

Microwave properties of $\text{Ba}_{1-x}\text{Pb}_x\text{Nd}_2\text{Ti}_5\text{O}_{14}$ dielectric resonators

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The $\text{Ba}_{1-x}\text{Pb}_x\text{Nd}_2\text{Ti}_5\text{O}_{14}$ (BNT: Pb) ceramics are appropriate for microwave devices due to their high dielectric constant and low loss in the microwave domain. Samples with x Pb content in the range $0 \div 0.5$ were prepared by solid-state reaction and sintered at temperatures $T_s = 1230 \div 1260$ °C. XRD and SEM analysis indicate very good crystalline structure and polyhedral well formed grains. Controlled temperature coefficient of resonant frequency τ_f is essential for dielectric resonators. The temperature coefficient of the resonant frequency τ_f takes values from -15 ppm/°C to $+70$ ppm/°C. High-density values and adequate microwave parameters were obtained for $x = 0.5$ Pb content. The BNT: Pb ceramics sintered at 1250 °C and 1260 °C for 2 hours are suitable for dielectric resonators for frequencies up to 5 GHz, $\epsilon_r = 76 \div 87$ and $Q \times f \sim 5000$ GHz).

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1. Introduction

Dielectric materials continue to have a decisive influence on the evolution of the electrical and electronic engineering, communications and information technology. These materials, which exhibit high dielectric constant, low dielectric losses, and good temperature stability are required to reduce the size and weight of equipment, enhance its reliability, and lower the manufacturing and operational costs. Ceramics are from far the most utilized as they offer cost-effective solutions for applications [1, 2].

The dielectric materials used for microwaves resonators and filters are of particular interest to materials science. These materials are presently employed as bulk ceramics in microwave communication devices, as discrete components in hybrid circuits. The ceramic pieces are designed to be dielectric resonators, resonating at the frequency of the carrier signal to allow that signal to be efficiently separated from other signals in the microwave band. The resonant frequency of the dielectric resonator depends on the dielectric constant of the material and on the size of the resonator. The size of the resonator for any particular resonant frequency depends on the inverse of the square root of the dielectric constant of the material, and thus, the larger the dielectric constant the smaller the ceramic component needed. For example, a 1/6 size-reduction was achieved when using ZST dielectric resonator instead a vacuum cavity [3].

The BNT dielectric materials, which are compositions based on the BaO - Nd_2O_3 - TiO_2 ternary system, are very

attractive for microwave devices due to their high dielectric constant and low losses in the microwave range [1, 2]. These materials exhibit a dielectric constant in the range of $\epsilon_r = 70 \div 80$, depending on the Nd_2O_3 and TiO_2 content. In principle, the addition of highly polarisable ions can increase dielectric permittivity of BNT materials. For this reason, the Pb effect, which substitutes the Ba ions, on the dielectric parameters was investigated for $\text{Ba}_{1-x}\text{Pb}_x\text{Nd}_2\text{Ti}_5\text{O}_{14}$ compounds. When Pb is added to the BNT, the dielectric constant is increased to $80 \div 90$ with a slight increase in dielectric loss. The lead addition changes also the temperature coefficient τ_f [4]. The temperature coefficient of the resonance frequency f_0 of a dielectric resonator is defined by

$$\tau_f = \frac{1}{f_0} \frac{\Delta f}{\Delta t}, \quad (1)$$

where Δf is the shift in the resonance frequency for a temperature variation Δt . Therefore, the Pb addition is a way to obtain a desired value of τ_f . A controllable τ_f is another feature that makes $\text{Ba}_{1-x}\text{Pb}_x\text{Nd}_2\text{Ti}_5\text{O}_{14}$ materials very attractive to microwave applications.

2. Experimental

The $\text{Ba}_{1-x}\text{Pb}_x\text{Nd}_2\text{Ti}_5\text{O}_{14}$ samples based on BaO-PbO- Nd_2O_3 - TiO_2 system were prepared by the solid-state reaction technique. The starting materials TiO_2 , PbO, Nd_2O_3 , and BaCO_3 powders of purity higher than 99 % were weighted for the desired stoichiometry. The raw

materials were ball-milled in water for two hours and then calcined at 1200 °C. The powder was crushed and milled again for 2 hours. Mixing was carried out for 2 hours in an agate mortar with agate balls. The mixture was pressed into pellets, which were sintered at temperatures between 1230 °C and 1260 °C for 2 hours. In order to obtain high densities at low sintering temperatures, 0.2 wt % NiO was added for some samples. The NiO sintering addition acts as a grain-growth inhibitor improving the quality factor Q_o in microwave domain.

The bulk densities of the sintered pellets were measured by Archimede's method. Structural and morphological analyses were performed on $Ba_{1-x}Pb_xNd_2Ti_5O_{14}$ samples by X-ray diffraction (XRD) analysis, and electron microscopy (SEM). The patterns were recorded in a 2θ range from 20° to 60° on a Seifert Debye Flex 2002 diffractometer into the $2\theta - \theta$ mode. Measurements were performed at room temperature using a Ni - filtered Cu K_α radiation, and a counter scan speed of 5°/min.

Accurate measurements of the dielectric constant were carried out in microwave domain by using the Hakki-Coleman method [5]. The dielectric resonators were sandwiched between two large conducting plates, and magnetically coupled to the microwave field. The resonant frequency was measured and, from that, in combination with the geometry of the resonator, the complex dielectric constant was calculated. A computer aided measurement system containing an HP 8757 C scalar network analyzer and an HP 8350 B sweep oscillator was utilized.

3. Results and discussion

$Ba_{1-x}Pb_xNd_2Ti_5O_{14}$ samples with $x = 0, 0.33$ and 0.5 Pb content were investigated in order to study the modifications on morpho-*structural* and dielectric properties of the BNT: Pb ceramics with the increase of the Pb concentration. The sintered ceramics were polished and etched in order to remove the surface layer and to obtain plan parallel surfaces. A good compactness was obtained for rectified samples for all sintering temperatures. The bulk density versus sintering temperature of $Ba_{1-x}Pb_xNd_2Ti_5O_{14}$ samples is shown in Fig. 1.

Structural investigations of $Ba_{1-x}Pb_xNd_2Ti_5O_{14}$ ceramics were made using XRD. For $x = 0$, the X-ray diffraction pattern shown in Fig. 2 contain the diffraction lines of the single-phased $BaNd_2Ti_5O_{14}$ with the specific orthorhombic structure [6]. With the increase of the Pb content x , the XRD peaks intensity increases and the secondary-phase $Nd_4Ti_9O_{24}$ appears [7].

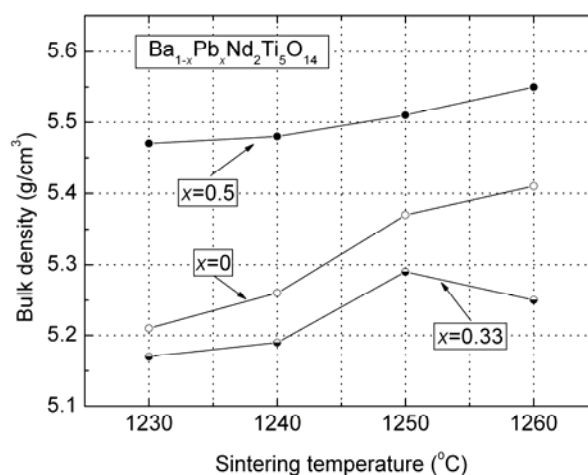


Fig. 1. Bulk density versus sintering temperature of $Ba_{1-x}Pb_xNd_2Ti_5O_{14}$ samples.

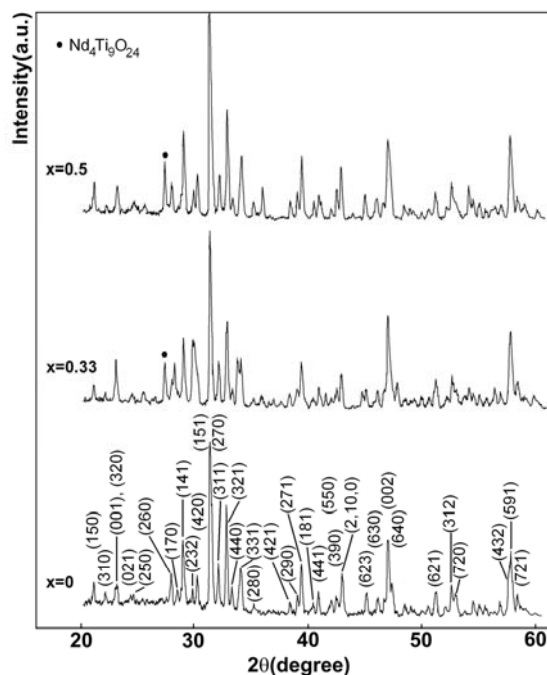


Fig. 2. X-ray diffraction patterns for $Ba_{1-x}Pb_xNd_2Ti_5O_{14}$ ceramic samples sintered at 1250/2h.

The SEM morphology of $Ba_{1-x}Pb_xNd_2Ti_5O_{14}$ samples sintered at 1250 °C for 2 hours is shown in Figs. 3-5. Spherical or polyhedral grains and pores appear in all the images. The size of the grains ($1 \div 8 \mu\text{m}$) increases with the increase in the Pb concentration. For samples with $x = 0$ or 0.33 Pb content, the crystallites dimensions vary between 0.5 and $3 \mu\text{m}$ (Fig. 3 and Fig. 4). At $x = 0.5$ Pb concentration, the large aggregates with dimensions $d > 10 \mu\text{m}$ bonded by high sizes pores disappear, as can be seen in Fig. 5. For samples with $x = 0.5$, the ceramics exhibit a good densification due to the high crystallites size in the range $2 \div 4 \mu\text{m}$.

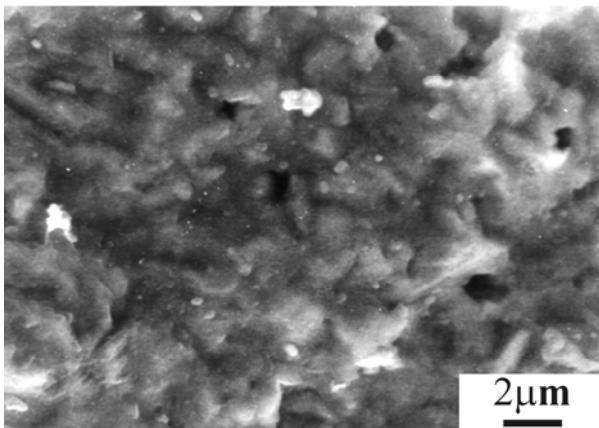


Fig. 3. SEM image of $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ sintered at 1250°C for 2 hours.

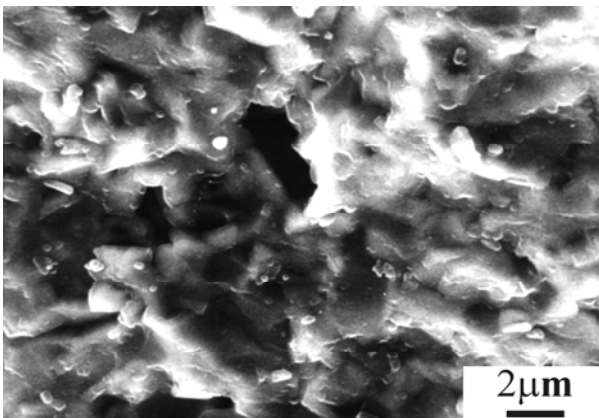


Fig. 4. SEM image of $\text{Ba}_{0.66}\text{Pb}_{0.33}\text{Nd}_2\text{Ti}_5\text{O}_{14}$ sintered at 1250°C for 2 hours.

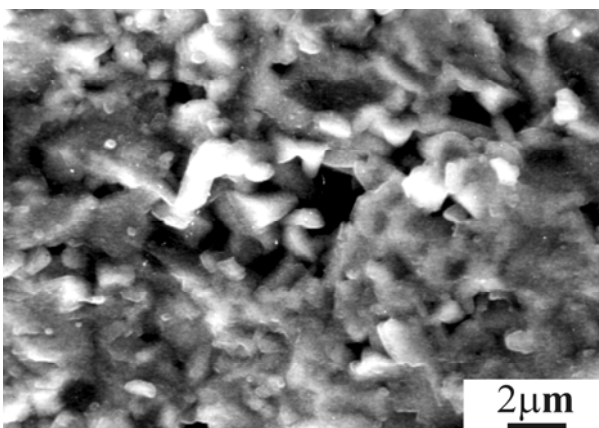


Fig. 5. SEM image of $\text{Ba}_{0.5}\text{Pb}_{0.5}\text{Nd}_2\text{Ti}_5\text{O}_{14}$ sintered at 1250°C for 2 hours.

The microwave measurements were performed in the 2÷5 GHz frequency range. A plot of few resonating modes of a $\text{Ba}_{0.5}\text{Pb}_{0.5}\text{Nd}_2\text{Ti}_5\text{O}_{14}$ dielectric resonator of 18.15 mm diameter and 10.78 mm height, placed in a Courtney holder, is depicted in Fig. 6. In order to accurately correct for the coupling losses, the external couplings were reduced and the TE_{011} resonance peak was investigated not very far from the noise floor. Corrections for the conduction loss in the parallel plates were considered also for accurate measurements of the dielectric resonator intrinsic quality factor Q_o .

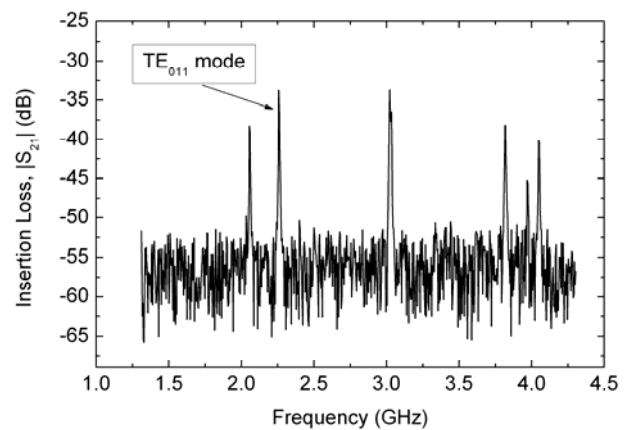


Fig. 6. Resonance peaks in microwave range of a $\text{Ba}_{0.5}\text{Pb}_{0.5}\text{Nd}_2\text{Ti}_5\text{O}_{14}$ dielectric resonator with 18.15 mm diameter and 10.78 mm height.

The microwave measurements on $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ samples, which do not contain Pb, show an increase of the dielectric constant with the increase in the sintering temperature as shown in Table 1. However, the quality factor exhibits a maximum value for the samples sintered at 1250°C for 2 hours. For an $x = 0.33$ Pb content, the dielectric constant increases with the increase of the sintering temperature as shown in Table 2. Nonetheless, the variation of the Qxf_o is in correlation with the variation of the bulk density showed in Fig. 1. The temperature coefficient τ_f takes slightly smaller values as in the case of $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$.

Table 1. Microwave characteristics of the BaNd₂Ti₅O₁₄ samples versus sintering temperature.

Sample	T _s /t _p (°C/h)	h (mm)	D (mm)	f ₀ (GHz)	ε _r	tan δ (x 10 ⁻⁴)	Q _o	Q _o x f _o (GHz)	τ _f (ppm/°C)
1	1230/2	5.17	9.94	4.72	76.1	5.9	1690	7978	+60 ÷ +70
2	1240/2	5.15	9.93	4.71	76.8	5.7	1730	8148	
3	1250/2	5.14	9.91	4.68	78.2	5.3	1900	8890	
4	1260/2	5.15	9.91	4.65	79.3	6.3	1580	7350	

Table 2. Microwave characteristics of Ba_{0.66}Pb_{0.33}Nd₂Ti₅O₁₄ versus sintering temperature.

Sample	T _s /t _p (°C/h)	h (mm)	D (mm)	f ₀ (GHz)	ε _r	tan δ (x 10 ⁻⁴)	Q _o	Q _o x f _o (GHz)	τ _f (ppm/°C)
5	1230/2	5.13	10.23	4.52	81.6	6.7	1500	6780	+50 ÷ +55
6	1240/2	5.65	10.27	4.22	83.5	6.4	1570	6625	
7	1250/2	5.12	10.20	4.48	83.4	7.8	1280	5734	
8	1260/2	5.08	10.01	4.45	85.3	6.9	1430	6364	

The highest values of the dielectric constant were achieved for a $x = 0.5$ Pb content on Ba_{0.5}Pb_{0.5}Nd₂Ti₅O₁₄ (Table 3). The dielectric constant somewhat increases with the sintering temperature. On the other hand, the dielectric

constant in microwave range can be correlated with the bulk density: both parameters exhibit the highest values for $x = 0.5$ and they both increase with the increase in sintering temperature.

Table 3. Microwave characteristics of Ba_{0.5}Pb_{0.5}Nd₂Ti₅O₁₄ versus sintering temperature.

Sample	T _s /t _p (°C/h)	h (mm)	D (mm)	f ₀ (GHz)	ε _r	tan δ (x 10 ⁻⁴)	Q _o	Q _o x f _o (GHz)	τ _f (ppm/°C)
9	1230/2	4.90	9.73	4.67	84.2	9.3	1080	5040	-10 ÷ -15
10	1240/2	4.87	9.68	4.67	85.1	8.8	1130	5270	
11	1250/2	4.86	9.65	4.64	86.5	8.8	1130	5240	
12	1260/2	4.78	9.58	4.70	86.6	9.1	1100	5170	

Furthermore, the lowest value of the temperature coefficient $|\tau_f| < 15$ ppm/°C was achieved for the Ba_{0.5}Pb_{0.5}Nd₂Ti₅O₁₄ samples. However, the quality factor, which practically does not depend on the sintering temperature, is smaller than in the previous cases of $x = 0$ or $x = 0.33$.

5. Conclusions

The Pb addition can increase the bulk density and can improve the microwave dielectric parameters of the BNT samples. A dielectric constant of ~ 87 at 4.6 GHz and a low temperature coefficient $|\tau_f| < 15$ ppm/°C were achieved for a $x = 0.5$ Pb content. Such BNT materials are very attractive for temperature stable applications at a few GHz working frequency. However, when a product $Q \times f$ higher than 6000 is required in order to use the BNT materials at higher frequency, then the Pb content can result from the trade off between a small temperature coefficient τ_f and a high quality factor Q .

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