Dielectric resonators in $BaO–Ln_2O_3–5TiO_2$ system (Ln = La, Pr, Nd, Sm)

H. Sreemoolanadhan, M. T. Sebastian, and P. Mohanan

Ceramics of composition $BaO–Ln_2O_3–5TiO_2$ have been prepared with four lanthanide elements (Ln = La, Pr, Nd, Sm) by a conventional solid state ceramic preparation route and the dielectric properties measured in the microwave frequency range. The dielectrics had high values for the dielectric constant ε_r in the range 72–88 and quality factor Q_u values of up to 24 000. The phase constitution and microstructures of the materials were characterised using X-ray diffraction and scanning electron microscopy, respectively. The observed properties indicate that these are promising materials for use as microwave dielectric resonators.

Dr Sreemoolanadhan and Dr Sebastian are in the Regional Research Laboratory (CSIR), Thiruvananthapuram-695 019, India. Dr Mohanan is in the Department of Electronics, Cochin University of Science and Technology, Kochi-682 022, India. *Manuscript received 13 March 1995.*

INTRODUCTION

With the increasing demand for miniaturisation of microwave communication systems such as cellular telephones, ceramic dielectrics with high permittivity and low loss have become indispensable for microwave integrated circuits (MICs). These ceramics, called 'dielectric resonators' (DRs) offer small size, light weight, temperature stability, and integrability by virtue of the unique combination of properties they possess.[1,2] Ceramics used for DR applications need relative permittivity or dielectric constant ε_r in the range 25–100, $\tan\delta < 5 \times 10^{-4}$, where $\tan\delta$ is dielectric loss, and τ_f (coefficient of thermal variation of resonant frequency) within ± 20 ppm K^{-1}. The resonant frequency of a DR (usually $TE_{01\delta}$ for practical applications is selected by taking the ε_r of the material and the dimensions into consideration. In pursuit of appropriate materials, a few ceramics such as $Ba_2Ti_9O_{20}$ (Refs. 3–5), $(Zr,Sn)TiO_4$ (Refs. 6–8), $Ba(Zn,Ta)O_3$ (Refs. 9–11), $Ba(Mg.Ta)O_3$ (Ref. 12), $Ba(Re.Nb)O_3$ (Refs. 13, 14), $Ba_5Nb_4O_{15}$ (Ref. 15) have been investigated. All the above ceramics have $\varepsilon_r < 45$ and hence their use in 800 MHz band is limited by the large size. Development of microwave dielectric resonators still with high ε_r is required for frequencies <2 GHz where the wavelength is large, and can be reduced through high ε_r dielectrics. *A dielectric constant in the range 70–90 is* commonly needed in the 800 MHz mobile telephone system and in L or S band frequencies for miniaturisation of circuits. More recently $BaNd_2Ti_5O_{14}$ and $BaSm_2Ti_5O_{14}$ have been reported[16–26] as high ε_r dielectric ceramics for the above applications. The ε_r of $BaNd_2Ti_5O_{14}$ based materials varies in the range 77–95 and τ_f from +90 to +123 whereas in $BaSm_2Ti_5O_{14}$ based ceramics ε_r varies in the range 66–77 and τ_f from −30 to +12. The quality factor varies from 1000 to 20 000. These variations in the dielectric properties are attributed[16–26] to the presence of secondary phases such as $Ba_2Ti_9O_{20}$, $BaTi_4O_9$, TiO_2, $Nd_2Ti_2O_7$, $Sm_2Ti_2O_7$, etc. Partial substitution of Ba by Sr or Pb or addition of Bi_2O_3 enhances the ε_r and improves τ_f in the above systems.[16,17,19,24] In the present paper the preparation, characterisation, and dielectric properties of $BaLn_2Ti_5O_{14}$ (Ln = La, Pr, Nd, Sm) are reported.

EXPERIMENTAL PROCEDURES

Sample preparation

High purity $BaCO_3$, TiO_2, La_2O_3, Pr_2O_3, Nd_2O_3 and Sm_2O_3 were mixed in the molecular proportions $BaO:Ln_2O_3:TiO_2 = 1:1:5$ with distilled water for ~30 min in an agate mortar. The powders were calcined in alumina crucibles at 1120–1200°C for 4 h with intermediate grinding, then mixed with PVA binder, and ground for 1 h. They were pressed into 10 mm diameter compacts at 350 MPa and subsequently sintered in air at 1300–1350°C for 4 h. The density of the sintered compacts was determined from the dimensions. X-ray diffraction (XRD) studies were carried out on powdered samples using Cu K_α radiation and the microstructures examined by SEM.

Microwave dielectric property measurements

The dielectric constant was measured using an HP 8510 B network analyser and accessories by the post resonator method as proposed by Hakki and Coleman[27] and modified by Courtney.[28] First, the cylindrical sample is resonated in the end shorted condition. The E-field probes couple the microwave to the sample and the $TE_{01\delta}$ resonance corresponding to a frequency f_0 in the transmission mode is taken. Using a Hewlett Packard 9000/300 series computer, which controls the network analyser, the ε_r is calculated using the relation

$$\varepsilon_r = 1 + \left(\frac{\lambda_0}{\pi D}\right)^2 (\alpha_1^2 + \beta_1^2) \quad . \quad . \quad . \quad (1)$$

where β_1 is a function of the resonant frequency and sample dimensions given by

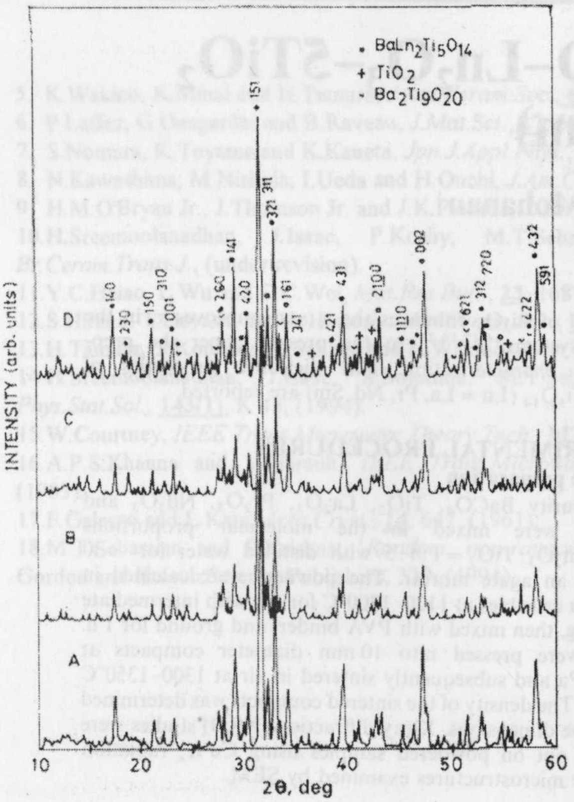
$$\beta_1 = \frac{\pi D}{\lambda_0}\left[\left(\frac{\lambda_0}{2L}\right)^2 - 1\right]^{1/2} \quad . \quad . \quad . \quad (2)$$

Here, λ_0 is the free space wavelength corresponding to f_0, and D and L are the specimen diameter and height respectively. α_1 is taken from a mode chart given in Ref. 27. The selection of resonant frequency and the calculation of ε_r are done entirely by the computer.

The conduction loss in the above method is quite high *and comparable to the loss of the dielectric material itself.*[1] Hence this method cannot be used for the Q_u measurement. In this work the 'stripline method' proposed by Khanna and Garault[29] for estimating the Q_u value was used. In this method the dielectric ceramic coupled to a stripline of 50 Ω acts as a band rejection filter. The least transmission coefficient S_{21} corresponding to f_0 is taken. From this, the width of the resonant curve Δf corresponding to the transmission coefficient S_{21u} given by

$$S_{21u} \approx S_{21}\left(\frac{2}{1 + S_{21}^2}\right)^{1/2} \quad . \quad . \quad . \quad (3)$$

is taken. The unloaded quality factor, Q_u, is calculated from



A $BaLa_2Ti_5O_{14}$; B $BaPr_2Ti_5O_{14}$; C $BaNd_2Ti_5O_{14}$; D $BaSm_2Ti_5O_{14}$

1 Powder X-ray diffraction patterns of $BaLn_2Ti_5O_{14}$ ceramics obtained using Cu K_α radiation

the relation

$$Q_u = f_0/\Delta f \qquad (4)$$

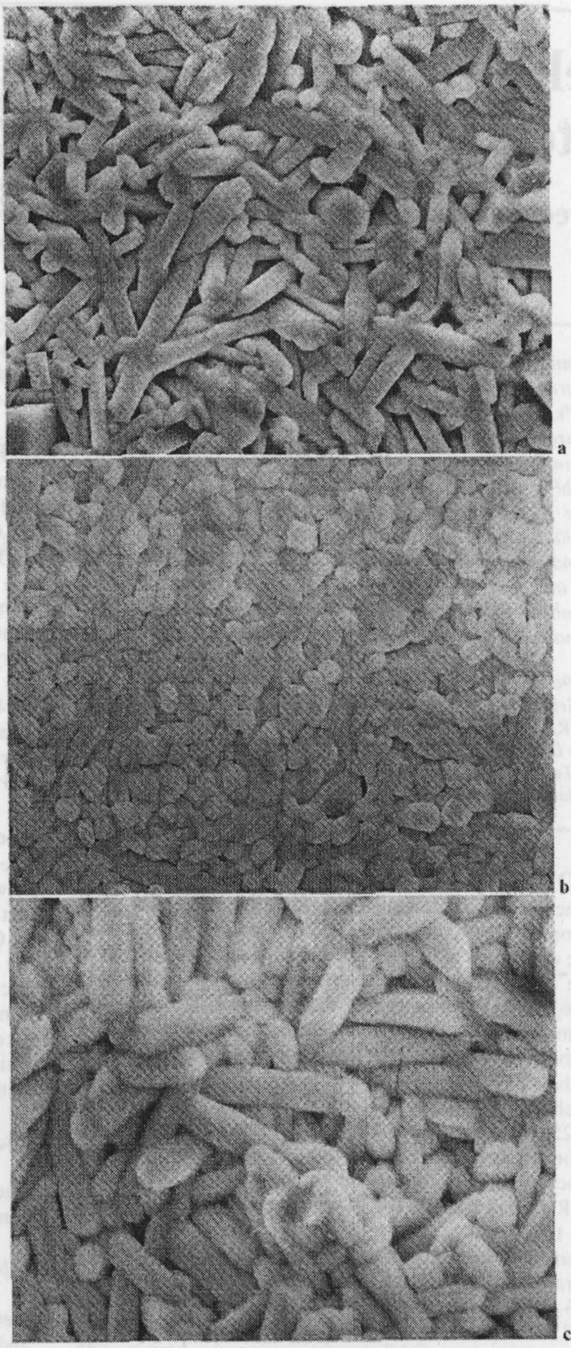
Here, also, the frequency selection and the calculation are completely done by the computer. This method is straightforward and is reproducible. Moreover, the Q value obtained is almost equal to Q_u since proper shielding is provided (using a brass cavity of size 5 × 5 × 3 cm) to prevent radiation loss. Most of the applications of DR involve coupling using striplines. In fact, the present method is superior to all other existing methods since the measurement is made in an actual working environment.

The temperature variation of the resonant frequency τ_f was obtained by placing the ceramic at the centre of the bottom of an aluminium cavity, 4 cm dia. × 7 cm high, and by keeping the top open. Here the cavity dimensions are four times those of the dielectric ceramic. Using an E-field probe, the resonant frequency f_0 and the shift during heating were determined in the range 25–80°C. A graph drawn between resonant frequency and temperature, whose slope gives $\Delta f/\Delta T$ and the τ_f was obtained using the following equation

$$\tau_f = \frac{1}{f_0}\left(\frac{\Delta f}{\Delta T}\right) \qquad (5)$$

RESULTS AND DISCUSSION

The powder XRD patterns obtained for the four ceramics, $BaLa_2Ti_5O_{14}$, $BaPr_2Ti_5O_{14}$, $BaNd_2Ti_5O_{14}$, and $BaSm_2Ti_5O_{14}$ are shown in Fig. 1. The patterns are similar for all the samples and show that the 1:1:5 is the major phase. The patterns contain additional diffraction peaks corresponding to that of $Ba_2Ti_9O_{20}$ and TiO_2. The microwave dielectric properties such as ε_r, $Q_u \times f$, and τ_f are shown in Table 1. A study of Table 1 indicates that, in general, ε_r and τ_f decrease with the substitution of a smaller ion at the Ln^{3+} site. The value of $Q \times f$ increases with the decrease in ionic radius of the lanthanide. Similar variations in dielectric properties were observed by Fukuda *et al.*[30] However, Nishigaki *et al.*[24] and Sun *et al.*[25] observed an increase in the ε_r and τ_f and a decrease in Q when the smaller Sr ion was substituted for Ba in $BaSm_2Ti_5O_{14}$. The Sr substitution for Ba was reported to suppress the formation



a $BaPr_2Ti_5O_{14}$, × 3000; *b* $BaNd_2Ti_5O_{14}$, × 3000; *c* $BaSm_2Ti_5O_{14}$, × 4000

2 SEM of $BaLn_2Ti_5O_{14}$ ceramics

Table 1 Microwave dielectric properties of $BaLn_2Ti_5O_{14}$ ceramics

Material	ε_r	$Q \times f$, GHz	τ_f, ppm K^{-1}	Bulk density, g cm^{-3}
$BaLa_2Ti_5O_{14}$	88·02	2200	+70	4·95
$BaPr_2Ti_5O_{14}$	76·48	6700	+37	5·12
$BaNd_2Ti_5O_{14}$	77·55	17600	+40	5·14
$BaSm_2Ti_5O_{14}$	72·15	24000	−14	5·36

of $Ba_2Ti_9O_{20}$ and enhance the formation of TiO_2 phase. They reported that the increase in ε_r and τ_f are due to the presence of TiO_2.

The microstructures of these ceramics, thermally etched at 1200°C for 1 h, show a typical grain size of 2–3 µm (Fig. 2), with $BaLn_2Ti_5O_{14}$ being the major phase. The presence of secondary phases such as $Ba_2Ti_9O_{20}$, TiO_2, etc. is very common[16–26] in these types of compounds. The bulk densities of the samples are given in Table 1 but the presence of the secondary phases precludes the comparison of experimental density with theoretical density. The presence of secondary phases alters the ε_r, τ_f, and Q_u values and, in certain cases, improves the dielectric properties. For example, the presence of a small amount of TiO_2 ($\varepsilon_r = 100$; $Q = 10\,000$; $\tau_f = +420$ ppm K^{-1}) increases the ε_r and Q values and brings the τ_f towards positive in negative τ_f materials.

CONCLUSIONS

$BaLn_2Ti_5O_{14}$ (Ln = La, Pr, Nd, Sm) ceramics have been prepared by the conventional solid state ceramic route. The $BaSm_2Ti_5O_{14}$ composition with ε_r of 72·15, $Q \times f$ of 24 000, and τ_f of −14 ppm K^{-1} is a useful material for application in cellular telephones.

ACKNOWLEDGEMENTS

The authors are grateful to Dr A. D. Damodaran and Professor K. G. Nair for their keen interest and encouragement. Dr Sreemoolanadhan is grateful to CSIR for the award of a Research Fellowship.

REFERENCES

1. D. KAJFEZ and P. GUILLON: 'Dielectric resonators'; 1986, Norwood, MA, Artech House.
2. J. K. PLOURDE and C. L. REN: *IEEE Trans. Microwave Theory Tech.*, 1981, **MTT-29**, (8), 754–770.
3. J. K. PLOURDE, D. F. LINN, H. M. O'BRYAN, Jr, and J. THOMSON, Jr: *J. Am. Ceram. Soc.*, 1975, **58**, 418–420.
4. H. M. O'BRYAN, Jr, J. THOMSON, Jr, and J. K. PLOURDE: *J. Am. Ceram. Soc.*, 1974, **57**, 450–453.
5. H. SREEMOOLANADHAN, J. ISAAC, P. KOSHY, M. T. SEBASTIAN, K. A. JOSE, and P. MOHANAN: *Br. Ceram. Trans.*, 1995, **94**, (4), 157–160.
6. G. WOLFRAM and H. E. GOBEL: *Mater. Res. Bull.*, 1981, **16**, 1455–1463.
7. F. AZOUGH and R. FREER: in Proc. 7th IEEE Int. Symp. on 'Applied ferroelectrics' (ISAF 90), 198–201; 1991, New York, IEEE.
8. D. M. IDDLES, A. J. BELL, and A. J. MOULSON: *J. Mater. Sci.*, 1992, **27**, 6303–6310.
9. H. TAMURA, D. A. SAGALA, and K. WAKINO: *Jpn J. Appl. Phys. 1*, 1986, **25**, (6), 787–791.
10. K. WAKINO, M. MURATA, and H. TAMURA: *J. Am. Ceram. Soc.*, 1986, **69**, 34–37.
11. S. KAWASHIMA, M. NISHIDA, I. UEDA, and H. OUCHI: *J. Am. Ceram. Soc.*, 1983, **66**, 421–423.
12. S. NOMURA, K. TOYAMA, and K. KANETA: *Jpn J. Appl. Phys.*, 1982, **21**, L624–L626.
13. M. TAKATA and K. KAGEYAMA: *J. Am. Ceram. Soc.*, 1989, **72**, (10), 1955–1959.
14. H. SREEMOOLANADHAN, J. ISAAC, M. T. SEBASTIAN, A. D. DAMODARAN, K. A. JOSE, P. MOHANAN, U. RAVINDRANATH, and S. DEY: Proc. 4th Int. Symp. on 'Recent advances in microwave technology', 565–568; 1993, New Delhi, Wiley Eastern.
15. H. SREEMOOLANADHAN, J. ISAAC, S. SOLOMON, M. T. SEBASTIAN, K. A. JOSE, and P. MOHANAN: *Phys. Status Solidi a*, 1994, **143**, (1), K45–K48.
16. D. KOLAR, S. GABERSCEK, Z. STADLER, and D. SUVOROV: *Ferroelectrics*, 1980, **27**, 269–272.
17. J. M. DURAND and J. P. BOILOT: *J. Mater. Sci. Lett.*, 1987, **6**, 134–136.
18. A. YAMADA, Y. UTSUMI, and H. WATARAI: *Jpn J. Appl. Phys. 1*, 1991, **30**, (9B), 2350–2353.
19. K. WAKINO, K. MINAI, and H. TAMURA: *J. Am. Ceram. Soc.*, 1984, **67**, 278–281.
20. J. P. MERCURIO, M. MANIER, and B. FRIT: *Mater. Lett.*, 1989, **8**, (4), 112–114.
21. J. M. WU, M. C. CHANG, and P. C. YAO: *J. Am. Ceram. Soc.*, 1990, **73**, (6), 1599–1605.
22. P. LAFFEZ, G. DESGARDIN, and B. RAVEAU: *J. Mater. Sci.*, 1992, **27**, 5229–5238.
23. X. M. CHEN, Y. SUZUKI, and N. SATO: *Mater. Lett.*, 1993, **16**, (2, 3), 75–78.
24. S. NISHIGAKI, H. KATO, S. YANO, and R. KAMIMURA: *Am. Ceram. Soc. Bull.*, 1987, **66**, (9), 1405–1410.
25. J. S. SUN, C. C. WEI, and L. WU: *J. Mater. Sci.*, 1992, **27**, 5818–5822.
26. J. P. GUHA: *J. Am. Ceram. Soc.*, 1991, **74**, (4), 878–880.
27. B. W. HAKKI and P. D. COLEMAN: *IRE Trans. Microwave Theory Tech.*, 1960, **MTT-8**, 402–410.
28. W. E. COURTNEY: *IEEE Trans. Microwave Theory Tech.*, 1970, **MTT-18**, (8), 476–485.
29. A. P. S. KHANNA and Y. GARAULT: *IEEE Trans. Microwave Theory Tech.*, 1983, **MTT-31**, 261–264.
30. K. FUKUDA, I. FUJII, R. KITOH, Y. CHO, and I. AWAI: *Jpn J. Appl. Phys. 1*, 1993, **32**, 1712–1715.