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Effects of the sintering atmosphere on Nb-based dielectrics

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Abstract

The effects of a forming atmosphere on the stability, the sintering and the dielectric properties of $Ba_5Nb_4O_{15}$, $BaNb_2O_6$, $ZnNb_2O_6$ and $Zn_3Nb_2O_8$ ceramics were investigated, because of the primary importance of the sintering atmosphere in relation to copper sintering. These Nb-based materials were sintered in air and in $Ar/H_2$10%. Zn-containing samples are very sensitive to the reductive atmosphere. ZnO volatilises at 800–850 °C and the resulting compound does not exhibit the expected properties. $BaNb_2O_6$ and $Ba_5Nb_4O_{15}$ are more stable in term of relative weight loss. Nevertheless, the phase analysis reveals a modification of the $BaNb_2O_6$ phase, what induces the degradation of the dielectric property stability versus temperature. The properties of $Ba_5Nb_4O_{15}$ are not modified by a sintering in reductive atmosphere. A relative permittivity of 38.8, a permittivity temperature coefficient of -150 ppm °C^{-1} and an insulating resistivity of $10^{10.9}$ Ω cm were obtained for this latter.

Keywords: A. Sintering; C. Dielectric properties; D. Niobates

1. Introduction

The key point in multilayer ceramics capacitors (MLCC) manufacturing is the compatibility between the dielectric ceramic and the electrodes during the sintering process. Until the 1990s, the MLCC were manufactured with very expensive inner electrodes using noble metals like Pt, Pd, ... These metallic electrodes actually present two advantages. Firstly, their high melting points (>1500 °C) are compatible with the high sintering temperature needed for the dielectrics which are commonly used in capacitors namely $BaZn_{1/3}Ta_{2/3}O_3$ [1], $BaMg_{1/3}Ta_{2/3}O_3$ [2], $BaZn_{1/3}Nb_{2/3}O_3$ [3] and $MgTiO_3$ [4]. Secondly, these metals are not sensitive to an oxidant atmosphere even at temperature as high as 1500 °C. Nevertheless, the cost lowering of such components is becoming indispensable to be able to compete in this very high competitive field. The most promising way for that is to substitute noble metals by more basic ones like silver or copper. This substitution obviously imposes to lower the sintering temperature of the ceramic at a temperature inferior to the silver or copper melting points, respectively, 961 °C and 1084 °C. Copper is less constraining as regards to sintering temperature than silver but there is a real drawback when copper is used. The capacitors must be fired in a forming atmosphere to protect the copper from oxidation and it is obvious that such sintering condition can influence the ceramic and its properties.

From the sintering temperature aspect, Nb-based dielectrics such as $ZnNb_2O_6$ [5], $Zn_3Nb_2O_8$ [6], $BaNb_2O_6$ [7] and $Ba_5Nb_4O_{15}$ [8] are practically interesting since they all exhibit a relatively low sintering temperature of 1200 °C. It can be mentioned that usual dielectric ceramics require a temperature as high as 1400 °C to be well densified. Considering this advantage, it is reasonable to predict that niobate-based dielectrics will be easily sinterable at lower temperatures using additives or sintering aids permitting base metal co-sintering. To illustrate this assumption, it can be mentioned the work of Kim et al. in which the authors showed that $Ba_5Nb_4O_{15}$ can be correctly sintered at 925 °C owing to the addition of a small amount of B_2O_3 [9]. It must be also precise that all these dielectrics offer attractive dielectric properties corroborating by an ε_r between 20 and 45, very low dielectric losses ($\tan\delta < 10^{-3}$) and high insulating resistivity ($>10^{10}$ Ω cm) at high frequencies (>1 MHz). Taking into account all of these, the sintering atmosphere is of primary importance in view of copper co-sintering, and thus the niobates sintering in a forming atmosphere is considered in this work. The aim of this paper is to show clear evidence of the effect of forming atmosphere on the stability, the sintering and the dielectric properties of

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Nb-based dielectrics. For this goal, Nb-based materials were sintered in both atmospheres (air and forming ones). The sintered products have been characterised in terms of phase analysis and dielectric properties.

2. Experimental procedure

The 504, 102, 012 and 032 (respectively, $Ba_5Nb_4O_{15}$, $BaNb_2O_6$, $ZnNb_2O_6$ and $Zn_3Nb_2O_8$) phases have been synthesised by solid-state reaction. Precursor powders of $BaCO_3$ (Diopma, 99.99%), ZnO (Cerac, 99.995%) and Nb_2O_5 (HCS Starck, 99.9%) were mixed in appropriate proportions and ground in a Teflon jar using zircon balls (1 mm in diameter) in an ammoniac solution for 2 h. The resulting slurry was subsequently dried under infrared lamps and manually reground. The 504, 102 and 012 were heat treated at 1100 °C and the 032 mixture at 1000 °C in air for 2 h with a heating and cooling rate of 200 °C h^{-1}. The resulting powder was reground in a Teflon jar using the same process as the one used before the calcination step. The powder composition was determined by X-ray diffraction (XRD) using the Cu Kα radiation (Philips X'Pert diffractometer).

The weight loss of the compounds was studied by themogravimetric analysis (TGA Setaram) in air and in a reductive atmosphere. The forming atmosphere systematically used was Ar/$H_2$10% with saturated moisture. Cylindrical pellets were shaped using a 28 kN uniaxial load to perform a dilatometry experiment (TMA Setaram) and a sintering for dielectric measurements. The pellets were sintered at 1200 °C for 2 h with a heating and cooling rate of 200 °C h^{-1}.

For the dielectric properties characterisation, In–Ga electrodes were manually deposited on each face of the disks. The dielectric measurements performed at 1 MHz were carried out versus temperature (from −60 °C to +160 °C) using a RLC Bridge (Flucke PM6306). The resistivity was measured using a SEFELEC DM500A megohmeter.

3. Results and discussion

The influence of sintering atmosphere on the phase stability has been carried out by both ATG and XRD analysis. Fig. 1 shows the weight losses versus temperature of each compound in reductive atmosphere. In air, the four compounds are stable as expected (curves are not plotted). In reductive atmosphere, the weight loss of the Ba compounds is very low whereas the weight loss of the Zn compounds is dramatically high and mainly occurs in the temperature range 800–1200 °C. In such atmosphere and after a heat treatment at 1200 °C, the weight losses of 504, 102, 012 and 032 achieve, respectively, −0.3%, −2.4%, −21.7% and −34.9%. These results indicate that the volatilisation of ZnO probably occurs for Zn-based dielectrics when sintering is performed in a forming atmosphere.

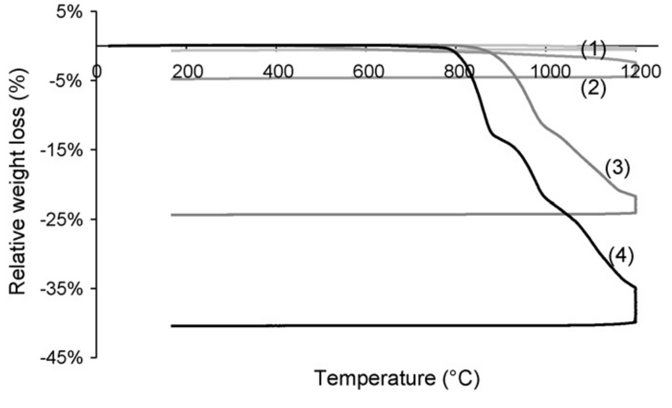

Fig. 1. Relative weight losses vs. temperature of: 504 (1), 102 (2), 012 (3) and 032 (4) in reductive atmosphere.

Fig. 2 shows the XRD patterns of 504, 102, 032 and 012 after calcination (as reference) and after sintering at 1200 °C for 2 h in Ar/H_2 atmosphere. The XRD pattern of the $Ba_5Nb_4O_{15}$ sintered in a forming atmosphere is similar to the reference. No phase modification occurred as it was previously suggested by the ATG experiment. For the 102 compound, the XRD pattern indicates a partial reduction of the niobium from Nb^{V} to Nb^{IV} as it is testified by the presence of $Ba_3Nb^{IV}Nb^{V}_4O_{15}$ phase. Moreover, a modification of the crystal system has been observed for the $BaNb_2O_6$ phase. This latter is monoclinic whereas the system was initially orthorhombic. The resulting compact is then mainly composed of a mixture of $Ba_3Nb^{IV}Nb^{V}_4O_{15} + BaNb^{V}_2O_6$ phases. The slight weight loss (−2.4%) is in good agreement with this observation.

The XRD patterns of the 032 and of the 012 compounds sintered in forming atmosphere reveal that both compounds are mainly composed by $Nb^{IV}_2Nb^{V}_{10}O_{29}$ after the heat treatment. The absence of the peaks belonging to the $Zn_3Nb_2O_8$ phase is evidenced for the 032 compound whereas some traces of the $ZnNb_2O_6$ are still observable for the 012 compound. These results show that Zn-based compounds decompose at high temperature in Ar/H_2 atmosphere to form Nb_2O_5 and ZnO which volatilises. Then, the Nb_2O_5 is partially reduced into $Nb^{IV}_2Nb^{V}_{10}O_{29}$. Examination of the ATG analysis (Fig. 1) gives additional information about the departure of ZnO in both cases. The weight loss curve indicates that ZnO starts to volatilise at 900 °C for $ZnNb_2O_6$ whereas $Zn_3Nb_2O_8$ starts to decompose at 800 °C. The profile of the curve after 900 °C seems to be similar for both compounds which suggests a departure of ZnO from $Zn_3Nb_2O_8$ in this manner:

$$Zn_3Nb_2O_8 \rightarrow ZnNb_2O_6 + 2ZnO \text{ from } 800\,^{\circ}C$$

$$ZnNb_2O_6 \rightarrow Nb_2O_5 + ZnO \text{ from } 900\,^{\circ}C$$

Fig. 3 shows the XRD pattern of $Zn_3Nb_2O_8$ heated in Ar/H_2 atmosphere at 900 °C. At this temperature, the sample is composed by $Zn_3Nb_2O_8$ and $ZnNb_2O_6$ that confirms the ZnO departure from $Zn_3Nb_2O_8$ in two steps as described before.

The shrinkage curves versus temperature and atmosphere are shown in Fig. 4. For the 504 compound, the forming atmosphere induces a slight delay of the sintering temperature of around 50 °C. Usually, sintering in forming atmosphere induces a slight lowering of the sintering temperature since it may provoke the formation of anionic vacancies due to a partial cationic reduction. As it is not observed here, a partial reduction of the niobium in 504 does probably not occur. One can only

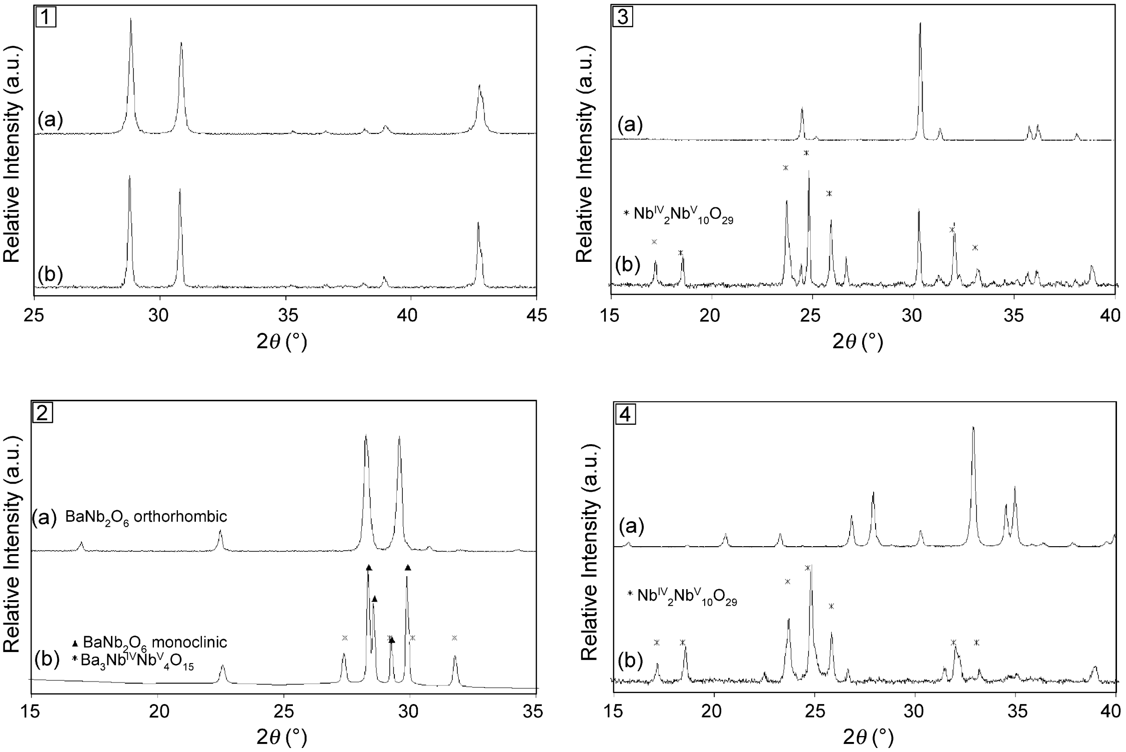

Fig. 2. XRD pattern of: 504 (1), 102 (2), 012 (3) and 032 (4), after the calcination step (a) and sintering in reductive atmosphere (b).

suggest that forming atmosphere modifies the transport of matter notably by vapour/condensation route that induces a slight increase of the sintering temperature. For the 102 compound, the forming atmosphere conducted to the formation of a small amount of $Ba_3Nb^{IV}Nb^{V}_4O_{15}$ which is probably more refractory than $BaNb_2O_6$ since a slight increase of the 102's sintering temperature is here evidenced. For the Zn-containing compounds, TMA curves exhibit some accidents inherent to the compounds decomposition. As material decomposition is detrimental for copper co-sintering, it seems not interesting to examine more accurately on these TMA curves.

The degradation of the dielectric properties of Zn-containing materials after sintering in forming atmosphere is in good agreement with their decomposition (Fig. 5). Table 1 shows that the reductive atmosphere in comparison with the oxidant one leads to a significant decrease of the insulating resistivity and a significant increase of the permittivity as well as the temperature coefficient of ε_r. The properties are becoming not suitable for the applications when reductive atmosphere is used for sintering. Such result can be easily explained by the decomposition/reduction phenomenon as previously demonstrated.

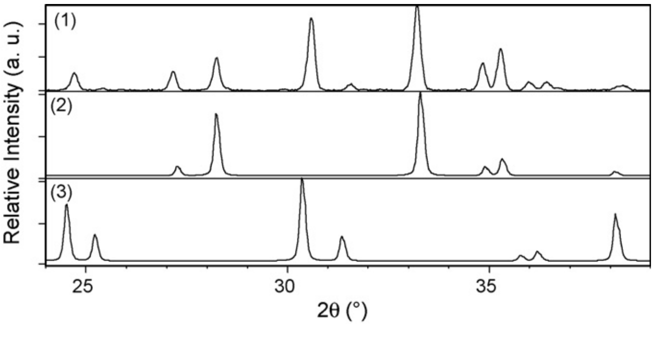

Fig. 3. XRD pattern of: (1) 032 heated at 900 °C in reductive atmosphere, (2) $Zn_3Nb_2O_8$ (00-013-0472 JCPDS file) and (3) $ZnNb_2O_6$ (00-025-1027 JCPDS file).

The most important point stands in the achievement of the expected properties for the Zn free compounds even when sintering is performed in Ar/H_2 atmosphere. The $Ba_5Nb_4O_{15}$ compound has a permittivity around 39, a temperature coefficient of permittivity of -150 ppm $°C^{-1}$ and an insulating resistivity of $10^{10.9}$ Ω cm. These properties are similar to those measured on pellet sintered in air but slightly lower, due to the delay in densification step observed in Fig. 4. As comparison, the relative densities of the 504 compounds sintered in air and in reductive atmosphere are 95% and 92.5%, respectively. The good stability of the properties is well related to the chemical stability of this compound in forming atmosphere. Concerning the $BaNb_2O_6$ compound, the main dielectrics properties are

Table 1
Dielectric properties at 1 MHz of each compound sintered at 1200 °C for 2 h in air (A) and in reductive atmosphere (R)

Compounds	ε_r (at 25 °C)		τ_ε (ppm $°C^{-1}$)		log[ρ (Ω cm)]	
	(A)	(R)	(A)	(R)	(A)	(R)
504	42.2	38.8	−171	−150	11.5	10.9
102	42.2	48	+330	+2185	11	9.8
032	22.2	34.6	+197	+620	12.5	6.9
012	22.8	19,280	+217	–[a]	11.4	–[a]

[a] These values cannot be measured.

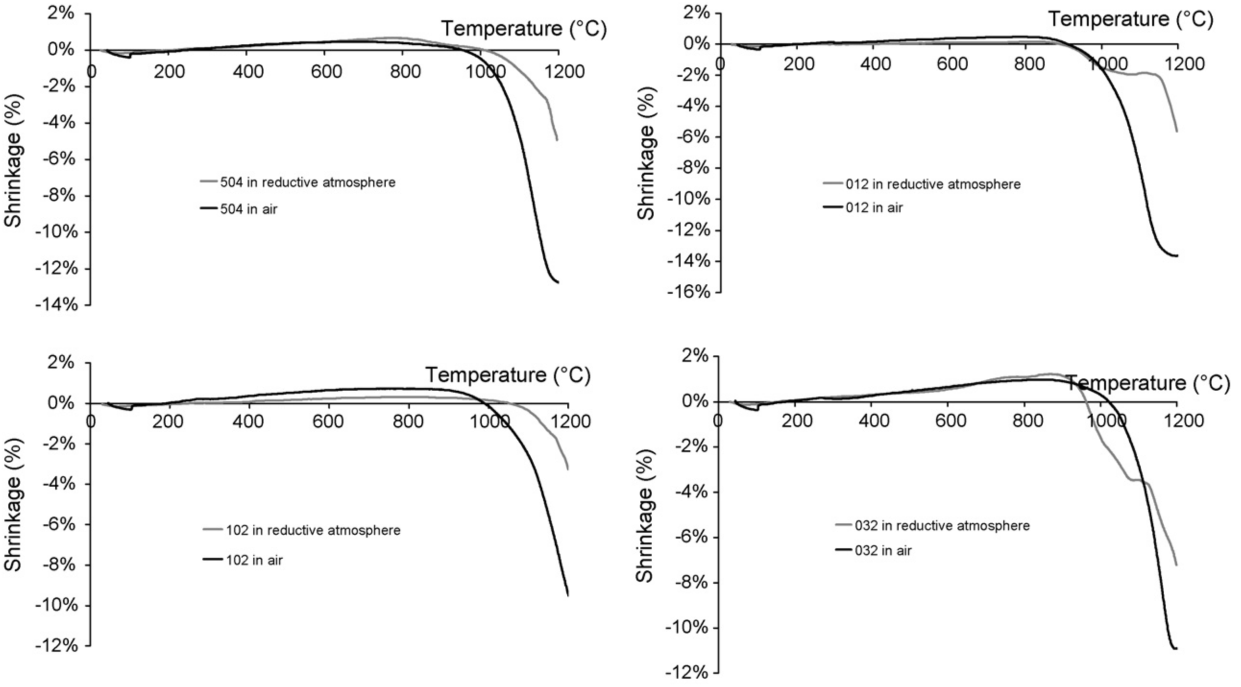

Fig. 4. Shrinkage curves of 504, 102, 012 and 032 vs. temperature in air and in reductive atmosphere.

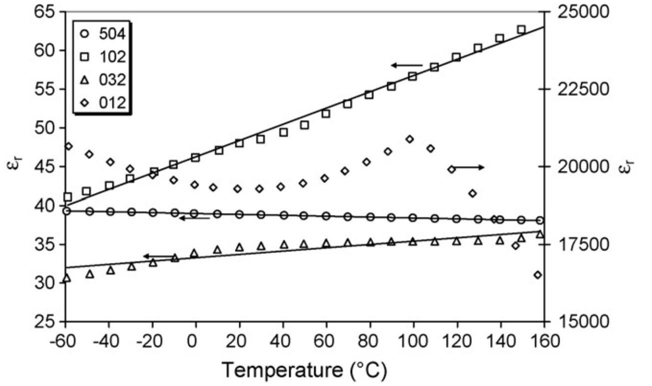

Fig. 5. Relative permittivity vs. temperature of each compound sintered at 1200 °C in reductive atmosphere for 2 h.

maintained: a permittivity around 49, a resistivity of $10^{9.8}$ Ω cm. Nevertheless, the temperature coefficient of the permittivity has considerably increased for sample sintered in Ar/H_2, which can be related to the presence of $Ba_3Nb^{IV}Nb^{V}_4O_{15}$, as noticed before.

4. Conclusion

This work was devoted to explore the effect of a reductive atmosphere on the sintering of some Nb-based dielectrics. Materials $ZnNb_2O_6$, $Zn_3Nb_2O_8$, $BaNb_2O_6$ and $Ba_5Nb_4O_{15}$ were synthesised by solid-state reaction and subsequently sintered in air to characterise their dielectrics properties. In these usual conditions, all materials are synthesised as single phase and exhibits the expected properties in terms of permittivity, temperature coefficient and insulating resistivity. As a result the $Ba_5Nb_4O_{15}$ phase exhibits a permittivity of around 42.2, a temperature coefficient of -170 ppm °C^{-1} and an insulating resistivity of $10^{11.5}$ Ω cm.

In view of a copper co-sintering, a mixture Ar/$H_2$10% atmosphere compatible with Cu was used to sinter all materials. Using these new conditions, it was shown that Zn-containing samples decompose into ZnO, going out from the material, and Nb_2O_5. Then a partial reduction of Nb_2O_5 into $Nb^{IV}_2Nb^{V}_{10}O_{29}$ occurs. A two-step mechanism of ZnO volatilisation has been also evidenced in the case of $Zn_3Nb_2O_8$. First, $Zn_3Nb_2O_8$ decomposes into ZnO and $ZnNb_2O_6$ from 800 °C and second, $ZnNb_2O_6$ decomposes into ZnO and Nb_2O_5 after 900 °C. This behaviour forbids the use of these niobates for some copper co-sintering applications.

The Zn free niobates are more stable for sintering in Ar/$H_2$10% atmosphere. For $BaNb_2O_6$, a beginning of reduction of Nb has been noticed, what induced an increase in temperature coefficient. Finally, the $Ba_5Nb_4O_{15}$ compound is stable in Ar/H_2 atmosphere and sintered specimens in such atmosphere exhibit similar properties as those obtained in air. This latter is a good dielectric candidate for applications requiring sintering in a forming atmosphere owing to its high stability.

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