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Preparation and sintering of $Ba_2Ti_9O_{20}$-based ceramics and their properties for dielectric resonators

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Abstract

The present paper was intended to study the grain-size influence of the oxide reagents used and the chemical treatment method applied of dibarium nonatitanate-based dielectric ceramics used as dielectric resonators in high-frequency fields. On the obtained samples, the main ceramic and electric properties were determined. The dielectric characterization of the resonators obtained, as well as the effects determined by their utilization within a stable frequency oscillator, was achieved by measurements in a high-frequency field. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Among the materials with electric properties used in electronic instruments and devices operating in the field of microwaves, a particular place is occupied by dielectric ceramic materials of low permitivity and small dielectric losses, that work as dielectric resonators. This type of electric material also includes ceramics with the composition corresponding to the $Ba_2Ti_9O_{20}$ compound, situated within the more than 80% mol TiO_2 zone of the BaO–TiO_2 system [1]. O'Brian and Thomson [2] mentioned that the realization of such dielectric ceramics of the polytitanate type requires a severe control on component stoichiometry, of the desire to be obtained phases, and of the sintering temperature. Wu and Wang [3] characterized the titanate compounds prepared by the conventional method, from kinetic and phasal points of view. O'Bryan et al. [4] have been shown that a chemical purification treatment applied to polytitanates can increase the phasal stability and quality factor of useful compounds.

The electric properties of interest, relating to this type of dielectric material, fall within high-frequencies zones (GHz); their utilization and measurement being carried out on the principle of resonant cavity with plane-parallel walls [5].

In the present paper the possibilities for improving the electric characteristics of the dielectric ceramic resonators based on dibarium nonatitanate were studied from the point of view of using them in a high-frequency IMPATT diode-equipped oscillator.

For this purpose the following were aimed at: -influence of raw materials grain-size on the synthesis manner and on properties; -influence of the obtained route by combining dry conventional mixed oxide techniques synthesis with wet chemical purification treatment of the obtained main compound; -the ceramic, structural and electric properties as well as the behavior at high frequency of the dielectric ceramics achieved.

2. Experimental procedure

The polytitanate dielectric ceramic materials based on $Ba_2Ti_9O_{20}$ were obtained by using reagent-grade titanium dioxide and barium carbonate (purity 99.2%) as starting materials. The powdery reagents were ground for various times of 3, 6, 9 and 12 h. Grinding was carried out in ceramic mills having Al_2O_3 balls as grinding bodies and using acetone as grinding medium. The resulting grain-sizes were determined by means of a laser granulometer type Cilas-Delcita 715 (France). The impurity acquired during processing was Al_2O_3—from 0.02 wt% for 3 h milling to 0.05 wt% for 12 h milling. The raw materials batch was made according to the compound stoichiometry (Ba:Ti = 2:9 in molar ratio). The oxide powders were homogenized and given by pressing a cylindrical shape of 12.1 mm in diameter and

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approx. 15.5 mm in height. Sample presintering was carried out in an electric kiln at 1150°C temperature for 4 h. On the obtained samples the following ceramic properties were measured: initial and final density, porosity, water absorption and apparent density. Then the samples were ground to powders for 6 and 12 h. On these samples, a chemical treatment with nitric acid of 7.85% mol concentration was carried out for non-atitanate purification. The chemical attack by the nitric acid, which eliminates compounds of higher barium content, which affect negatively the dielectric properties, was performed in more than 6 h when powder grain-size was greater than 10 μm and in less than 2 h when it was smaller than 2 μm; therefore for the grain size obtained after 12 h grinding time required by chemical attack on high barium content compounds was 4 h. After chemical treatment the powders were neutralized and prepared for sintering by shaping them, by pressing into a cylindrical form of 12.3 mm in diameter and 13.3 mm in height. The final sintering process was carried out in the electrical kiln at 1330°C temperature for 3 h. Sample cooling was done slowly at a cooling speed of 10°C/min. The samples obtained after sintering were characterized from a ceramic point of view (shrinkage, weight loss, absolute and apparent density, porosity) by standardized methods.

The electric properties were determined in high-frequency field (between 2 and 8.28 GHz) by means of a Hewlett–Packard measuring apparatus and of a parallel plane testing equipment. The measured samples were made to have a cylindrical shape as successful as possible, of approx. 6 mm in diameter and 4 mm in height.

The functional properties of the dielectric ceramics based on $Ba_2Ti_9O_{20}$ were measured by introducing them into a high frequency oscillator with IMPATT diode.

3. Results and discussion

As resulted from Fig. 1, the TiO_2 optimum grinding time periods suitable for achieving a continuous grain-size distribution as homogeneous as possible [6], were those of 9 and 12 h when particle sizes of 1–12 μm were obtained. With increasing the grinding duration, the > 16 μm fraction changed into the fine fraction of < 2 μm.

Fig. 2 shows $BaCO_3$ grain-size distributions versus various grinding time periods. The optimum $BaCO_3$ grain-size distributions required 9 h of grinding to result in dimensional uniformity of 1–12 μm size particles. With increasing the grinding duration, the 4–48 μm fractions changed into fine fractions of 1–8 μm and even < 2 μm.

It can be seen from Table 1 that after the presintering process of $Ba_2Ti_9O_{20}$, weight and volume losses show slight increases with increase in grinding time, which proves that grains fineness intervenes in increasing the physical–chemical interactions between reactant particles, with advantageous effects on compound characteristics. The final densities of ceramic bodies show an increase, except for the ceramics obtained from 9 h ground powders, but the sintering degree shown has an increasing tendency by almost 40% as a result of 12 h ground powders compared to ungrounded ones. At the same time, the apparent density confirms this increase of ceramic body density, which concludes that physical–chemical processes are taking place within the ceramic body. Along with densification, simultaneous decrease in absorption and porosity took place, too.

The presintered samples were ground for 6 and 12 h, to ensure the required optimum grain-size distribution for purification with nitric acid. The most granulometric fractions of 1–8 μm were greater in the case of 12 h grinding time, an advantageous condition for chemical attack by nitric acid in view of eliminating the compound with the higher content of BaO. The weak TiO_2 excess as a result of the chemical treatment avoid the appearance of the $Ba_6Ti_{17}O_{40}$ and $Ba_4Ti_{13}O_{30}$ at the sintering temperature. These compounds are in the phase diagram near to the $Ba_2Ti_9O_{20}$ phase. This phase contributes to the formation of the microwave phases-$Ba_2Ti_9O_{20}$ and also small amounts of $BaTi_4O_9$ as shown in the Fig. 3. After the sintering treatment was carried out on the presintered and chemically treated samples, the ceramic characteristics given by Table 2 were obtained.

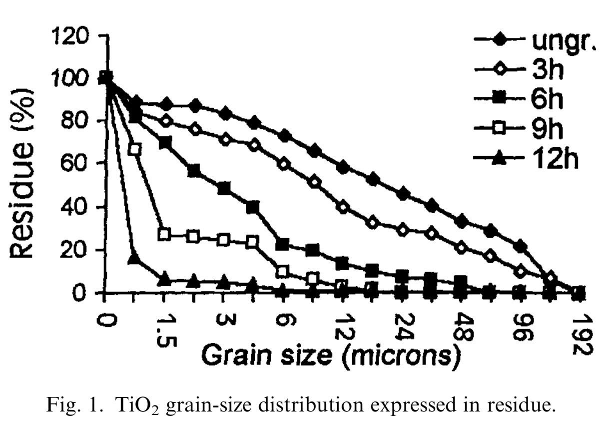

Fig. 1. TiO_2 grain-size distribution expressed in residue.

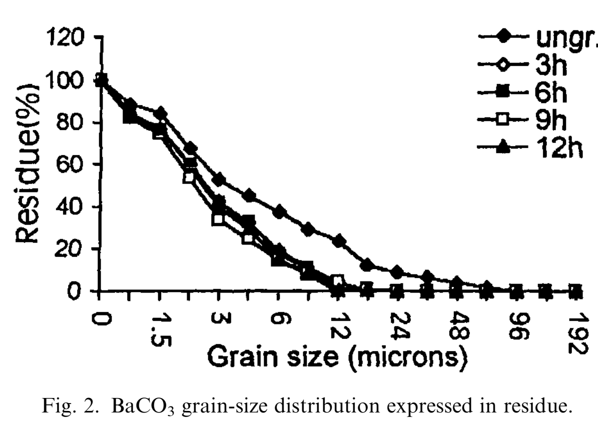

Fig. 2. $BaCO_3$ grain-size distribution expressed in residue.

Table 1
Ceramic properties of the presintered samples having $Ba_2Ti_9O_{20}$ composition

No. properties		Unground	Grinding times			
			3 h	6 h	9 h	12 h
1	Fire shrinkage (%)	21.70	31.80	35.80	37.40	44.00
2	Weight loss (g)	0.38	0.47	0.53	0.31	0.50
3	Initial density (g/cm^3)[a]	2.24	2.42	2.34	2.27	2.25
4	Final density (g/cm^3)[a]	2.64	3.10	3.31	3.28	3.63
5	Porosity (%)	39.80	23.70	27.30	25.90	9.10
6	Water absorption (%)	16.12	7.05	7.74	6.12	2.05
7	Apparent density (g/cm^3)	2.49	3.37	4.04	4.24	4.48
8	Sintering degree[b]	1.17	1.27	1.44	1.47	1.61

[a] Before and after firing, respectively.
[b] Final to initial densities ratio.

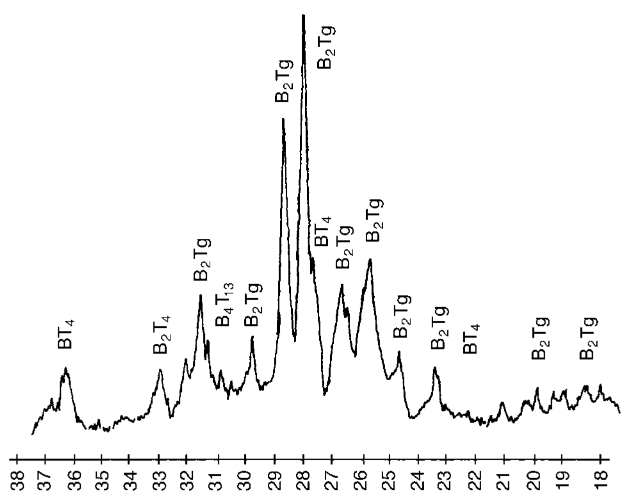

Fig. 3. X-ray diffractometry for the $Ba_2Ti_9O_{20}$ sintered samples.

The dielectric ceramics based on $Ba_2Ti_9O_{20}$, as shown, showed that weight and volume decreased and that more than 3 h grinding is necessary to obtain acceptable ceramic characteristics. Sample shrinkage showed similar magnitude order values for all grinding times, slightly varying around 23%.

Density values indicate a very slight increasing variation, the maximum ones being attained with samples obtained from 9 h ground powders. Final density of this sample was 4.10 g/cm^3 and the maximum value of apparent density was 4.25 g/cm^3.

Porosity of the sintered samples obtained from ground powders shows decreasing values but generally it is higher than those of the samples obtained from unground powders. A porosity of 3.46% is attained with samples made from 9 h ground powder due to the sintering having been optimum (Table 2).

The sintering degree achieved for the samples having $Ba_2Ti_9O_{20}$ composition indicates good values so that it can be appreciated that efficiency of the sintering process is about 14% at 12 h grinding.

Table 3 emphasizes that $Ba_2Ti_9O_{20}$ based resonators realized from unground reagents show a resonant frequency bandwidth (Δf) of 14.5 MHz for a permitivity (ε) of 32.3. The quality factors are low, having values of 700 and 800 for the one under load (Q_L) and for that specific to the resonator (Q_0), respectively. The loss angle tangent (tan δ) has implicitly increased values of approx. 1.2×10^{-3}. Variation in resonant frequency versus temperature ($\pm\Delta f_r$) appears good with these ceramics, having low values both when increasing (from 15 to 60°C) and decreasing (from 60 to 15°C). The electric effect of temperature variation was a compensating one, of ± 3 MHz, governing the resonator frequency (τ_f) versus temperature variation coefficient which had the value of $+6$ ppm/°C.

Table 2
Ceramic properties of the sintered samples having $Ba_2Ti_9O_{20}$ composition

No. properties		Unground	Grinding times			
			3 h	6 h	9 h	12 h
1	Fire shrinkage (%)	23.80	22.30	22.60	25.70	23.30
2	Weight loss (g)	0.02	0.03	0.03	0.04	0.08
3	Initial density (g/cm^3)	2.95	2.99	3.02	3.07	3.24
4	Final density (g/cm^3)	3.87	3.85	3.89	4.10	3.96
5	Porosity (%)	3.06	9.05	6.05	3.46	1.67
6	Water absorption (%)	0.73	2.29	1.50	0.06	1.66
7	Apparent density (g/cm^3)	4.12	3.95	4.04	4.25	3.77
8	Sintering degree	1.30	1.28	1.29	1.34	1.48

Table 3
Dielectric properties of $Ba_2Ti_9O_{20}$ dielectric ceramics samples

No.	Sample	D (mm)	h (mm)	f_r GHz	Δf (MHz)	Q_l	ε_r	Q_o	tan δ ×1000	Δ_{fr} 15–60°C (MHz)	Δ_{fr} 60–15°C (MHz)	τ_f (ppm/°C)
1	B2T9 unground	6.02	4.1	10.3	14.6	715	32.3	810	1.24	3.5	−2.8	6.1
2	B2T9/3 h/ch.trat	6.00	4.1	10.9	9.6	1135	29.3	1390	0.72	9.1	−5.9	12.0
3	B2T9/6 h/ch.trat.	5.89	3.9	11.0	10.0	1100	30.6	1358	0.73	6.4	−3.2	6.5
4	*B2T9/9 h/ch.trat.*	*6.04*	*4.1*	*10.2*	*3.3*	*3096*	*33.5*	*6849*	*0.14*	*9.6*	*−9.6*	*20.8*
5	B2T9/12 h/ch.trat.	6.00	3.9	11.3	12.0	942	28.6	1126	0.88	9.6	−4.0	7.8
6	B2T9/12 h/untrat.	6.13	4.1	11.4	12.0	955	26.3	1131	0.88	15.5	−5.5	30.1

Compared to earlier presented data the electric property values of the dielectric resonators with similar dimensions, obtained from powders ground for various periods of time and chemically treated, proved the beneficial influences conferred by the grinding process particularly by chemical treatment, as shown by Table 3.

Comparing the sample ground for 12 h (6 in Table 3) with the ungrounded sample (1 in Table 3) made obvious the effect of the advanced grinding on the electric properties, which consists in determining resonant frequency increasing to 11.4 GHz, band width narrowing to 12 MHz and quality factors advancing to 955, when under load, and 1131 in the case of that specific to the resonator, respectively. The ground and chemically treated samples permit the obtaining of a quality factor of 1100–3096. In addition to this, the loss angle tangent value of the chemically treated samples decreased to $0.72–0.88\times10^{-3}$. Unfavorable values were given by dielectric permitivity (which decreases to 26) and particularly by the resonant frequency versus temperature variation coefficient which increased significantly, but not so much for the ground and chemically treated samples.

The dielectric resonators with the best dielectric properties were obtained for a 9 h grinding of reactant powders followed by chemical treatment of presintered powders. These resonators showed a resonant frequency of 10.2 GHz, a bandwidth of 3.3 MHz (more selectively) and a dielectric permitivity of 33.5. The quality factors of these ceramics were very good for this range of frequency, of approx. 3000 and 7000 for that under load and for that specific to the resonator, respectively. In accordance with these, the loss angle tangent value appeared very good, 0.14×10^{-3}. The variation of resonant frequency with temperature increasing and decreasing fell within a range of ±9.6 MHz, which determined a resonant frequency versus temperature variation coefficient of +20 ppm/°C. Freer [1] presents, for microwave dielectric ceramic $Ba_2Ti_9O_{20}$, the following data: dielectric permitivity of 40 and quality factor of 8000 at 4 GHz frequency. Also Freer shows the representation of the variation of relative permitivity and dielectric Q value at microwave frequencies which consist of an exponential increase of the quality factor versus a decrease of the frequency. Thus, a value of about 7000 for the quality factor at 10 GHz represents a good value for these dielectric ceramics we obtained.

The resonant ceramics based on $Ba_2Ti_9O_{20}$ were inserted within an IMPATT diode oscillator, with the cylindrical dielectric resonator being arranged at a given distance from the microstrip line. By resonating it according to $Te_{01\delta}$ mode, the microstrip line impedance change took place.

Introduction of the dielectric resonator into the oscillator produced modification of the properties, as shown in Table 4.

It has been found that using resonators achieved from powders ground for 9 h and chemically treated, resulted in improvement of IMPATT diode-equipped oscillator properties. It also resulted in the frequency spectrum increasing by 4.7 dBc at a distance of 100 kHz from the signal carrier, resonant frequency variation improving at ±1 MHz, in uniform increase of power versus polarization current and in resonant frequency versus temperature variation improving over a 45°C temperature range at only ±5 MHz.

Table 4
Properties of the IMPATT diode equipped oscillator

No.	Property	With resonator	Without resonator
1	Frequency spectrum	−36 dBc	−40 dBc
2	Resonant frequency variation	35 MHz	1 MHz
3	Output power of the signal generated for IMPATT diode polarization currents of: 25 mA	4.07 mW	9.74 mW
	30 mA	34 mW	23.1 mW
	35 mA	53 mW	45 mW
4	Resonant frequency versus temperature variation ($\Delta t = 45°C$)	18 MHz	5 MHz

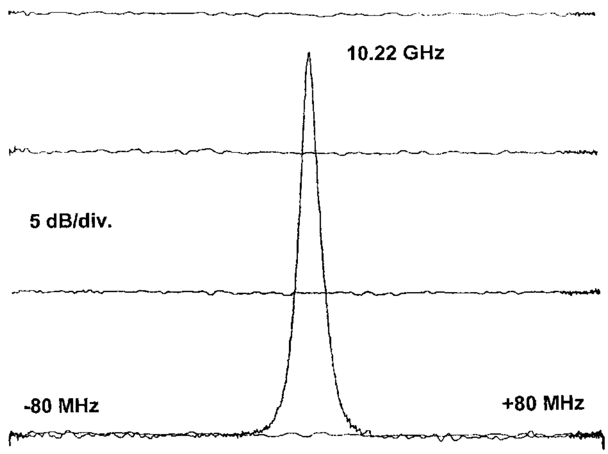

Fig. 4. The operating characteristics of the dielectric resonator.

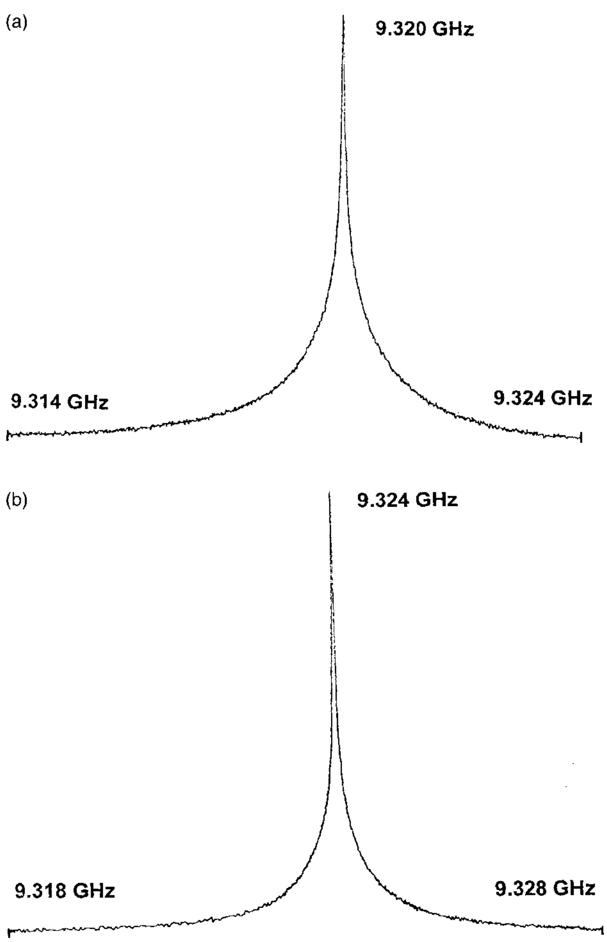

Fig. 5. (a) Oscillator signal under dielectric absence condition. (b) Oscillator signal under dielectric presence conditions.

The electric characteristic measured for the dielectric resonator made of $Ba_2Ti_9O_{20}$ based dielectric ceramics is plotted in Fig. 4. In addition to this, Figs. 5(a) and (b) illustrate the operating characteristics of the high-frequency IMPATT diode-equipped oscillator when the dielectric resonator is absent [Fig. 5(a)] and present [Fig. 5(b)].

4. Conclusions

- Ceramic dielectric materials based on $Ba_2Ti_9O_{20}$ were obtained by using presintered samples with various grinding times. The presintered samples were chemically treated with nitric acid and then sintered at 1330°C for 3 h.
- It was found that for the ceramics based on $Ba_2Ti_9O_{20}$ the most advantageous values of the ceramic properties were obtained when using reagent powders ground for 9 h, when reactant particles were of 1–12 μm.
- The dielectric properties of the $Ba_2Ti_9O_{20}$-based ceramics, obtained from 9 h ground powders, proved that: (1) raw materials grinding resulted in resonant frequency increasing by 1.5 GHz, in a band width narrowing by 2.5 MHz, in quality factors enhancing by 250 and 300 for that under load and for that specific to the resonator, respectively, and in loss angle tangent decreasing by 0.4×10^{-3}; (2) the chemical treatment on presintered powders and the advanced grinding resulted in the frequency band decreasing by 11.2 MHz and in quality factors increasing by 2300 and 6200 for that under load and for that specific to the resonator, respectively.

  The variation coefficient versus temperature was of +20 ppm/°C at the frequency of 10.2 GHz.
- Using the ceramics within the IMPATT diode-equipped oscillator led to a frequency spectrum improvement as a result of the phase noise reducing by 4.7 dB at the distance of 100 kHz from the carrier and to frequency stability improvement versus the polarization current of the IMPATT diode at a resonant frequency variation of ±1 MHz. The output power of the signal increased by 4.3 mW when the polarization current was low (25 mA). The variation factor of the oscillator resonant frequency versus temperature attained only ±5 MHz for a temperature range of 45°C.

References

[1] R. Freer, Silicates Industriels (1993) 191.
[2] H.M. O'Bryan, J. Thomson, Journal of American Ceramic Society 68 (2) (1985) 70.
[3] J.M. Wu, H.W. Wang, Journal of American Ceramic Society 71 (10) (1988) 869.
[4] H.M. O'Bryan, J. Thomson, J.K. Plourde, Ber. Dt. Keram. Ges. 55(7) (1978).
[5] Y. Kobayashi, IEEE Trans on MTT, MTT 33 (1985) 586.
[6] I. Teoreanu, N. Ciocea, A. Barbulescu, N. Ciontea, Tehnologia produselor ceramice si refractare, Ed. Tehnica, Bucareşti 1 (1985) 146–149.