

# Preparation, characterization and microwave dielectric properties of $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$ [ $\text{B}' = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Y}, \text{Yb}$ and $\text{In}$ ] ceramics

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## Abstract

Microwave dielectric resonators (DRs) based on  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  [ $\text{B}' = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Y}, \text{Yb}$ , and  $\text{In}$ ] complex perovskites have been prepared by conventional solid state ceramic route. The dielectric properties (relative permittivity,  $\epsilon_r$ ; quality factor,  $Q$ ; and resonant frequency,  $\tau_f$ ) of the ceramics have been measured in the frequency range 4–6 GHz using resonance methods. The resonators have relatively high dielectric constant in the range 36–45, high quality factor and small temperature variation of resonant frequency. The dielectric properties are found to depend on the tolerance factor ( $t$ ), ionic radius ( $r$ ), and lattice parameter ( $a_p$ ).

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**Keywords:** Dielectric resonators; Complex perovskites; Double perovskites; Microwave ceramics; Dielectric ceramics

## 1. Introduction

Dielectric resonators (DRs) are ceramics with high relative permittivity ( $\epsilon_r$ ), low dielectric loss (or high quality factor  $Q$ ), and small temperature variation of resonant frequency ( $\tau_f$ ) that are used in place of bulky cavity resonators and lossy stripline resonators in modern microwave integrated circuits for reducing the size and weight of the components [1,2]. Typically, ceramics with  $20 < \epsilon_r < 100$ ,  $Q > 2000$ , and  $\tau_f < 20 \text{ ppm}/^\circ\text{C}$  are useful for various kinds of applications ranging from 800 MHz (UHF) to 20 GHz (K band) of microwave spectrum. This limits the number of materials available for practical applications. The important dielectric resonator materials so far studied include  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  [3],  $\text{Zr}(\text{Sn},\text{Ti})\text{O}_4$  [4],  $\text{BaO-Ln}_2\text{O}_3\text{-TiO}_2$  [5,6] ( $\text{Ln} = \text{rare earth}$ ),  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  [7] and complex perovskites [8,9]. Still the search for new ceramics with better characteristics is in progress.

Several workers [8–12] investigated the dielectric resonator properties of  $\text{A}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$  ceramics where  $\text{A} = \text{Ba}, \text{Sr}$ ;  $\text{B}' = \text{Zn}, \text{Mg}$ ; and  $\text{B}'' = \text{Nb}, \text{Ta}$ . Although a considerable amount of work has been done on the  $\text{A}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$  perovskites, only a little attention has been paid to the microwave dielectric properties of  $\text{A}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$  type complex perovskite ceramics where  $\text{B}'$  is a trivalent ion and  $\text{B}''$  is a pentavalent-ion. Agranovskaya [13] in 1960 outlined the dielectric properties of  $\text{A}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$  complex perovskites. A detailed description about the structure and properties of a large number of this type of compounds is given by Galasso [14]. Takata and Kageyama [15] were the first to investigate the microwave dielectric properties of  $\text{A}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$  type perovskites ( $\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$ ;  $\text{B}' = \text{La}, \text{Nd}, \text{Sm}, \text{Yb}$ , and  $\text{B}'' = \text{Nb}, \text{Ta}$ ). They obtained  $\epsilon_r$  in the range 30–45 and found that niobates and tantalates of Ba have positive  $\tau_f$  while those of Sr and Ca have negative  $\tau_f$ . Recently, several authors [16–20] reported the microwave dielectric properties of a few of the  $\text{A}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$  type ceramics by direct microwave or spectroscopic methods. It was reported that the  $\epsilon_r$  value of  $\text{Ba}(\text{Nd}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ,  $\text{Ba}(\text{Sm}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ,  $\text{Ba}(\text{Eu}_{1/2}\text{Nb}_{1/2})\text{O}_3$ , and  $\text{Ba}(\text{Pr}_{1/2}\text{Nb}_{1/2})\text{O}_3$  as 12, 9, 11,

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and 15, respectively in the microwave frequency region [20] which were different from the report of Ikawa and Takemoto [21], and Zurmuhlen et al. [17]. Since the dielectric constants reported by various research groups [15–17,19,20] on some of the  $A(B'_{1/2}Nb_{1/2})O_3$  compounds are found to be contradicting, we have undertaken a detailed study on the preparation, characterization and microwave dielectric properties of  $Ba(B'_{1/2}Nb_{1/2})O_3$  [ $B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, \text{ and } In$ ] ceramics.

## 2. Experimental

The ceramic resonators  $Ba(B'_{1/2}Nb_{1/2})O_3$  [ $B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Yb, \text{ and } In$ ] were prepared by the conventional solid state ceramic route. Starting materials were high purity  $BaCO_3$  (Aldrich Chemicals; 99.9%),  $Nb_2O_5$  (Nuclear Fuel Complex, Hyderabad; 99.9%) and rare earth oxides (Indian Rare Earths Ltd.; 99.99%). These powders were ball milled using distilled water for 36 h. The slurry was then dried and calcined in platinum crucibles at temperature 1375 °C for 4 h. After an intermediate grinding the powders were recalcined at the same temperature for the same duration and again ground well. The calcined powders were ground for 2 h in an agate mortar to get fine powders and mixed thoroughly with 4 wt.% PVA solution. The slurry was dried and uniaxially pressed into cylindrical compacts of 11–14 mm diameter under a pressure of about 150 MPa. The green compacts were initially fired at a rate of 6 °C/min up to 800 °C and then at a rate of 12 °C/min to the sintering temperature. An intermediate soaking at 800 °C for 30 min was given to expel the binder (PVA). The sintering temperatures of the different  $Ba(B'_{1/2}Nb_{1/2})O_3$  compounds were in the range 1575–1600 °C for 4 h in air. The materials with tolerance factor,  $t > 0.98$  were found to have poor sinterability. Materials with  $t > 0.98$  were sintered with the use of 0.5–1 wt.% of  $CeO_2$ , as sintering aid, which was added to the calcined powder. In the case of  $Ba(In_{1/2}Nb_{1/2})O_3$  ceramic  $La_2O_3$  or  $MoO_3$  was used as sintering aid.  $Ba(B'_{1/2}Nb_{1/2})O_3$  materials whose tolerance factor  $t < 0.98$  were sintered well without any sintering aid. The bulk densities ( $D$ ) of the sintered samples were measured by Archimedes method. Well polished samples were used for microwave measurements and powders of sintered specimens were used for recording X-ray diffraction (XRD) patterns.

The microwave dielectric properties of the samples were measured using HP 8510C Network Analyzer. The dielectric constant was obtained by the Hakki and Coleman method [22] using  $TE_{011}$  mode. Quality factor was calculated from  $TE_{018}$  mode by the cavity method [23]. The temperature variation of the resonant frequency was obtained by heating the sample and noting the variation of the resonant frequency ( $f_0$ ) at different temperatures.

## 3. Results and discussion

The  $Ba(B'_{1/2}Nb_{1/2})O_3$  [ $B' = In, Yb, Y, Ho, Dy, \text{ and } Tb$ ] ceramics with  $t > 0.98$  when fired without additive, showed a very poor sinterability and did not show any sign of sintered appearance, shrinkage or mechanical strength, even after firing at 1650 °C for 4 h. The tolerance factor was calculated using the following equation [24] modified for  $Ba(B'_{1/2}Nb_{1/2})O_3$  complex perovskite,

$$t = \frac{r_{Ba} + r_0}{\sqrt{2}} \left[ \frac{r_{B'} + r_{Nb}}{2} + r_0 \right]^{-1} \quad (1)$$

where  $r_A, r_{B'}, r_{Nb}$ , and  $r_0$  are the ionic radii of the constituent ions [25].

The percentage densities of the ceramics with  $t \geq 0.98$  though fired at 1650 °C were very poor (see Table 1). But addition of 0.5–1 wt.% of  $CeO_2$  [1 wt.% of  $La_2O_3$  or 0.5 wt.%  $MoO_3$  in the case of  $Ba(In_{1/2}Nb_{1/2})O_3$ ] to the calcined powders, reduced the sintering temperature to 1575–1600 °C and enhanced the sintered density to 96–98% of the theoretical density with a corresponding improvement in their microwave dielectric properties. The percentage density of materials having tolerance factor,  $t < 0.98$  were in the range 97–98% without using sintering aid except for  $Ba(Gd_{1/2}Nb_{1/2})O_3$  ceramics. A comparison of measured density ( $D_M$ ) and theoretical density ( $D_T$ ) against ionic radii are given in Fig. 1. The density decreases with the increase of ionic radii. However, the behaviors of Y and In are different and is due to the fact that they do not belong to the lanthanide group. It may be noted that the theoretical density is calculated assuming cubic symmetry. The perovskite cell parameter ( $a_p$ ) in terms of the ionic radii of the ions forming a perfect cube was calculated using the following equation [24,25]

$$a_p = \frac{(r_A + r_0)}{\sqrt{2}} + 0.5r_{B'} + 0.5r_{Nb} + r_0 \quad (2)$$

The equation assumes the unit cell as an ideal cube. The ionic radii are taken from Shannon [25] for the appropriate co-ordination numbers. The addition of sintering aid improves the densification by solid solution effect [26].

To understand the effect of  $CeO_2$ , we studied five different compositions of  $Ba(Eu_{1/2}Nb_{1/2})O_3$  with 0.5, 1, 2, 5, and

Table 1  
Variation of percentage density of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics having  $t > 0.98$  with and without the sintering aid

$B'$ element	Percentage density (without sintering aid)	Percentage density (with sintering aid)
In	56	98
Yb	60	97
Y	74	96
Ho	76	97
Dy	77	96
Tb	92	98

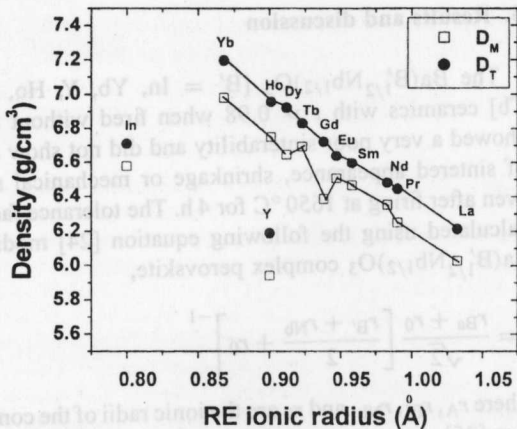


Fig. 1. Variation of theoretical density ( $D_T$ ) and measured density ( $D_M$ ) of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics with ionic radius of  $B'$  ion.  $D_T$  was calculated assuming the cubic symmetry.

10 wt.% of  $CeO_2$  as a sintering aid. Variations of the dielectric constant ( $\epsilon_r$ ) and the normalized  $Q$  factor ( $Q_{xf}$ ) with the addition of  $CeO_2$  in different wt.% are shown in Fig. 2. It can be seen that the addition of  $CeO_2$  decreases the  $\epsilon_r$  and  $Q$  factor in the microwave frequency range. But the bulk density and temperature coefficient of resonant frequency of these samples did not show any significant variation beyond 0.5 wt.% of  $CeO_2$  content. Hence 0.5–1 wt.% of  $CeO_2$  was chosen as optimum. Addition of  $MoO_3$  instead of  $La_2O_3$  to  $Ba(In_{1/2}Nb_{1/2})O_3$  enhanced its densification and dielectric properties to a greater extent. By the addition of 0.5 wt.%  $MoO_3$  to the calcined  $Ba(In_{1/2}Nb_{1/2})O_3$  powder, its density

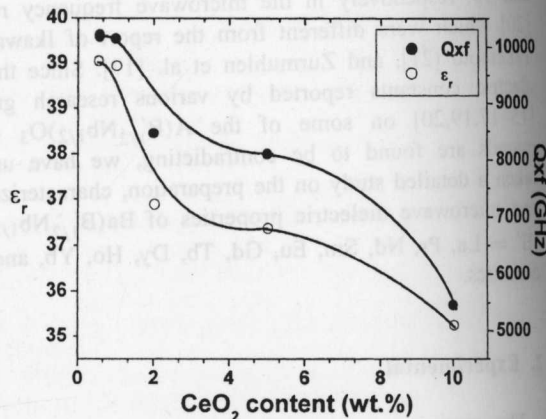


Fig. 2. Variation of  $\epsilon_r$  and  $Q_{xf}$  of  $Ba(Eu_{1/2}Nb_{1/2})O_3$  ceramic with the addition of  $CeO_2$ .

and dielectric constant were increased by 6%, normalized quality factor improved by 106% and there was no change in  $\tau_f$ .

Fig. 3 shows the X-ray diffraction patterns recorded from the powdered samples and are in agreement with earlier reports (JCPDS files 24-1144, 24-1142, 24-1053, 24-1042, 24-1030, 37-858, 31-137, 37-857, 14-116, 37-856 and [14,15]). However, XRD patterns of some of the materials showed splitting of the main reflections indicating a non-cubic symmetry. Crystal symmetries of  $Ba(B'_{1/2}Nb_{1/2})O_3$  perovskites are slightly different from cubic due to the large difference in ionic radii between  $B'^{3+}$  and  $Nb^{5+}$  [27]. From the XRD pattern (Fig. 3), it is

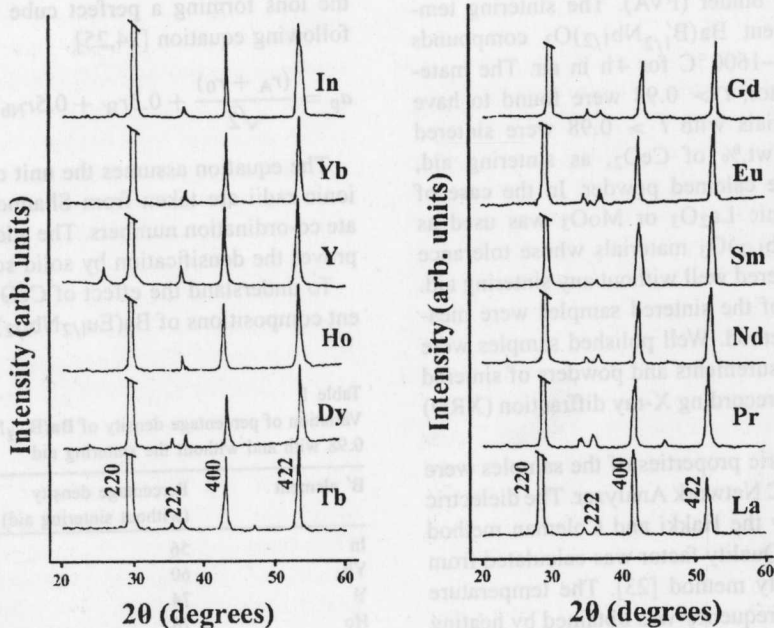


Fig. 3. XRD patterns of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics show a gradual increase in the splitting of main peaks with the lowering of symmetry. (\*) represents an unidentified peak at  $2\theta \approx 35^\circ$ .

clear that the amount of splitting of the main reflections increased with the decrease of tolerance factor. Galasso [14] reported these compounds as face centered cubic with  $(\text{NH}_4)_3\text{FeF}_6$  structure. But some of the earlier as well as recent studies [16–18,28,29] and JCPDS files 37–856, 857, 858 have shown that the room temperature symmetry of these compounds may be different from cubic. These studies showed that the room temperature symmetry of  $\text{A}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$  can be cubic, tetragonal, orthorhombic or monoclinic depending on the tolerance factor ( $t$ ) [16,17,26,27,30]. It was suggested that the difference in the crystal symmetry is due to the tilting of anion octahedra. A detailed description about the tilting of octahedra and their effect on the symmetry of perovskites was reported by Glazer [30,31]. It was shown [16–18] that compounds with  $t < 0.985$  the symmetry is reduced from cubic due to antiphase or in-phase tilting of octahedra. Hence the splitting observed in some of our XRD patterns could be attributed to the lowering of symmetry. It is difficult to establish the correct symmetry and structure of these compounds from XRD because the scattering power of oxygen sub lattice is low and the tilt angle is being small [16–18,29]. Several authors [16–18,29] reported that complex perovskite compounds with non-cubic symmetry at room temperature are transformed to cubic at high temperature. Recently, these compounds have been reported as cubic by Koshy et al. [20,32], as tetragonal by Zurmuhlen et al. [17], as monoclinic by Henmi et al. [27] and as cubic by Brixner [33] except  $\text{Ba}(\text{La}_{1/2}\text{Nb}_{1/2})\text{O}_3$  which is tetragonally distorted. In our XRD patterns an additional peak at  $2\theta \approx 35^\circ$  is observed in all the compounds with  $t < 0.985$  whereas it is completely absent in the materials with  $t > 0.985$  (see Fig. 3). Neutron diffraction and Raman spectroscopic studies are needed to determine precisely the structure and symmetry of these compounds. A detailed report on the structure and symmetry of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  as studied using neutron diffraction, synchrotron radiation and spec-

troscopic methods is in progress and will be published elsewhere.

The microwave dielectric properties of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics are given in Table 2. The different  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  compounds have high  $\epsilon_r$  which are in the range 36–45. The  $\epsilon_r$  of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics was also calculated using the following Clausius–Mosotti equation are given in Table 2

$$\epsilon_r = \frac{3V + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} \quad (3)$$

where  $\alpha_D$  is the total dielectric polarizability and  $V_m$  is the molar volume. The observed dielectric polarizability was calculated by Clausius–Mosotti equation, given by

$$\alpha_{\text{observed}} = \frac{3V_m(\epsilon_r - 1)}{4\pi(\epsilon_r + 2)} \quad (4)$$

and the theoretical dielectric polarizability by the total polarizabilities of constituent elements [34]. Theoretical dielectric polarisabilities show a shift from the observed ones. The variations in calculated  $\epsilon_r$  (using Eq. (3)) from the experimental  $\epsilon_r$  of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics are due to this shift of  $\alpha_{\text{theoretical}}$  from  $\alpha_{\text{observed}}$ .

The percentage shift of theoretical dielectric polarizability from the observed value is calculated by the following equation [35]

$$\frac{\alpha_{\text{observed}} - \alpha_{\text{theoretical}}}{\alpha_{\text{observed}}} \times 100\% \quad (5)$$

Experimentally obtained  $\epsilon_r$  is greater than the calculated  $\epsilon_r$  since  $\alpha_{\text{observed}}$  is greater than  $\alpha_{\text{theoretical}}$ . Since the correct symmetry of all the compounds are not known, the cell volumes are calculated using cubic perovskite cell parameter ( $a_p$ ) using Eq. (2). The actual unit cell symmetry may slightly deviates from cubic for each  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramic. Qualitatively, the deviation is directly related to  $t$ .

Table 2  
Some lattice constants and microwave dielectric properties of different  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  perovskites

B' element	$r$ (Å)	$a_p$ (Å)	(%) $D$	$t$	$\alpha_{\text{theoretical}}$	$\alpha_{\text{observed}}$	(%) $\Delta\alpha$	$\epsilon_{\text{observed}}$	$\epsilon_{\text{calculated}}$	$\Delta\epsilon_r$	$Q \times f$ (GHz)	$\tau_f$ (ppm/°C)
La	1.032	4.2961	97	0.95633	17.45	17.730	1.579	45	36.2	8.8	5,700	7.0
Pr	0.990	4.2751	97	0.96557	17.08	17.459	2.199	44.5	33.3	11.2	28,500	-22
Nd	0.983	4.2716	98	0.96712	16.92	17.403	2.775	44	31.0	13.0	11,700	10
Sm	0.958	4.2591	98	0.97272	16.79	17.224	2.549	43	31.2	11.8	18,400	9.0
Eu	0.947	4.2536	98	0.97521	16.68	17.070	1.406	40	33.6	6.4	40,200	6.7
Gd	0.938	4.2491	95	0.97725	16.60	17.015	2.439	40	30.0	10.1	5,700	4.6
Tb	0.923	4.2416	98	0.98067	16.54	16.894	2.095	39	30.5	8.5	52,400	-2.0
Dy	0.912	4.2361	96	0.98320	16.45	16.825	2.229	38.9	30.0	8.9	20,600	-3.6
Ho	0.901	4.2306	97	0.98573	16.40	16.746	2.066	38	30.2	7.8	21,600	-10.8
Y	0.900	4.2301	96	0.98597	16.32	16.689	2.211	37	29.0	8.1	49,600	15
Yb	0.868	4.2141	97	0.99343	16.21	16.404	1.213	36	30.3	5.9	38,100	2.0
ln <sup>a</sup>	0.800	4.1801	98	1.00967	15.73	16.069	2.140	36	28.5	7.5	14,200	17
ln <sup>b</sup>	0.8	4.1801	98	1.00967	15.73	16.169	2.746	39	28.5	10.5	30,700	17

Percent  $D$  represents the percentage density, percent  $\alpha$  represent the percentage shift in dielectric polarisability.

<sup>a</sup> Sintered with  $\text{La}_2\text{O}_3$  additive.

<sup>b</sup> Sintered with  $\text{MoO}_3$ .

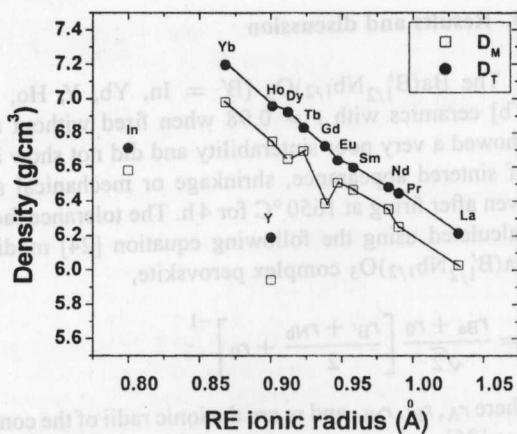


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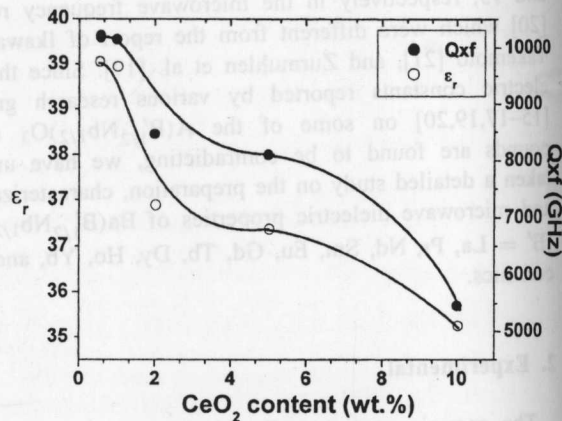


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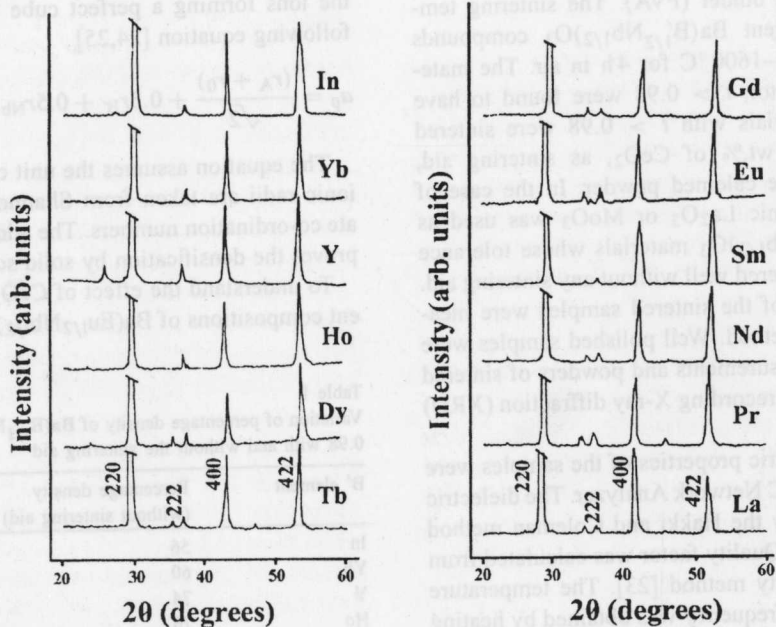


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clear that the amount of splitting of the main reflections increased with the decrease of tolerance factor. Galasso [14] reported these compounds as face centered cubic with  $(\text{NH}_4)_3\text{FeF}_6$  structure. But some of the earlier as well as recent studies [16–18,28,29] and JCPDS files 37–856, 857, 858 have shown that the room temperature symmetry of these compounds may be different from cubic. These studies showed that the room temperature symmetry of  $\text{A}(\text{B}'_{1/2}\text{B}''_{1/2})\text{O}_3$  can be cubic, tetragonal, orthorhombic or monoclinic depending on the tolerance factor ( $t$ ) [16,17,26,27,30]. It was suggested that the difference in the crystal symmetry is due to the tilting of anion octahedra. A detailed description about the tilting of octahedra and their effect on the symmetry of perovskites was reported by Glazer [30,31]. It was shown [16–18] that compounds with  $t < 0.985$  the symmetry is reduced from cubic due to anti-phase or in-phase tilting of octahedra. Hence the splitting observed in some of our XRD patterns could be attributed to the lowering of symmetry. It is difficult to establish the correct symmetry and structure of these compounds from XRD because the scattering power of oxygen sub lattice is low and the tilt angle is being small [16–18,29]. Several authors [16–18,29] reported that complex perovskite compounds with non-cubic symmetry at room temperature are transformed to cubic at high temperature. Recently, these compounds have been reported as cubic by Koshy et al. [20,32], as tetragonal by Zurmuhlen et al. [17], as monoclinic by Henmi et al. [27] and as cubic by Brixner [33] except  $\text{Ba}(\text{La}_{1/2}\text{Nb}_{1/2})\text{O}_3$  which is tetragonally distorted. In our XRD patterns an additional peak at  $2\theta \approx 35^\circ$  is observed in all the compounds with  $t < 0.985$  whereas it is completely absent in the materials with  $t > 0.985$  (see Fig. 3). Neutron diffraction and Raman spectroscopic studies are needed to determine precisely the structure and symmetry of these compounds. A detailed report on the structure and symmetry of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  as studied using neutron diffraction, synchrotron radiation and spec-

troscopic methods is in progress and will be published elsewhere.

The microwave dielectric properties of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics are given in Table 2. The different  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  compounds have high  $\epsilon_r$  which are in the range 36–45. The  $\epsilon_r$  of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics was also calculated using the following Clausius–Mosotti equation are given in Table 2

$$\epsilon_r = \frac{3V + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} \quad (3)$$

where  $\alpha_D$  is the total dielectric polarizability and  $V_m$  is the molar volume. The observed dielectric polarizability was calculated by Clausius–Mosotti equation, given by

$$\alpha_{\text{observed}} = \frac{3V_m(\epsilon_r - 1)}{4\pi(\epsilon_r + 2)} \quad (4)$$

and the theoretical dielectric polarizability by the total polarizabilities of constituent elements [34]. Theoretical dielectric polarisabilities show a shift from the observed ones. The variations in calculated  $\epsilon_r$  (using Eq. (3)) from the experimental  $\epsilon_r$  of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics are due to this shift of  $\alpha_{\text{theoretical}}$  from  $\alpha_{\text{observed}}$ .

The percentage shift of theoretical dielectric polarizability from the observed value is calculated by the following equation [35]

$$\frac{\alpha_{\text{observed}} - \alpha_{\text{theoretical}}}{\alpha_{\text{observed}}} \times 100\% \quad (5)$$

Experimentally obtained  $\epsilon_r$  is greater than the calculated  $\epsilon_r$  since  $\alpha_{\text{observed}}$  is greater than  $\alpha_{\text{theoretical}}$ . Since the correct symmetry of all the compounds are not known, the cell volumes are calculated using cubic perovskite cell parameter ( $a_p$ ) using Eq. (2). The actual unit cell symmetry may slightly deviates from cubic for each  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramic. Qualitatively, the deviation is directly related to  $t$ .

Table 2  
Some lattice constants and microwave dielectric properties of different  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  perovskites

B' element	$r$ (Å)	$a_p$ (Å)	(%) $D$	$t$	$\alpha_{\text{theoretical}}$	$\alpha_{\text{observed}}$	(%) $\Delta\alpha$	$\epsilon_{\text{observed}}$	$\epsilon_{\text{calculated}}$	$\Delta\epsilon_r$	$Q \times f$ (GHz)	$\tau_f$ (ppm/°C)
La	1.032	4.2961	97	0.95633	17.45	17.730	1.579	45	36.2	8.8	5,700	7.0
Pr	0.990	4.2751	97	0.96557	17.08	17.459	2.199	44.5	33.3	11.2	28,500	-22
Nd	0.983	4.2716	98	0.96712	16.92	17.403	2.775	44	31.0	13.0	11,700	10
Sm	0.958	4.2591	98	0.97272	16.79	17.224	2.549	43	31.2	11.8	18,400	9.0
Eu	0.947	4.2536	98	0.97521	16.68	17.070	1.406	40	33.6	6.4	40,200	6.7
Gd	0.938	4.2491	95	0.97725	16.60	17.015	2.439	40	30.0	10.1	5,700	4.6
Tb	0.923	4.2416	98	0.98067	16.54	16.894	2.095	39	30.5	8.5	52,400	-2.0
Dy	0.912	4.2361	96	0.98320	16.45	16.825	2.229	38.9	30.0	8.9	20,600	-3.6
Ho	0.901	4.2306	97	0.98573	16.40	16.746	2.066	38	30.2	7.8	21,600	-10.8
Y	0.900	4.2301	96	0.98597	16.32	16.689	2.211	37	29.0	8.1	49,600	15
Yb	0.868	4.2141	97	0.99343	16.21	16.404	1.213	36	30.3	5.9	38,100	2.0
In <sup>a</sup>	0.800	4.1801	98	1.00967	15.73	16.069	2.140	36	28.5	7.5	14,200	17
In <sup>b</sup>	0.8	4.1801	98	1.00967	15.73	16.169	2.746	39	28.5	10.5	30,700	17

Percent  $D$  represents the percentage density, percent  $\alpha$  represent the percentage shift in dielectric polarisability.

<sup>a</sup> Sintered with  $\text{La}_2\text{O}_3$  additive.

<sup>b</sup> Sintered with  $\text{MoO}_3$ .

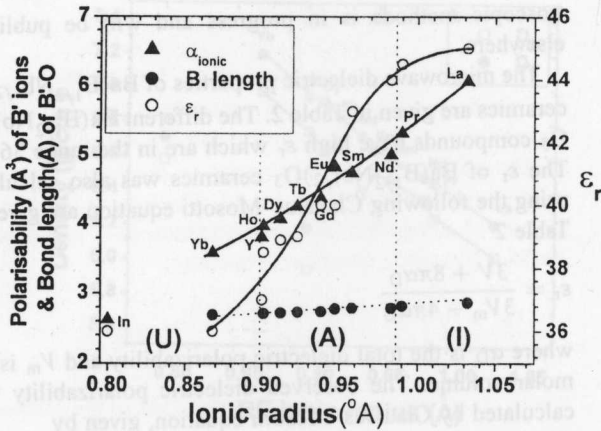


Fig. 4. Variation of dielectric constant, ionic polarizability, and bond valence with ionic radii of  $B'$  ions. Dotted lines separate the unilted (U), antiphase tilted (A), and inphase tilted (I) regions given by Reaney et al. [18]. In and Y are non lanthanides.

Fig. 4 shows the variation of  $\epsilon_r$  of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics with ionic radii of  $B^{3+}$  ions. The dielectric constant increases with the increase in ionic radius. The ionic polarizability of  $B'$  ions also increase with the increase in ionic radius. The variation of dielectric constant with tolerance factor ( $t$ ) is shown in Fig. 5, which is in agreement with that of Reaney et al. [18]. The small differences in  $t$  may be due to the fact that, Reaney et al. used the ionic radii given by Muller and Roy [36] to calculate the tolerance factor. In the present case we have calculated the tolerance factor using the ionic radii given by Shannon [25]. The inphase, antiphase, and unilted regions are marked in Figs. 4–7. Anti-phase tilting is within the tolerance factor range 0.967–0.987 (Fig. 5). Corresponding to this antiphase tilting the ionic radii range is 0.9–0.983 (Fig. 4). The  $\epsilon_r$  of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics decrease with increase in  $t$  as shown in Fig. 5. Since  $t$

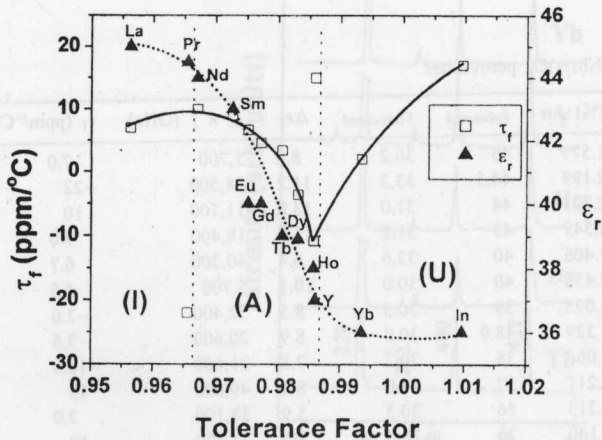


Fig. 5. Variation of dielectric constant and temperature coefficient of resonant frequency with the tolerance factor. Dotted lines separate the unilted (U), antiphase tilted (A), and inphase tilted (I) regions given by Reaney et al. [18].

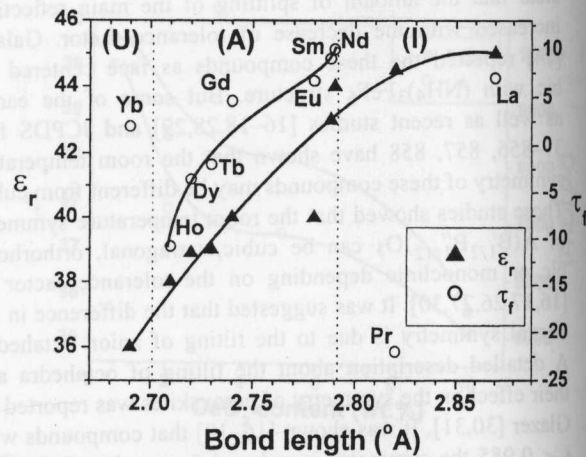


Fig. 6. Variation of  $\epsilon_r$  and  $\tau_f$  of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics with bond length of  $B'-O$ . (U), (A), and (I) are unilted, antiphase tilted and inphase tilted regions with respect to the corresponding tolerance factor ranges.

is related to packing of ions in the perovskite cell, when deviates from 1, the perovskite cell gets deformed and the symmetry is lowered from cubic. Any deviation from cubic symmetry results in extra polarization, which is reflected in the dielectric constant [26]. Thus, larger the deviation from the cubic symmetry, larger is the  $\epsilon_r$  (see Table 2). The value of  $\epsilon_r$  reported here are in good agreement with earlier reports on some of the compounds for which data is available, measured by direct microwave methods or spectroscopic methods [15–17], but very different from a recent report [20]. The  $\epsilon_r$  of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics increases with increase in dielectric polarizability (Table 2), in agreement with earlier reports [35,37,38].

The different  $Ba(B'_{1/2}Nb_{1/2})O_3$  compounds have relatively high quality factor ( $Q_{xf}$ ) up to 50,000 (see Table 2). The temperature coefficient of resonant frequency ( $\tau_f$ ) of  $Ba(B'_{1/2}Nb_{1/2})O_3$  compositions are given in Table 2. The

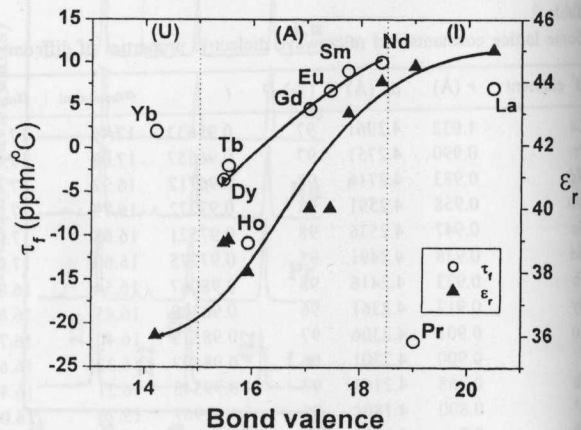


Fig. 7. Variation of  $\epsilon_r$  and  $\tau_f$  with bond length  $B'-O$  of  $Ba(B'_{1/2}Nb_{1/2})O_3$  ceramics. (U), (A), and (I) are unilted, antiphase tilted and inphase tilted regions with respect to the corresponding tolerance factor ranges. Non lanthanides Y and In are excluded.

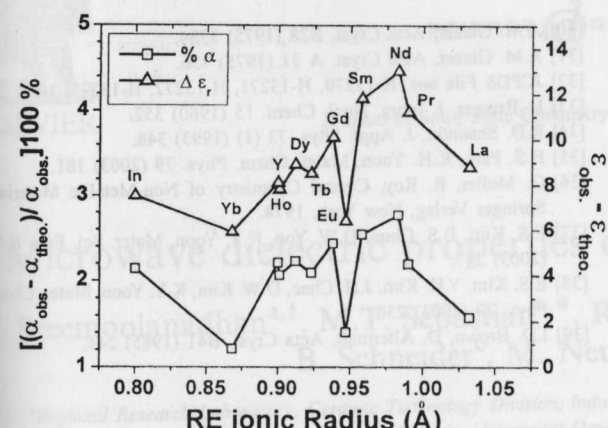


Fig. 8. Percentage shift of dielectric polarizability and shift of dielectric constant of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics are plotted against the ionic radii of  $\text{B}'$  ions.

$\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics have low  $\tau_f$  values in the range from  $-22$  to  $+17$  ppm/ $^\circ\text{C}$ . The values vary non-linearly with tolerance factor as shown in Fig. 5.

The bond valence was calculated from the bond parameters of Brown et al. [39]. Figs. 6 and 7 show the variation of  $\epsilon_r$  and  $\tau_f$  with bond length and bond valence. The  $\epsilon_r$  increases with the increase in bond length and bond valence. The  $\tau_f$  of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics increases with bond length and bond valence in the antiphase tilted region. Park and Yoon [35] and Kim et al. [38] reported a similar relation between bond valence and  $\tau_f$  in  $(\text{Pb}_{1-x}\text{Ca}_x)(\text{Ca}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , and  $(\text{Pb}_{1-x}\text{Ca}_x)(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ . Both the theoretical and observed dielectric polarizabilities ( $\alpha_{\text{theoretical}}$  and  $\alpha_{\text{observed}}$ ) decrease with increase in tolerance factor (shown in Table 2). Due to tilting the effective size of the ion in the center of the oxygen octahedra is changed [25] and hence there is a variation in the shift of  $\alpha_{\text{theoretical}}$  from  $\alpha_{\text{observed}}$ . The percentage shift of  $\alpha_{\text{theoretical}}$  from  $\alpha_{\text{observed}}$  is shown in Table 2. Fig. 8 shows the percentage shift of  $\alpha_{\text{observed}}$  from  $\alpha_{\text{theoretical}}$  and the shift of  $\epsilon_{\text{observed}}$  from  $\epsilon_{\text{theoretical}}$  as a function of ionic radii of  $\text{B}'$  ions. These shifts are maximum for Nd and minimum for Yb. The  $\alpha_{\text{theoretical}}$  and  $\alpha_{\text{observed}}$  were calculated based on the assumed cubic symmetry. Therefore, the larger shift in  $\epsilon_{\text{observed}}$  and  $\alpha_{\text{observed}}$  from their theoretical values may be due to the deviation of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics from the cubic symmetry.

#### 4. Conclusion

The  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  [ $\text{B}' = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Y}, \text{Yb}$ , and  $\text{In}$ ] were prepared by conventional solid state ceramic route. The compounds based on  $\text{In}, \text{Yb}, \text{Y}, \text{Ho}, \text{Dy}$ , and  $\text{Tb}$  have poor sinterability. Addition of 0.5 wt.% of  $\text{CeO}_2$  as sintering aid improved their sinterability except in the case of  $\text{In}$ .  $\text{La}_2\text{O}_3$  and  $\text{MoO}_3$  are found to be good sintering aids for  $\text{Ba}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ . The use of  $\text{MoO}_3$  as sin-

tering aid increased the Q factor of  $\text{Ba}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$  without affecting its  $\tau_f$ . The  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics show high  $\epsilon_r$  in the range 36–45, high quality factor and low  $\tau_f$ . The microwave dielectric properties are found to be related to the tolerance factor and octahedral tilts. The  $\epsilon_r$  of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics increase with the dielectric polarizability, bond valence, bond length and ionic radii of the  $\text{B}'$  ions. The  $\tau_f$  of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics increase with the bond length and bond valence in the antiphase tilted region. The percentage shift of dielectric polarizability and the shift of obtained dielectric constant from their theoretical values indicate a lowering of symmetry of  $\text{Ba}(\text{B}'_{1/2}\text{Nb}_{1/2})\text{O}_3$  ceramics from cubic.

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