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High decrease in $CaZrO_3$ sintering temperature using complex fluoride fluxes

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Abstract

The effects of complex fluoride flux on the sintering and the electric/dielectric properties of $CaZrO_3$ ceramics are investigated. Four fluoride mixtures are tested: LiF–CaF_2–SrF_2, LiF–CaF_2–BaF_2, LiF–SrF_2–BaF_2 and LiF–BaF_2–B_2O_3. They are used because each of their associated phase diagrams shows the existence of an eutectic composition having a low melting temperature. This liquid phase is used to promote the densification at low temperature. The effect of various additions (nature and quantity) are also investigated to optimise the resulting thermal and physical properties. In terms of sintering behaviour, the results are unambiguous, leading to a drastic decrease of the densification temperature with all the non-boric additions ($\leq$1000 °C). The dc/ac measurements carried out on the materials sintered at low temperature (900 and 1000 °C) and either in air or in reductive atmosphere follow the same trend when using non-boric additions, with high permittivities ($\geq$25), low dielectric losses ($<10 \times 10^{-4}$), low temperature coefficients of the permittivity (<100 ppm/K) and high insulating resistivities (up to 10^{15} Ω cm); the high frequency measurements lead to similar conclusions revealing high QF products (up to 40 THz) using non-boric additions. The effect of the sintering temperature, the sintering atmosphere, the flux composition and its amount on these properties are also discussed.

Keywords: Capacitors; Sintering

1. Introduction

The multilayer ceramic capacitors' (MLCC) market has been growing in pace with the development of communication technologies. Almost half of this production is based on noble metals (Pt, Pd, Ag), which are expensive, and the development of cheaper base metal electrode MLCC (BME-MLCC) is being preferred. The base metals classically wished to be used in such applications are either Ni or Cu. The main disadvantage of the former is its ferromagnetism[1] which prohibits its use in the framework of applications using a magnetic field. The second one is diamagnetic[2] moreover it possesses a higher conductivity[2] that can lower the equivalent serial resistance (ESR). An alternative to the use of either the copper or nickel could be the silver since it is even more diamagnetic than the copper and also better conductor.[1,2] The main advantage of this alternative stands in the fact that the behavior of this metal is already well known in the MLCC's industry. Even more expensive than the base metals, the silver keeps interesting if one compares the cost of its use to the one of the production of new BME-MLCCs which are necessarily produced using atmosphere controlled equipments with reductive flows.[3]

The $CaZrO_3$ material was chosen because it exhibits a relatively high permittivity (25–30), low dielectric losses ($<10^{-4}$) and a high insulating resistivity (>1012 Ω cm) and also for its inertia to the reductive atmosphere. It has already been shown that the sintering temperature of $CaZrO_3$ could be decreased below the nickel melting point[3,4] and the copper melting point.[4,5] The aim of this study is to still decrease the sintering temperature of the $CaZrO_3$ material (1550–1600 °C) below the copper melting point (1083 °C) to improve the properties and reliability of the capacitors[6] and even bellow the silver melting point (961 °C) while maintaining the good electric and dielectric properties of the material.

This study details the results obtained using several fluorides based fluxes. The parameters reported are the effect

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Table 1
Characteristics of the fluxes used to lower the sintering temperature; the composition described are those of the eutectics (see references)

System	LiF (%)	CaF_2 (%)	SrF_2 (%)	BaF_2 (%)	B_2O_3 (%)	$T_{Melting}$ (°C)	Ref.
LCS	57.6	20.2	22.2			740	7
LCB	52	25		23		710	8
LSB	54.8		19.8	25.4		750	9
LBBo	35.8			32.3	31.9	752	10

of several fluxes on the sintering temperature, the electric properties and dielectric properties at low (1 MHz) and high frequencies (GHz).

2. Experimental details

Four different ternary fluxes were tested for this study. All were chosen because of the low melting of the eutectic composition (Table 1).

A stoichiometric $CaZrO_3$ phase was prepared using industrial reagents $CaCO_3$ (Merck, 99.95% purity) and ZrO_2 (Daiichi, DK1, 99.5% purity).[5] The different materials for the flux (Prolabo, ≥99% purity) were added using several concentration (Table 2). The powders were wet-ball-milled in ethanol for 45 min. using an agate mortar with agate balls. The mixture was dried using infrared lamps and manually de-agglomerated in an agate mortar. The powders were then mixed with an organic binder and uniaxially pressed to form green discs (2100 kg/6.36 mm discs for dilatometric measurements; 3880 kg/8.06 mm discs for sintering). The dilatometric measurements were carried out in static air using a SETARAM TMA92 dilatometer. For all the measurements, the samples were heated/cooled at 2 K/min with a dwell at 1200 °C for 1 h. A load of 1 g was applied during the measurements. A heat/cool ramp of 2.5 K/min was chosen for the sintering in a tubular furnace, with a thermal cycle dependent upon the dilatometric results; the sintering atmosphere was static air or a mixture of 10% H_2/90% Ar, moisture saturated at room temperature. Electrical measurements were realized on shaped discs painted, when needed, on both faces with Copper. Insulating resistance measurements were made using a SEFELEC DM500A megohmmeter and the dielectric characteristics [ε, tg(δ)] were acquired at 1 MHz with a FLUCKE 6306 LCRmeter and in the GHz domain through the cavity method.

3. Results

Fig. 1 shows the results of the dilatometric measurements. Both the shrinkage curves and their first derivative (inserts) are plotted. The first general observation is that all the fully fluorides based fluxes allow a high decrease in the sintering temperature of $CaZrO_3$. For all these fluxes, the temperatures for a maximum shrinkage rate (T_{SRM}; see the first derivative curves) are between 850 and 950 °C. With the LCS flux, the effect of the amount rapidly saturates and 10 at.% are sufficient to obtain a low densification temperature; the effect of the doubling of the LiF content (LCS10d) simply gives an intermediate result between LCS5 and LCS10 and does not allow any improvement in the sintering behavior.

Table 2
Summary of the studied compositions

Compound	at.% Li	wt%					
		LiF	CaF_2	SrF_2	BaF_2	B_2O_3	Total
LCS5	**5**	0.7	0.8	1.4			2.84
LCS10	**10**	1.4	1.5	2.7			5.67
LCS20	**10**	1.4	0.8	1.4			3.56
LCS10d	**20**	2.9	3.1	5.4			11.35
LCB5	**5**	0.7	1.0		2.2		3.93
LCB10	**10**	1.4	2.1		4.3		7.87
LCB20	**10**	1.4	1.0		2.2		4.66
LCB10d	**20**	2.9	4.2		8.7		15.73
LSB5	**5**	0.7		1.3	2.3		4.26
LSB10	**10**	1.4		2.5	4.5		8.51
LSB20	**10**	1.4		1.3	2.3		4.98
LSB10d	**20**	2.9		5.1	9.1		17.02
LBBo10	**10**	1.4			8.8	3.5	13.73
LBBo20	**10**	1.4			4.4	1.7	7.59
LBBo10d	**20**	2.9			17.6	6.9	27.46

The flux additions are expressed as a function of the lithium content relative to the $CaZrO_3$ molar content (in bold character). The compounds including the letter "d" in their name (i.e. LCS10d . . .) have a doubled amount of lithium compared to the eutectic composition (i.e. the LiF quantity is the same in XXX10 and XXX10d but the amount for the other flux's compounds is divided per 2).

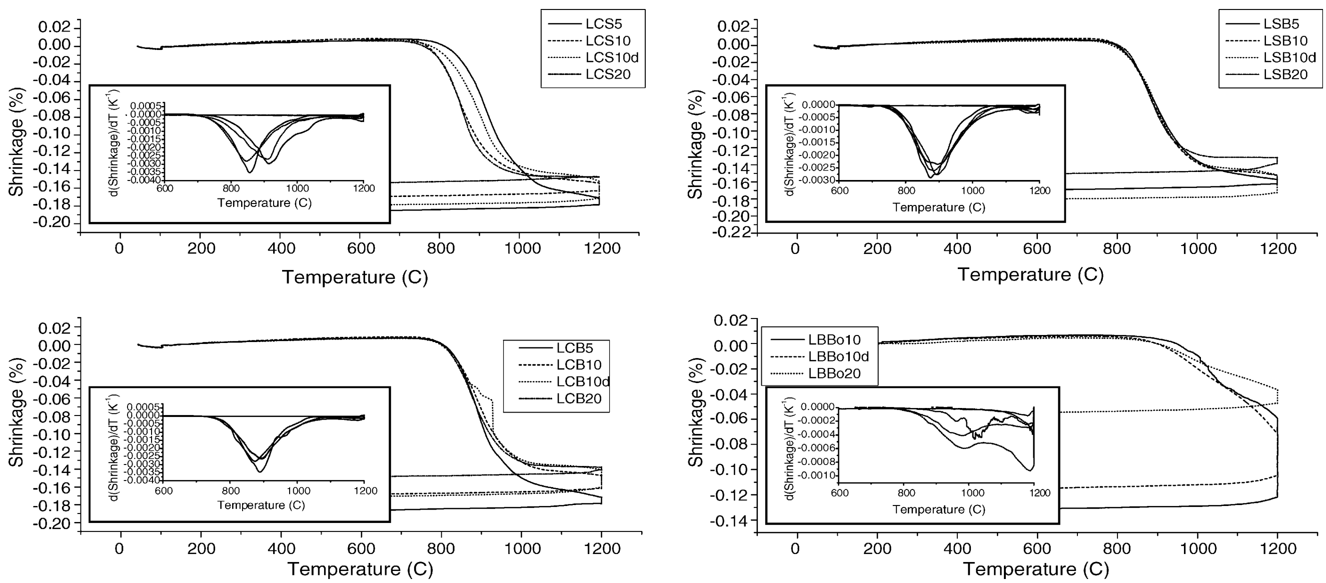

Fig. 1. Dilatometric measurements using the four different fluxes; the inserts show the plots of the first derivative of the shrinkage (with respect to the temperature).

The results with LCB and LSB fluxes are quite similar with nearly no effect of the amount (with the compositions used for these tests); in the same way, the doubling of the LiF content in the fluxes seems to have no effect on the sintering. The results obtained with the flux containing boron oxide are the worst and this flux has simply been discarded since the densification of the materials hardly starts below the copper melting point. All the compounds based on fully fluorides fluxes have been sintered at 900 °C/12 h and 1000 °C/4 h using an air atmosphere or a reductive one. This system, using two different temperatures, two different atmospheres, three different fluxes and three different concentrations has been analyzed using a simple $3^2 2^2$ experiments plan.[11,12] Since we also have tried to observe the influence of the doubling of the LiF content in the flux, we have analyzed two different experiments plans (Table 3).

The properties analyzed are the density, the permittivity, the QF product, the temperature coefficient of the resonance frequency and of the permittivity and the insulating resistivity. For these two last properties, the samples have been heated a second time after the painting of each face with a copper ink. This annealing was made at only 850 °C to limit the effect the thermal treatment on the 900 °C sintered samples.

Table 3
Factors and levels used for the experiments plans; the numbers 1 and 2 refers to the two different plans; the details concerning the formalism can be found in the references given in the text

Level	Factor			
	Flux	Concentration	Sintering temperature	Atmosphere
−1	LCS	5	900 °C/12 h	Air
0	LCB	10 (1); 10d (2)		
1	LSB	20	1000 °C/4 h	Ar/H_2

Fig. 2 summarizes the electrical and dielectric results. The effects of the factors and their interactions for the first plan are given in Table 4. The last row in the table shows the uncertainties for the different parameters to see which of the calculated effects are pertinent (bold characters).

Most of the factors have few influences on the measured parameters; moreover, none of the ternary and quaternary interaction has any significant influence. (i) The nature of the flux has an impact only on the temperature coefficient and tends to make it decrease while changing from LCS to LCB and then to LSB. (ii) The amount of flux is the most influent factor. Its increase contributes to the rise in the quality factor and the temperature coefficient of the permittivity (what is particularly visible with flux LCS; see Fig. 2). On the other hand, it makes decrease the permittivity and probably the density, even if the effect is slightly lower than the uncertainty noted in the table (note that it is here an average uncertainty but it actually depends on the geometrical characteristics and weight of each sample). Even if it seems interesting to increase the concentration to increase the quality factor, this solution can only have an academic interest since owing to the TEMEX engineers, for both technical and environmental purposes, none of the fluorides addition should have a concentration higher than 5 wt% to allow the use of these compounds in an industrial process. (iii) The sintering using a reductive atmosphere involves a slight decrease in the quality factor but raises the temperature coefficient of the permittivity. (iv) The rise in the sintering temperature induces a decrease in the quality factor. (v) Except the various effects on the temperature coefficients, the only significant binary interaction is the combination [flux/composition] which has a deleterious effect on the quality factor when both changing the flux from LCS to LCB and finally to LSB and the composition from 5 to 10 and then to 20. The analysis of the second

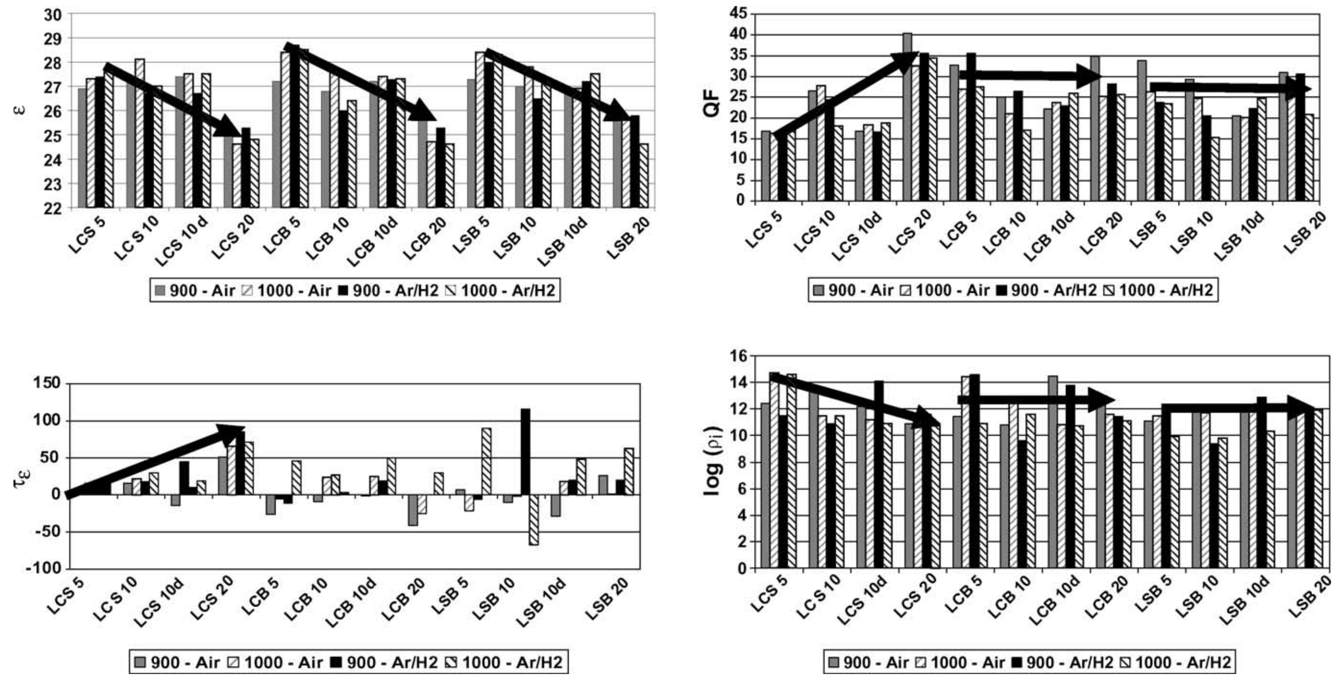

Fig. 2. Electric and dielectric properties of the materials sintered using the fully fluorides fluxes; the thick arrows are guide for the eyes; the insulating resistivity in the right bottom part is expressed as $\log(\rho_i)$, with ρ_i in Ω cm.

Table 4
Effect of the factors and their interactions for the first plan (using the compositions XXX5, XXX10, XXX20)

	Q	ε	$\%d$	τ_f	τ_ε	$\mathrm{Log}(\rho_i)$
Flux (*F*)	0.0%	0.4%	0.5%	−0.1%	−31.1%	−2.4%
Concentration (*C*)	5.8%	−3.3%	−0.9%	0.2%	33.0%	−2.4%
Atmosphere (*A*)	−5.8%	−0.4%	−0.1%	0.0%	70.0%	−3.0%
Sintering temperature (*T*)	−9.5%	0.2%	0.1%	0.3%	12.4%	0.8%
F/*C*	−8.0%	−0.1%	0.1%	0.3%	−27.3%	2.8%
F/*A*	−2.3%	−0.1%	0.1%	0.3%	24.3%	−0.3%
F/*T*	−2.0%	0.1%	0.2%	−0.5%	−18.9%	−1.1%
C/*A*	−0.6%	−0.5%	0.0%	−0.6%	2.9%	0.2%
C/*T*	−1.5%	−0.8%	−0.4%	−1.0%	−14.4%	−1.3%
A/*T*	−0.1%	−0.4%	0.0%	0.4%	−4.4%	−1.2%
F/*C*/*A*	1.0%	−0.1%	−0.1%	0.1%	−11.3%	0.1%
F/*C*/*T*	0.3%	−0.1%	−0.1%	0.1%	−6.1%	1.7%
F/*A*/*T*	0.2%	−0.1%	−0.2%	0.4%	3.3%	−1.0%
C/*A*/*T*	0.4%	0.2%	0.0%	0.4%	−16.1%	1.8%
F/*C*/*A*/*T*	−2.0%	−0.1%	−0.2%	−0.2%	−4.1%	0.9%
Average	3140.02	26.69	92.35%	0.9284	14.7	11.7
Uncertainty	5%	1%	1%	1%	20%	4%

plan (with XXX10d) leading to similar conclusions, it will not be more discussed.

4. Conclusion

We achieved in obtaining formulations which allow the sintering of $CaZrO_3$ at low temperature both in oxidative and reductive atmospheres. The sintered materials exhibit good electrical and dielectrical properties. The plan analysis highlights that all the tested fully fluorides fluxes seem to be nearly equivalent. The concentration of the flux is the most influent factor. It is needed to sinter the material using the lowest temperature as possible and using the atmosphere the least impoverished in oxygen (keeping in mind that it is necessary that the temperature remains sufficiently high to densify the material and that the atmosphere should remain sufficiently reductive to not oxidize the base metals). All these results make these formulations of $CaZrO_3$ added with fluorides fluxes, excellent candidates to produce BME-MLCC.

Tests are presently carried out with the Temex Company to study the reliability of prototypes containing either silver or copper electrodes.

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