

Ba(Tb_{1/2}Nb_{1/2})O₃: A new ceramic microwave dielectric resonator

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Abstract

A new microwave dielectric resonator Ba(Tb_{1/2}Nb_{1/2})O₃ has been prepared and characterized in the microwave frequency region. 1 wt% CeO₂ is used as additive to reduce the sintering temperature. The sintered samples were characterized by XRD, SEM and Raman spectroscopic methods. Microwave DR properties such as ϵ_r , Q factor and temperature-coefficient of resonant frequency (τ_f) have been measured using a HP 8510 B Network Analyzer. Cylindrical DRs of Ba(Tb_{1/2}Nb_{1/2})O₃ showed high ϵ_r (~ 37), high Q ($\sim 3,200$) and low τ_f (~ -10 ppm/°C) at 4 GHz and hence are useful for practical applications. © 1997 Elsevier Science B.V.

Keywords: Perovskites; Dielectric resonators; Microwave ceramics; Barium terbium niobate

1. Introduction

Recent progress in microwave integrated systems for telecommunication and satellite television demand the development of a variety of hyper frequency devices for filters and frequency stabilized oscillators. The dielectric resonators (DRs) provide significant advantages in terms of compactness, light weight, temperature stability and relatively low cost of production of microwave devices as compared with the same devices without them. The important characteristics of dielectric resonator ceramics are high dielectric constant (ϵ_r), high Q factor ($> 1,000$) and small temperature-coefficient of resonant frequency (τ_f). Recently DRs with relative permittivity in the range 20 to 100 such as Ba₂Ti₉O₂₀, (Zr,

Sn)TiO₄, Complex perovskites, BaO-RE₂O₃-TiO₂, and Ba₅Nb₄O₁₅ have been investigated [1–8] for practical applications. The A²⁺(B_{1/3}²⁺B_{2/3}⁵⁺)O₃ type complex perovskites such as Ba(Mg_{1/3}Ta_{2/3})O₃ and Ba(Zn_{1/3}Ta_{2/3})O₃ [3,9–13] have been extensively studied as DR ceramics. These ceramics, with ordered structure, showed very high Q factors ($> 10,000$ at 10 GHz) and $\epsilon_r < 30$. When compared with this type of complex perovskites, the dielectric resonator property studies on A²⁺(B_{1/2}³⁺B_{1/2}⁵⁺)O₃ complex perovskites are relatively less. In 1969, in his book, Galasso [14] gave a detailed account about the preparation, characterization and properties of complex perovskites, including A²⁺(B_{1/2}³⁺B_{1/2}⁵⁺)O₃ type compounds. Recently Takata and Kageyama [4], Reaney et al. [15] and Zurmuhlen et al. [16–18] studied the microwave DR properties of some complex perovskites of the A(B_{1/2}B_{1/2})O₃ type. In the

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present paper we report the preparation, characterization and properties of a new DR material $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ belonging to the above family.

2. Experimental procedure

The DR samples were prepared by the conventional solid state ceramic route. Stoichiometric amount of high purity BaCO_3 , Nb_2O_5 and Tb_4O_7 were weighed and wet mixed using distilled water for about 1 h. The mixture was dried and calcined at 1325°C for 4 h. The calcined powder was ground well into fine powder. This powder was pressed into cylindrical discs under a pressure of 200 MPa and sintered at 1480°C for 4 h. As a sintering aid 1 wt% of CeO_2 was added to the calcined powder. The sintered samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopic methods.

The ϵ_r and unloaded Q at microwave frequency were measured by a HP 8510 B Network Analyzer and HP 8514 B Reflection–Transmission unit. The cylindrical resonators were kept end-shortened between two gold-plated brass plates and the TE_{011} mode of resonance were identified [19]. The ϵ_r was obtained from the frequency of the TE_{011} resonance and the dimensions of the samples using the relation of Hakki and Coleman [20]:

$$\epsilon_r = 1 + \left(\frac{c}{\pi D f_0} \right)^2 (\alpha_1^2 + \beta_1^2) \quad (1)$$

where D is the diameter of the resonator and f_0 is the resonant frequency. The α_1 and β_1 are two constants determined from the mode chart [20] using the dimensions and the resonant frequency of the sample. During the identification of TE_{011} mode, care was taken to ensure that the mode is well-separated from other modes.

For the measurement of Q factor, the resonators were coupled to a microstripline enclosed in a brass cavity of size $5 \times 5 \times 3 \text{ cm}^3$. The DR enclosed in the cavity acts as a band rejection filter. The resonance, whose quality factor has to be measured was selected and the span of the Network Analyzer was reduced to 200 MHz by keeping this mode as center frequency. Then the DR was removed and the system

was calibrated for full transmission to ensure that no adjacent modes are present and the system has 100% transmission at the resonant frequency. Again the DR was coupled to the stripline and the resonant frequency f_0 and the transmission coefficient S_{21} were noted. Using the relation of Khanna and Gaurault [21], the parameter S_{21u} was calculated:

$$S_{21u} = S_{21} \sqrt{\frac{2}{1 + S_{21}^2}} \quad (2)$$

The width of the resonant curve corresponding to S_{21u} was taken as Δf . The Q factor was determined from the quotient $(f_0/\Delta f)$.

To study the temperature dependence of the resonant frequency, the DR under end-shortened condition was heated slowly ($\sim 2^\circ\text{C}/\text{min}$). The shift of the TE_{011} mode in the temperature range $25\text{--}75^\circ\text{C}$ was noted. A graph is plotted with $(\Delta f/f)$ along the Y -axis and temperature along the X -axis. The slope of the curve gives the τ_f .

3. Results and discussion

The $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramics did not sinter into dense ceramics even by firing at a temperature of 1600°C . But addition of 1 wt% CeO_2 into the calcined powder as a sintering aid reduces the sintering temperature and enhances the sinterability. The CeO_2 addition creates cation vacancies and enhances diffusion mechanism [5]. The bulk density of the pellets were found to be 6.61 g/cm^3 . The theoretical density calculated using $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ formula and perovskite cell parameter a_T is 6.886 g/cm^3 . The a_T was calculated using the following equation.

$$a_T = \frac{R_{\text{Ba}} + R_{\text{O}}}{\sqrt{2}} + \frac{R_{\text{Tb}} + R_{\text{Nb}}}{2} + R_{\text{O}} \quad (3)$$

where R represent the ionic radii given by Shannon and Prewitt [22]. Fig. 1 shows the typical microstructure of $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ obtained using SEM. The microstructure consists of uniform polygonal grains of approximately 3μ size.

The powder XRD patterns obtained using $\text{CuK}\alpha$ radiation showed good agreement with earlier reports [14]. But the crystal symmetry at room temperature cannot be unambiguously determined based solely

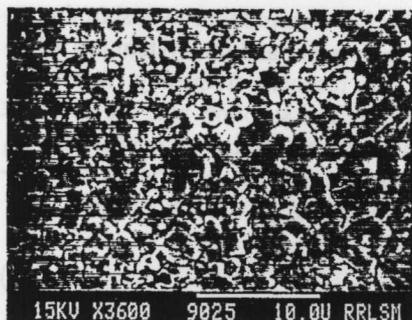


Fig. 1. Surface microstructure of a typical Ba(Tb_{1/2}Nb_{1/2})O₃ ceramic obtained using SEM.

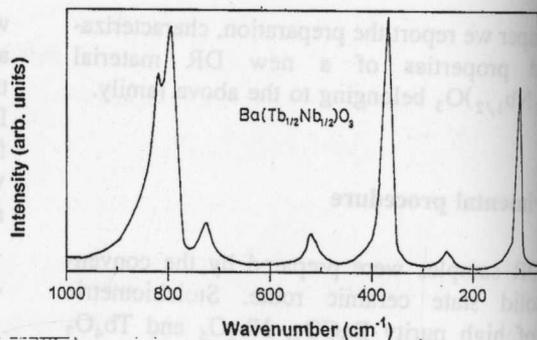


Fig. 2. Raman spectrum of Ba(Tb_{1/2}Nb_{1/2})O₃ in the 50 to 1000 cm⁻¹ region.

on XRD [23–25]. Earlier reports of Filiptev and Fesenko [26] and recent reports of Gregoria et al. [27] and Zurmuhlen et al. [16–18] have confirmed the existence of subtle phase transition in complex perovskites. The recent reports showed that the phase transition temperature depends inversely on the tolerance factor (t). They suggested that the room temperature symmetry of complex perovskites can be monoclinic, orthorhombic or tetragonal depending upon t and transform to cubic at high temperatures. According to these reports, complex perovskites with $t < 0.985$ possess non-cubic symmetry at room temperature. Hence it follows that the crystal symmetry of this material is slightly different from cubic since the tolerance factor (t) is 0.978. Since the tilting of the octahedra and the deviation in symmetry is very small, it is difficult to detect the transition and the symmetry through routine DTA, DSC or XRD. Hence TEM and neutron diffraction experiments are recommended for precise structure determination [16–18]. Since Raman spectroscopy is sensitive to the molecular level, FT-Raman spectrum of Ba(Tb_{1/2}Nb_{1/2})O₃ was taken in the 50–1000 cm⁻¹ region (see Fig. 2). The spectrum is nearly similar to that of Ba(Y_{1/2}Ta_{1/2})O₃ [26] which is cubic at room temperature. The three strong bands at 802, 376, 103 cm⁻¹ are similar to those obtained for Ba(Y_{1/2}Ta_{1/2})O₃. However, the presence of shoulder near 802 cm⁻¹ and other additional bands in Fig. 2 indicate that the symmetry of Ba(Tb_{1/2}Nb_{1/2})O₃ slightly deviates from cubic.

Fig. 3 shows the TE₀₁₁ resonance at 5.93 GHz of a typical sample which was 13.3 mm diameter and 5.2 mm length and was used for obtaining the ϵ_r .

The dielectric constant of the sample is 37.6. The ϵ_r is also calculated theoretically using Clausius–Mosotti equation and the ionic polarisabilities [28]

$$\epsilon_r = \frac{3V_m + 8\pi\alpha}{3V_m - 4\pi\alpha} = 37 \quad (4)$$

where V_m (75.045 Å³) is the cell volume. The cell volume is obtained from the theoretical lattice parameter a_T [29] using the Eq. (3). The α (16.54 Å³) is the total dielectric polarisability of the compound and can be calculated as a simple linear combination of individual ion polarisabilities given

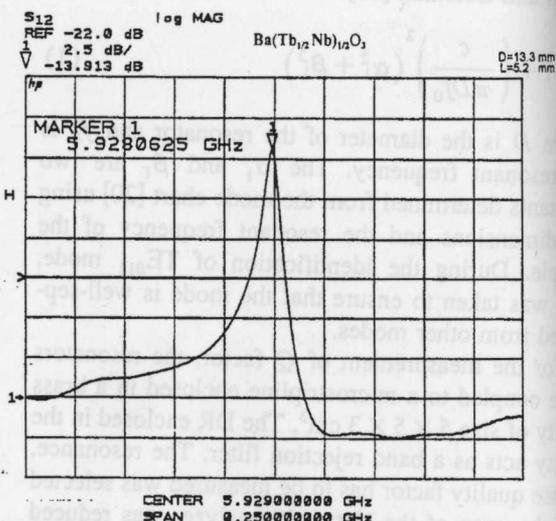


Fig. 3. TE₀₁₁ resonance of a typical Ba(Tb_{1/2}Nb_{1/2})O₃ DR obtained under the endshorted condition.

by Shannon [28]. The ϵ_{cal} is 37 and is in agreement with the measured value.

The band rejection filter using the DR, coupled to the microstripline and enclosed in a brass cavity $5 \times 5 \times 3 \text{ cm}^3$, showed resonances as shown in Fig. 4 (left). The right hand side figure shows the resonances of the cavity without sample. The first resonance corresponds to $\text{TE}_{01\delta}$ mode and the second one to another unknown mode. When duly coupled and measured after calibration, $\text{TE}_{01\delta}$ mode gave a Q factor of 3,200 at 4.355 GHz and the Q factor obtained for the other mode was 77,300 at 4.7063 GHz. The normalized unloaded quality factor ($Q \times f$) of the DR of $\text{TE}_{01\delta}$ mode is 1.39×10^{13} and for the other mode is 3.64×10^{14} . The mode at 4.7 GHz was found to be highly sensitive to the position of the DR near stripline and tuning. The high Q factor was obtained with the help of impedance chart by carefully adjusting the position and tuning. This high Q may be due to the particular structure of the measurement cavity and the sample. The reason for the very high Q obtained for the mode at 4.7 GHz as well as its applicability for practical circuits are under investigation.

The variation of the resonant frequency ($\Delta f/f$) with temperature is shown in Fig. 5. The resonant frequency decreases indicating an increase in ϵ_r with respect to temperature. The τ_f of $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ as obtained from the slope of Fig. 5 is $-10 \text{ ppm}/^\circ\text{C}$. More recently, we found

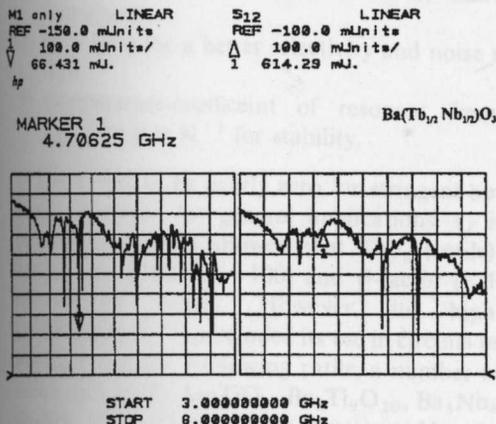


Fig. 4. Various resonances of the $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ DR when coupled to a microstripline in the 3 to 8 GHz band. The right hand figure corresponds to the resonances of the stripline alone, i.e. without the DR.

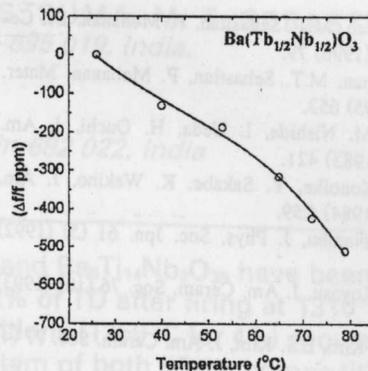


Fig. 5. Variation of resonant frequency with respect to temperature. ($\Delta f/f$ is taken in ppm along the Y axis).

that partial replacement of B^{3+} element by bismuth in $\text{Ba}(\text{Bi}_{0.2}\text{D}_{0.3}^{3+})\text{Nb}_{0.5}\text{O}_3$ ($\text{D}^{3+} = \text{Y, Pr, Sm, Gd, Dy, Er}$) increases the ϵ_r and improves the τ_f [30]. In a similar way the ϵ_r and τ_f of $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ could be improved by bismuth substitution.

4. Conclusion

The $\text{Ba}(\text{Tb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ complex perovskite compound has been synthesized as a ceramic at 1480°C by adding 1 wt% CeO_2 . The dielectric resonator properties such as ϵ_r ($= 37$), Q factor (3,200 at 4.355 GHz) and τ_f ($-10 \text{ ppm}/^\circ\text{C}$) have been measured using standard techniques and are found to be useful for practical applications. The Raman spectrum shows that the room temperature crystal symmetry slightly deviates from cubic.

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