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Temperature compensated niobate microwave ceramics with the columbite structure, $M^{2+}Nb_2O_6$

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Abstract

Of the niobate ceramics with the formula $M^{2+}Nb_2O_6$, several compounds (M^{2+} = Zn, Mg, Ca and Co) have Qf values (at f = 1–10 GHz) between 40 000 and 90 000 GHz, offering potential in dielectric resonator applications. However, their temperature coefficient of resonant frequency (τ_f) values are too high for commercial development, at between −50 and −90 ppm. This paper details the doping of these materials with dielectric ceramics having a large positive τ_f, in an attempt to reduce the overall τ_f to zero, whilst maintaining a high quality factor (Q). It was also found that doping increased the relative permitivity (ε_r) of the niobates. Several materials have been made with near-zero τ_f, such as 90% $CoNb_2O_6$/10% $CaTiO_3$ (τ_f = +2.0 ppm, ε_r = 25.2 and Qf = 21 700 GHz), and 94% $CoNb_2O_6$/6% TiO_2 (τ_f = +4.4 ppm, ε_r = 29.6 and Qf = 20 300 GHz)

Keywords: Columbites; Dielectric properties; Microwave properties; Niobates; Tcf (or τ_f)

1. Introduction

With the continuing proliferation of wireless communications technologies operating at microwave frequencies, there is an ever-increasing demand for cheap, but nonetheless high performance, dielectric ceramics. To be effective dielectric resonator materials they should have a sufficiently high relative permittivity to allow miniaturisation of the component ($\varepsilon_r > 10$), low dielectric losses at microwave frequencies to improve selectivity ($Q > 5000$, where $Q = 1/\tan\delta$), and a temperature coefficient of resonant frequency near zero for temperature stability ($\tau_f < \pm 20$ ppm per °C).[1]

Microwave ceramics are currently available with low τ_f and $Qf > 100\,000$ ($Qf = Q \times f_r$). However, these are usually made from complex perovskites, such as the mixed metal tantalate perovskites $BaZn_{0.33}Ta_{0.67}O_3$ (BZT) and $BaMg_{0.33}Ta_{0.67}O_3$ (BMT).[2–4] These complex perovskites require fairly high sintering temperatures (> 1400 °C), and the structures and properties of the complex perovskites (often with four or more cations) are proving difficult to predict, and depend strongly upon the degree of ordering.[5] Furthermore, tantalum is a relatively expensive metal, the ore tantalite (60% Ta_2O_5) costing $150 per kg,[6] whereas niobium is over 20 times cheaper, with the mineral columbite costing just $8 per kg.[6]

The binary niobate ceramics, with the formula MNb_2O_6 where M is a divalent cation, are one of the end members of the perovskite $BaM_{0.33}Nb_{0.67}O_3$ group (the other being BaO), and they are mostly isostructural with the orthorhombic mineral columbite ($ZnNb_2O_6$, space group = Pnca (60)).[7] The transition metal columbite niobates sinter between 1100 and 1200 °C, much lower than the perovskites,[7–10] and Q of the columbite niobates is higher than that of the $M^{2+}Ta_2O_6$ compounds, which do not have the columbite structure.[8] As niobium is so much cheaper than tantalum, and because the chemistry of the binary compounds should be easier to investigate than that of the complex perovskites, a study was made of these binary niobates, and these results have been previously reported.[11,12] Amongst the niobates investigated, four in particular exhibited potential for commercial application: these were $ZnNb_2O_6$ (ZnNO), $MgNb_2O_6$ (MgNO), $CaNb_2O_6$ (CaNO) and $CoNb_2O_6$ (CoNO). The properties of these materials are shown in Table 1, and it can be seen that these materials have good quality factors, especially considering the low cost and simplicity of the materials compared with the complex perovskites. The τ_f values,

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Table 1
Properties of optimum samples of TiO_2 and $CaTiO_3$ doped niobate ceramics, along with the pure parent compounds

Material	Temperature (°C)	% Sintering	ε_r	Qf (GHz)	τ_f (ppm K^{-1})
TiO_2 (rutile)[13,14]	1400	>95	100	48 000	+420
$CaTiO_3$[15]	1500	>95	170	3600	+800
Pure $ZnNb_2O_6$[11,12]	1200	94.4	21.54	84 500	−75.6
85% $ZnNb_2O_6$/15% TiO_2	1150	90.3	29.82	46 000	−69.6
78% $ZnNb_2O_6$/22% TiO_2	1200	76.6	29.59	27 700	+21.7
70% $ZnNb_2O_6$/30% TiO_2	1150	92.2	52.00	26 500	+110.3
91% $ZnNb_2O_6$/9% $CaTiO_3$	1250	88.6	21.83	31 500	−64.5
80% $ZnNb_2O_6$/20% $CaTiO_3$	1200	88.2	22.21	14 800	−27.4
75% $ZnNb_2O_6$/25% $CaTiO_3$	1150	76.4	22.50	15 000	−14.8
Pure $MgNb_2O_6$[11,12]	1300	93.9	18.42	79 600	−72.0
93% $MgNb_2O_6$/7% TiO_2	1350	95.5	22.56	47 400	−48.8
90% $MgNb_2O_6$/10% TiO_2	1300	89.0	25.36	19 000	−23.1
87% $MgNb_2O_6$/13% TiO_2	1300	96.5	37.97	21 800	+80.0
93% $MgNb_2O_6$/7% $CaTiO_3$	1300	89.9	19.95	78 600	−52.8
80% $MgNb_2O_6$/20% $CaTiO_3$	1300	90.2	18.35	73 700	−45.0
Pure $CaNb_2O_6$[11,12]	1350	97.5	17.31	49 600	−52.9
89% $CaNb_2O_6$/11% TiO_2	1300	97.2	23.09	6700	−11.3
88% $CaNb_2O_6$/12% TiO_2	1300	96.4	22.32	3600	+5.2
85% $CaNb_2O_6$/15% TiO_2	1250	98.3	24.66	2100	+36.7
94% $CaNb_2O_6$/6% $CaTiO_3$	1300	95.1	19.54	69 500	−65.4
92% $CaNb_2O_6$/8% $CaTiO_3$	1300	95.1	30.14	10 800	+39.7
90% $CaNb_2O_6$/10% $CaTiO_3$	1300	95.7	33.90	17 600	+72.7
Pure $CoNb_2O_6$[11,12]	1150	95.6	20.46	41 700	−66.6
95% $CoNb_2O_6$/5% TiO_2	1150	96.5	27.51	20 100	−10.6
94% $CoNb_2O_6$/6% TiO_2	1150	94.2	29.56	20 300	+4.4
86% $CoNb_2O_6$/14% TiO_2	1100	94.0	28.40	12 100	+145.2
92% $CoNb_2O_6$/8% $CaTiO_3$	1150	96.0	22.76	29 000	−12.2
90% $CoNb_2O_6$/10% $CaTiO_3$	1150	95.4	25.19	21 700	+2.0

whilst being fairly small compared with materials like titania or calcium titanate, were still too large for many resonator applications. Therefore, the effects of using dopants in an attempt to lower the τ_f of these niobate compounds were investigated. Because all of the niobates have negative τ_f values, dopants with large positive τ_f values and good microwave properties were added. The dopants used were commercially available forms of doped TiO_2 (rutile), which has $\tau_f = +420$ ppm K^{-1} and $Qf = \sim 48\,000$ GHz,[13,14] and $CaTiO_3$ which has a $\tau_f = +800$ ppm K^{-1} and $Qf = \sim 3600$ GHz.[15]

2. Experimental

2.1. Sample preparation

All niobate samples were prepared by a standard ceramics mixed-oxide route (oxides at least 99.9% pure). A stoichiometric mixture of the oxides needed to form each columbite compound was ball milled in deionised water with zirconia balls for 2 days, and then dried on a rotary evaporator. The resultant powder was then calcined at a temperature between 1000 and 1200 °C for 12 h in air, and then ball milled again in deionised water with zirconia balls for 2 weeks, and again dried on a rotary evaporator.

Doped samples were produced by adding the required amounts of TiO_2 (ISK Ltd., Osaka, Japan) or $CaTiO_3$ (Pi-Kem Ltd., Shropshire, UK) to the niobate powder, and then dry ball milling (with no solvent) the doped powder for 24 h to mix.

The powders were uniaxially pressed to form pellets (no binder was necessary), under a pressure of 100 MPa using an 8 mm diameter die. All samples were then sintered in air, at temperatures between 1000 and 1400 °C. The samples were all heated at a rate of 5 °C min^{-1} to the sintering temperature, sintered at that temperature for 2 h, and then cooled to 40 °C at a rate of 5 °C min^{-1}.

2.2. Sample characterisation

2.2.1. Density and sintering

The density of the samples was calculated from their measured volume and mass. The theoretical density of the doped niobates was calculated using the law of mixtures and the x-ray densities of the niobate and dopant compounds, obtained from JCPDS files, with the equation:

$$\rho_{total} = (Vf_1 \times \rho_1) + (Vf_2 \times \rho_2) \quad (1)$$

where Vf_1 and Vf_2 = volume fraction of components 1 and 2 and ρ_1 and ρ_2 = X-ray density of components 1 and 2. The degree of sintering was calculated by dividing the sample density by the maximum theoretical density of the ceramic, and expressed as a percentage.

2.2.2. Microwave measurements

The quality factor (Q) and relative permittivity (ε_r) were measured at frequencies between 6 and 10 GHz, using the resonant $TE_{01\delta}$ mode of the sample.[16] The sample was placed in an oxygen-free high-conductivity copper cavity, supported on a 4 mm high low-loss quartz spacer. The cavity was 30 mm in diameter, with adjustable height. This height was adjusted so that the space above and below the sample was 4 mm, approximately the same as the sample thickness. The diameter of the sample was also approximately 1/3 of the diameter of the cavity, as recommended by Kajfez and Guillon.[16] The surface resistance of the copper was calculated from the Q value of the TE_{011} resonance of the empty cavity, to allow the results to be corrected for any loss due to the cavity walls.[16] The $TE_{01\delta}$ mode was examined using a Hewlett-Packard HP8720D Vector Network Analyser, with a resolution of one Hz. The Q values are corrected for losses due to the measurement equipment, and so can be assumed to be the Q of the dielectric ceramic. Measurements were made on the as-fired samples, at room temperature.

The temperature coefficient of resonant frequency (τ_f) was obtained by measuring the variation in resonant frequency (f_r) of the sample every 5 K, between 250 and 300 K, while cooling at a rate of 2 K min^{-1}. A linear fit was then made to these data using Microcal Origin software, and τ_f derived from the gradient. The fitting was made using the least squares method to 10 data points, the standard error of all slope values was less than 0.2% and the standard deviation of all fits was less than 1×10^{-4}, with the correlation coefficient giving a level of confidence greater than 99.99%. The results are quoted in ppm K^{-1} of f_r at room temperature (e.g. 1 ppm of 7 GHz = 7 kHz). The samples were cooled by placing the cavity in a closed-cycle cooling system using a CTI Cryogenics Model 22 refrigerator and 8200 cryo-compressor, and the temperature controlled and measured using a Lakeshore 330 Temperature Controller and specially written software.

3. Results and discussion

Initial doping levels were chosen assuming that the total τ_f of the doped niobate would be simply additive from the proportions of the two individual components. It was not expected that the τ_f would be so easily predictable, and this indeed proved to be the case. Then, based upon the results of these first experiments, further doping levels were chosen for each niobate. These doping levels are shown in Table 1, as wt.%. In our investigations of the columbite niobate compounds we observed that there is an optimum sintering temperature for each of the compounds, which is that temperature at which density, Q and ε_r is maximised. Sintering below this optimum resulted in low density and hence low ε_r, and above the optimum usually resulted in de-densification and exaggerated grain growth, with rapid loss of Q.

Therefore, each of the doped niobates was sintered over a range of temperatures, and their density, Q and ε_r were measured. However, it was found that the highest Q material was not always that with the highest density, particularly in the $CaTiO_3$ doped niobates, indicating that the properties of the doped niobates would be difficult to predict and their behaviour complex. The densities of many of the doped ZnNO samples is lower as they began to melt at lower temperatures, before becoming fully dense.

The τ_f values quoted are those for the sample with the highest Qf for each doped niobate, and the properties of these samples are given in Table 1. As can be seen, these results were very unpredictable, with a wide variation in effects of doping between the different parent niobate compounds, seemingly unrelated to any trends observed in the pure niobate compounds.[11,12] The scope of this paper is to investigate the effect of doping upon τ_f, and the properties of the optimum sample of each mixture. A more detailed study of the effect of sintering temperature upon density, Qf and ε_r of these doped niobates can be found in Ref. 17. An investigation is also currently underway into their structures and crystalline phases.

Plots of τ_f against wt.% of dopant are shown in Figs. 1 and 2. It can be seen that in all cases the plots cross zero with TiO_2 addition, and near-zero τ_f materials have been achieved for doped CaNO (12%, $\tau_f = +5.2$ ppm) and CoNO (6%, $\tau_f = +4.4$ ppm). However, the proper-

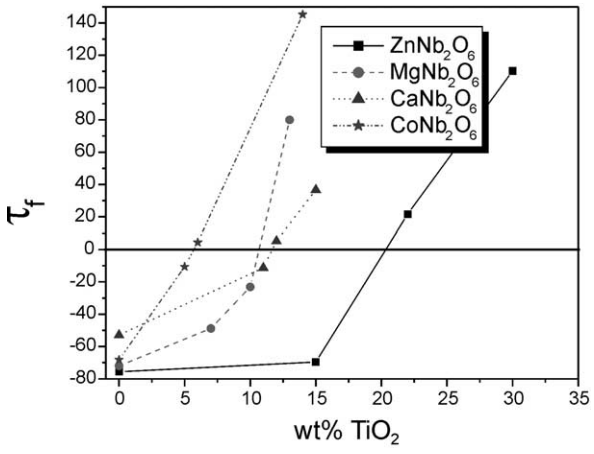

Fig. 1. Variation in τ_f with wt.% addition of TiO_2.

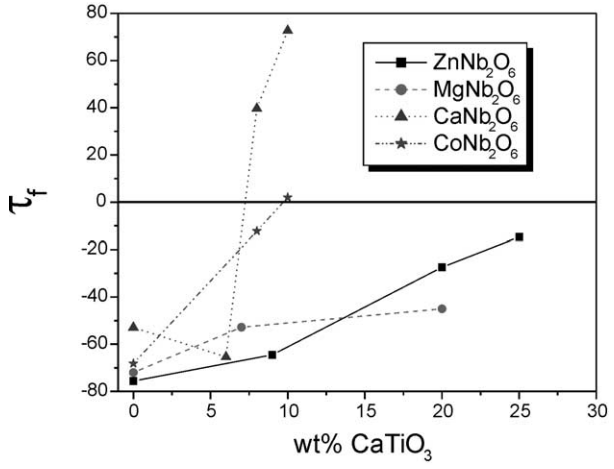

Fig. 2. Variation in τ_f with wt.% addition of $CaTiO_3$.

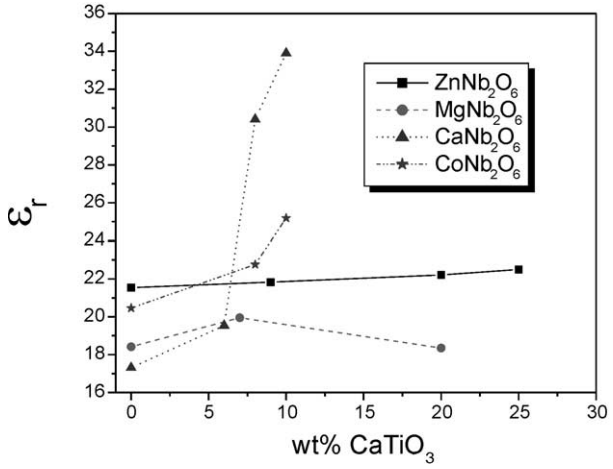

Fig. 4. Variation in ε_r with wt.% addition of $CaTiO_3$.

ties are less easily predicted when using $CaTiO_3$ as a dopant. While a near-zero τ_f material has already been achieved with CoNO (10%, $\tau_f = +2.0$ ppm), and doped CaNO passes through zero between 6 and 8%, the evidence suggests that much larger amounts will have to be added to ZnNO and MgNO if they are to be temperature compensated. Extrapolation of the plots from current data suggest that a ZnNO containing material may have a zero τ_f, but that $CaTiO_3$-doped MgNO will never reach zero. However, as pure $CaTiO_3$ has a large positive τ_f, it may be that $CaTiO_3$ doped with a minority of MgNO may be temperature compensated.

It can be seen from Fig. 3 that ε_r generally increases with TiO_2 doping, particularly in the case of ZnNO and MgNO, for which materials ε_r has more than doubled. However, with the $CaTiO_3$ doped niobates (Fig. 4) there was little change in ε_r with doping, except in the case of CaNO, which also exhibited a doubling of ε_r. Therefore, many of these near-zero τ_f niobates also posses improved ε_r over the pure material, enabling the miniaturisation of any resulting microwave components.

As can be observed in Figs. 5 and 6, in almost all cases addition of the dopants causes a large increase in dielectric loss. Although CaNO with 12% $CaTiO_3$ has a τ_f of only $+5.2$ ppm, the Qf is reduced to only 3600 GHz, rendering this material unusable in resonator applications. CoNO only suffers a decrease of $\sim$50% in both near-zero τ_f compositions, resulting in low τ_f materials with Qf values of around 20,000 GHz. The results also indicate that zero τ_f materials should exist in the ZnNO– and MgNO–TiO_2 systems with Qf values exceeding 20,000 GHz in both cases. The relationship between Q and doping is less clear in the $CaTiO_3$ doped samples. The Qf of MgNO hardly changes even with an addition of 20% $CaTiO_3$, but τ_f and ε_r also remain largely unaffected. ZnNO suffers a large increase in losses with initial addition, but with additions over 20% Qf seems to stabilise, while τ_f continues to gradually approach zero. CaNO doped with $CaTiO_3$ has anomalous properties, with an initial increase in both negativity of τ_f and magnitude of Qf with an addition of 6%, after which point the material behaves in a similar

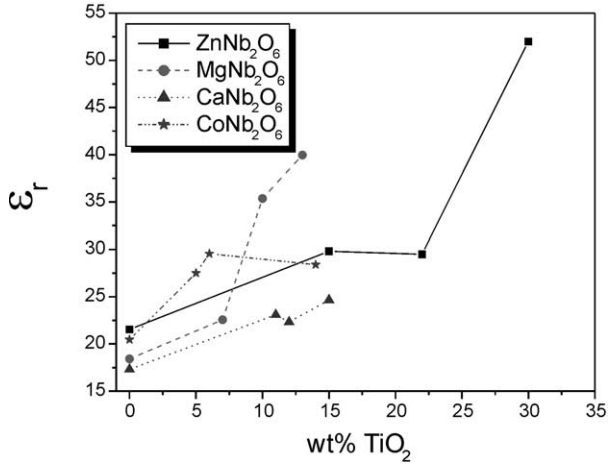

Fig. 3. Variation in ε_r with wt.% addition of TiO_2.

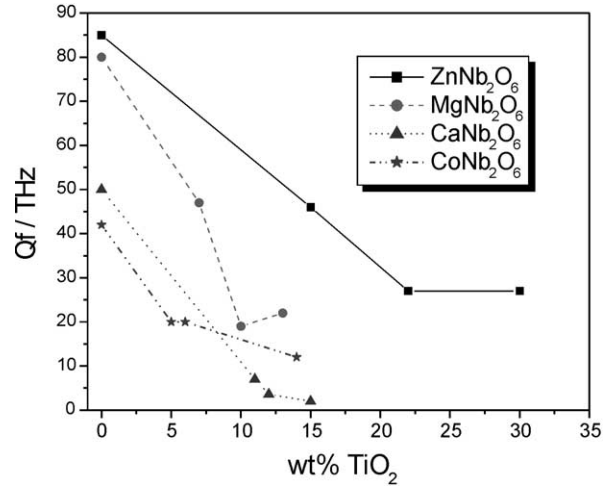

Fig. 5. Variation in Qf with wt.% addition of TiO_2.

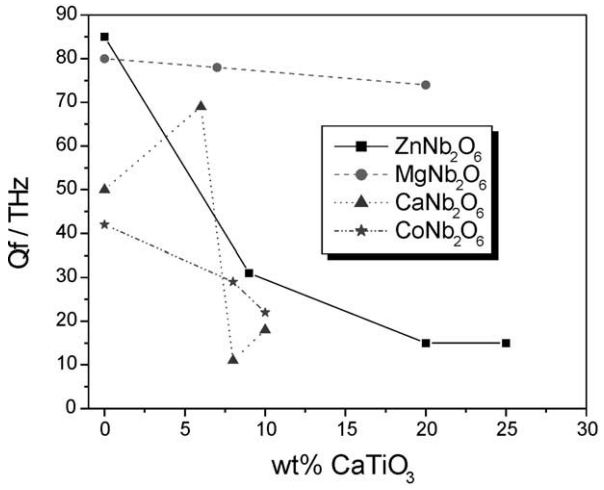

Fig. 6. Variation in Qf with wt.% addition of $CaTiO_3$.

fashion to the other niobates, with τ_f becoming positive and Qf decreasing significantly. The reason for this different behaviour is currently being investigated. It should be noted that these measurements of Q must be treated with some caution, especially for poorly sintered samples which contain porosity. In previous work on Al_2O_3 we have demonstrated that while ε_r falls linearly with an increase in porosity, a porosity of 5% can decrease Q by over 50%, so the true Qf values of such materials may be much higher.[18]

4. Conclusions

It is evident from this study that the behaviour of these four, structurally and chemically very similar, columbite niobate compounds are different from one-another, and difficult to predict, when doped with TiO_2 and $CaTiO_3$. It can be generally stated that an increasing amount of dopant increases ε_r, decreases Q and changes τ_f from negative to positive, passing through zero at some point. While many of the materials investigated have Qf values too low for practical use as microwave resonator materials, two near-zero τ_f materials with reasonably good microwave dielectric properties have been produced; 90% $CoNb_2O_6$/10% $CaTiO_3$ ($\tau_f = +2.0$ ppm, $\varepsilon_r = 25.2$ and $Qf = 21\,700$ GHz), and 94% $CoNb_2O_6$/6% TiO_2 ($\tau_f = +4.4$ ppm, $\varepsilon_r = 29.6$ and $Qf = 20\,300$ GHz). These results also indicate that with further work in both systems more zero τ_f materials with $Qf > 20\,000$ GHz and an enhanced ε_r should be possible.

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