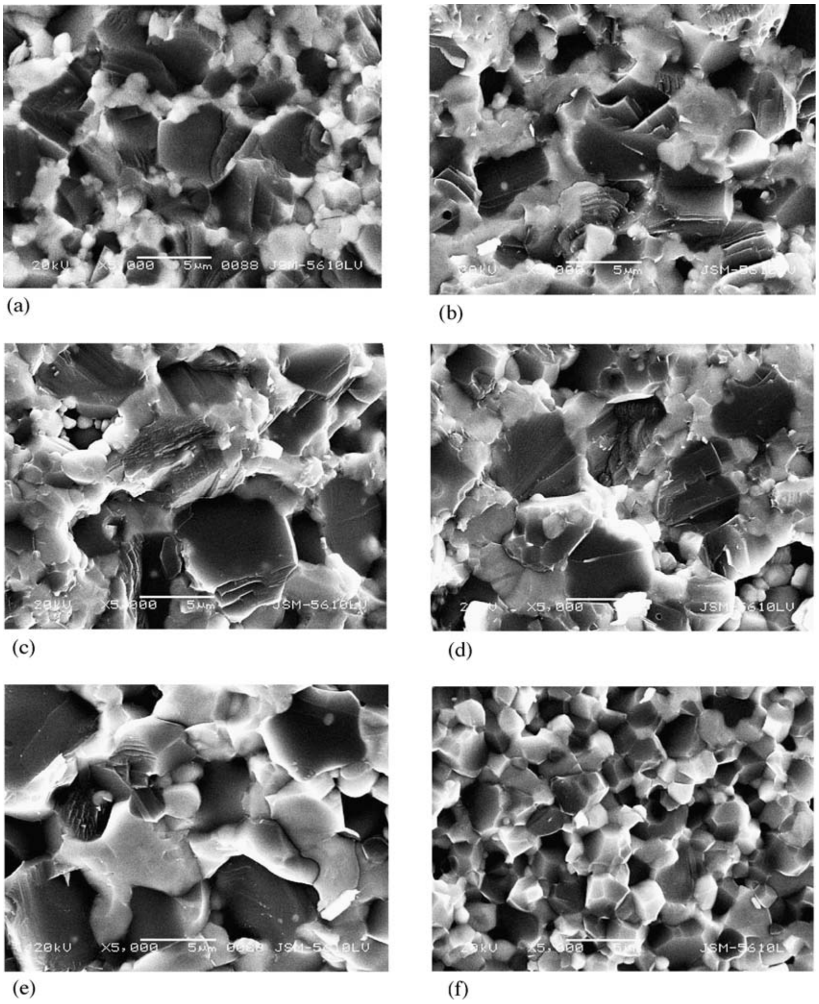

Fig. 1. SEM micrographs of BSTM sintered at 1550 °C with La_2O_3 added where (a) 0 wt%, (b) 0.2 wt%, (c) 0.4 wt%, (d) 0.8 wt.%, (e) 1.0 wt.% and (f) 2.0 wt%.

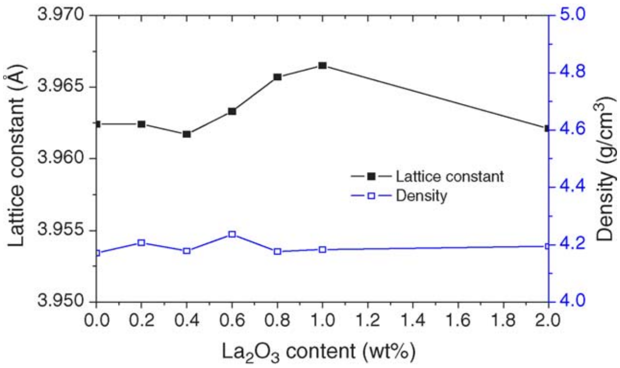

Fig. 3. The variation of lattice constant and bulk density with amounts of La_2O_3 added into BSTM.

increasing La content. This peak broadening indicates a decrease in grain size. The perovskite structure is preserved despite the addition of La_2O_3. Fig. 3 shows the variation of lattice constant and bulk density as a function of the addition of La_2O_3 sintered at 1550 °C. With increasing the amount of La_2O_3 addition, the lattice constant initially decreases to a minimum at $x = 0.4$ wt%, and then increases again to a maximum at $x = 1.0$ wt%. Further additions of La_2O_3 decrease the lattice constant. Densities are not significantly affected by addition of La_2O_3.

In an ideal cubic perovskites ABO_3, the coordination numbers of the A- and B-sites are 12 and 6, respectively, $t = 0.77–1.1$. The ionic radii of Ba, Sr, Ti, O, Mg and La are summarized as follows: A-site (12 coordinate): $Ba^{2+} = 1.61$ Å, $Sr^{2+} = 1.58$, $La^{3+} = 1.36$; B-site (6 coordinate): $Mg^{2+} = 0.72$, $Ti^{4+} = 0.605$, $La^{3+} = 1.032$; $O^{2-} = 1.40$.[11] Accordingly, the Mg^{2+} would occupy the B sites of the perovskite structure. La^{3+} is too large for the B-site and would occupy the A-sites with Ba^{2+} and Sr^{2+}. When La^{3+} and Mg^{2+} substitute A- and B-site, respectively, the incorporation reactions are as follows:

$$\mathrm{MgO} \Leftrightarrow \mathrm{Mg}''_{\mathrm{Ti}} + \mathrm{V}_{\mathrm{O}}^{\bullet\bullet} + \mathrm{O}_{\mathrm{O}} \tag{1}$$

$$\mathrm{La_2O_3} \Leftrightarrow 2\mathrm{La}^{\bullet}_{\mathrm{Ba}} + \mathrm{V}''_{\mathrm{Ba}} + 3\mathrm{O}_{\mathrm{O}} \tag{2}$$

$$\mathrm{null} \Leftrightarrow \mathrm{V}_{\mathrm{O}}^{\bullet\bullet} + \mathrm{V}''_{\mathrm{Ba}} \tag{3}$$

$$2\mathrm{O}_{\mathrm{O}} \Leftrightarrow \mathrm{O}_2 \uparrow + \mathrm{V}_{\mathrm{O}}^{\bullet\bullet} + 2\mathrm{e}' \tag{4}$$

The measured XRD intensity ratios of $I_{MgO(2\,0\,0)}/I_{BST(1\,1\,0)}$ of samples are 0.62, 0.61, 0.54, 0.55, 0.56, 0.57, 0.52, respectively. $I_{MgO(2\,0\,0)}$ and $I_{BST(1\,1\,0)}$ are the XRD intensity for MgO(2 0 0) peak and BST(1 1 0) peak, With increasing content of La_2O_3, the rate of $I_{MgO(2\,0\,0)}$ and $I_{BST(1\,1\,0)}$ simulated the same trend as the variation in lattice constant. In addition, the amount of second phase-MgO changed with the doping of La_2O_3. As mentioned above, La^{3+} would occupy A-site and Mg^{2+} would substitute B-site in perovskite structure. Therefore, the changes of lattice constant are determined by the cation substitution. B-site substitution of the Ti ions by the larger Mg^{2+} cations will cause the increase of the lattice parameter. The decrease in lattice parameter can be attributed to A-site substitution of Ba and Sr ions by the smaller La^{3+} ions. La_2O_3 addition results in a decrease in oxygen vacancy, based on reaction Eqs. (1)–(3). Deficiency of oxygen vacancies can causes more Ti^{4+} substituted by Mg^{2+}. It is confirmed by XRD, the XRD pattern shows the intensity ratio of $I_{MgO(2\,0\,0)}/I_{BST(1\,1\,0)}$ decreases after La_2O_3 doping. However, when doped with small amounts of La_2O_3, not exceeding the solubility limit of Mg in BST, the $I_{MgO(2\,0\,0)}/I_{BST(1\,1\,0)}$ changed slightly. The lattice constant variation depends on the dominant ionic substitution. When La_2O_3 additive less than 0.4 wt%, there is more La^{3+} substituted Ba^{2+} and Sr^{2+}. The lattice constant decrease with increasing of La_2O_3 and reach to the minimum at $x = 0.40$ wt%. Keeping increase the La doping will increase MgO solubility. There are more Ti^{4+} are substituted by Mg^{2+}. It is a dominant ionic substitution when La_2O_3 additive is more than 0.4 wt%. The lattice constant increases with the increasing of doping and reaches to a maximum at the 1.0 wt%. However, further increasing the additive of La_2O_3 will cause an increase in oxygen vacancies, based on reactive Eq. (4). Higher concentration of oxygen vacancy prevents further substitution of Ti^{4+} by Mg^{2+}. It stops the increment of lattice constant. Higher doping of La_2O_3 also change the solubility of MgO, the XRD pattern shows a decrease of the intensity ratios of $I_{MgO(2\,0\,0)}/I_{BST(1\,1\,0)}$ at $x = 2.0$ wt%.

3.2. Dielectric properties

Table 1 shows dielectric properties of the ceramics at 10 kHz. The dielectric tunability of the ceramics is defined as $\{C(0) - C(E)\}/C(0)$, where C is the capacitance and E is the applied dc electric field. The dielectric constant of pure BST is ~3680. The addition of non-ferroelectric oxide MgO and La_2O_3 will cause a dramatic decrease in the relative permittivity of BST. As the content of La_2O_3 increased, from 0.2 wt% to 2 wt%, the relative dielectric constant ε_r decreased from 154.39 to 58.23, while the loss reduced and the tunability decreased.

The change in the dielectric constant and tunability with the La_2O_3 addition is correlated with the change in the phase transition peak with La_2O_3. Fig. 4 shows the temperature depen-

Table 1
Dielectric properties of the BSTM with addition of x wt% La_2O_3 at 10 kHz and 20 °C

La_2O_3 content (wt%)	Relatively dielectric constant, ε_r	Loss tangent	Tunability (%)	dc electric field (kV/mm)
$x = 0$	167.26	0.0005	18.36	2.976
$x = 0.2$	154.39	0.0006	16.26	3.571
$x = 0.4$	137.62	0.0006	12.00	3.125
$x = 0.6$	121.10	0.0006	10.77	3.289
$x = 0.8$	113.91	0.0006	8.12	3.125
$x = 1.0$	76.14	0.0005	3.60	2.659
$x = 2.0$	58.23	0.0004	<1.00	>3.000

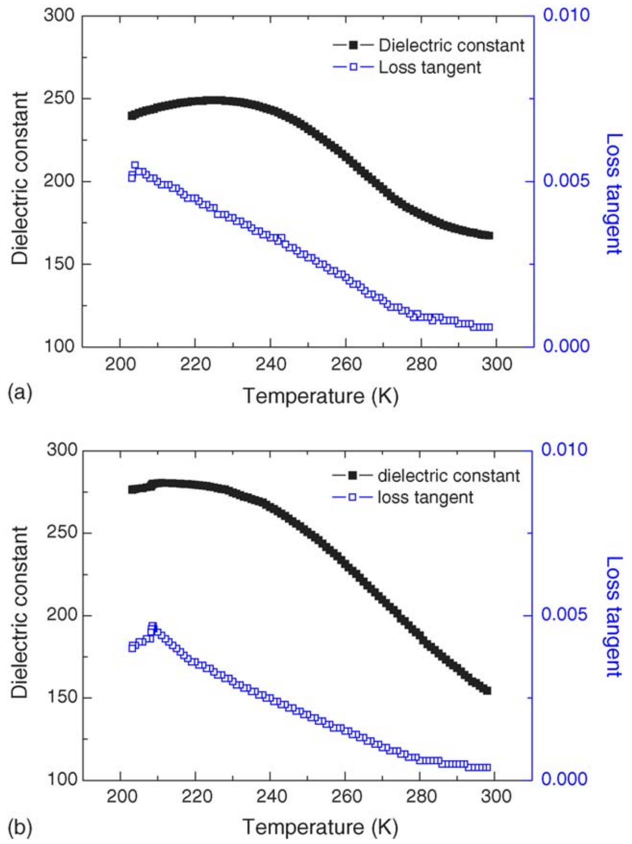

Fig. 4. Temperature dependence of the dielectric constant and loss of BSTM sintered at 1550 °C (a) without La_2O_3 additive, (b) with addition of 0.2 wt% La_2O_3.

dence of the dielectric constant and loss tangent of BSTM and BSTM–0.2 wt% La_2O_3. With La_2O_3 additions, the dielectric constant maximum (k_{max}) is shifted towards lower temperatures, also becoming very broad. K_{max} for BSTM ceramics is −30 °C (Fig. 4a), while 0.2 wt% La_2O_3 doped BSTM ceramic shows peak maximum at −60 °C (Fig. 4b). La^{3+} substitution broadens and shifts k_{max} to a lower temperature in BSTM ceramic. So the dielectric constant and loss decreased with increasing content of La_2O_3. The change in permittivity with dc electric field is associated with the anharmonic interactions of Ti^{4+} ions. With the addition of La_2O_3, the ferroelectricity and interactions of Ti^{4+} ions weakened, it causes the decrease of tunability.

Table 2
Dielectric properties of the BSTM with addition of x wt% La_2O_3 at microwave frequency and 20 °C

La_2O_3 content (wt%)	Relatively dielectric constant, ε_r	Measure frequency (GHz)	Loss tangent, tan δ
$x = 0$	112.51	2.756	0.015
$x = 0.2$	94.05	2.853	0.012
$x = 0.4$	85.73	2.973	0.011
$x = 0.6$	76.56	3.153	0.009
$x = 0.8$	70.13	3.273	0.007
$x = 1.0$	64.73	3.333	0.006
$x = 2.0$	44.84	4.357	0.003

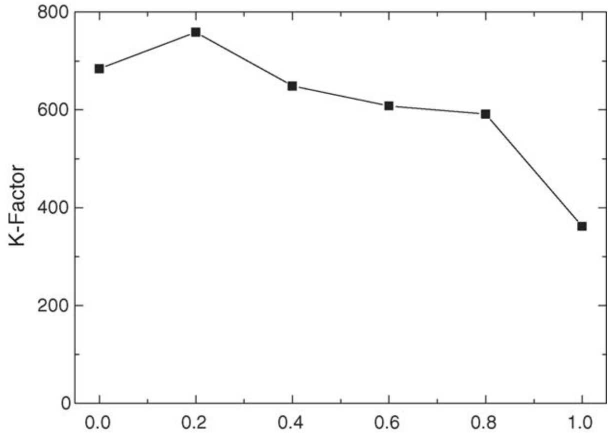

Fig. 5. The change in K-factor with addition of La_2O_3 to BSTM ceramics at 2.2 kV/mm.

The dielectric properties of the samples at microwave frequency are shown in Table 2. The dielectric constant decreases and loss increases at X-band compared with the properties at 10 kHz. It is due to relaxation of polarization mechanisms at higher frequencies. With the increase of La_2O_3 additive, the dielectric constant and loss tangent decrease. When doped with >1 wt% La_2O_3, the dielectric constant and dielectric losses are low, but the tunability is also adversely affected.

A figure of merit[12] often used to evaluate a ferroelectric RF material is given as

$$K\text{-factor} = \frac{\text{tunability}}{\tan\delta} \times 100$$

The K-factors of BSTM with La_2O_3 additions at 2.2 kV/mm bias condition are showed in Fig. 5. It indicates that K-factor first increases with small amount of La_2O_3, then decreases with more La_2O_3 additive. This result suggests that BSTM with 0.2 wt% La_2O_3 additive should perform better than BSTM. Otherwise its dielectric constant is lower than BSTM, so it is a better candidate for phase shifter.

4. Conclusions

The microstructure and dielectric properties of 40 wt% $Ba_{0.6}Sr_{0.4}TiO_3$–60 wt% MgO ceramic composites doped with La_2O_3 have been discussed. La_2O_3 additions suppressed the grain growth especially at 2 wt%. XRD analysis revealed there were only BST and MgO phases in La_2O_3 doped BSTM ceramics. With increasing amount of La_2O_3, the lattice constant of BSTM showed non-monotonic behavior. Excess La_2O_3 changed the solubility of MgO in BST. The dielectric constant and loss tangent decreased with increasing additions of La_2O_3, while the tunability decreased. With increasing of La_2O_3 content, the K-factor reached maximum at 0.2 wt%, then decreased monotonously. With 0.2 wt% La_2O_3 additive, the ceramic was suitable for phase shifter with the following properties: $\varepsilon_r = 94.05$, $\tan\delta = 0.012$ (at 2.853 GHz), and tunability = 16.26% (at 3.57 kV/mm).

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References

1. Sengupta, L. C. and Drach, W. C., Investigation of the electric properties of doped $Ba_{1-x}Sr_xTiO_3$ phase shifting materials. *Ferroelectrics*, 1994, **153**, 359–364.
2. Hui, C., Xu, A. L. and Gao, S. H., A novel BSTO electro-optic phase shifters for phase array antennas. *J. Xidian University*, 1999, **26**, 514–518.
3. Mueller, C. H., Romanofsky, R. R. and Miranda, F. A., Ferroelectric thin film and broadband satellite systems. *IEEE Potentials*, 2001, **20**, 36–39.
4. Gevorgian, S. S. and Kollberg, E. L., Do we really need ferroelectrics in paraelectric phase only in electrically controlled microwave devices? *IEEE Trans. Microwave Theory Tech.*, 2001, **49**, 2117–2124.
5. Korn, D. S. and Wu, H. D., Comprehensive review of microwave system requirements on thin-film ferroelectrics. *Int. Ferroelectr.*, 1999, **24**, 215–237.
6. Chang, W. and Sengupta, L. C., MgO-mixed $Ba_{0.6}Sr_{0.4}TiO_3$ bulk ceramics and thin films for tunable microwave applications. *J. Appl. Phys.*, 2002, 92.
7. Sengupta, L.C., Ngo, E., O'Day, M.E., Stowell, S. and Lancto, R., Fabrication and characterization of barium strontium titanate and non-ferroelectric oxide composites for use in phased antennas and other electronic devices. In *ISAF '94, Proceedings of the Ninth IEEE International Symposium on Applications of Ferroelectrics*, 7 August 1991, pp. 622–625.
8. Sengupta, L.C. *et al.*, *Ceramics Ferroelectric Composite Material-BSTO-MgO*. U.S. Patent 5427988.
9. Chiu, L.H., Sengupta, L.C. and Sengupta, S. *et al.*, *Ceramic ferroelectric composite for waveguides in phased array antennae, dielectrics in capacitors etc., comprises barium strontium titanate, compound of magnesium and oxygen, and rare earth oxide*. U.S. Patent 6074971, 2000-06-13.
10. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive capacitance in the millimeter range. *IRE Trans. Microwave Theory Tech.*, 1960, 402–410.
11. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, 1976, **A32**, 751–767.
12. Feteira, A., Sinclair, D. C., Reaney, I. M., Somiya, Y. and Lanagan, M. T., $BaTiO_3$-based ceramics for tunable microwave applications. *J. Am. Ceram. Soc.*, 2004, **87**, 1082–1087.