

# Tailoring the microwave dielectric properties of $\text{BaRE}_2\text{Ti}_4\text{O}_{12}$ and $\text{BaRE}_2\text{Ti}_5\text{O}_{14}$ ceramics by compositional variations

S. SOLOMON, N. SANTHA, I. N. JAWAHAR, H. SREEMOOLANADHAN, M. T. SEBASTIAN

Regional Research Laboratory, Trivandrum-695 019, India

E-mail: mailadils@yahoo.com

P. MOHANAN

Department of Electronics, Cochin University of Science and Technology, Cochin 682022 India

Ceramic dielectric resonators in the  $\text{BaO-RE}_2\text{O}_3\text{-TiO}_2$  (RE = rare earth) system have been prepared by the conventional solid state ceramic route. The dielectric properties have been tailored by substitution of different rare earth oxides and by bismuth oxide addition. The dielectric constants increased with Bi addition whereas the  $Q$  decreased. The temperature coefficient of the resonant frequency improved with bismuth addition.

© 2000 Kluwer Academic Publishers

## 1. Introduction

Ceramic compositions in the system  $\text{BaO-RE}_2\text{O}_3\text{-TiO}_2$  ( $\text{RE}_2\text{O}_3$ -rare earth oxide) are extensively used in the manufacture of electronic components. These compositions have high relative permittivity or dielectric constant ( $\epsilon_r \sim 80$ ) which are useful above 500 MHz, especially for applications like cellular telephones. In pursuit of high- $Q$  ceramics possessing high quality factor ( $Q$ ) and temperature compensation (zero  $\tau_f$ ), binary oxides of the  $\text{RE}_2\text{O}_3\text{-TiO}_2$  system [1, 2] and ternary oxides of the  $\text{BaO-RE}_2\text{O}_3\text{-TiO}_2$  system [3–20] (RE=La, Pr, Nd, Sm) have been studied by many researchers. The  $\text{BaO-RE}_2\text{O}_3\text{-TiO}_2$  ceramics (RE=Nd, Sm) with stoichiometry near to  $\text{BaRE}_2\text{Ti}_5\text{O}_{14}$  and  $\text{BaRE}_2\text{Ti}_4\text{O}_{12}$  have been widely studied [3–33]. Following earlier reports the  $\text{BaRE}_2\text{Ti}_4\text{O}_{12}$  ( $\text{BaO} : \text{RE}_2\text{O}_3 : 4\text{TiO}_2$ ) and  $\text{BaRE}_2\text{Ti}_5\text{O}_{14}$  ( $\text{BaO} : \text{RE}_2\text{O}_3 : 5\text{TiO}_2$ ) are represented in this article as 114 and 115 compounds, respectively, for convenience.

Optimization and tailoring of microwave dielectric properties of the ceramics can be achieved by compositional modifications such as doping, partial substitution and solid solution formation to meet the specific needs of the device design engineer. They can also improve the temperature variation of the resonant frequency [8–11]. Several authors [12, 13] reported that substituting Sr for Ba decreased the  $Q$  factor and improved the  $\tau_f$ . Lee and Lin [14] reported that Pb substitution for Ba in  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  decreased  $\epsilon_r$ , increased  $Q$  and improved  $\tau_f$ . Addition of commercial glass is reported to decrease the sintering temperature,  $\epsilon_r$ ,  $Q$  and  $\tau_f$  in  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  [7]. Valant *et al.* [4] found that addition of  $\text{WO}_3$  increased the  $Q$  but decreased the  $\epsilon_r$  whereas Mn addition [5] improved the  $\tau_f$  keeping  $\epsilon_r$  nearly constant. Al-substitution at the Ti site decreased the  $\epsilon_r$ ,  $Q$  and  $\tau_f$  [6].

Addition of rutile decreased the sintering temperature, and  $\epsilon_r$ , and increased the  $Q$  and  $\tau_f$  [6]. Several authors [19, 21, 29–32] reported the effect of  $\text{Bi}_2\text{O}_3$  substitution on Nd-based 114 and 115 ceramics. The present study was undertaken to investigate the effect of  $\text{Bi}_2\text{O}_3$  addition on the microwave dielectric properties of Nd, Sm, Pr and La-based 114 and 115 ceramics.

## 2. Experimental

(a) The undoped 114 and 115 ceramics were prepared by weighing high purity (99.9%)  $\text{BaCO}_3$ ,  $\text{RE}_2\text{O}_3$  ( $\text{Pr}_6\text{O}_{11}$  for Pr) in stoichiometric proportions and wet mixed with distilled water and ground in an agate mortar for 1 h and then dried. The dried powders were calcined in platinum crucibles at  $1210^\circ\text{C}$  for 4 h. The calcined powder was again ground well for half an hour and PVA (5%) was added and mixed well. It is then dried and again ground well for half an hour. This fine powder was pressed into cylindrical compacts of about 11 mm diameter and 5–8 mm height under a pressure of about 150 to 175 MPa. The samples were then sintered at appropriate optimized temperatures.

(b) For the Bi-doped 114 and 115 ceramics, the chemicals  $\text{BaCO}_3$ ,  $\text{RE}_2\text{O}_3$  ( $\text{Pr}_6\text{O}_{11}$  for Pr) and  $\text{TiO}_2$  were weighed in stoichiometric ratios. The powders were mixed well and calcined as described above for undoped ceramics. The calcined powder was then divided into 4 parts. 1 wt %  $\text{Bi}_2\text{O}_3$  was added to the first part, 3 wt % of  $\text{Bi}_2\text{O}_3$  to the second part, 5 wt % of  $\text{Bi}_2\text{O}_3$  to the third and 10 wt % of  $\text{Bi}_2\text{O}_3$  to the fourth part. Dielectric resonators were prepared from the powders by the method described above in (a).

(c) For the partial substitution using Bi in  $\text{Ba}(\text{RE}_{1.95}\text{Bi}_{0.05})\text{Ti}_5\text{O}_{14}$  ceramics, stoichiometric amounts of  $\text{Bi}_2\text{O}_3$  and other oxides were weighed and mixed well. The resonator samples were prepared as described in (a). The samples were sintered at  $1320^\circ\text{C}$  for 4 h.

(d) For the Bi-doped and undoped compositions of  $\text{Ba}(\text{Nd}_x\text{Sm}_{2-x})\text{Ti}_4\text{O}_{12}$  and  $\text{Ba}(\text{Nd}_x\text{Sm}_{2-x})\text{Ti}_5\text{O}_{14}$  ( $x = 0, 0.5, 1, 1.5, 2$ ), stoichiometric amounts of  $\text{BaCO}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$  and  $\text{TiO}_2$  were weighed and mixed well. The bismuth-doped samples were prepared by adding 1 wt % of  $\text{Bi}_2\text{O}_3$  to the calcined powder. The resonator samples were prepared as described in section (a).

The bulk densities of the compacts were measured by the Archimedes method. The sintered pellets were polished and thermally etched near the sintering temperature for 30 min and the surface microstructure studied using scanning electron microscopy (SEM). The phase purities and composition were studied from X-ray diffraction patterns obtained using  $\text{CuK}_\alpha$  radiation. Microwave dielectric resonator properties such as  $\epsilon$ , unloaded  $Q$  and  $\tau_f$  were measured using standard techniques, as explained elsewhere [15].

### 3. Results and discussion

#### 3.1. Sintered density and sintering temperature

Fig. 1 shows the variation of bulk densities and sintering temperatures of different 115 ceramics as a function of the percentage addition of  $\text{Bi}_2\text{O}_3$ . The addition of  $\text{Bi}_2\text{O}_3$  decreased the sintering temperature and increased the density. Fig. 2 shows the variation of bulk densities and sintering temperatures of different 114 ceramics as a function of the percentage addition of  $\text{Bi}_2\text{O}_3$ . It can be seen from the figure that the sintered densities of all the compounds increased when a small percentage of  $\text{Bi}_2\text{O}_3$  is added. The densities of La and Pr-based 114

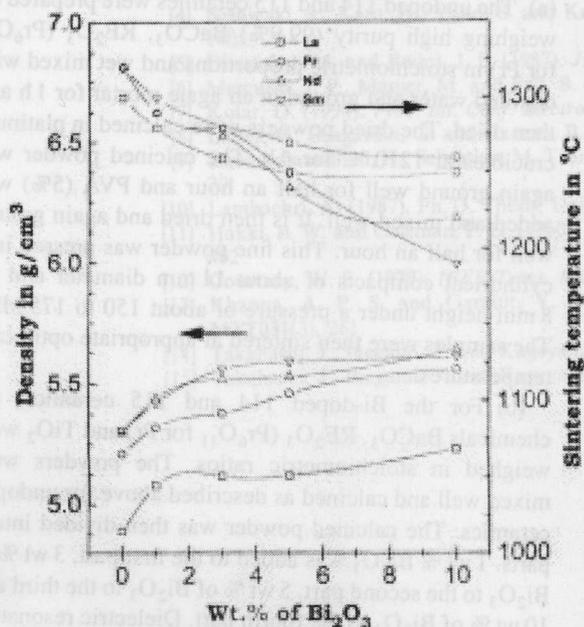


Figure 1 Variation of bulk densities and sintering temperatures of 115 ceramics due to the addition of  $\text{Bi}_2\text{O}_3$ .

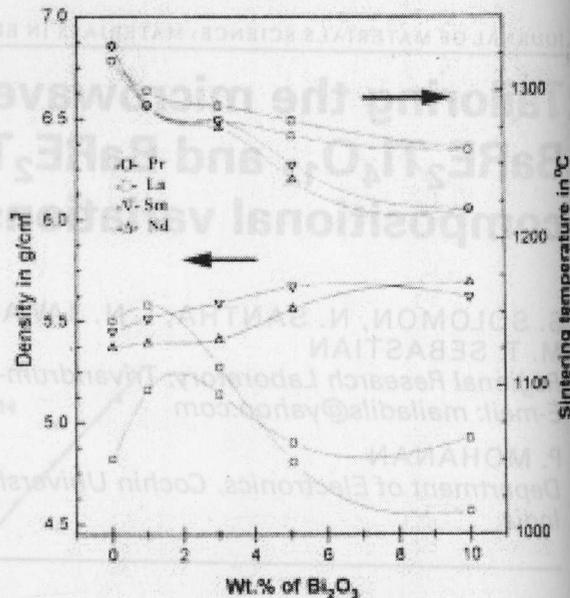


Figure 2 Variation of bulk densities and sintering temperatures of 114 ceramics due to the addition of  $\text{Bi}_2\text{O}_3$ .

compounds showed a decrease in density beyond 1 or 3 wt % addition of  $\text{Bi}_2\text{O}_3$ . This may be due to the porosity that larger amounts of  $\text{Bi}_2\text{O}_3$  produces.

Table I shows that the variation in densities of  $\text{BaRE}_{1.95}\text{Bi}_{0.05}\text{Ti}_5\text{O}_{14}$  ceramics due to  $\text{Bi}_2\text{O}_3$  substitution is relatively small; the values in between those of respective undoped 115 ceramics and those doped with 1% of  $\text{Bi}_2\text{O}_3$ . The sintering temperature of  $\text{BaRE}_{1.95}\text{Bi}_{0.05}\text{Ti}_5\text{O}_{14}$  ceramics also decreased by a small factor only. In general, addition of a small amount of  $\text{Bi}_2\text{O}_3$  increased the density of the sintered samples and lowered the sintering temperature.

#### 3.2. X-ray diffraction and electron microscopy

The X-ray diffraction (XRD) patterns obtained for the representative compounds of  $\text{Bi}_2\text{O}_3$  doped 115 and 114 ceramics using  $\text{CuK}_\alpha$  radiation are shown in Fig. 3 and Fig. 4, respectively. The patterns are in agreement with earlier reports [16–18]. Kolar *et al.* [19] had observed faint super-structure reflections in their XRD due to doubling of the  $c$ -axis. Rawn *et al.* [20] have taken into account the super-structure reflections in the refinement of the data. It has been reported that these ceramics may contain many secondary phases such as  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ,  $\text{TiO}_2$ ,  $\text{RE}_2\text{Ti}_2\text{O}_7$ ,  $\text{BaTi}_4\text{O}_9$ ,  $\text{RE}_4\text{Ti}_9\text{O}_{24}$ ,  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ , etc. [5, 6, 12, 14, 19, 21–26] and it is difficult to get a single phase material. Among these,  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  and  $\text{TiO}_2$  are found to be present as secondary phases more frequently.

The crystal system of these ceramics is reported to be tungsten-bronze type orthorhombic. Rawn *et al.* [20] also arrived at an orthorhombic crystal system with doubling of the lattice parameter and space group  $\text{Pnma}$ . It can be described as consisting of an infinite network of  $\text{TiO}_6$  corner-shared octahedra. The RE ions are in the perovskite-like columns surrounded by  $\text{TiO}_6$  octahedra. The addition of  $\text{Bi}_2\text{O}_3$  to 115 and 114 ceramics does not show any significant variation in the XRD patterns. Matveera *et al.* [27] were the first to make an XRD study

	Density (g/cc)	TE <sub>011</sub> (GHz)	ε	Q × f (GHz)	τ <sub>r</sub> (ppm°C <sup>-1</sup> )
La	5.01	3.8197	89	3290	330
Pr	5.29	3.5286	86	7190	134
Nd	5.35	3.7248	80	10800	69
Sm	5.40	3.6097	73	6200	-30

of the structure of these types of compounds. They reported the crystal structure of Ba<sub>3.75</sub>Pr<sub>0.5</sub>Ti<sub>18</sub>O<sub>54</sub> single crystals as made up of corner-sharing perovskite-like TiO<sub>6</sub> octahedra. Further to that, pentagonal and rhombic channels existed in this framework of linked TiO<sub>6</sub> octahedra, which can be occupied by Ba or RE ions. The occupancies of the pentagonal and rhombic sites are found to be different in different reports [20]. Accordingly [28], a solid solution, described by the general formula Ba<sub>6-x</sub>RE<sub>8+2/3x</sub>Ti<sub>8</sub>O<sub>54</sub> extends from x=0 through to x=3 for La-containing compounds have been proposed. The solid solutions can have different cations, large size Ba<sup>2+</sup> and/or RE<sup>3+</sup>. The variations in composition occur due to possible replacement of Ba<sup>2+</sup> with RE<sup>3+</sup>. Thus, to maintain charge neutrality three Ba<sup>2+</sup> ions should be replaced with two RE<sup>3+</sup> ions and a vacancy. The concentration of vacancies and ratio of Ba/Sm in the shared channel depend on the composition (x) of the solid solution.

The surface microstructure of typical Bi<sub>2</sub>O<sub>3</sub>-added 115 and 114 ceramics obtained using scanning electron microscopy (SEM) are shown in Fig. 5 a to d. The figures show the secondary electron images of polished and thermally etched surfaces of sintered ceramics. Most of the ceramics had columnar grains up to 5 μm in size. The

SEM pictures showed relatively low levels of porosity in the ceramics. Ceramics doped with larger amounts of Bi<sub>2</sub>O<sub>3</sub> show secondary phases.

### 3.3. Dielectric resonator properties

#### 3.3.1. 115 Ceramics

The relative dielectric constants (ε<sub>r</sub>) of the ceramics are obtained using the TE<sub>011</sub> resonant frequencies and dimensions of the resonator. The samples showed sharp TE<sub>011</sub> resonances in the 3–5 GHz range. Table II lists the TE<sub>011</sub> mode resonant frequencies and ε<sub>r</sub> of these ceramics. It can be seen that Bi<sub>2</sub>O<sub>3</sub> addition increases the ε<sub>r</sub> of the ceramics. Fig. 6 shows the variation of ε<sub>r</sub> with respect to the percentage of Bi<sub>2</sub>O<sub>3</sub> addition. The increase in ε<sub>r</sub> with Bi<sub>2</sub>O<sub>3</sub> addition showed a behavior similar to the increase in density with Bi<sub>2</sub>O<sub>3</sub> addition. The ε<sub>r</sub> increases with Bi<sub>2</sub>O<sub>3</sub> doping up to 10 wt %. In the case of Sm-based ceramics the ε increased up to 5 wt % addition of Bi<sub>2</sub>O<sub>3</sub> and further addition decreased ε<sub>r</sub>. The BaRE<sub>1.95</sub>Bi<sub>0.05</sub>Ti<sub>5</sub>O<sub>14</sub> ceramics show a small increase in the dielectric constant (see Table I). This can be supported by the fact that the increase in density by the Bi-substitution is also very small.

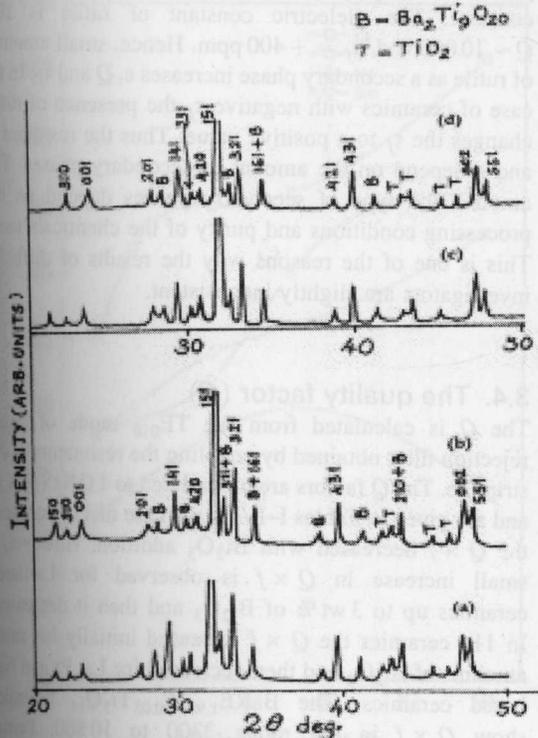


Figure 3 X-ray diffraction (XRD) patterns of typical 115 ceramics (a) La-compound, (b) La-compound with 5% Bi<sub>2</sub>O<sub>3</sub> added (c) Nd-compound and (d) Nd-compound with 5% Bi<sub>2</sub>O<sub>3</sub> added.

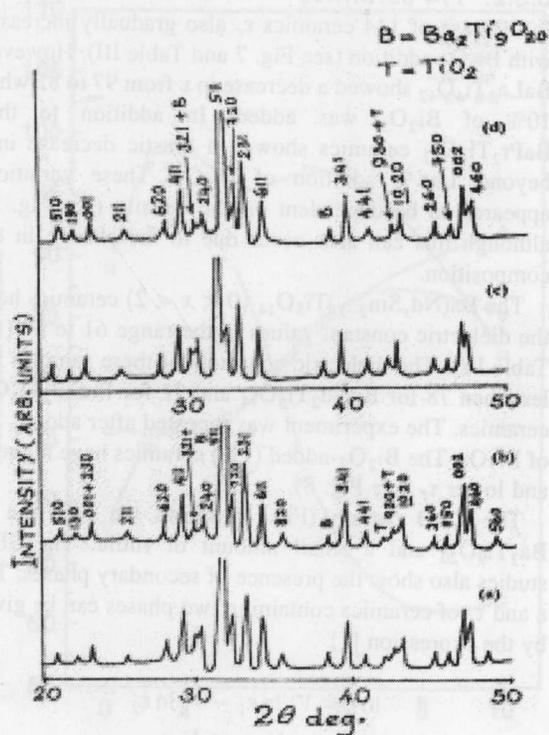
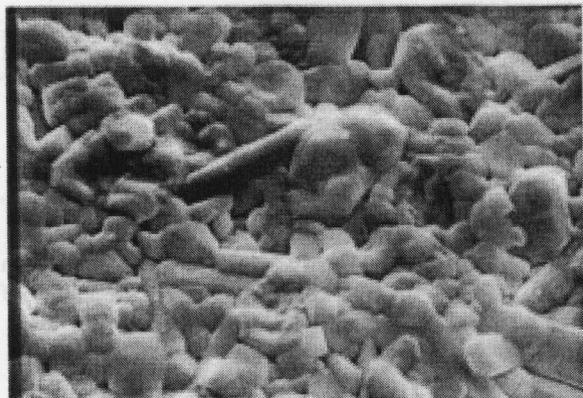
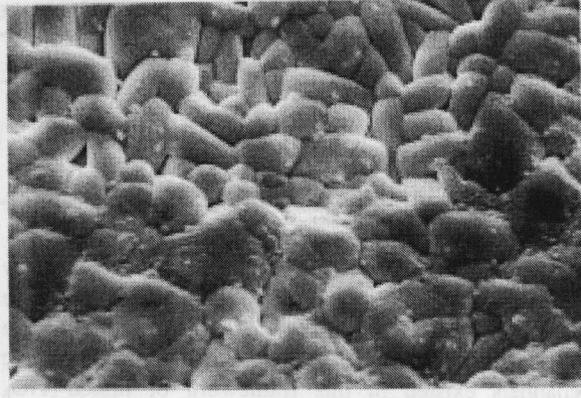


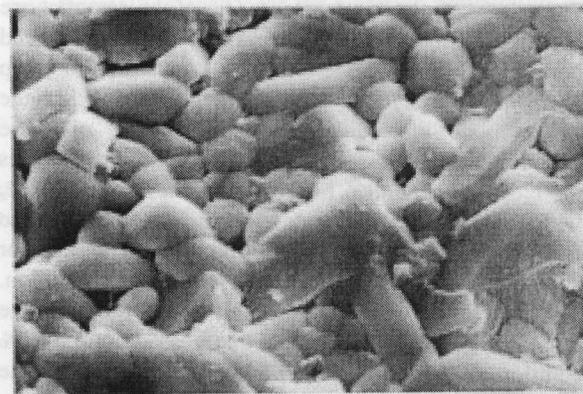
Figure 4 X-ray diffraction (XRD) patterns of typical 114 ceramics (a) La-compound, (b) La-compound with 5% Bi<sub>2</sub>O<sub>3</sub> added (c) Nd-compound and (d) Nd-compound with 5% Bi<sub>2</sub>O<sub>3</sub> added.



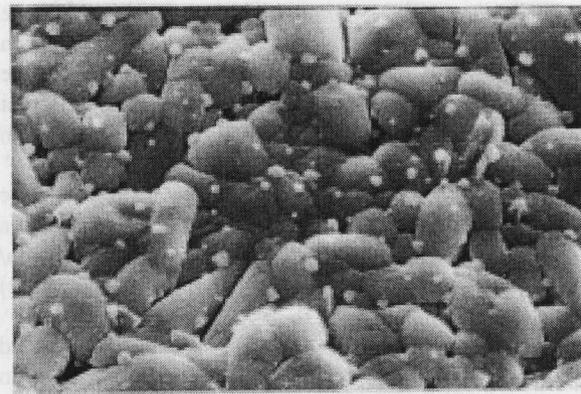
(a)



(b)



(c)



(d)

Figure 5 Secondary electron images of the etched surfaces of 115 ceramics (a) Nd-compound (b) Nd-compound with 10%  $\text{Bi}_2\text{O}_3$  added. Similar images obtained for 114 ceramics (c) Nd-compound, (d) Nd-compound with 10%  $\text{Bi}_2\text{O}_3$  added.

### 3.3.2. 114 ceramics

In the case of 114 ceramics  $\epsilon_r$  also gradually increased with  $\text{Bi}_2\text{O}_3$  addition (see Fig. 7 and Table III). However,  $\text{BaLa}_2\text{Ti}_4\text{O}_{12}$  showed a decrease in  $\epsilon$  from 97 to 82 when 10% of  $\text{Bi}_2\text{O}_3$  was added. In addition to this,  $\text{BaPr}_2\text{Ti}_4\text{O}_{12}$  ceramics showed a drastic decrease in  $\epsilon$  beyond 1 wt % addition of  $\text{Bi}_2\text{O}_3$ . These variations appeared to be dependent on the density (see Fig. 2), although this can also occur due to the change in the composition.

The  $\text{Ba}(\text{Nd}_x\text{Sm}_{2-x})\text{Ti}_5\text{O}_{14}$  ( $0 < x < 2$ ) ceramics have the dielectric constant values in the range 61 to 80 (see Table IV). The dielectric constants of these samples are less than 78 for  $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$  and 72 for  $\text{BaSm}_2\text{Ti}_5\text{O}_{14}$  ceramics. The experiment was repeated after adding 1% of  $\text{Bi}_2\text{O}_3$ . The  $\text{Bi}_2\text{O}_3$ -added (1%) ceramics have higher  $\epsilon$  and lower  $\tau_f$  (see Fig. 8).

The XRD pattern (Fig. 4) shows the presence of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  and a small amount of rutile. The SEM studies also show the presence of secondary phases. The  $\epsilon$  and  $\tau_f$  of ceramics containing two phases can be given by the expression [1]

$$\ln \epsilon = V_1 \ln \epsilon_1 + V_2 \ln \epsilon_2$$

$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2}$$

where  $V_1$  and  $V_2$  are the volume fractions of the two phases and  $\epsilon_1$  and  $\epsilon_2$  are their dielectric constants. The

presence of  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  with  $\epsilon_r = 39$  lowers the dielectric constant. The dielectric constant of rutile is 104,  $Q \sim 10\,000$  and,  $\tau_f = +400$  ppm. Hence, small amounts of rutile as a secondary phase increases  $\epsilon$ ,  $Q$  and  $\tau_f$ . In the case of ceramics with negative  $\tau_f$  the presence of rutile changes the  $\tau_f$  to a positive value. Thus the resultant  $\tau_f$  and  $\epsilon$  depend on the amount of secondary phases. The amount and type of secondary phases depend on the processing conditions and purity of the chemicals used. This is one of the reasons why the results of different investigators are slightly inconsistent.

### 3.4. The quality factor ( $Q$ )

The  $Q$  is calculated from the  $\text{TE}_{018}$  mode of band-rejection filter obtained by coupling the resonators to the stripline. The  $Q$  factors are normalized to 1 GHz ( $Q \times f$ ) and are given in Tables I–IV. In the case of 115 ceramics the  $Q \times f$  decreased with  $\text{Bi}_2\text{O}_3$  addition. However, a small increase in  $Q \times f$  is observed for La-based ceramics up to 3 wt % of  $\text{Bi}_2\text{O}_3$  and then it decreased. In 114 ceramics the  $Q \times f$  increased initially for small amounts of  $\text{Bi}_2\text{O}_3$  and then decreased for La, Pr and Nd-based ceramics. The  $\text{BaRE}_{1.95}\text{Bi}_{0.05}\text{Ti}_5\text{O}_{14}$  ceramics show  $Q \times f$  in the range 3300 to 10800. Partial substitution of  $\text{Bi}^{3+}$  for RE increased the  $Q$  (see Table I).  $\text{Ba}(\text{Nd}_x\text{Sm}_{2-x})\text{Ti}_5\text{O}_{14}$  ceramics possess high  $Q$  (see Table IV) with  $Q \times f$  in the range 7000 to 11000. The

TABLE II Microwave dielectric resonant properties of Bi<sub>2</sub>O<sub>3</sub>-doped BaRE<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> ceramics

	Wt % Bi <sub>2</sub> O <sub>3</sub>	D (mm)	L (mm)	TE <sub>011</sub> (GHz)	ε	Q × f (GHz)	τ <sub>f</sub> (ppm°C <sup>-1</sup> )
La	0	9.91	11.37	3.2163	85	2800	345
	1	9.43	6.48	3.8979	92	3000	324
	3	9.42	7.71	3.62265	95	3250	213
	5	9.44	7.61	3.618	96	3000	160
	10	9.41	8.2	3.3167	106	1900	139
Pr	0	9.77	8.87	3.6388	78	7090	147
	1	9.48	9.35	3.652	79	5830	132
	3	9.70	9.92	3.428	82	5300	109
	5	9.69	9.31	3.373	90	3400	98
	10	9.71	10.08	3.1499	96	2870	80
Nd	0	9.5	8.83	3.731	78	8900	82
	1	9.47	6.87	4.07875	80	8800	74
	3	9.34	8.37	3.736	84	7400	60
	5	9.38	8.14	3.7046	86	6500	45
	10	9.38	6.51	3.883	93	4400	41
Sm	0	9.56	7.18	4.1872	72	8750	-42
	1	9.75	5.58	3.835	74	7800	-18
	3	9.42	7.52	3.9894	78	8000	-2
	5	9.48	6.37	4.2185	80	6200	-5
	10	9.48	9.39	3.775	74	2000	*

compounds containing Bi<sub>2</sub>O<sub>3</sub> > 10 wt % did not show resonance. This may be due to the very low quality factor of the samples.

### 3.5. Temperature coefficient of resonant frequency (τ<sub>f</sub>)

The temperature variation of resonant frequencies of Bi<sub>2</sub>O<sub>3</sub> added 115 and 114 ceramics, obtained from the slope of the variation of resonant frequency versus temperature are given in Tables II and III respectively.

The τ<sub>f</sub> values decrease with increase in the percentage of addition of Bi<sub>2</sub>O<sub>3</sub>. Valant *et al.* [19] also have reported that Bi<sub>2</sub>O<sub>3</sub> addition up to 6.5 wt % lowers τ<sub>f</sub> and further addition increases the τ<sub>f</sub> in BaNd<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> ceramics.

In the case of BaSm<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub>, τ<sub>f</sub> improves from -42 ppm°C<sup>-1</sup> to -5 ppm°C<sup>-1</sup>. Figs 9 and 10 show the variation in τ<sub>f</sub> with respect to the addition of Bi<sub>2</sub>O<sub>3</sub> in 115 and 114 ceramics, respectively. Bi<sup>3+</sup> added compounds show lower τ<sub>f</sub> when compared to their corresponding undoped samples (see Table II and III).

Fig. 11 shows the variation in the resonant frequency

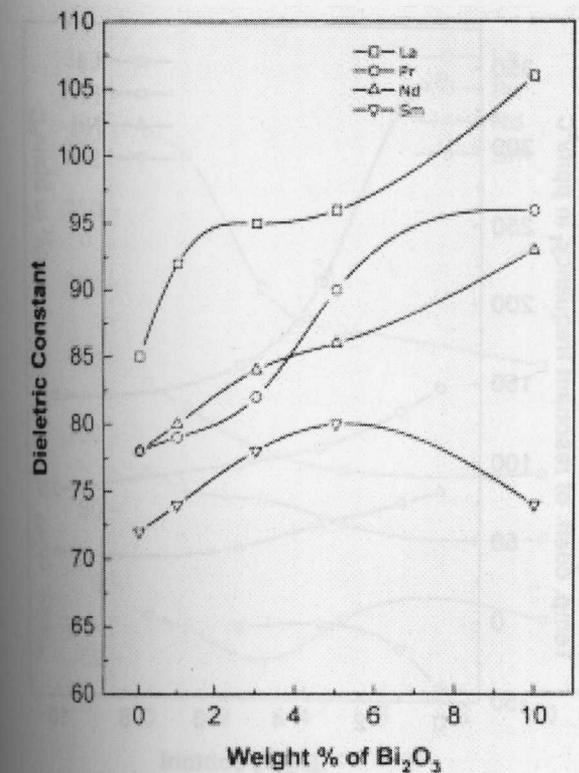


Figure 6 Effect of Bi<sub>2</sub>O<sub>3</sub> addition on the dielectric constants (ε<sub>r</sub>) of 115 ceramics.

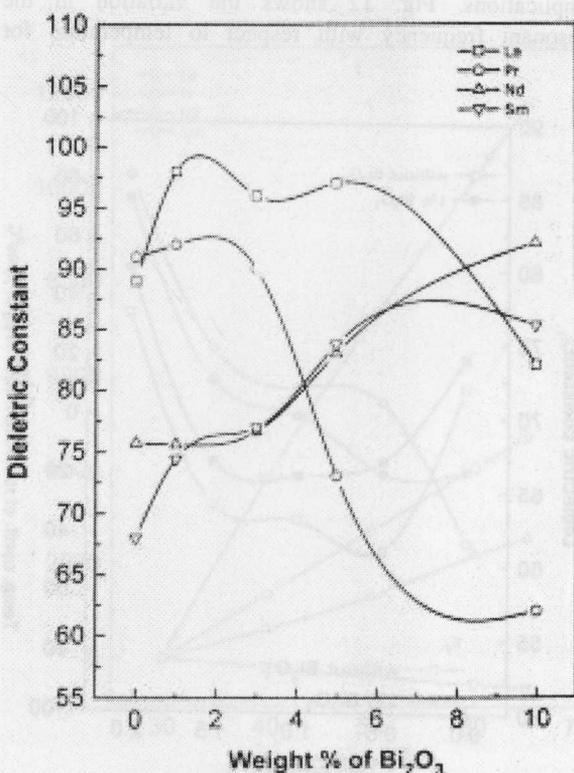


Figure 7 Effect of Bi<sub>2</sub>O<sub>3</sub> addition on the dielectric constants (ε<sub>r</sub>) of 114 ceramics.

TABLE III Microwave dielectric resonator properties of Bi<sub>2</sub>O<sub>3</sub>-doped BaRE<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> ceramics

	Wt % Bi <sub>2</sub> O <sub>3</sub>	D (mm)	L (mm)	TE <sub>011</sub> (GHz)	ε	Q × f (GHz)	τ <sub>f</sub> (ppm °C <sup>-1</sup> )
La	0	9.65	6.14	4.04097	89	1900	301
	1	9.53	6.11	3.8807	98	2100	286
	3	9.55	5.97	3.935	96	2450	197
	5	9.53	8.38	3.4211	97	2250	169
	10	9.91	8.32	3.6121	82	1650	144
Pr	0	9.32	8.35	3.5883	91	5600	135
	1	9.47	5.8	4.1555	92	5650	118
	3	9.59	5.86	4.1385	90	5350	89
	5	9.81	10.16	3.5753	73	4850	75
	10	10.04	9.44	3.939	62	4200	72
Nd	0	9.7	7.19	4.0584	75.7	5600	77
	1	9.79	5.9	4.4575	75.6	6350	63
	3	9.85	8.25	3.778	76.6	4950	56
	5	9.83	9.64	3.4396	83	3100	39
	10	9.77	6.08	3.9604	92.1	2300	28
Sm	0	9.69	6.59	3.429	68	3600	-21
	1	9.65	7.64	4.0303	74.4	3150	-30
	3	9.59	8.04	3.8733	76.9	2000	-52
	5	9.54	7.34	3.8797	83.7	1950	-25
	10	9.7	8.14	3.6375	85.2	2300	-27

with respect to temperature for the Bi<sup>3+</sup>-substituted BaRE<sub>1.95</sub>Bi<sub>0.05</sub>Ti<sub>5</sub>O<sub>14</sub> compounds. The values of τ<sub>f</sub> are lower than that of the pure samples.

The τ<sub>f</sub> of BaNd<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> is 82 and that of BaSm<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> is -42. Therefore it should be possible to tune τ<sub>f</sub> by making solid solution between these compounds. The solid solutions with the general formula Ba(Nd<sub>x</sub>Sm<sub>2-x</sub>)Ti<sub>5</sub>O<sub>14</sub> have τ<sub>f</sub> values between those of the above two compounds. When x=0.5, i.e. Ba(Nd<sub>0.5</sub>Sm<sub>1.5</sub>)Ti<sub>5</sub>O<sub>14</sub> τ<sub>f</sub> = +5 ppm °C<sup>-1</sup>. The τ<sub>f</sub> for x=1, i.e. Ba(NdSm)Ti<sub>5</sub>O<sub>14</sub> is +10 ppm °C<sup>-1</sup>. When 1 wt % of Bi<sub>2</sub>O<sub>3</sub> is added to this compound, the τ<sub>f</sub> value is reduced to 0.4 and this is useful for practical applications. Fig. 12 shows the variation in the resonant frequency with respect to temperature for

Ba(Nd<sub>x</sub>Sm<sub>2-x</sub>)Ti<sub>5</sub>O<sub>14</sub> ceramics. Table IV shows the microwave dielectric resonator properties of Ba(Nd<sub>x</sub>Sm<sub>2-x</sub>)Ti<sub>5</sub>O<sub>14</sub> ceramics. The variation in τ<sub>f</sub> and ε<sub>r</sub> with respect to x for pure and 1% Bi<sub>2</sub>O<sub>3</sub>-added Ba(Nd<sub>x</sub>Sm<sub>2-x</sub>)Ti<sub>5</sub>O<sub>14</sub> ceramics are given in Fig. 8. The Ba(Nd<sub>x</sub>Sm<sub>2-x</sub>)Ti<sub>4</sub>O<sub>12</sub> ceramics have a very low Q and hence the τ<sub>f</sub> could not be measured.

The beneficial influence of bismuth addition on the dielectric properties of the ceramics with ternary compositions from the BaO-Nd<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> system was first reported by Kolar *et al.* [19]. They noticed that by increasing the Bi content, the ε<sub>r</sub> and τ<sub>f</sub> increased. Several authors [29–32] confirmed the observations of Kolar.

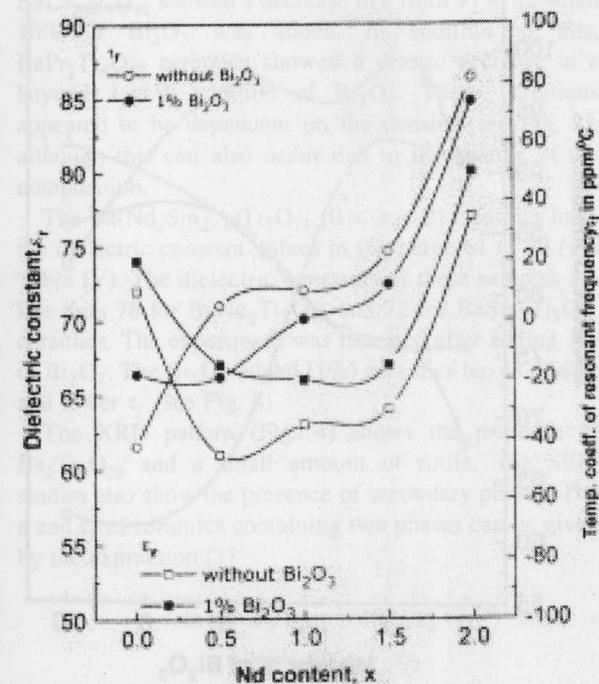


Figure 8 Influence of substitution (x) and Bi<sub>2</sub>O<sub>3</sub> addition on the dielectric constants (ε<sub>r</sub>) of Ba(Nd<sub>x</sub>Sm<sub>2-x</sub>)Ti<sub>5</sub>O<sub>14</sub> ceramics.

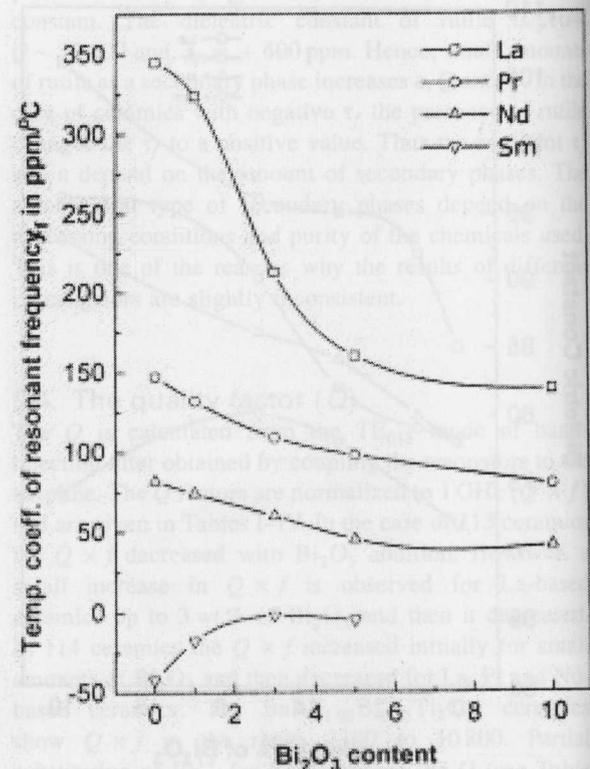


Figure 9 Effect of Bi<sub>2</sub>O<sub>3</sub> addition on the temperature coefficient of resonant frequencies (τ<sub>f</sub>) of 115 ceramics.

X	Wt % Bi <sub>2</sub> O <sub>3</sub>	D (mm)	L (mm)	ρ (g cm <sup>-3</sup> )	TE <sub>011</sub> (GHz)	ε	Q × f (GHz)	τ <sub>f</sub> (ppm °C <sup>-1</sup> )
0.0	-0-	9.56	7.18	5.31	4.19	72	8750	-42.0
	1.0	9.75	5.58	5.42	3.38	74	7450	-18.0
0.5	-0-	9.44	5.66	5.31	5.05	61	8200	5.0
	1.0	9.39	6.72	5.39	4.35	67	7200	-19.0
1.0	-0-	9.31	7.35	5.33	4.48	63	8800	10.0
	1.0	9.28	6.46	5.36	4.68	66	9000	0.4
1.5	-0-	9.24	7.67	5.31	4.38	64	11 000	23.0
	1.0	9.36	7.37	5.37	4.38	67	9200	12.0
2.0	-0-	9.50	8.83	5.30	3.73	78	8900	82.0
	1.0	9.47	6.87	5.44	4.08	80	8800	74.0

However, the role of Bi in optimizing the dielectric properties is still a matter of discussion. Recently, it has been reported [32] that Bi<sup>3+</sup> substitutes for Nd<sup>3+</sup> in the crystal structure of the BaNd<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> up to the solubility limit, which was determined to be 2.5 mol%. After exceeding the solubility limit, additional Bi<sub>2</sub>O<sub>3</sub> concentrates as a Bi-enriched phase at the grain boundaries, causing considerable reduction in the Q and increases τ<sub>f</sub>. Moreover, Valant *et al.* [33] made a detailed EXAFS (extended X-ray absorption time spectroscopy) study on Ba<sub>4.5</sub>Nd<sub>9-y</sub>Bi<sub>y</sub>Ti<sub>18</sub>O<sub>54</sub> (y = 0, 0.5, 1). Due to very similar environments of the equivalent sites in the subcells, only EXAFS can distinguish the different channels. Their results indicate that Bi<sup>3+</sup> do not substitute for Nd<sup>3+</sup> randomly on all possible sites. The Bi<sup>3+</sup> selectively enters one of the following possible channels i.e., R: x = 0.9484, y = 0.2500, z = 0.2939 and/or x = 0.0455, y = 0.2500, z = 0.6928 previously occupied by Nd<sup>3+</sup>.

A practical problem in the synthesis of these bismuth-substituted materials is related to the conditions

necessary to maintain exact stoichiometry and reproducibility due to the vaporization of Bi<sub>2</sub>O<sub>3</sub> at elevated temperatures. Slight changes in stoichiometry can lead to large changes in the microstructure development during sintering. Incomplete substitution of Bi<sup>3+</sup> for Nd<sup>3+</sup> due to the evaporation of Bi<sub>2</sub>O<sub>3</sub> during sintering leads to the formation of multiphase ceramics. In such ceramics, the additional phases can increase or decrease ε<sub>r</sub> and τ<sub>f</sub> of 114 and 115 ceramics and hence the microwave dielectric properties vary according to the contributions of each phase. This is one of the reasons for different dielectric properties reported by different research groups.

### 4. Conclusion

BaRE<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> and BaRE<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> ceramics have been prepared with different trivalent ions for RE and also using different percentages of Bi<sub>2</sub>O<sub>3</sub> as additive and sintered into dense ceramics. The dielectric resonator

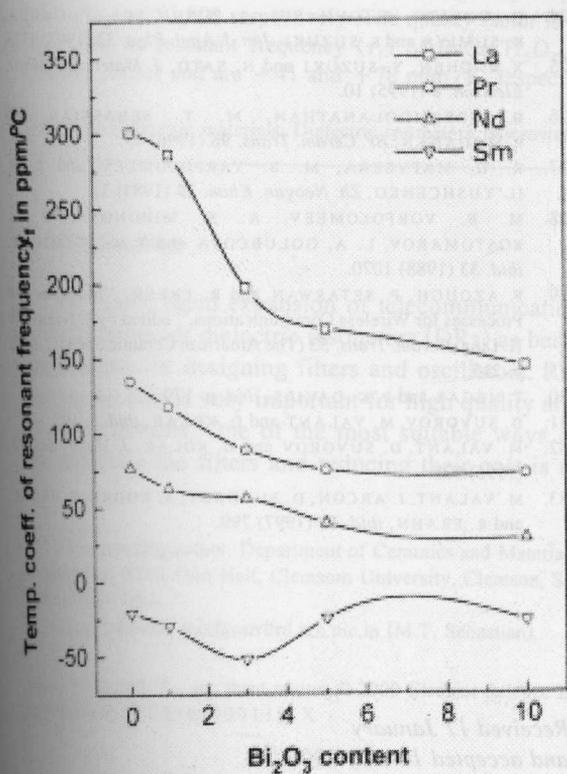


Figure 10 Effect of Bi<sub>2</sub>O<sub>3</sub> addition on the temperature coefficient of resonant frequencies (τ) of 114 ceramics.

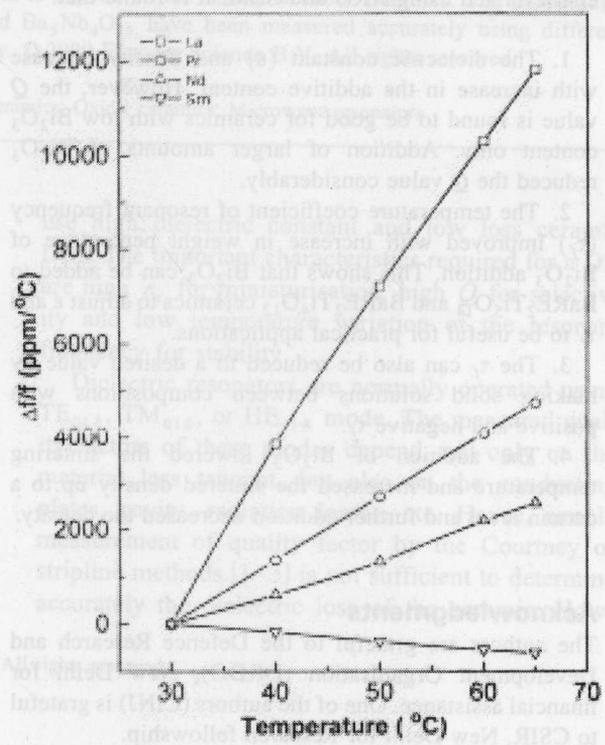


Figure 11 Variation of (Δf/f) as a function of temperature in Ba(RE<sub>1.95</sub>Bi<sub>0.05</sub>)Ti<sub>5</sub>O<sub>14</sub> ceramics.

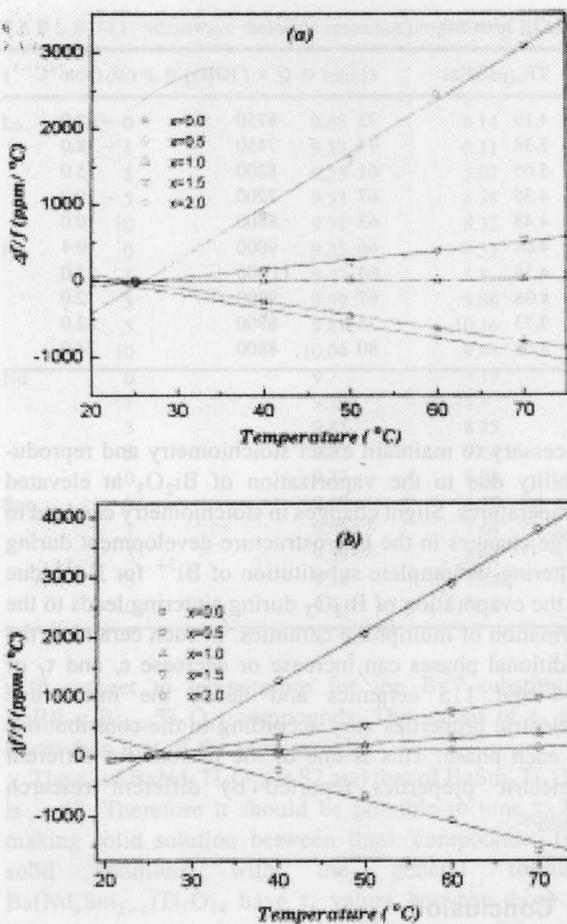


Figure 12 Variation of ( $\Delta f/f$ ) as a function of temperature in  $\text{Ba}(\text{Nd}_x\text{Sm}_{2-x})\text{Ti}_5\text{O}_{14}$  ceramics. (a) undoped (b) lwt %  $\text{Bi}_2\text{O}_3$ .

properties of these ceramics have been measured in the microwave frequency range. The ceramics have been characterized using XRD and SEM. It is found that:

1. The dielectric constant ( $\epsilon$ ) and density increase with increase in the additive content. However, the  $Q$  value is found to be good for ceramics with low  $\text{Bi}_2\text{O}_3$  content only. Addition of larger amounts of  $\text{Bi}_2\text{O}_3$  reduced the  $Q$  value considerably.

2. The temperature coefficient of resonant frequency ( $\tau_f$ ) improved with increase in weight percentage of  $\text{Bi}_2\text{O}_3$  addition. This shows that  $\text{Bi}_2\text{O}_3$  can be added to  $\text{BaRE}_2\text{Ti}_5\text{O}_{14}$  and  $\text{BaRE}_2\text{Ti}_4\text{O}_{12}$  ceramics to adjust  $\epsilon$  and  $\tau_f$  to be useful for practical applications.

3. The  $\tau_f$  can also be reduced to a desired value by making solid solutions between compositions with positive and negative  $\tau_f$ .

4. The addition of  $\text{Bi}_2\text{O}_3$  lowered the sintering temperature and increased the sintered density up to a certain level and further addition decreased the density.

## Acknowledgments

The authors are grateful to the Defence Research and Development Organisation (DRDO), New Delhi for financial assistance. One of the authors (CINJ) is grateful to CSIR, New Delhi for Research fellowship.

## References

1. A. E. PALASHINO, *J. Am. Ceram. Soc.* **54** (1971) 168.
2. J. TAKAHASHI, K. KAGEYAMA and K. KODAIRA, *Jpn. J. Appl. Phys.* **32** (1993) 4327.
3. D. KOLAR, Z. STADLER, S. GABERSCEK and D. SUVOROV, *Ber. Dr. Keram. Ges.* **55** (1978) 346.
4. M. VALANT, D. SUVOROV and D. KOLAR, Proc. III Euro-Ceramics, edited by P. Duran and J. F. Fernandez, Faenza Editrice Iberica S.L. **2** (1993) 235.
5. M. MIZATE, K. UENOYAMA, H. OHSATO, S. NISHIGAKI and T. OKUDA, *Jpn. J. Appl. Phys.* **35** (1996) 5065.
6. H. OHSATO, A. KOMURA, Y. TAKAGI, S. NISHIGAKI and T. OKUDA *ibid.* **37** (1998) 5357.
7. C. C. LEE and P. LIN, *ibid.* **37** (1998) 6048.
8. H. SREEMOOLANADHAN, PhD Thesis, University of Kerala (1997).
9. H. TAKAHASHI, Y. BABA, K. EZAKI, V. OKAMOTA, K. SHIBATA and K. KUROTO, US Patent 5 244 851 (1993).
10. H. TAKAMI, S. YANO and M. ABE, US Patent 5 185 304 (1993).
11. T. FUJIMURA, T. YONEDA and H. TAKI, US Patent 5 256 639 (1993).
12. J. S. SUN, C. C. WEI and L. WU, *J. Mater. Sci.* **27** (1992) 5818.
13. S. NISHIGAKI, KATO, YANO and R. KAMIMURA, *Am. Ceram. Soc. Bull.* **66**(9) (1987) 1405.
14. C. C. LEE and P. LIN, *Jpn. J. Appl. Phys.* **37** (1998) 779.
15. R. RATHEESH, H. SREEMOOLANADHAN, P. MONAHAN and M. T. SEBASTIAN, *Ferroelectrics* (1998) 211.
16. JCPDS file 35-331.
17. J. TAKAHASHI, T. IKEGAMI and K. KAGAYAMA, *J. Am. Ceram. Soc.* **74** (1991) 1873; *ibid.* 1868.
18. H. OHSATO, T. OHASHI, H. KATO, S. NISHIGAKI and T. OKUDA, *Jpn. J. Appl. Phys.* **34** (1993) 187.
19. M. VALANI, D. KOLAR, and D. SUVOROV, Proc. III Euro-Ceramics, edited by P. Duran and J. F. G. Fernandez **2** (1993) 235.
20. C. J. RAWN, D. P. BIRNICA, M. A. BRUCK, J. H. ENEMARK and R. S. ROTH, *J. Mater. Res.* **13** (1998) 187.
21. J. M. DURAND and J. P. BOILOT, *J. Mater. Sci. Lett.* **6** (1987) 134.
22. J. M. WU, M. C. CHANG and P. C. YAO, *J. Am. Ceram. Soc.* **73** (1990) 1599.
23. P. LAFFEZ, G. DESGARDIN and B. RAVEAU, *J. Mater. Sci.* **27** (1992) 5229.
24. H. OHSATO, T. OHASHI, S. NISHIGAKI, T. OKUDA, K. SUMIYA and S. SUZUKI, *Jpn. J. Appl. Phys.* **32** (1993) 4323.
25. X. M. CHEN, Y. SUZUKI and N. SATO, *J. Mater. Sci. Mater. Electron.* **6** (1995) 10.
26. H. SREEMOOLANATHAN, M. T. SEBASTIAN and P. MOHANAN, *Br. Ceram. Trans.* **95** (1996) 79.
27. R. G. MATVEERA, M. B. VARFOLOMEEV and L. S. IL'YUSHCENKO, *Zh. Neogan. Khim.* **29** (1984) 31.
28. M. B. VORFOLOMEEV, A. S. MIRONOVA, U. S. KOSTOMAROV, L. A. GOLUBCOVA and T. A. ZOLOTOVA, *ibid.* **33** (1988) 1070.
29. F. AZOUGH, P. SETASWAN and R. FREER, "Materials and Processes for Wireless Communications," edited by T. Negas and H. Ling. *Ceram. Trans.* **53** (The American Ceramic Society, 1995) p. 215.
30. T. NEGAS and P. K. DAVIES, *ibid.* p. 179.
31. D. SUVOROV, M. VALANT and D. KOLAR, *ibid.* p. 197.
32. M. VALANT, D. SUVOROV and D. KOLAR, *J. Mater. Res.* **11** (1996) 928.
33. M. VALANT, I. ARCON, D. SUVOROV, A. KODRE, T. NEGAS and R. FRAHN, *ibid.* **12** (1997) 799.

Received 17 January  
and accepted 10 July 2000