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Tuning of the $Ba_5Nb_4O_{15}$ permittivity temperature coefficient

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Abstract

The $Ba_5Nb_4O_{15}$ ceramic offers attractive dielectric properties ($\varepsilon_r \sim 39$, $\tan(\delta) < 10^{-3}$, $\rho_i \sim 10^{12}\ \Omega\,\text{cm}$) but exhibits a high permittivity temperature coefficient ($\tau_\varepsilon \sim -171\ \text{ppm}\ {}^\circ\text{C}^{-1}$). In order to tune this parameter, substitutions on the Ba and Nb sites by, respectively, Mg, Ca, Sr and V, Ta, Sn have been investigated. Two interesting formulations have been identified, $Ba_{2.5}Mg_{2.5}Nb_4O_{15}$ and $Ba_5Nb_3SnO_{14.5}$ as nominal compositions, with temperature coefficients of -44 and $-30\ \text{ppm}\ {}^\circ\text{C}^{-1}$, respectively. More attention has been paid to the $Ba_5Nb_3SnO_{14.5}$ compound (named 504Sn25) in which $BaSnO_3$ has been clearly identified as a secondary phase. $BaSnO_3$, having a positive and very high temperature coefficient ($+393\ \text{ppm}\ {}^\circ\text{C}^{-1}$), seems to be responsible for the τ_ε lowering of 504Sn25. Furthermore B_2O_3 addition as sintering aid has been successfully investigated for increasing the $Ba_5Nb_3SnO_{14.5}$ sample density. In terms of dielectric properties, it induces an increase of the permittivity and of the insulating resistivity, while the control of τ_ε is maintained. Finally, the formulation 504Sn25 + 15 mol% B_2O_3 sintered at 1200 °C has a value of 17.8 as dielectric constant and $-1\ \text{ppm}\ {}^\circ\text{C}^{-1}$ as τ_ε value, that evidences the potentiality of this material to be used as temperature stable capacitor.

Keywords: Niobate; Dielectric properties; Capacitors

1. Introduction

The ceramic $Ba_5Nb_4O_{15}$ offers attractive properties for potential applications in passive electronic components. This compound exhibits at high frequency (from MHz to GHz) an ε_r of 39, very low dielectric losses ($\tan(\delta) < 10^{-3}$), a high insulating resistivity ($\cong 10^{12}\ \Omega\,\text{cm}$) and a sintering temperature around 1380 °C.[1] This later aspect is a real advantage compared to the sintering temperature which is usually required for sintering barium perovskites based dielectrics ($\cong$1500 °C).[2–5] Nevertheless, this material has a high permittivity temperature coefficient ($\tau_\varepsilon \cong -171\ \text{ppm}\ {}^\circ\text{C}^{-1}$)[1,6] that constitutes a real drawback for type I capacitors applications. Basically, two methods can be used for tuning τ_ε. The first one consists in the modulation of the volume fraction of two different materials with coefficients of opposite sign by stacking two cylindrical pellets or by mixing powders. However, this latter method is not easy to conduct for obtaining a well-controlled temperature coefficient because of the possible reactivity between the different phases during the sintering process. The second one is based on the crystal lattice modification induced by some substitutions. It is indeed expected that substitutions should modify the distances between atoms and consequently the physical properties such as the polarizability and/or the thermal expansion coefficient. It can be reminded the Bosman and Havinga's law which links the permittivity temperature coefficient with the above physical parameters:

$$\tau_\varepsilon = \frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon}\frac{1}{3\alpha}\left(\frac{\partial\alpha}{\partial T}\right)_P - \alpha_l{}^{7},$$

where α is the polarizability and α_l the linear thermal expansion coefficient.

In the present work, the influence of substitutions on Ba and Nb sites by, respectively, Mg, Ca ($r_{ca^{2+}}[\text{XII}] = 1.34$ Å [8]), Sr ($r_{Sr^{2+}}[\text{XII}] = 1.44$ Å [8]) and V ($r_{V^{5+}}[\text{VI}] = 0.54$ Å [8]), Ta ($r_{Ta^{5+}}[\text{VI}] = 0.64$ Å [8]) has been investigated, in order to control the $Ba_5Nb_4O_{15}$ τ_ε parameter. These substituting elements were chosen according to their ionic radii and their belonging to the same group than the substituted elements (group IIA for Ba and group VA for Nb). A substitution with Sn has been also carried out on the Nb site because of their similar ionic radius in octahedral environment ($r_{Sn^{4+}}[\text{VI}] = 0.69$ Å). Moreover, this element has been already successfully used to tune the permittivity temperature coefficient of some microwave ceramics.[8] The effects of these various substituting elements are presented in terms of structure and dielectric properties.

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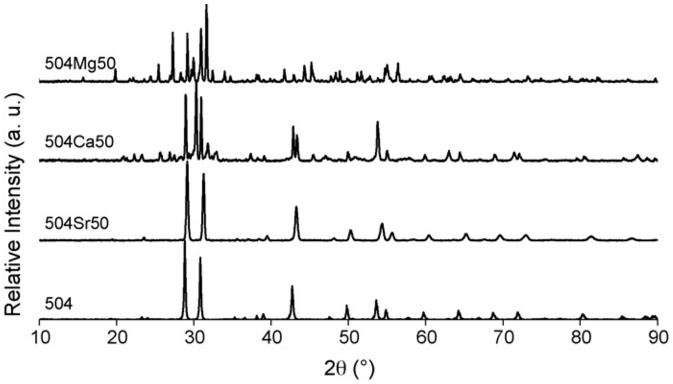

Fig. 1. XRD patterns of 504, 504Mg50, 504Ca50 and 504Sr50 powders after the calcination step at 1100 °C.

2. Experimental procedure

All compounds have been synthesized by solid state reaction. Precursor powders of $BaCO_3$ (Diopma, 99.99%), Nb_2O_5 (HCS Starck, 99.9%), $MgCO_3$ (Cerac, 99.95%), $CaCO_3$ (Cerac, 99.95%), $SrCO_3$ (Diopma, 99.99%), V_2O_5 (Rectapur, 99.50%), Ta_2O_5 (Cerac, 99.99%), SnO_2 (Prolabo) were mixed according to these six nominal compositions: $Ba_{2.5}Mg_{2.5}Nb_4O_{15}$ (named 504Mg50), $Ba_{2.5}Ca_{2.5}Nb_4O_{15}$ (504Ca50), $Ba_{2.5}Sr_{2.5}Nb_4O_{15}$ (504Sr50), $Ba_5Nb_3VO_{15}$ (504V25), $Ba_5Nb_3TaO_{15}$ (504Ta25) and $Ba_5Nb_3SnO_{14.5}$ (504Sn25). These powders were ground for 30 min in ethanol in an agate mortar using a planetary grinder. The resulting slurry was subsequently dried under infrared lamps and manually reground. The powders were heat treated at 1100 °C in air for 2 h with a heating and cooling rate of 200 °C h^{-1}. The resulting powder was manually reground in an agate mortar. The powder composition was determined by X-ray diffraction (XRD) using the Cu Kα radiation (Philips X'Pert diffractometer). Cylindrical green samples (6 and 8 mm in diameter, 2–3 mm in thickness) were shaped using a 28 kN uniaxial load and the sintering temperature was determined by dilatometry (TMA Setaram). The pellets were then sintered for 2 h at the dwell temperature previously determined and the heating and cooling rate was systematically fixed at 200 °C h^{-1}. For the dielectric properties characterization, In–Ga based electrodes were manually deposited on each face of disks. The dielectric measurements performed at 1 MHz were carried out versus temperature (from −60 to +160 °C) using a RLC Bridge (Flucke PM6306) and the resistivity was measured using a SEFELEC DM500A megohmeter.

3. Results and discussion

3.1. Substitutions on the Ba site

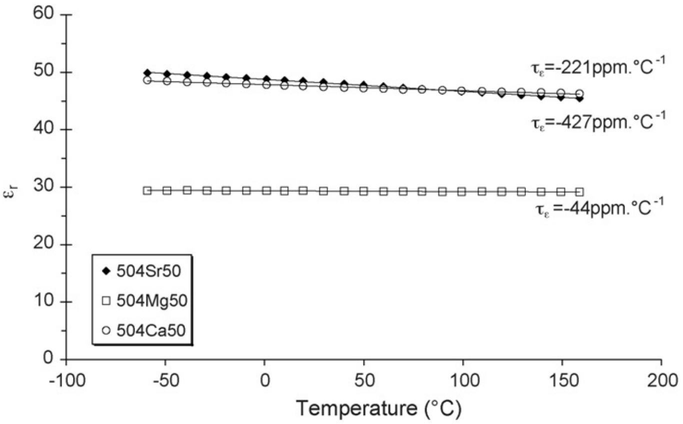

Fig. 2. Relative permittivity vs. temperature at 1 MHz of 504Mg50, 504Ca50 and 504Sr50 compounds, respectively, sintered at 1300, 1300 and 1200 °C.

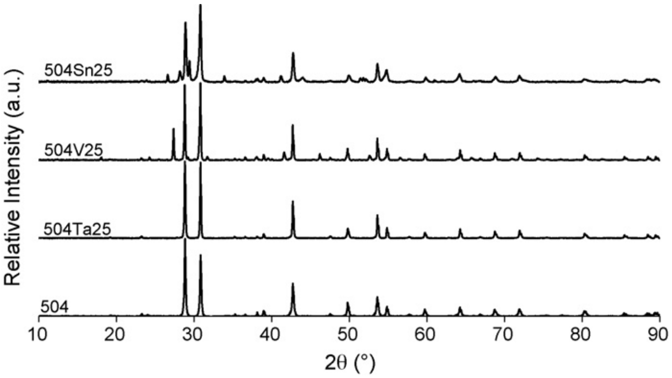

Fig. 3. XRD patterns of 504, 504V25, 504Ta25 and 504Sn25 powders after the calcination step at 1100 °C.

Fig. 1 shows the XRD patterns of $Ba_5Nb_4O_{15}$ (named 504) as reference and the three powders 504Mg50, 504Ca50 and 504Sr50, after the calcination step. For the 504Sr formulation, a solid solution is clearly evidenced. For the two others, many secondary phases appear. Fig. 2 shows the relative permittivity versus temperature of each sintered pellet. For all compounds, the temperature dependence of the relative permittivities is linear. The 504Ca50 and 504Sr50 compounds have relatively high permittivities, respectively, 47.6 and 48.5 at 20 °C, but their temperature coefficients are degraded. For 504Mg50, the temperature coefficient is reduced to −44 ppm °C^{-1} with a RT permittivity around 29.4.

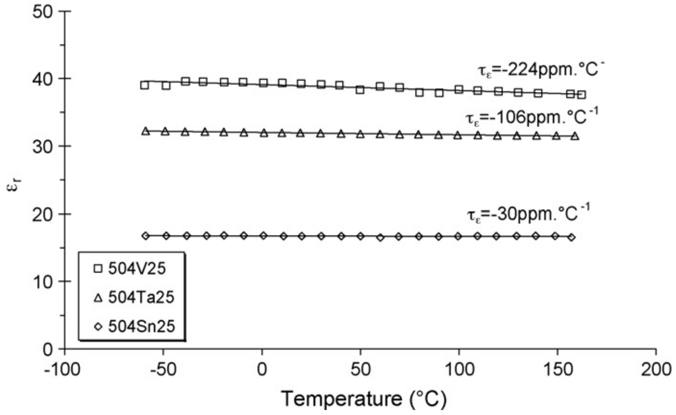

Fig. 4. Relative permittivity vs. temperature at 1 MHz of 504V25, 504Ta25 and 504Sn25 compounds, respectively, sintered at 1200, 1350 and 1450 °C.

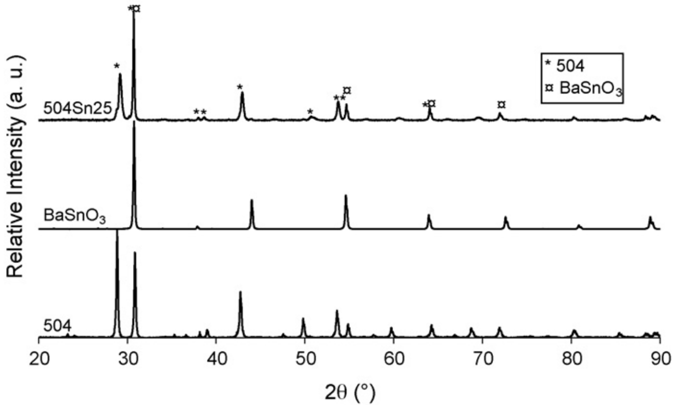

Fig. 5. XRD patterns of the 504Sn25 compound sintered at 1450 °C and of the $BaSnO_3$ and 504 powders after the calcinations step at 1100 °C.

3.2. Substitutions on the Nb site

Fig. 3 shows the XRD patterns of 504 as reference and the three powders 504V25, 504Ta25 and 504Sn25. Only the Ta element authorizes a solid solution formation. It seems that the V and Sn elements do not enter in Nb site.

In terms of dielectric properties, Fig. 4 shows the linear dependence of ε_r versus temperature for these three compounds. The 504Ta25 and 504Sn25 compounds, respectively, sintered at 1350 and 1450 °C, have lower temperature coefficients than the 504 compound. In the case of 504Ta25, the τ_ε value achieves $-106\,\mathrm{ppm}\,^\circ\mathrm{C}^{-1}$, with a room temperature permittivity of 32. The 504Sn25 compound has a relative permittivity of 16.5 at room temperature and a temperature coefficient of $-30\,\mathrm{ppm}\,^\circ\mathrm{C}^{-1}$. This τ_ε lowering is very interesting, whereas its low insulating resistivity value of $7.10^8\,\Omega\,\mathrm{cm}$ is redhibitory. It can be attributed to the low density of 4.50 and/or to the possible presence of SnO_2 which is known to be semiconductor.[9]

3.3. Tuning of τ_ε with the Sn element

In terms of τ_ε tuning, the most attractive result has been obtained with the Sn addition. The XRD pattern of 504Sn25 has been carefully examined and reveals mainly the presence of 504 and $BaSnO_3$ mixture (Fig. 5). In order to clarify the effect of $BaSnO_3$ on the τ_ε value, a $BaSnO_3$ pellet has been sintered and characterized.

3.4. $BaSnO_3$ characterization

$BaSnO_3$ powder has been prepared by solid state reaction. Single phase of $BaSnO_3$ has been synthesized as it is testified by the XRD pattern (Fig. 5). In terms of dielectric properties, the $BaSnO_3$ compound sintered at 1380 °C exhibits relative permittivity of 69.4 at RT and a temperature coefficient of $+393\,\mathrm{ppm}\,^\circ\mathrm{C}^{-1}$. Consequently, the presence of $BaSnO_3$ in 504Sn25 could explain the tuning of τ_ε in our ceramic according to the mixing rule. In order to characterize more accurately the dielectric properties of 504Sn25, the increase of the final density is crucial, that is the reason why sintering additives have been used.

3.5. Improving of the 504Sn25 density by B_2O_3 additions

B_2O_3 has been added to improve the densification. Three additions of B_2O_3 (7.5, 15 and 30 mol%) and three sintering temperatures have been tested. Table 1 shows the dielectric properties obtained for each compound. The resistivity is clearly higher than that of the 504Sn25 compound sintered at 1450 °C. Moreover, most of the sintered pellets exhibit a loss factor lower than 3×10^{-3}.

Table 1 also presents the temperature coefficients versus B_2O_3 additions and sintering temperatures. Two formulations exhibit very low τ_ε values: 504Sn25 + 15 mol% B_2O_3 and 504Sn25 + 30 mol% B_2O_3 sintered at 1200 °C, with, respectively, -1 and $-5\,\mathrm{ppm}\,^\circ\mathrm{C}^{-1}$. Their relatively low dielectric constant (respectively, 17.8 and 19.1) can be explained by the densification which is probably not complete at 1200 °C, the porosity lowering the relative permittivity value ($\varepsilon_r(\mathrm{air}) = 1$). Fig. 6 shows the microstructure of the 504Sn25 + 15 mol% B_2O_3 compound sintered at 1200, 1250 and 1350 °C; higher the sintering temperature, lower the porosity, higher the permittivity. However, 504Sn25 + B_2O_3 based formulations have dielectric properties suitable to manufacture temperature stable capacitors. However, a low content of $BaNb_2O_6$ ($\tau_\varepsilon \sim +400\,\mathrm{ppm}\,^\circ\mathrm{C}^{-1}$) due to the B_2O_3 addition being possible,[10] additional investigations are needed to more precisely understand the reasons of the tem-

Table 1
Dielectric properties of the 504Sn25 + B_2O_3 compounds at 1 MHz

B_2O_3 (%mol)	$T_{\mathrm{sintering}}$(°C)	Apparent density (g cm^{-3})	ε_r at 20°C	Log[ρi(Ω cm)]	τ_ε (ppm °C^{-1})
7.5	1200	4.14	15.1	11.4	−47
	1250	4.34	15.9	10.4	25
	1300	4.60	18.2	11.2	17
15	1200	4.84	17.8	11.3	−1
	1250	5.01	19.9	10.9	25
	1300	5.48	21.9	12.2	9
30	1200	5.07	19.1	11.6	−5
	1250	5.33	20.2	12.3	25
	1300	5.46	22.3	12.1	9

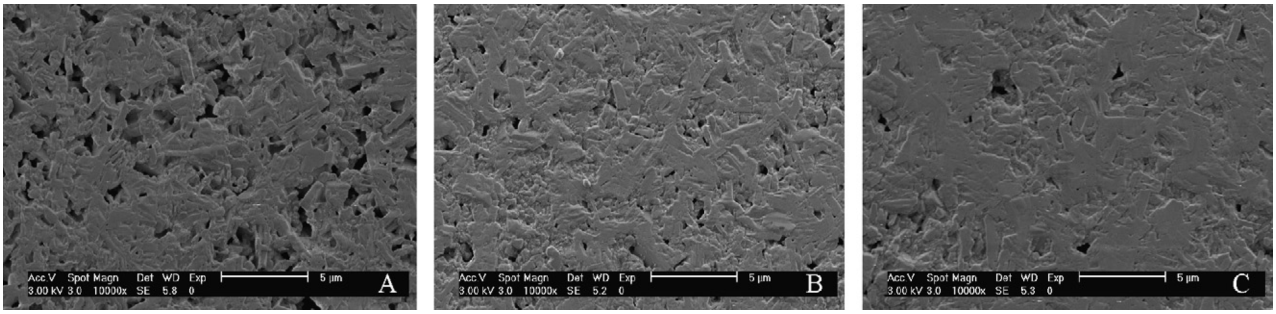

Fig. 6. Microstructures of the 504Sn25 + 15 mol% B_2O_3 compound sintered at 1200 °C (A), 1250 °C (B) and 1300 °C (C).

perature coefficient modification in the $Ba_5Nb_4O_{15}/Sn/B_2O_3$ system. Nevertheless the B_2O_3 amount having no major effect on the 504Sn25 temperature coefficient for the same sintering temperature (Table 1), $BaSnO_3$ phase is suspected to be responsible for the τ_ε tuning.

4. Conclusion

The influence of some elements, namely Mg, Ca, Sr, V, Ta and Sn, on the dielectric properties of the $Ba_5Nb_4O_{15}$ dielectric ceramic has been carried out, in order to tune its permittivity temperature coefficient ($\tau_\varepsilon \cong -171$ ppm $°C^{-1}$). From the structural point of view, only the Sr and Ta elements enter in Ba site and Nb site, respectively, without improving the temperature stability of ε_r. With the other elements, multiphase materials have been obtained and some of them exhibit improved temperature coefficient, namely 504Mg50 and 504Sn25 with temperature coefficients of −44 and −30 ppm $°C^{-1}$, respectively. Interesting results on the 504Sn25compound have encouraged us to focus on it. As Sn element has conducted to the formation of $BaSnO_3$, this compound has been synthesized and characterized. Its temperature coefficient is positive and very high ($\tau_\varepsilon = +393$ ppm $°C^{-1}$), that could explain the τ_ε tuning for the 504Sn25 compound ($\tau_\varepsilon = -30$ ppm $°C^{-1}$) according to the mixing rule. The B_2O_3 additions in 504Sn25 allowed to improve its densification, in resulting an increase of the permittivity and the insulating resistivity. Because τ_ε is globally inferior to 50 ppm $°C^{-1}$, the results obtained for the 504Sn25 + B_2O_3 formulations are very interesting. For example, the 504Sn25 + 15 mol% B_2O_3 formulation sintered at 1200 °C has 17.8 as dielectric constant and −1 ppm $°C^{-1}$ as τ_ε value.

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