Microwave dielectric properties of MO–La2O3–TiO2 (M = Ca, Sr, Ba) ceramics

— Source link ⬈

I N Jawahar, Narayana Iyer Santha, Mailadil Thomas Sebastian, Pezholil Mohanan

Institutions: Council of Scientific and Industrial Research, Cochin University of Science and Technology

Related papers:

- Dielectric polarizabilities of ions in oxides and fluorides

- Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides

- A Dielectric Resonator Method of Measuring Inductive Capacities in the Millimeter Range

- Microwave dielectric properties of hexagonal perovskites

- Microwave ceramics for resonators and filters

Microwave dielectric properties of MO–La$_2$O$_3$–TiO$_2$ (M = Ca, Sr, Ba) ceramics

Isuhak Naseemabeevi Jawahar, Narayana Iyer Santha, and Mailadil Thomas Sebastian[a)]
Regional Research Laboratory, Council of Scientific and Industrial Research, Trivandrum, 695 019, India

Pezholil Mohanan
Department of Electronics, Cochin University of Science and Technology, Cochin 682 022, India

Single-phase polycrystalline ceramics in the MO–La$_2$O$_3$–TiO$_2$ (M = Ca, Sr, Ba) system, such as cation-deficient hexagonal perovskites CaLa$_4$Ti$_4$O$_{15}$, SrLa$_4$Ti$_4$O$_{15}$, BaLa$_4$Ti$_4$O$_{15}$, and Ca$_2$La$_4$Ti$_5$O$_{18}$ and the orthorhombic phases CaLa$_4$Ti$_5$O$_{17}$ and CaLa$_8$Ti$_9$O$_{31}$, were prepared through the solid-state ceramic route. The phases and structure of the ceramics were analyzed through x-ray diffraction and scanning electron microscopy. The microwave dielectric properties of the ceramics were studied using a network analyzer. The investigated ceramics show high ϵ_r in the range 42 to 54, high quality factors with $Q \times f$ in the range 16,222 to 50,215 GHz, and low τ_f in the range −25 to +6 ppm/°C. These high dielectric constant materials with high $Q \times f$ up to 50,215 GHz are suitable for applications where narrow bandwidth and extremely low insertion loss is necessary, especially at frequencies around 1.9 GHz.

I. INTRODUCTION

The dramatic advancements during the last two decades in the microwave integrated circuit technology have brought a revolution in telecommunication systems. Dielectric resonators (DRs) provide a compact, low-cost, and highly reliable choice as resonator elements in microwave circuits, and they now replace the conventional metallic cavity and microstrip resonators more frequently than ever before. The size of the microwave circuit is inversely proportional to the square root of its dielectric constant. The constraints due to size, frequency of operation, frequency stability, and selectivity allow only those materials with high dielectric constant (20–100), high Q factor (>2000), and low temperature coefficient of resonant frequency ($\tau_f < \pm 20$ ppm/°C) for DR applications.

Most of the commercial DRs available at present fall into two groups: (i) ceramics with low dielectric constant ($20 < \epsilon_r < 40$) and high Q factor ($Q \times f > 50,000$ GHz) such as Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$, Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$, their solid-solution modifications, Ba$_2$Ti$_9$O$_{20}$, (Zr,Sn)TiO$_4$, etc.; (ii) ceramics with high dielectric constant (>65) and low Q factor ($Q \times f < 10,000$), such as the tungsten–bronze type materials in the BaO–RE$_2$O$_3$–TiO$_2$ system. Though high dielectric constant materials can give better miniaturization, the applications requiring narrow bandwidth and

extremely low insertion loss (0.3 dB) enables the use of ceramics having even $\epsilon_r = 38$.[1] Dielectric materials with $\epsilon_r > 40$ and $Q \times f > 45,000$ GHz can allow for further miniaturization of the devices without much compromise in quality. Materials with ϵ_r in the range 40 to 65 suitable for such applications are few, and the search for such materials is one of the current areas of research in microwave dielectrics. The Ba$_5$Nb$_4$O$_{15}$-type cation-deficient hexagonal perovskites are characterized by high dielectric constant and high quality factor. The microwave dielectric properties of Ba$_5$Nb$_4$O$_{15}$, Ba$_{5-x}$Sr$_x$Nb$_4$O$_{15}$, Ba$_5$Ta$_4$O$_{15}$, and (Ba,La)$_n$Ti$_{n-1}$O$_{3n}$ (n = 5, 6) have already been reported.[2–6] The ceramics are characterized by high dielectric constants up to 50.6 and $Q \times f$ up to 44,000 GHz. Veneis *et al.*[3] reported the microwave dielectric properties of BaLa$_4$Ti$_4$O$_{15}$ and Ba$_2$La$_4$Ti$_5$O$_{18}$, and the ceramics show high dielectric constants and quality factors with small temperature coefficients of resonant frequency.[3] In the present paper, we report the preparation, characterization, and microwave dielectric properties of the cation-deficient hexagonal phases (M,La)$_n$Ti$_{n-1}$O$_{3n}$ (M = Ca, Sr, Ba; n = 5, 6) and the orthorhombic type CaLa$_4$Ti$_5$O$_{17}$, Ca$_2$La$_4$Ti$_6$O$_{20}$, and CaLa$_8$Ti$_9$O$_{31}$ ceramics belonging to the CaO–La$_2$O$_3$–TiO$_2$ system. The microwave dielectric properties of the Ca- and Sr-based ceramics are reported for the first time.

The (M,La)$_n$Ti$_{n-1}$O$_{3n}$ (M = Ca, Sr, Ba; n = 5, 6) ceramics, i.e., CaLa$_4$Ti$_4$O$_{15}$, SrLa$_4$Ti$_4$O$_{15}$, BaLa$_4$Ti$_4$O$_{15}$, and Ca$_2$La$_4$Ti$_5$O$_{18}$, crystallize in a hexagonal

[a)]e-mail: mailadils@yahoo.com

structure.[7–12] The above compounds belong to the cation-deficient hexagonal perovskite family A$_n$B$_{n-1}$O$_{3n}$ (n = 5, 6, or 8) where the M and La ions occupy the A sites, and Ti ions occupy the B sites. The crystal lattice of the cation-deficient perovskite-related phases A$_n$B$_{n-1}$O$_{3n}$ (n = 5, 6, 8) can be derived from the basic perovskite structure by the periodic introduction of intrinsic stacking faults in the cubic close packing of the AO$_3$ mixed layers with hexagonal structure. Alternatively, the structure may be defined as consisting of identical perovskite like blocks of n corner sharing octahedra where successive blocks are shifted by $1/3 \langle 10\bar{1}0 \rangle$ vector. One nth of the octahedral holes are kept vacant in such a way that B cations are omitted from the face sharing octahedral holes to form the cation-deficient structure. The A site ions are 12-fold coordinated whereas B site ions are 6-fold coordinated. The lattice parameters and the atom positions of the homologous phases BaLa$_4$Ti$_4$O$_{15}$ and Ba$_2$La$_4$Ti$_5$O$_{18}$ were precisely determined by Harre *et al.*[10,11] based on single-crystal x-ray diffraction (XRD) and later confirmed by neutron diffraction studies.[12]

II. PREPARATION AND CHARACTERIZATION

The ceramics were prepared through the solid-state ceramic route. High-purity CaCO$_3$ (99+%), BaCO$_3$ (99+%), and SrCO$_3$ (99.9%), and TiO$_2$ (99.9%) (Aldrich Chemicals Company, Inc., Milwaukee, WI) were used as the starting oxide powders. La$_2$O$_3$ (99.99%, Indian Rare Earths, Kerala, India) was heated at 1000 °C for 3 h before weighing to remove any hydroxides. The powders were weighed according to the stoichiometry and ball milled in distilled water medium for 24 h in a plastic bottle using zirconia balls. The wet mixed powder was dried and calcined at 1200 °C for 4 h, then ground and again calcined at 1400–1450 °C for 4 h. The calcined mixture was ground well. Then 3 wt% PVA was added as the binder, the powder was mixed, dried, and again ground. The resultant fine powder was uniaxially pressed in a tungsten carbide die under a pressure of 150 MPa such that the pressed disks were 6–8 mm high and 14 mm in diameter. Stearic acid was used as a lubricant. The green pellets were sintered at different temperatures in the range 1500–1675 °C for 4 h. The sintering temperatures were optimized for maximum density. The sintered samples were typically annealed at 1400–1450 °C for 12 h to minimize the reduction of titanium ions. The sintered pellets were polished well, and the bulk densities were measured using the Archimedes method. The phase purity of the sintered samples was studied by XRD using a Rigaku x-ray diffractometer (Dmak 1C, Tokyo, Japan). The surface morphology of the samples was studied using scanning electron microscopy (SEM). The sintered samples were thermally etched at temperatures 50 °C lower than their respective sintering temperature for 30 min and were used for recording SEM.

The microwave dielectric properties were measured using an HP 8510C network analyzer (Hewlett-Packard, Palo Alto, CA). The microwave dielectric constant was measured by the dielectric post resonator method suggested by Hakki and Coleman and modified by Courtney.[13,14] The resonator was placed between two gold-coated copper metallic plates, and microwave energy was coupled through E-field probes to excite various resonant modes. Among the various resonant modes, the TE$_{011}$ mode was selected for the measurement. The quality factors of the samples were measured at the TE$_{018}$ mode resonant frequency using a transmission mode cavity.[15] The temperature coefficient of resonant frequency (τ_f) was measured from the slope of the graph plotted between resonant frequency and temperature. The measurement is usually done in the range 20–80 °C.

III. RESULTS AND DISCUSSION

The ceramics were sintered into dense bodies. The percentage densities of the sintered samples are given in Table I. The MaLa$_4$Ti$_4$O$_{15}$ (M = Ca, Sr, Ba) ceramics show densities in the range 95–98% of their theoretical densities, whereas Ca$_2$La$_4$Ti$_5$O$_{18}$ shows only 93.6% of its theoretical density. The CaLa$_4$Ti$_5$O$_{17}$ and CaLa$_8$Ti$_9$O$_{31}$ were densified to 98.2% and 92.1% of their respective theoretical densities. The BaLa$_4$Ti$_4$O$_{15}$ ceramic was sintered well at 1550 °C for 4 h, whereas its strontium counterpart was sintered well at 1625 °C for 2 h. The calcium-based compounds were sintered into dense bodies in the temperature range 1650–1670 °C for 4 h.

A. XRD and SEM analysis

The XRD patterns recorded for the ceramics were compared with standard data.[16] The XRD patterns of the MLa$_4$Ti$_4$O$_{15}$ (M = Ca, Sr, Ba) and Ca$_2$La$_4$Ti$_5$O$_{18}$ ceramics are shown in Fig. 1, and those of the orthorhombic CaLa$_4$Ti$_5$O$_{17}$ and CaLa$_8$Ti$_9$O$_{31}$ are shown in Fig. 2. The obtained compounds were phase pure. The CaLa$_4$Ti$_4$O$_{15}$, BaLa$_4$Ti$_4$O$_{15}$, and SrLa$_4$Ti$_4$O$_{15}$ ceramics

TABLE I. Microwave dielectric properties of MO–La$_2$O$_3$–TiO$_2$ ceramics (M = Ca, Sr, Ba).

Material	Percentage density	ϵ_r	ϵ_r (corrected)	τ_f (ppm/°C)	Q_0	f (GHz)	$Q_0 \times f$ (GHz)
CaLa$_4$Ti$_4$O$_{15}$	95.2	41.6	44.7	−25	8100	4.31	34911
SrLa$_4$Ti$_4$O$_{15}$	98.0	43.8	45.1	−14	12100	4.15	50215
BaLa$_4$Ti$_4$O$_{15}$	96.2	46.3	49.1	−13	3150	5.15	16222
Ca$_2$La$_4$Ti$_5$O$_{18}$	93.6	44.7	49.3	+6	4800	4.19	20112
CaLa$_4$Ti$_5$O$_{17}$	98.2	53.7	55.2	−20	4730	3.67	17359
CaLa$_8$Ti$_9$O$_{31}$	92.1	48.6	54.9	−6	5300	3.65	19345

crystallized in a hexagonal structure, and the close similarity of their XRD patterns is well evident in Fig. 1. The calculated lattice parameters were found to agree closely with the reported values. The pattern recorded for $BaLa_4Ti_4O_{15}$ was indexed by doubling the unit cell along the c axis to account for some very weak maxima in the pattern so that the unit cell contains ten perovskite layers.[7,10,12] $SrLa_4Ti_4O_{15}$ crystallizes in the hexagonal structure with $hhccc$ stacking.[8] $CaLa_4Ti_4O_{15}$ belongs to $A_5B_4O_{15}$ with $hcccch$ stacking ($p\bar{3}m$), and $Ca_2La_4Ti_5O_{18}$ belongs to $A_6B_5O_{18}$ with $hccccchhccccchhccccchh$ stacking [$R\bar{3}m$] and crystallizes within the trigonal system with $Z = 3$.[9] $A_nB_{n-1}O_{3n}$ compounds usually show a severe distortion of TiO_6 octahedra and the presence of short Ti–O bonds. The decrease in difference between charges of the cations reduces the effect of ordering on the stability of the structure and hence a distorted distribution of the Ca and La cations is found in $Ca_2La_4Ti_5O_{18}$.[9] Especially in those cases where hexagonal polytypes of the perovskites are also possible for ABO_3, the stability of phases with an ordered distribution of vacancies decreases as the Goldschmidt "t" criterion[17] increases and above 1450 °C the hexagonal $A_6B_5O_{18}$ phases

decompose slowly in the solid state.[9] Figure 3 shows typical SEM pictures recorded for $BaLa_4Ti_4O_{15}$ and $CaLa_4Ti_5O_{17}$. The $BaLa_4Ti_4O_{15}$ grains are elongated and up to about 10 μm in length. The $CaLa_4Ti_5O_{17}$ grains are large and up to 15 μm in size. Other samples also showed similar microstructures. The SEM pictures confirmed the single-phase nature of the compounds. The near-to-melting appearance of the ceramics [Fig. 3(b)] may be due to higher sintering temperatures. These DR samples are optimized to have the best Q at these temperatures.

B. Microwave dielectric properties

The ceramics showed excellent microwave dielectric properties. The $TE_{01\delta}$ modes of the samples were obtained in the range of 4–6 GHz. The microwave dielectric properties of the ceramics are given in Table I. The variation of $(\Delta f/f)$ with temperature for the compounds is given in Fig. 4. The $BaLa_4Ti_4O_{15}$ shows $\epsilon_r = 46.3$ and $\tau_f = -13$ ppm/°C with quality factor of 3150 (at 5.15 GHz) for 96.2% dense samples. Veneis et al. have reported that $BaLa_4Ti_4O_{15}$ has ϵ_r of 43 and Q of 1430 (at 8.10 GHz) with τ_f of -17 ppm/°C for 93.7% dense ceramics.[3] The higher densification of the present ceramic may be the reason for the increase in dielectric constant and quality factor of the ceramics. The $SrLa_4Ti_4O_{15}$ ceramics had ϵ_r of 43.8 with very high Q factor of 12,100 (at 4.149 GHz) and a low τ_f of -14 ppm/°C. $Ca_2La_4Ti_5O_{18}$ showed a quality factor of 4800 at 4.19 GHz whereas it was 8100 at 4.31 GHz for $CaLa_4Ti_4O_{15}$. German and Kovba have reported that $Ca_2La_4Ti_5O_{18}$ has a more diffuse infrared and Raman
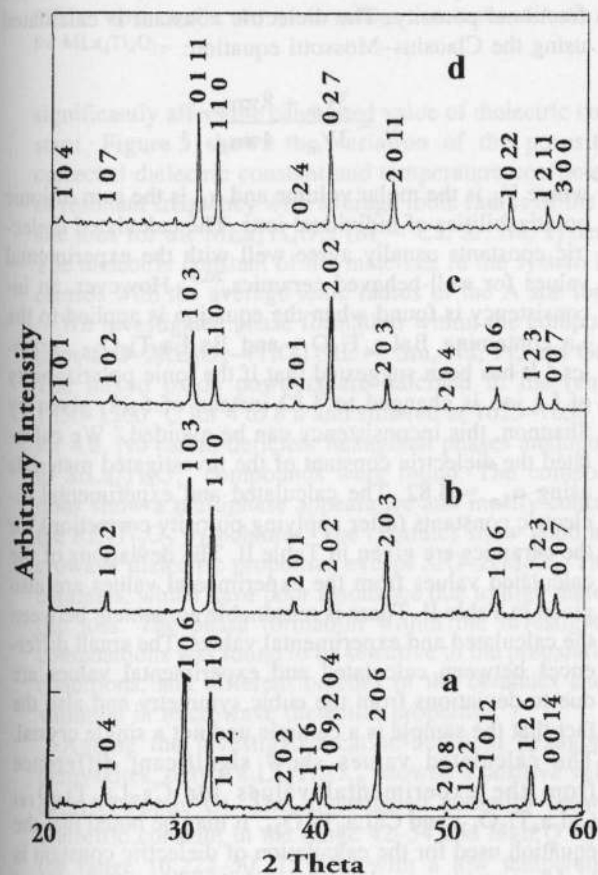
FIG. 1. X-ray diffraction patterns of (a) $BaLa_4Ti_4O_{15}$, (b) $SrLa_4Ti_4O_{15}$, (c) $CaLa_4Ti_4O_{15}$, and (d) $Ca_2La_4Ti_5O_{18}$.
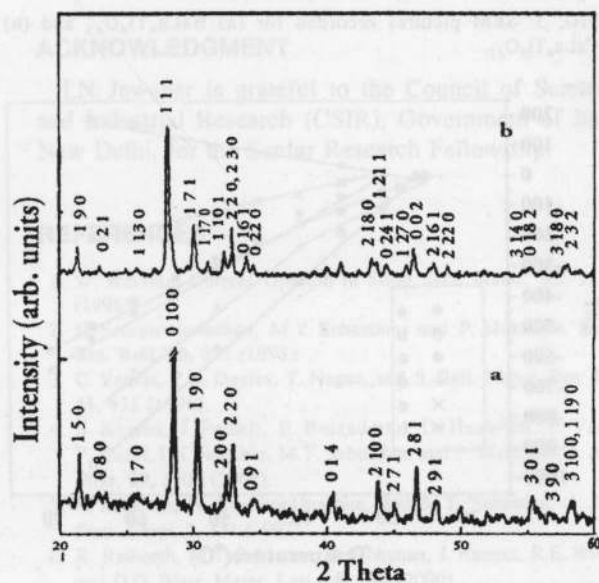
FIG. 2. X-ray diffraction patterns of (a) $CaLa_4Ti_5O_{17}$ and (b) $CaLa_8Ti_9O_{31}$.
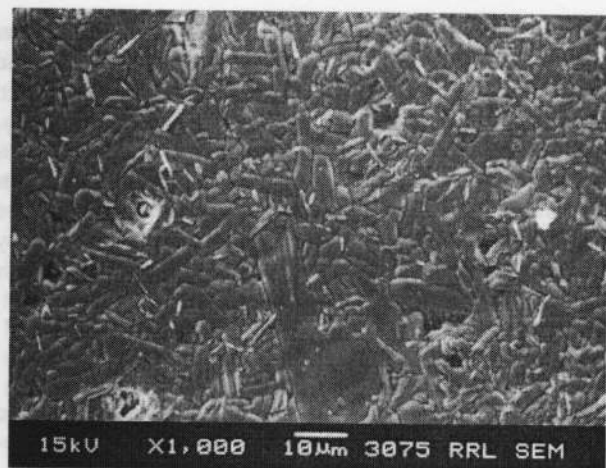
(a)
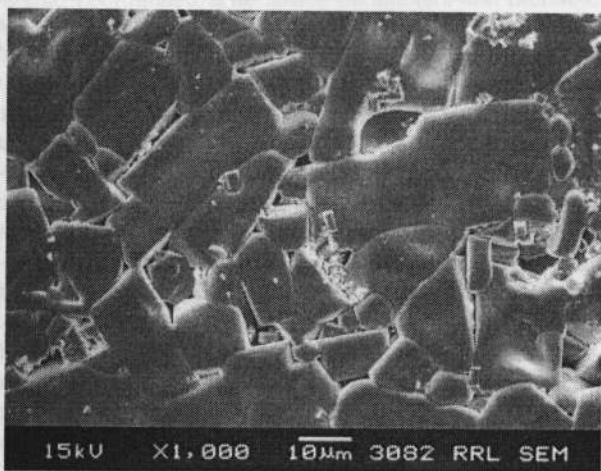
(b)

FIG. 3. SEM pictures recorded for (a) BaLa$_4$Ti$_4$O$_{15}$ and (b) CaLa$_4$Ti$_5$O$_{17}$.
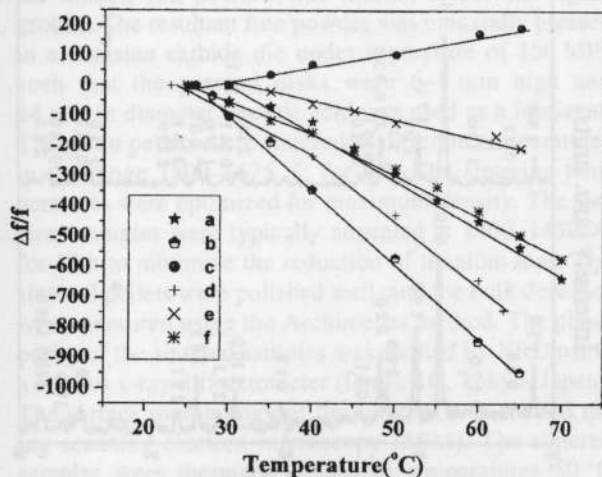
FIG. 4. Plot of $\Delta f/f$ against temperature (a) SrLa$_4$Ti$_4$O$_{15}$, (b) CaLa$_4$Ti$_4$O$_{15}$, (c) Ca$_2$La$_4$Ti$_5$O$_{18}$, (d) Ca$_2$La$_4$Ti$_5$O$_{17}$, and (e) CaLa$_8$Ti$_9$O$_{31}$.

spectra than CaLa$_4$Ti$_4$O$_{15}$.[9] They have suggested a distorted distribution of the Ca and La cation among the equivalent positions to interpret the spectra. This statistical distribution and the resultant disorder of the Ca and La ions may cause lower quality factors of the Ca$_2$La$_4$Ti$_5$O$_{18}$ compared to CaLa$_4$Ti$_4$O$_{15}$ apart from the higher porosity. Usually the broadening of the Raman spectra indicates disorder in crystals.[18] The orthorhombic CaLa$_4$Ti$_5$O$_{17}$ and CaLa$_8$Ti$_9$O$_{31}$ were also characterized by very good microwave dielectric properties with ϵ_r of 53.7 and 48.6, quality factors of 4730 (at 3.67 GHz) and 5300 (at 3.65 GHz) and low τ_f of –20 and –6 ppm/°C, respectively. Ca$_2$La$_4$Ti$_6$O$_{20}$ showed poor resonance due to very high dielectric loss and is therefore not useful for DR applications.

The values of the microwave dielectric constant obtained for the ceramics were corrected for porosity (refer to Table II) using the following equation:[19]

$$\acute{\epsilon} = \epsilon_m\left(1 - \frac{3P(\epsilon_m - 1)}{2\epsilon_m + 1}\right),$$

where ϵ_m is the dielectric constant corrected for porosity, ϵ' is the experimental dielectric constant, and P is the fractional porosity. The dielectric constant is calculated using the Clausius–Mossotti equation:

$$\epsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D},$$

where V_m is the molar volume and α_D is the sum of ionic polarizabilities of individual ions. The calculated dielectric constants usually agree well with the experimental values for well-behaved ceramics.[20,21] However, an inconsistency is found when the equation is applied to the La containing BaLa$_4$Ti$_4$O$_{15}$ and Ba$_2$La$_4$Ti$_5$O$_{18}$ ceramics.[3] It has been suggested that if the ionic polarizability of La ion is changed to 4.82 instead of 6.12, given by Shannon, this inconsistency can be avoided.[3] We calculated the dielectric constant of the investigated materials using $\alpha_{La} = 4.82$. The calculated and experimental dielectric constants (after applying porosity correction) for the ceramics are given in Table II. The deviations of the calculated values from the experimental values are also given in Table II. There is reasonable agreement between the calculated and experimental values. The small differences between calculated and experimental values are due to deviations from the cubic symmetry and also the fact that the sample is a ceramic and not a single crystal. The calculated values show significant difference from the experimental values for Ca$_2$La$_4$Ti$_5$O$_{18}$, CaLa$_4$Ti$_5$O$_{17}$, and CaLa$_8$Ti$_9$O$_{31}$. It may be noted that the equation used for the calculation of dielectric constant is highly sensitive to the value of the denominator, and even a small error in determining the cell volume can

J. Mater. Res., Vol. 17, No. 12, Dec 2002

3087

TABLE II. Comparison of values of experimental and calculated dielectric constants.

Material	α_D (α_{La} = 4.82)	V_m (Å^3)	Space group	ϵ_r (corrected)	Calculated ϵ_r	Deviation (%)
CaLa$_4$Ti$_4$O$_{15}$	64.31	291.98	$P\bar{3}m$	44.7	36.74	17.4
SrLa$_4$Ti$_4$O$_{15}$	65.39	295.22	$P\bar{3}m$	45.1	39.53	12.4
BaLa$_4$Ti$_4$O$_{15}$	67.55	302.48	$P\bar{3}m$	49.1	44.45	9.5
Ca$_2$La$_4$Ti$_5$O$_{18}$	76.43	349.5	$R\bar{3}m$	49.3	33.71	31.6
CaLa$_4$Ti$_5$O$_{17}$	72.34	336.43	...	55.2	28.2	48.9
CaLa$_8$Ti$_9$O$_{31}$	131.48	613.47	...	54.9	27.34	50.0
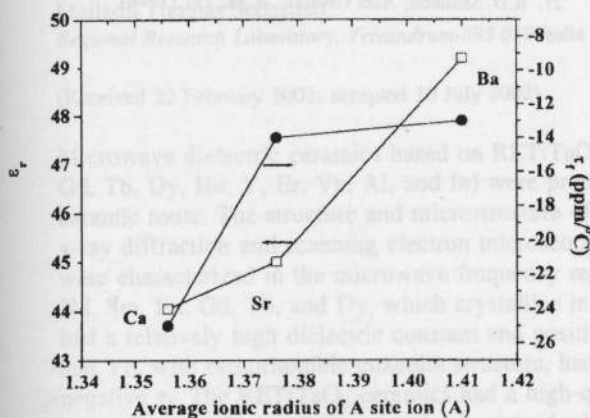
FIG. 5. Variation of ϵ_r and τ_f with average ionic radius of A site ion for MLa$_4$Ti$_4$O$_{15}$.

significantly affect the calculated value of dielectric constant. Figure 5 shows the variation of the porosity-corrected dielectric constant and temperature coefficient of resonant frequency with average ionic radius of the A site ions for the MLa$_4$Ti$_4$O$_{15}$ (M = Ca, Sr, Ba) system. The dielectric constant of the materials in the system increases with the average ionic radius of the A site ions.

We investigated phase formation within the compositions SrO–2RE$_2$O$_3$–4TiO$_2$ (RE = Sm, Nd, Pr, and Gd). The mixed oxide powders are calcined in the range 1350–1500 °C for 4 to 8 h and sintered at 1625–1650 °C for 4 h. No cation-deficient hexagonal phases analogous to SrLa$_4$Ti$_4$O$_{15}$ compounds were found. The compositions show a multiphase appearance and mostly contain the RE$_2$Ti$_2$O$_7$ pyrochlores. The ceramics show good microwave dielectric properties except SrO–2Gd$_2$O$_3$–TiO$_2$ ceramics, which have poor resonance due to high dielectric loss. The phase formation within the investigated compositions was found to be sensitive to the preparation conditions, and different batches of the ceramics show variation in microwave dielectric properties.

Among the investigated cation-deficient hexagonal perovskites, only Ca$_2$La$_4$Ti$_5$O$_{18}$ showed a positive value of τ_f (+6 ppm/°C). The investigated ceramics showed dielectric constant in the range 42–54 and high $Q \times f$ in the range 16,222–50,215 GHz with a low temperature coefficient of resonant frequency in the range +6 to −25 ppm/°C. The investigated ceramics are potential

candidates for practical applications. These high dielectric constant materials with high $Q \times f$ up to 50,215 GHz are suitable for applications where narrow bandwidth and extremely low insertion loss is necessary, especially at frequencies around 1.9 GHz.

IV. CONCLUSION

Cation-deficient hexagonal perovskites CaLa$_4$Ti$_4$O$_{15}$, SrLa$_4$Ti$_4$O$_{15}$, BaLa$_4$Ti$_4$O$_{15}$, and Ca$_2$La$_4$Ti$_5$O$_{18}$ and the orthorhombic phases CaLa$_4$Ti$_5$O$_{17}$ and CaLa$_8$Ti$_9$O$_{31}$ were prepared through the solid-state ceramic route. The phases and structure of the ceramics were analyzed through XRD and SEM. The microwave dielectric properties of the ceramics were studied. The ceramics showed high ϵ_r in the range 42–54, high quality factors with $Q \times f$ in the range 16,222–50,215 GHz, and low τ_f in the range of −25 and +6 ppm/°C. Their high dielectric constants and high quality factors of $Q \times f$ up to 50,215 GHz with low temperature coefficients of resonant frequency make them suitable for applications where narrow bandwidth and extremely low insertion loss are necessary, especially at frequencies around 1.9 GHz.

REFERENCES

1. W. Wersing, Current Opinion in Solid State Mater. Sci. **1**, 715 (1996).
2. H. Sreemoolanadhan, M.T. Sebastian, and P. Mohanan, Mater. Res. Bull. **30**, 653 (1995).
3. C. Veneis, P.K. Davies, T. Negas, and S. Bell, Mater. Res. Bull. **31**, 431 (1996).
4. S. Kamba, J. Petzelt, E. Buixaderas, D. Haubrich, P. Vanek, P. Kuzel, I.N. Jawahar, M.T. Sebastian, and P. Mohanan, J. Appl. Phys. **89**, 3900 (2001).
5. R. Ratheesh, H. Sreemoolanadhan, and M.T. Sebastian, *J. Solid. State. Chem.* **2**, 131 (1997).
6. R. Ratheesh, M.T. Sebastian, P. Mohanan, J. Harnett, R.E. Woode, and D.G. Blair, Mater. Lett. **45**, 279 (2000).
7. V.A. Saltikova, O.V. Melnikova, N.V. Leonova, and N.F. Fedorov, Russ. J. Inorg. Chem. **30**, 105 (1985).

8. V.A. Saltikova, O.V. Melnikova, and N.F. Fedodov, Russ. J. Inorg. Chem. **34,** 758 (1989).

9. M. German and L.M. Kovba, Russ. J. Inorg. Chem. **30,** 176 (1985).

10. N. Harre, D. Mercurio, G. Trolliard, and B. Frit, Mater. Res. Bull. **33,** 1537 (1998).

11. N. Harre, D. Mercurio, G. Trolliard, and B. Frit, Eur. J. Solid State Inorg. Chem. **35,** 77 (1998).

12. N. Teneze, D. Mercurio, G. Trolliard, and B. Frit, Mater. Res. Bull. **35,** 1603 (2000).

13. B.W. Hakki and P.D. Coleman, IRE Trans. Microwave Theory Tech. **MTT8,** 402 (1960).

14. W.E. Courtney, IEEE Trans. Microwave Theory Tech. **MTT18,** 476 (1970).

15. J. Krupka, K. Derzakowsky, B. Riddle, and J.B. Jarviz, Meas. Sci. Technol. **9,** 1751 (1998).

16. JCPDS Powder Diffraction File Nos. 39-831, 36-1278, 36-1278, 36-1279, 27-1057, 27-1058, 24-1059 (Joint Committee for Powder Diffraction Standards, Newton Square, PA).

17. R.S. Roth, J. Res. Nat. Bur. Stand. **58,** 75 (1957).

18. E. Brük, R.K. Route, R.J. Raymakers, and R.S. Feigelson, J. Cryst. Growth **128,** 842 (1993).

19. S.J. Penn, N.M. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, and K. Schrapel, J. Am. Ceram. Soc. **80,** 1885 (1997).

20. R.D. Shannon, J. Appl. Phys. **73,** 348 (1993).

21. R.D. Shannon, Acta Crystall. A **32,** 751 (1976).