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Novel microwave dielectric LTCCs based upon V_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ compounds (M^{2+} = Zn, Co, Ni, Mg and Ca)

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Abstract

The copper-niobates, $M^{2+}Cu_2Nb_2O_8$ (M^{2+} = Zn, Co, Ni, Mg or Ca) have good microwave dielectric properties when sintered between 985–1010 °C and 1110 °C for $CaCu_2Nb_2O_8$. Therefore, they would be potential dielectric LTCC materials if they could be made to sinter below 960 °C (melting point of silver). To this end, additions of 3 wt.% V_2O_5 were made to $ZnCu_2Nb_2O_8$, $CoCu_2Nb_2O_8$, $NiCu_2Nb_2O_8$, $MgCu_2Nb_2O_8$ and $CaCu_2Nb_2O_8$, and their sintering and dielectric behaviour was investigated for samples fired between 800 and 950 °C. Doping lowered sintering temperatures to below the 960 °C limit in all cases. Doping had the general effect of reducing ε_r, density, Qf and τ_f, although doped $CaCu_2Nb_2O_8$ had a Qf value of 9300 GHz, nearly four times that of the best undoped sample. Doped $ZnCu_2Nb_2O_8$ fired to 935 °C had Qf = 10,200 GHz, and for doped $CoCu_2Nb_2O_8$ fired to 885 °C Qf = 7500 GHz. When doped and undoped samples all fired to 935 °C were compared, all doped samples had greater ε_r and density, and all except $ZnCu_2Nb_2O_8$ had a smaller τ_f. All doped samples had a more linear relationship between frequency and temperature in the range 250–300 K.

Keywords: LTCC; Sintering; Dielectric properties; Niobates; Functional applications

1. Introduction

The next generation of dielectric ceramic components need to be miniaturised, multilayer devices, leading to a recent growth in the study of low temperature co-fired ceramic (LTCC) materials suitable for use as dielectric resonators (DRs). However, to achieve this a new generation of DR materials must be developed that sinter at sufficiently low temperatures (ideally <960 °C, the melting point of silver), have the required dielectric properties at microwave frequencies, and are inexpensive. A DR ceramic must have very low dielectric losses (tan δ, where $Q = 1/\tan\delta$), a large relative permittivity (ε_r) to allow sufficient miniaturisation of the component, and a temperature coefficient of resonant frequency (τ_f) near zero for maximum temperature stability. There is also a need for low permittivity (ε_r = 10 to15) LTCCs with low losses. Due to the dominating losses from the metal layers, a massively low loss for current LTCC candidate materials is not necessary, and Qf = 10,000 GHz and over is sufficient. Much of the work on LTCC materials is based on the mixing of a low temperature glass with a dielectric ceramic, always to the detriment of the dielectric properties of the ceramic. At LSBU we are concentrating on achieving LTCC temperatures via the addition of non-glassy, oxide sintering aids such as CuO or V_2O_5, in small amounts, typically up to 3 wt.%, which generally have a less negative effect upon the microwave dielectric properties than glasses.

The authors have previously investigated the dielectric properties and sintering behaviour of several $M^{2+}Cu_2Nb_2O_8$ compounds (M^{2+} = Zn, Co, Ni, Mg and Ca). The only previously reported example of such materials is $(ZnCu_2)Nb_2O_8$, found as in intergranular phase when CuO was added to zinc niobate $ZnNb_2O_6$.[1] The authors have found these materials to have promise as LTCC DRs, as except for the calcium copper-niobate, they all form well-sintered ceramics, some with good dielectric properties, when fired between 985 and 1010 °C; and these results will be reported in another paper.[2] Therefore, these metal-copper-niobates, with the nominal formula $M^{2+}Cu_2Nb_2O_8$, were doped with 3 wt.% V_2O_5 as a sintering aid, their sintering behaviour has been examined, and their potential assessed as dielectric LTCC candidate materials.

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2. Experimental

All $M^{2+}Cu_2Nb_2O_8$ samples were prepared by a standard ceramics mixed-oxide route (oxides at least 99% pure), and are reported in detail in reference.[2] Doped samples were produced by adding 3 wt.% V_2O_5 to the $M^{2+}Cu_2Nb_2O_8$ powder, and then dry ball milling (with no solvent) for 24 h to mix. The powders were uniaxially pressed to form pellets under a pressure of 100 MPa using a 13 mm diameter die. All samples were then sintered in air, at temperatures between 800 and 1000 °C per 2 h, heated and cooled at a rate of 5 °C min^{-1}. The density of the samples was calculated from their measured volume and mass.

The change in length of a cylindrical sample, dL/L_0, with increasing temperature was measured at a rate of 5 °C min^{-1} using a Netzsch 402C dilatometer. This was expressed as a percentage change in length with temperature, to study the sintering behaviour of the samples.

The quality factor (Q) and relative permittivity (ε_r) were measured at frequencies around 8 GHz, using the resonant $TE_{01\delta}$ mode of the sample,[3] in an oxygen-free high-conductivity copper cavity, whose diameter was three times that of the sample, as recommended by Kajfez and Guillon.[3] The $TE_{01\delta}$ mode was examined using a Hewlett-Packard HP8720D Vector Network Analyser, and 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.[3] 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 results are given as Qf, that is $Q \times$ resonant frequency (f_r), and f_r was between 8.2 and 8.5 GHz in all cases.

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}, and τ_f derived from the gradient. The results are quoted in ppm K^{-1} of f_r at room temperature. The samples were cooled by placing the cavity in a closed-cycle cooling system using a CTI Cryogenics Model 22 refrigerator and 8200 cryocompressor and the temperature controlled and measured using a Lakeshore330 Temperature Controller and specially written software.

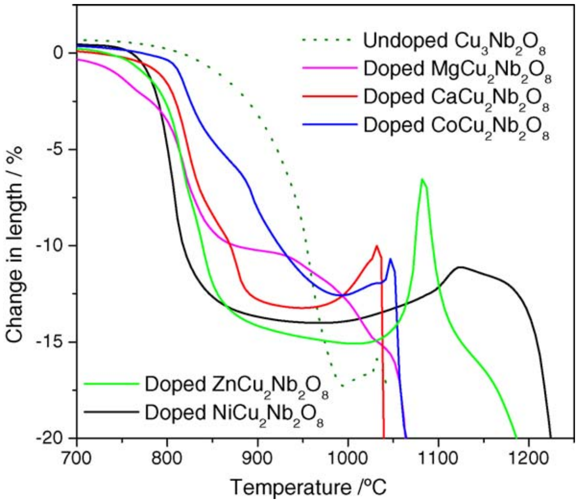

Fig. 1. Sintering plot of percentage change in length with temperature for 3 wt.% V_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ powders. Undoped $Cu_3Nb_2O_8$ is included as a reference point.

3. Results and discussion

The undoped $M^{2+}Cu_2Nb_2O_8$ ceramics were all found to sinter at temperatures between 985 and 1060 °C, except for $Cu_3Nb_2O_8$, which sintered at 910 °C.[2] With the exception of $Cu_3Nb_2O_8$, these sintering temperatures are too high for an LTCC material to be co-fired with silver contacts. The microwave dielectric properties of the samples with the highest Q value for each of the $M^{2+}Cu_2Nb_2O_8$ ceramics is given in Table 1. It can be seen that the cobalt and zinc copper-niobates are producing samples with reasonable properties just above the limit of LTCC temperatures, and that $Cu_3Nb_2O_8$ is a potential dielectric LTCC material without any further addition. Therefore, 3 wt.% V_2O_5 was added to the other five copper-niobate ceramics to see if well sintered samples, with useful dielectric properties, could be achieved at temperatures below the LTCC limit (<950 °C).

The shrinkage of the V_2O_5 doped samples with temperature can be seen in Fig. 1, which also has the shrinkage plot of undoped $Cu_3Nb_2O_8$ as a reference. It can clearly be seen that all of the doped samples sinter at temperatures less than that of $Cu_3Nb_2O_8$, and that all are fully dense by 950 °C. Despite this, the melting points of the samples are similar to those of the undoped copper-niobate ceramics. However, they all exhibit a large increase in thickness prior to melting not seen in the undoped ceramics, signifying de-densification probably due to massive discontinuous grain growth. This process has calamitous effects upon the microwave properties of the samples, but as it happens at temperatures well above the LTCC limit, it does not affect their potential as LTCCs. The microstructure

Table 1
Microwave dielectric properties of undoped $M^{2+}Cu_2Nb_2O_8$ ceramic samples with the highest Q values (f = 7.4 to 8.7 GHz)[2]

$M^{2+}Cu_2Nb_2O_8$	Sintering temperature (°C)	Density (g cm^{-3})	ε_r	Qf (GHz)	τ_f @295 K (ppm K^{-1})
$CoCu_2Nb_2O_8$	985	5.94	16.6	36,800	−37.0
$ZnCu_2Nb_2O_8$	985	3.95	8.9	23,350	−17.7
$NiCu_2Nb_2O_8$	985	5.32	12.8	4240	+481.6
$Cu_3Nb_2O_8$	910	4.79	11.2	25,560	−3.7
$MgCu_2Nb_2O_8$	1010	5.22	15.9	6780	−46.1
$CaCu_2Nb_2O_8$	1110	4.64	11.6	2300	−17.2

Table 2
Microwave dielectric properties of 3 wt.% V_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ ceramic samples with the highest Q values (f = 8.2–8.5 GHz)

$M^{2+}Cu_2Nb_2O_8$ + 3 wt.% V_2O_5	Sintering temperature (°C)	Density (g cm^{-3})	ε_r	Qf (GHz)	τ_f @295 K (ppm K^{-1})
$CoCu_2Nb_2O_8$	885	4.75	12.0	7530	−18.2
$ZnCu_2Nb_2O_8$	935	4.70	11.4	10,200	−23.0
$NiCu_2Nb_2O_8$	935	4.91	11.2	5760	−11.7
$MgCu_2Nb_2O_8$	935	4.40	11.3	2900	−27.4
$CaCu_2Nb_2O_8$	935	4.41	10.8	9300	−16.4

and composition during these changes is currently under investigation.

The microwave dielectric properties of the sample with the highest Q of each doped ceramic are shown in Table 2. It is apparent that all of the samples produce a maximum Q below the LTCC temperature limit, and that cobalt, zinc and calcium copper-niobates have reasonable Qf values for LTCC materials. Although most of the Qf values are less than half of the maximum Qf values obtained in the undoped copper-niobates (albeit at higher sintering temperatures), the doped $CaCu_2Nb_2O_8$ sample has a Qf of over 9000 GHz when sintered at 935 °C, nearly four times that of the best undoped sample. Density and ε_r is lower and τ_f of the sample with the highest Q is smaller in all doped copper-niobates, except for $ZnCu_2Nb_2O_8$, which also had an anomalous XRD pattern. The other samples all exhibited dissociated CuO and $M^{2+}Nb_2O_6$ on the surface of the sample, whereas zinc copper-niobate consisted of an as-yet unidentified, apparently single-phase material. Further investigations are currently underway into both this, and the true compositions of the materials below the penetration depth of the XRD beam (a few μm), and these results will be published in a future paper.

The behaviour of the microwave properties with sintering temperature is shown in Fig. 2. As would be expected, density mirrored the pattern of permittivity, as the two properties are intrinsically linked. However, Q is greatly affected by other factors such as grain sizes and boundaries, minor secondary phases, etc. With all samples except $CoCu_2Nb_2O_8$ a maximum in Qf was achieved as density and ε_r began to decrease from their maxima, contrasting with most of the undoped copper-niobates in which maxima in ε_r and Qf coincided. This is quite unusual, as often Qf decreases rapidly as density begins to decrease again due to over sintering causing discontinuous grain growth to occur. This leads to some grains being massively larger than others, resulting in porosity between the mis-matched grains and a collapse

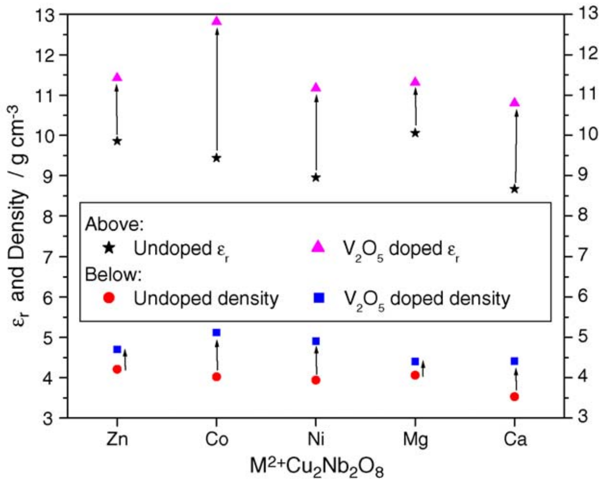

Fig. 3. Comparison of ε_r (top) and density (bottom) for undoped and 3 wt.% V_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ ceramics, all fired to 935 °C per 2 h (except for undoped Mg- and $CaCu_2Nb_2O_8$, which were fired to 960 and 1060 °C, respectively).

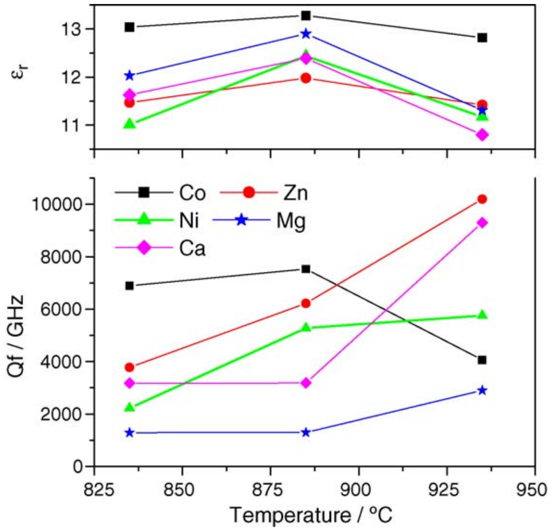

Fig. 2. Variation in ε_r (top) and Qf (bottom) with sintering temperature for 3 wt.% V_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ ceramics.

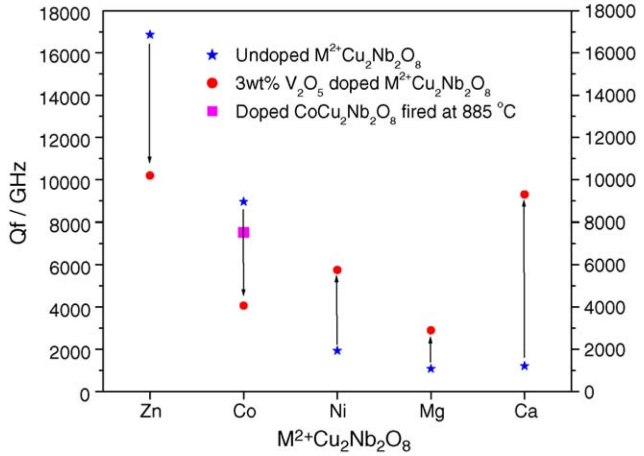

Fig. 4. Comparison of Qf for undoped and 3 wt.% V_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ ceramics, all fired to 935 °C per 2 h (except for undoped Mg- and $CaCu_2Nb_2O_8$, which were fired to 960 and 1060 °C, respectively). 3 wt.% V_2O_5 doped $CoCu_2Nb_2O_8$ fired to 885 °C is also included.

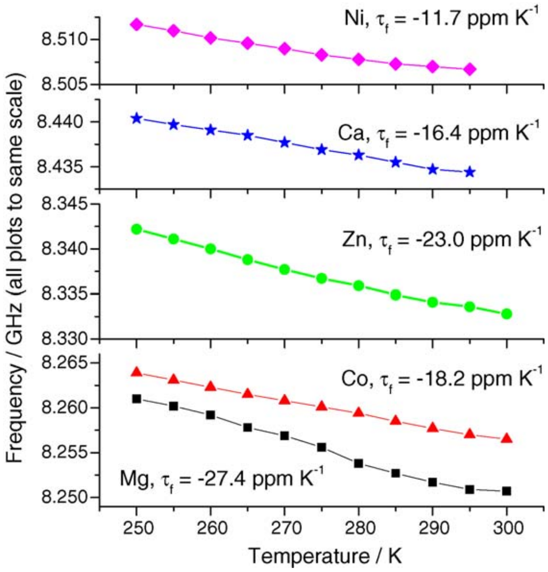

Fig. 5. Plots of frequency against measurement temperature for undoped and 3 wt.% V_2O_5 doped $M^{2+}Cu_2Nb_2O_8$ ceramics (maximum Qf samples from Table 2). τ_f is calculated from the slope of the plot. All plots are to the same scale, so slopes can be directly compared.

in Qf.[4] The internal microstructure of the doped copper-niobate samples is also currently under investigation in an attempt to explain this.

In Figs. 3 and 4, the ε_r, density and Qf values are compared between the undoped and V_2O_5 doped copper-niobate samples, all fired to 935 °C. This is except for undoped $MgCu_2Nb_2O_8$ and $CaCu_2Nb_2O_8$, which were samples fired to 960 and 1060 °C, respectively, as these were the lowest temperatures at which accurately measurable samples could be produced. Fig. 3 shows that both ε_r and density increased with doping in all cases, and as would be expected, these two values increased by similar degrees in each case. With Qf the effect of doping was not so easily predictable (Fig. 4). Doping increased Qf in nickel, magnesium and calcium copper-niobates; increasing greatly from 1200 to 9300 GHz in the case of $CaCu_2Nb_2O_8$. For zinc and cobalt copper-niobates, however, the Qf was considerably worse in the doped samples, even though they were better sintered than the undoped samples at those temperatures. Even when the doped $CoCu_2Nb_2O_8$ sample with the best Qf fired to 885 °C is included in Fig. 4, it still has a lower Qf than the undoped sample. The maximum Qf values were obtained at only 985 °C for undoped zinc, cobalt and nickel copper-niobates, and so if high Qf is the main criteria, the undoped $ZnCu_2Nb_2O_8$ and $CoCu_2Nb_2O_8$ ceramics are superior LTCCs than with 3 wt.% V_2O_5 doping.

However, τ_f is also an important property for microwave dielectrics, and in all cases except for $ZnCu_2Nb_2O_8$ doping reduced τ_f (Table 2; Fig. 5). Not only that, it also resulted in a considerably more linear relationship between temperature and frequency than that seen in the undoped samples, particularly in the case of $NiCu_2Nb_2O_8$, which saw a reversal from −19 ppm K^{-1} below 275 K to +481 ppm K^{-1} at room temperature.[2] By contrast, the doped $NiCu_2Nb_2O_8$ has a quite linear τ_f of −11.7 ppm K^{-1} between 250 and 295 K (Fig. 5).

4. Conclusions

Addition of 3 wt.% V_2O_5 to $ZnCu_2Nb_2O_8$, $CoCu_2Nb_2O_8$, $NiCu_2Nb_2O_8$, $MgCu_2Nb_2O_8$ and $CaCu_2Nb_2O_8$ lowered sintering temperatures to below the 960 °C limit for LTCC in all cases. Doping had the general effect of reducing ε_r, density, Qf and τ_f, although doped $CaCu_2Nb_2O_8$ had a Qf value of 9300 GHz, nearly four times that of the best undoped sample. For doped $ZnCu_2Nb_2O_8$ fired to 935 °C, Qf = 10,200 GHz, and for doped $CoCu_2Nb_2O_8$ fired to 885 °C, Qf = 7500 GHz. When doped and undoped samples all fired to 935 °C were compared, all doped samples had greater ε_r and density, and all except $ZnCu_2Nb_2O_8$ had a smaller τ_f. All doped samples had a more linear relationship between frequency and temperature in the range 250–300 K.

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