Microwave dielectric resonators based on $Ba[(Bi_{0.2}D_{0.3}^{3+})Nb_{0.5}]O_3$ $(D^{3+} = Y, Pr, Sm, Gd, Dy, Er)$

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Abstract

Dielectric resonator ceramics with composition formula $Ba[(D_{0.3}^{3+}Bi_{0.2})Nb_{0.5}]O_3$, where $D^{3+} = Y, Pr, Sm, Gd, Dy$ and Er, were prepared by the conventional ceramic preparation route. The dielectric properties at microwave frequencies were measured using a resonance method. The ceramics showed the dielectric constant (ϵ_r) above 40 and $Q \times f > 1.5 \times 10^{12}$. The temperature coefficient of resonant frequency (τ_f) varied from -27 to $+15$ ppm K^{-1}. The dielectric properties and low processing temperatures make these materials suitable for practical applications.

Keywords: Ceramics; Microwave dielectric resonators; $Ba[(Bi_{0.2}D_{0.3}^{3+})Nb_{0.5}]O_3$

1. Introduction

A low-loss dielectric material is required for use as a dielectric resonator (DR) in microwave circuits. With the progress in direct satellite broadcasting and cellular mobile telephones, there has been an ever-increasing demand for dielectric resonators. The versatility and adaptability of DRs to modern communication systems make them indispensable components for filters, oscillators, duplexers, etc. [1]. DRs reduce the size of a component by a factor of $\sqrt{\epsilon_r}$ where ϵ_r is the relative permittivity of the material. The important characteristics required for a dielectric resonator are: high ϵ_r (25–100), high unloaded quality factor $(Q_u > 1000)$ and a small coefficient of thermal

variation of resonant frequency $(\tau_f$ within 20 ppm/°C). In pursuit of suitable materials, a number of dielectric ceramics such as $Ba_2Ti_9O_{20}$ [2,3], $BaO–PbO–TiO_2–Nd_2O_3$ [4], $Ba(Zn, Ta)O_3–BaZrO_3$ [5], $(Zr, Sn)TiO_4$ [4,6], $(Ba, Sr)_5Nb_4O_{15}$ [7,8], etc. were investigated. Among them complex perovskite type oxides form a large class of materials, many of them having interesting dielectric properties. The $Ba(Mg_{1/3}Ta_{2/3})O_3$ [9] and $Ba(Zn_{1/3}Ta_{2/3})O_3$ [5] ceramics were extensively studied. Although these materials had very high Q values, the dielectric constants are relatively low $(\epsilon_r < 30)$, which made them unattractive in lower frequency bands. Agranovskaya [10] had outlined the dielectric properties of a number of complex perovskite materials and suggested the $A(B_{1/2}^{3+}B_{1/2}^{5+})O_3$ as excellent microwave resonator materials. Takata and Kageyama [11], Setter et al. [12] and Sreemoolanadhan et al.

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[13,14] reported the microwave characteristics of $A(B_{1/2}^{3+}B_{1/2}^{5+})O_3$ ceramics where A = Ba, Sr, Ca; B^{3+} is a trivalent lanthanide ion and B^{5+} = Nb, Ta with ϵ_r ranging up to 45. Several such complex perovskite samples were synthesized as monophase materials and the preparation and structure were described in detail by Galasso [15] in his book. Recently, bismuth based dielectric ceramics have been reported as useful materials for capacitor and DR applications [16–19]. The main advantage of these materials was the low sintering temperature ($\approx 1300°C$) compared to the conventional ceramics (> 1500°C). Even though the Q-factor was comparatively low, these systems offered high ϵ_r and temperature stability. In the present paper we report the preparation and microwave properties of $Ba[(D_{0.3}^{3+}Bi_{0.2})Nb_{0.5}]O_3$ ceramics. This work was aimed at reducing the sintering temperature and enhancing the ϵ_r of complex perovskite niobates.

2. Experimental procedure

2.1. Material synthesis

The samples were prepared by the conventional solid state ceramic route. High purity carbonates/oxides were wet mixed using distilled water in an agate mortar, dried and calcined at 900–1000°C for 8 h in air. The calcined powders were again ground and pressed into cylindrical compacts of 10 mm diameter under a pressure of 125 MPa. The samples were then sintered at 1250–1300°C for 8 h in air. X-ray diffraction studies were made on sintered samples using Cu Kα radiation and the microstructures were obtained using SEM.

2.2. Microwave characterisation

The ϵ_r of the DR was measured by the "post resonator" method proposed by Hakki and Coleman [20] and modified by Courtney [21]. The unloaded quality factor (Q_u) was measured by the "stripline method" proposed by Khanna and Garault [22]. The Q value thus obtained was very close to that of a DR used in a practical circuit [23]. The measurements of ϵ_r and Q_u were easily done automatically by a HP 9000, 300 series instrumentation computer, which controlled the HP 8510 B network analyser with synthesiser (HP 8341 B) and reflection–transmission test unit (HP 8514 B). Then the DR was slowly heated in the temperature range 25–80°C and the coefficient of thermal variation of resonant frequency (τ_f) was obtained. The details of the measurements are described elsewhere [3].

3. Results and discussion

The values of the dielectric constant (ϵ_r), normalised quality factor ($Q \times f$) and the coefficient of thermal variation of resonant frequency (τ_f) are given in Table 1. The dielectric constants in this system are relatively high (by about 45%) compared to other materials reported earlier [11,13,14]. 40% of bismuth substitution for D^{3+} ion at the B-site lowers the preparation temperature. The bismuth addition increases ϵ_r and temperature stability but decreases the Q value. It has been reported that the Q values of complex perovskite type materials depend on the extent of chemical order in the arrangement of the B site ions [24,25]. Hence, it is expected that the quality factor could be improved reasonably by annealing the sintered compacts at sufficiently high temperature for long time. In the XRD patterns obtained, shown in Fig. 1, the superstructure reflections due to chemical ordering of B-site ions are weak, which, presumably has caused high loss. Moreover, in bismuth containing systems densification is enhanced by liquid phase sintering which adversely affects the quality factor and sintered density. The temperature stability has been improved by partial bismuth substitution. The tolerance factor (t)

Table 1
Microwave dielectric properties of $Ba[(D_{0.3}^{3+}Bi_{0.2})Nb_{0.5}]O_3$ ceramics

Material (D^{3+})	ϵ_r	$Q \times f$ ($\times 10^9$ Hz)	τ_f (ppm K^{-1})
Pr	60.7	1500	15
Sm	50.8	1600	14
Gd	47.9	2100	5
Dy	48.6	2000	-3
Y	44.6	2000	6
Er	46.1	1500	-27

controlled the HP 8510 B network analyser with synthesiser (HP 8341 B) and reflection–transmission test unit (HP 8514 B). Then the DR was slowly heated in the temperature range 25–80°C and the coefficient of thermal variation of resonant frequency (τ_f) was obtained. The details of the measurements are described elsewhere [3].

3. Results and discussion

The values of the dielectric constant (ϵ_r, normalised quality factor $Q \times f_0$ at 5 GHz) and the thermal variation of resonant frequency (τ_f) are given in Table 1. The ϵ_r value in the present case are relatively high (by about 45%) compared to other materials reported [10,15,24]. 40% of Bismuth substitution for D^{3+} ion at the site lowers the sintering temperature. The bismuth addition increases the ϵ_r value and decreases the τ_f and Q values. For complex perovskite type materials depend on the extent of chemical order and the arrangement of the ions [6,15]. Here, it is suspected that the quality factor could be improved probably by annealing the sample at a higher sintering temperature for long time. In the XRD patterns obtained, super structure reflections due to chemical ordering of B-site ions were absent, which presumably has caused high dielectric loss. The Q value of these materials can therefore be improved by adopting either of the solutions mentioned above. Advanced processing methods, such as liquid phase sintering or partial isovalent cation substitution can also be
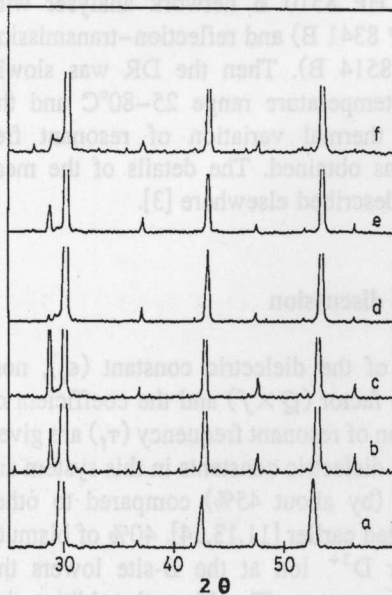

Fig. 1. Powder X-ray diffractograms of $Ba[(D_{0.3}^{3+} Bi_{0.2})Nb_{0.5}]O_3$ ceramics. (a) Pr, (b) Sm, (c) Gd, (d) Dy, (e) Y and (f) Er.

and the lattice parameter a_T for the different D^{3+} ions were calculated using the following formulae:

$$t = \frac{R_{Ba} + R_O}{\sqrt{2}\left[\frac{1}{2}(0.4R_{Bi} + 0.6R_D + R_{Nb}) + R_O\right]},$$

$$a_T = \frac{1}{2}(R_{Ba} + R_O) + \frac{1}{2}(0.4R_{Bi} + 0.6R_D + R_{Nb}) + R_O,$$

where R is the crystal radius of the respective ion indicated by the suffix. The expressions are derived from the formulae obtained by Megaw [26] and Brandle and Fratello [27] respectively. The tolerance factors of different compounds as calculated are given in Table 2. The values of the crystal or ionic
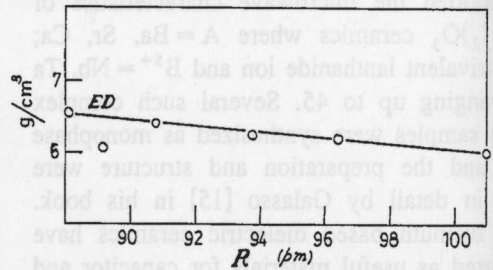

Fig. 2. Experimental density versus ionic radius (R) of D^{3+} ion.

radii are taken from Shannon and Prewitt [28]. The experimental density shows a smooth decrease with the increase in ionic radius of the D^{3+} ion except for Y^{3+} which is not a lanthanide (see Fig. 2). Fig. 3 shows the dependence of ϵ_r and τ_f on the tolerance factor.

Recently, it has been found [29] that the complex perovskites undergo a structural transition depending on the value of the tolerance factor. The high temperature phase is face-centred cubic with $(NH_4)_3FeF_6$ [15] structure with two formula units in the primitive cell. The transition temperature correlates [29,30] inversely with the tolerance factor t. The symmetry is lowered for materials with lower tolerance factor [29,31]. The materials with t in the range 0.985–1.03 do not undergo any phase transition and they have a cubic structure [29]. Materials with t less than 0.985 undergo a transformation from cubic to one with a lower symmetry (tetragonal, orthorhombic, or monoclinic). The lowering of the symmetry in perovskites is due to the tilting of the BO_6 octahedra [32]. In the present study all the compounds have tolerance factors less than 0.985 and hence are expected to un-
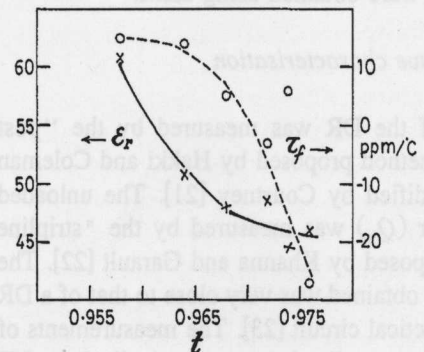
Table 2
Theoretically calculated values of the tolerance factor (t) and the lattice parameter

D^{3+} ion	Ionic radius R (Å)	Tolerance factor (t)	Lattice parameter (Å) theoretical (a_T)
Pr	1.010	0.958	8.526
Sm	0.964	0.964	8.496
Gd	0.938	0.968	8.484
Dy	0.908	0.972	8.466
Y	0.892	0.974	8.456
Er	0.881	0.976	8.450

Fig. 3. Variation of ϵ_r and τ_f of $Ba[(D_{0.3}^{3+} Bi_{0.2})Nb_{0.5}]O_3$ ceramics with respect to t.

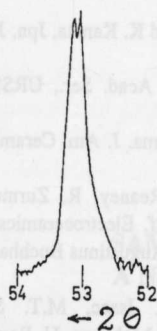Fig. 4. A slow-scanned XRD pattern of Ba(Bi, Sm, Nb)O$_3$ ceramic showing the splitting of a normal single X-ray peak.

Fig. 6. ϵ_r and τ_f versus lattice parameter (a_T) calculated for the pseudocubic structure of the Ba[(D$_{0.3}^{3+}$ Bi$_{0.2}$)Nb$_{0.5}$]O$_3$ ceramic.

dergo a phase transition from the cubic to one with a lower symmetry. X-ray diffraction is largely insensitive to scattering from the oxygen sublattice and therefore it is difficult to detect structural phase transition. The distortion of the cation sublattice is small and the associated peak splitting may be difficult to observe (see the splitting of the peak in Ba(Bi, Sm, Nb)O$_3$ in Fig. 4). Hence neutron scattering or electron microscopy experiments are needed to study the structure of these compounds [30,33,34] with certainty.

A straightforward analysis based on the tolerance factor, lattice parameter and ionic radius of the substituent D^{3+} ion, can easily explain the results obtained by the substitution. Fig. 5 shows a plot of the tolerance factor (t), ϵ_r and τ_f values versus the ionic radius (R) of the D^{3+} element. The linear nature of t versus R shows that the compounds are isostructural. As is evident from the figure, ϵ_r and τ_f show a
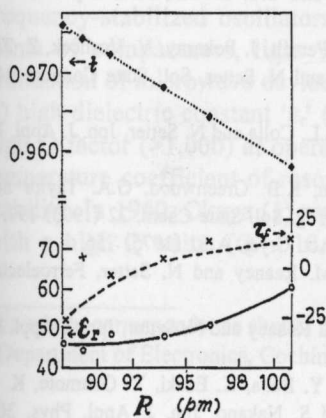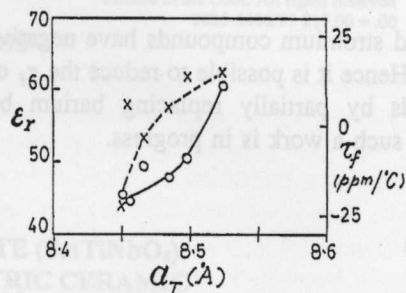
dependence on the ionic radii (R). Similar results for the dielectric properties as a function of composition were reported for Ba$_{1-x}$Sr$_x$(Nd$_{1/2}$Nb$_{1/2}$)O$_3$ [14] and (A$_{1/2}^{1+}$A$_{1/2}^{3+}$)TiO$_3$ [35]. A vivid picture of the effect of ionic size of homovalent and aliovalent substituents at A and B sites on the dielectric properties of A(B′B″)O$_3$ complex perovskites can be obtained based on this. ϵ_r and τ_f increase with ionic radius (R) with a minimum τ_f of -3 ppm/°C for Ba[(Dy$_{0.3}$Bi$_{0.2}$)Nb$_{0.5}$]O$_3$. The variation in ϵ_r and τ_f with lattice parameter (a_T) is as shown in Fig. 6. It is evident that the lattice parameter of complex cubic perovskites decreases with the ionic radius of the substituent ion. Hence, a similar variation as for the ionic radius can be expected for the lattice parameter in the case of ϵ_r and τ_f (see Fig. 6). A typical microstructure obtained for the Ba(Bi$_{0.2}$Er$_{0.3}$Nb$_{0.5}$)O$_3$ composition shows uniform grains of about 3 μm size (see Fig. 7).

The low τ_f value along with $\epsilon_r > 40$ make the Ba[(D$_{0.3}^{3+}$Bi$_{0.2}$)Nb$_{0.5}$]O$_3$ promising materials for use in dielectric resonators at low frequencies. It should be noted that barium compounds in general have a
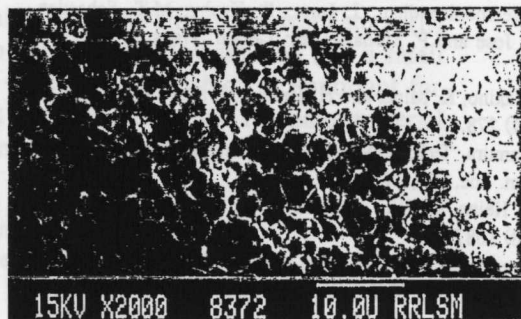

Fig. 5. t, ϵ_r and τ_f versus ionic radius (R) of D^{3+} ion.

Fig. 7. SEM photograph of Ba[(Er$_{0.3}$Bi$_{0.2}$)Nb$_{0.5}$]O$_3$ ceramic.

positive τ_f and strontium compounds have negative τ_f [11,13,14]. Hence it is possible to reduce the τ_f of Ba compounds by partially replacing barium by strontium and such a work is in progress.

4. Conclusion

Ceramics with composition $Ba[(D_{0.3}^{3+}$-$Bi_{0.2})Nb_{0.5}]O_3$ have been prepared and their microwave dielectric properties are measured. The dielectric constant and the coefficient of thermal variation of resonant frequency have been found to have a strong dependence on the tolerance factor and the ionic radius of the D^{3+} element. The compounds with $D^{3+} = Y$, Pr, Sm, Gd and Dy having $\epsilon_r > 40$, $Q \times f > 1500$ GHz and $\tau_f < +15$ ppm/°C are useful as dielectric resonators. The low preparation temperature makes these materials useful for industries.

Acknowledgements

References

[1] L.A. Trinogga, G. Kaizhou and I.C. Hunter, Practical microstrip circuit design (Ellis Horwood, 1991).

[2] H.M. O'Bryan Jr., J. Thomson Jr. and J.K. Plourde, J. Am. Ceram. Soc. 57 (1974) 450.

[3] H. Sreemoolanadhan, J. Isaac, P. Koshy, M.T. Sebastian, K.A. Jose and P. Mohanan, Br. Ceram. Trans. J. 94 (1995) 157.

[4] K. Wakino, K. Minai and H. Tamura, J. Am. Ceram. Soc. 67 (1984) 278.

[5] H. Tamura, T. Konoike, Y. Sakabe and K. Wakino, J. Am. Ceram. Soc. 67 (1984) C59.

[6] Y.C. Heiao, L. Wu and C.C. Wei, Mater. Res. Bull. 23 (1988) 1687.

[7] H. Sremoolanadhan, J. Isaac, S. Solomon, M.T. Sebastian, K.A. Jose and P. Mohanan, Phys. Stat. Sol. 143 (1994) K45.

[8] H. Sreemoolanadhan, M.T. Sebastian and P. Mohanan, Mater. Res. Bull. 30 (1995) 653.

[9] S. Nomura, K. Toyama and K. Kaneta, Jpn. J. Appl. Phys. 21 (1982) L624.

[10] A.I. Agranovskaya, Bull. Acad. Ser., URSS Ser. Phys. 24 (1960) 1271.

[11] M. Takata and K. Kageyama, J. Am. Ceram. Soc. 72 (1989) 1955.

[12] N. Setter, E. Colla, I. Reaney, R. Zurmuhlen and A.K. Tagantsev, Proc. Int. Conf. Electroceramics-IV, eds. Waser et al., Vol. 1 (Verlag der Augustinus Buchhandlung, 1994) p. 11.

[13] H. Sreemoolanadhan, J. Isaac, M.T. Sebastian, A.D. Damodaran, K.A. Jose, P. Mohanan, U. Ravindranath and S. Dey, Proc. 4th Int. Symp. Recent Advances in Microwave Technology (Wiley Eastern, New Delhi, 1993) p. 565.

[14] H. Sreemoolanadhan, J. Isaac, M.T. Sebastian, K.A. Jose and P. Mohanan, Ceram. Int. 21 (1995) 385.

[15] F. Galasso, Structure, properties and preparation of perovskite type compounds (Pergamon Press, Oxford, 1969).

[16] M. Manier, J.C. Champan, Mesjard, J.P. Mercurio, D. Bernache and B. Frit, Mater. Chem. Phys. 19 (1988) 167.

[17] H.C. Ling, M.F. Yan and W.W. Rhodes, J. Mater. Res. 5 (1990) 1752.

[18] M. Manier, J.P. Mercurio, D. Mercurio and B. Frit, J. de Phys. Colloq. C1 Supp. 47 (1986) C1-907.

[19] K. Fukuda, R. Kitoh and I. Awai, Jpn. J. Appl. Phys. 32 (1993) 4584.

[20] B.W. Hakki and P.D. Coleman, IRE Trans. Microwave Theory Tech. MTT-8 (1960) 402.

[21] W.E. Courtney, IEEE Trans. Microwave Theory Tech. MTT-18 (1970) 476.

[22] Aps Khanna and Y. Garault, IEEE Trans. Microwave Theory Tech. MTT-31 (1983) 261.

[23] D. Kajfez and P. Guillon, Dielectric resonators (Artech House, Massachusettes, 1986).

[24] D.A. Sagala and S. Nambu, J. Phys. Soc. Jpn. 61 (1992) 1791.

[25] R. Zurmuhlen, E. Colla, D.C. Dube, J. Petzelt, I. Reaney, A. Bell and N. Setter, J. Appl. Phys. 76 (1994) 5864.

[26] H.A. Megaw, Proc. Phys. Soc. 58 (1946) 133.

[27] C.D. Brandle and V.J. Fratello, J. Mater. Res. 5 (1990) 2160.

[28] R.D. Shannon and C.T. Prewitt, Acta Cryst. B 25 (1969) 925.

[29] I. Gregoria, I. Petzelt, J. Pokarny, V. Vorlicek, Z. Zikmund, R. Zurmuhlen and N. Setter, Sol. State Commn. 94 (1995) 899.

[30] I.M. Reaney, E.L. Colla and N. Setter, Jpn. J. Appl. Phys. 33 (1994) 3984.

[31] M.T. Anderson, K.B. Greenwood, G.A. Taylor and K.R. Poeppelmeir, Prog. Sol. State Chem. 22 (1993) 197.

[32] A.M. Glazer, Act. Cryst. A 31 (1975) 756.

[33] E.L. Colla, I.M. Reaney and N. Setter, Ferroelectrics 133 (1992) 217.

[34] E.L. Colla, I.M. Reaney and N. Setter, Jpn. J. Appl. Phys. 74 (1993) 3414.

[35] H. Takahashi, Y. Baba, K. Ezaki, Y. Okamoto, K. Shibata, K. Kuroki and S. Nakano, Jpn. J. Appl. Phys. 30 (1991) 2339.