Low temperature sintering of MgTiO$_3$ with bismuth oxide based additions

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Abstract : MgTiO$_3$ is a classical material for type I MLCC. However its densification temperature is too high to allow co-sintering with copper electrodes. Investigations on low temperature sintering of MgTiO$_3$ show the complexity of this problem particularly when co-sintering with copper electrodes and thus a reducing atmosphere are involved in the process. Though feasibility of MgTiO$_3$ / copper MLCC has been demonstrated, studies have pointed out several remaining problems. Investigations on low temperature sintering of MgTiO$_3$ are thus still necessary to find a formulation which is not detrimental to dielectric behaviour. Sintering aid capabilities and/or good dielectric properties of bismuth oxide based additives make them good candidate materials to lower MgTiO$_3$ sintering temperature without altering its final properties. In this study bismuth titanate is either formed in-situ by reaction-sintering of Bi$_2$O$_3$-B$_2$O$_3$ additives with MgTiO$_3$ or obtained by pre-calcination of Bi$_2$O$_3$ and TiO$_2$ powders and then added to MgTiO$_3$ prior to sintering. Bismuth titanate appears as a good sintering aid that allows sintering of MgTiO$_3$ under 1000°C. It is yet highly sensitive to the nature of the sintering atmosphere, oxidizing or reducing. Dielectric properties of sintered specimens are compatible with type I capacitors applications.

Keywords : Sintering, Dielectric Properties, Capacitors , Titanates, MLCC

1. Introduction

MgTiO$_3$ is a classical material for type I MLCC. The highly variable and high cost of the noble metals, palladium and silver, classically used to form the inner electrodes is a recurrent economical problem. Using non noble metals for these electrodes (for instance copper) could be a solution but would require to sinter the capacitors under a reducing atmosphere. This kind of process has been widely investigated with type II multilayer ceramic capacitors but few reports have been published related to the case of type I capacitors. Another way of investigation could lie in trying to get rid of palladium, the main source of economical problems, leading to a partial solution, the use of silver electrodes.

Both solutions have in common the same technological problem. Classical sintering temperatures of MgTiO$_3$ in air are around 1350°C. Sintering in a reducing atmosphere is also possible at 1350°C : this classically leads to reduction and thus conduction problems but it has been demonstrated that this drawback could be avoided when Ti^{4+} in the B site of the ilmenite structure of MgTiO$_3$ was substituted with equal atomic amounts of W^{6+} and Mn^{2+} acting as a couple of donor/acceptor in the same way that previously stated for type II BaTiO$_3$-based compositions[1,2]. The problem is that this temperature of 1350°C is totally inadequate for the use of copper or silver electrodes because the low melting points of these metals make the sintering temperature to be much lower than 1000°C. It is thus necessary to investigate on the possibility of lower the sintering temperature of MgTiO$_3$.

Recent studies have been devoted to the use of lithium compounds as additives[3,4,5]. These additives allow to sinter $MgTiO_3$ at temperatures lower than 1000°C, especially when excess magnesium is present in the ilmenite phase. Final dielectric properties are promising but, up to now, stability problems will hygrometry may remain[6]. The present work purpose is to try to find an alternative to this solution by using bismuth oxide based additives that seemed attractive by their sintering aid capabilities (Bi_2O_3-B_2O_3 eutectic composition and bismuth titanate have a low melting point) and well-known intrinsic dielectric properties (bismuth titanate) : boron containing additives have already been tested as sintering aid by other researchers[7].

2. Experimental Procedure

$MgTiO_3$ powder was synthesised by the classical solid-state route. The starting powders (MgO, TiO_2) were mixed together for one hour in water by attrition milling (Dyno Mill KDLA, WAB) using 0.8 mm diameter yttried stabilised zircon balls (YTZ grinding media TOSOH). We used the same material as the one developed in the previous studies ($MgTiO_3$ with Mg/Ti atomic ratio = 1.025). The powders were then calcined in air at 1000°C during one hour in order to form the ilmenite phase. The phase formation was controlled by X-ray diffraction. The diffraction patterns were collected using a SIEMENS 5005 diffractometer with $CuK\alpha$ ($\lambda = 1.5405$Å), in the range 15-85° (2θ)).

Bismuth oxide based additives were prepared by milling a mix of starting powders (Bi_2O_3 and B_2O_3 or TiO_2) in a planetary agitator (FRITSCH Pulverisette with agate bowl and balls). The first additive was an eutectic composition from the Bi_2O_3-B_2O_3 phase diagram (0.809mole-% Bi_2O_3 / 0.191mole-% B_2O_3). The second additive was a mix of 40mole-% Bi_2O_3 and 60mole-% TiO_2 calcinated in air at 800°C after milling.

Bismuth oxide based compounds were then added to the pre-calcinated $MgTiO_3$ and the powders were milled together in a planetary agitator.

The different compositions were pressed at 2000 kg.cm^{-2} to obtain disks 10 mm in diameter and around 1.5 mm thick. The disks were fired in air, N_2 or moist N_2-1vol.-%H_2 reducing atmosphere, with heating and cooling rates of 150°C.h^{-1} and dwell time of five hours at 960°C. Densification behavior was studied by dilatometric measurements performed in air or N_2 on TMA92 SETARAM dilatometer, with heating and cooling rates of 300°C.h^{-1}.

The faces of the disks were metallized using the indium-gallium eutectic. The insulation resistances were measured in a dry atmosphere at 25°C under a 1V.µm^{-1} DC bias (Sefelec (SIM 1000 A) megohmeter). Dielectric characterizations at 1kHz (C and tan δ) were realised with a RCL meter Fluke PM 6306 between –45 and 145°C (SECASI hot/cold oven with moisture rate regulated from 0 to 100% for temperatures higher than 10°C).

3. Results

3.1. $MgTiO_3$ + Bi_2O_3-B_2O_3 additives

Figure 1 compares the dilatometric behaviour of air-sintered samples containing various amounts of additives (1 to 5 wt.-%) of the eutectic composition 0.809Bi_2O_3-0.191B_2O_3 which melts around 622°C[8]. As the quantity of additives increases shrinkage curves are shifted

towards much lower temperatures than the typical sintering temperature of pure $MgTiO_3$. However the temperature at which shrinkage begins is different for every formulations and diminishes to 830°C with 5wt.-% additives.
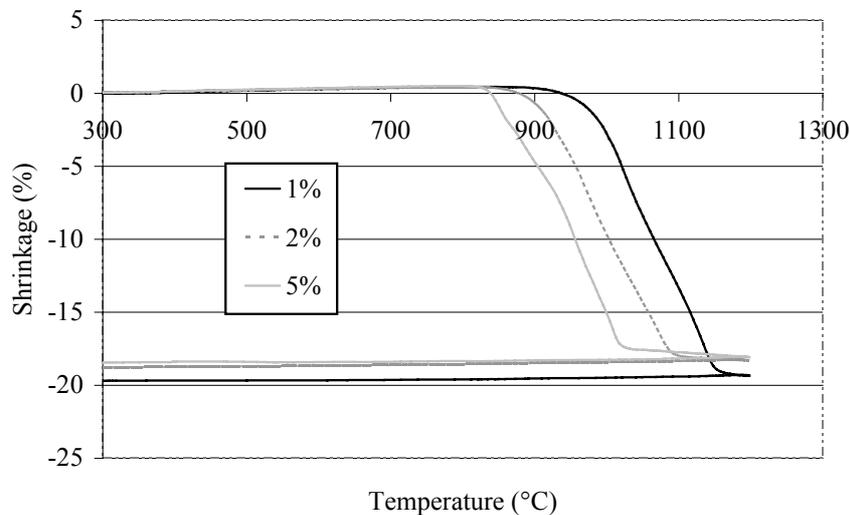
Fig. 1 – Dilatometric behaviour of MgTiO₃ 1.025 with eutectic additives
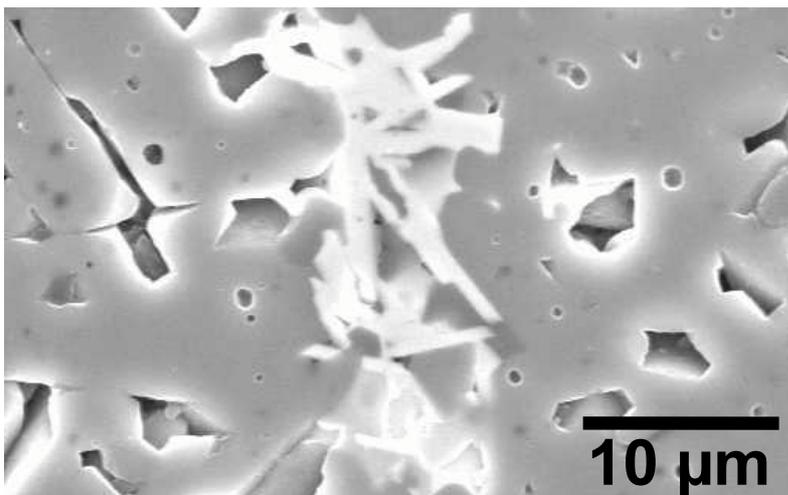
Fig. 2 - MgTiO₃ 1.025 + 5 wt.-% eutectic sintered in air (960°C x 5h)

The best composition ($MgTiO_3$ 1.025 + 5 wt.-% eutectic) was sintered in air. XRD measurements of sintered samples reveal that all samples contain $MgTiO_3$ and an additional phase which is a complex bismuth titanate, probably $Bi_4Ti_3O_{12}$. Traces of minor bismuth titanates were also detected but not any sign indicated the presence of boron within crystalline phases. Sintered samples are not fully dense as indicated by the micrographs on figure 2 : many small pores mainly intragranular together with empty triple points remain though linear shrinkage is estimated to around 15%. Grains of $MgTiO_3$ appear in grey, rare white grains are bismuth titanate. Some $MgTiO_3$ grains are large, more than 20μm for an average particle size of 3μm for raw materials which suggests exaggerate grain growth. Many needle-like grains are present throughout the microstructure, mainly close to triple points.

Sintering cycles have been performed under N_2 and N_2-1vol.-%H_2 atmospheres as these conditions could be of great interest for the use of non noble metal electrodes. Samples sintered in N_2-1vol.-%H_2 did not shrink at all. Shrinkage of samples sintered in N_2 are intermediate between them and those sintered in air. Only little shrinkage occurs and densification is poor. Figure 3 shows that dilatometric behaviours of $MgTiO_3$ 1.025 + 5 wt.-% eutectic under N_2 and air atmospheres are quite similar but shrinkage rate slows down around 900°C in N_2. XRD experiments indicate that bismuth titanate is not present after sintering under N_2-1vol.-%H_2 and is in very limited amounts after sintering in N_2.
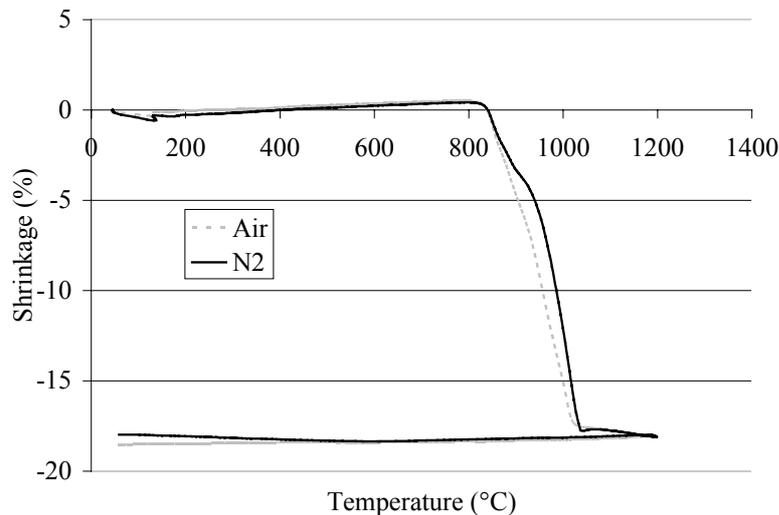

Fig. 3 – Effect of atmosphere on dilatometric behaviour of MgTiO₃ 1.025 + 5 wt% eutectic

The electrical resistivity of the samples sintered in air is higher than 10^{13} Ω.cm under 5% regulated moisture rate. This value decreases a little but remains higher than 10^{11} Ω.cm when hygrometry is shifted to 50%. Dielectric properties, permittivity and losses, are close to those of pure $MgTiO_3$, respectively around 13 and 0.2%.

3.2. $MgTiO_3$ + $Bi_3Ti_4O_{12}$ additives

6 wt.-% and 12wt.-% pre-calcinated bismuth titanate are added to $MgTiO_3$ 1.025. Among these two compositions the first one has exactly the same $Bi_2O_3/MgTiO_3$ ratio as in $MgTiO_3$ 1.025 + 5 wt.-% eutectic and this ratio is doubled for the second one.

Dilatometric results show figure 4 that this additive lowers as well the shrinkage temperature of pure excess magnesium $MgTiO_3$. The curves obtained with 6wt.-% bismuth titanate and 5wt.-% eutectic additives are similar but shrinkage rate is higher when bismuth titanate is used. A slightly lower sintering temperature is reached when doubling the quantity of additives : the end of shrinkage occurs at 1000°C with 12wt.-% titanate, around 30°C less than with only 6wt.-%.

Some samples have been sintered in air. XRD shows that all samples contain $MgTiO_3$, $Bi_4Ti_3O_{12}$ and some traces of other titanates. Densification seems good though the micrograph figure 5 shows a large number of intragranular pores. Also many empty triple points contribute to porosity. Some $MgTiO_3$ grains are large (even larger than with eutectic additives), especially for 12wt.-% bismuth titanate composition, and many of them have

needle-like shape, especially around triple points. The latter are also more developed when a larger amount of titanate has been used. Second phases seem present in higher amounts than with eutectic additives, even for the 6wt.-% composition.
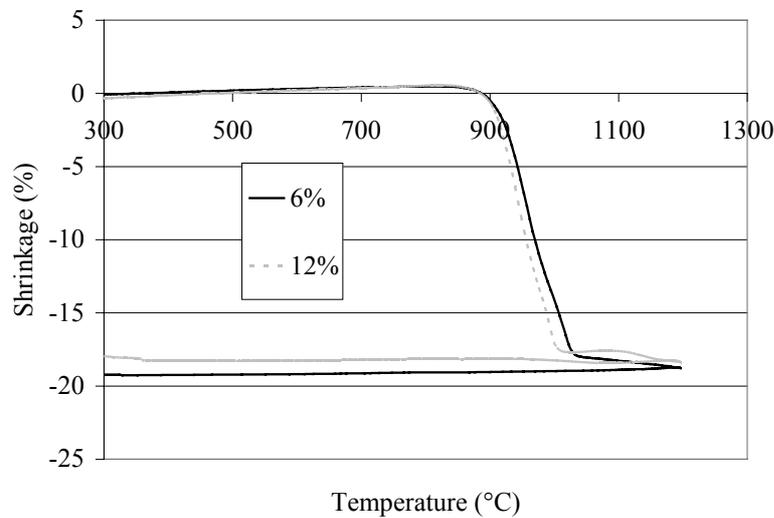

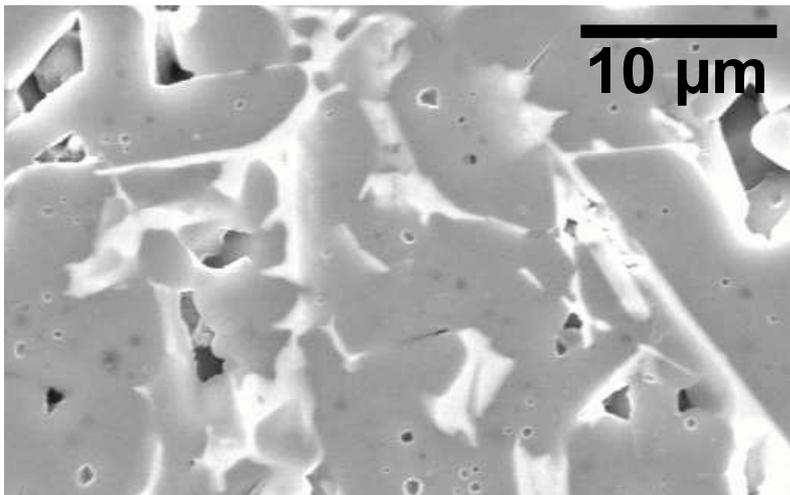*Fig. 4 - Dilatometric behaviour of MgTiO₃ 1.025 with Bi₄Ti₃O₁₂ additions*

Fig 5 - MgTiO₃ 1.025 + 6 wt% Bi₄Ti₃O₁₂ sintered in air (960°C x 5h)

Sintering was performed with the 6wt.-% bismuth titanate composition in N_2 and N_2-1vol.-%H_2. Both atmospheres do not lead to any densification. This is illustrated with figure 6 that compares shrinkage curves obtained in air and N_2 for this composition. Under N_2 atmosphere, the curve is shifted towards higher temperatures : shrinkage starts around 900°C in opposition with 850°C in air, and it stops at almost 1200°C instead of 1030°C. XRD measurements show that the samples sintered in air contain $MgTiO_3$, $Bi_4Ti_3O_{12}$ plus other titanates while not any titanate is present after sintering in N_2. Pre-calcination of bismuth titanate has been performed in N_2-1vol.-%H_2. While in air the calcinated powder is almost pure $Bi_4Ti_3O_{12}$ (with traces of excess Bi_2O_3), in N_2-1vol.-%H_2 only traces of $Bi_4Ti_3O_{12}$ are detected with Bi_2O_3 and TiO_2 as major phases.
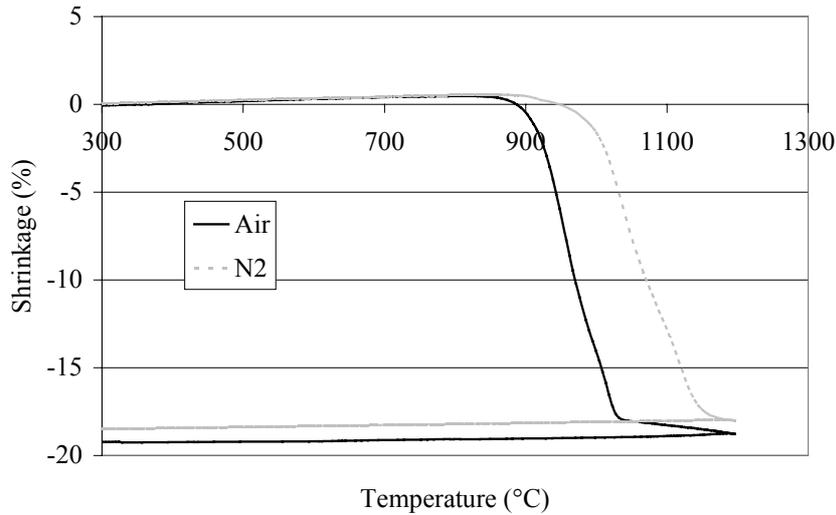
Fig. 6 - Effect of atmosphere on dilatometric behaviour of MgTiO$_3$ 1.025 + 6 wt% Bi$_4$Ti$_3$O$_{12}$

Samples sintered in air have been electrically tested. Resistivities are higher than 10^{13} Ω.cm under dry atmosphere (5% moisture). These values decrease with hygrometry but remains higher than 10^{11} Ω.cm in 50% moisture for 12wt.-% bismuth titanate additions : the 6wt.-% composition is more sensitive to hygrometry. Permittivities are respectively around 15 and 12, and dielectric losses are around 0,2%.

4. Discussion and conclusions

The sintering behaviour of MgTiO$_3$ with bismuth oxide based additives is very different from what was observed when Li compounds were used. Here it is unlikely that foreign atoms will enter the ilmenite structure of MgTiO$_3$. Boron cannot substitute with Mg or Ti in A or B site because it cannot get the 6 coordinence. Bismuth ion is too large (1.02 Å) when having the 6 coordinence compared to Mg^{2+} (0.72 Å) or Ti^{4+} (0.605 Å) : substitution with bismuth seems thus difficult to be considered. So shrinkage occurs at a lower temperature only because of the presence of a secondary phase that makes sintering easier. For every composition, the presence of Bi$_4$Ti$_3$O$_{12}$, pre-calcinated or formed in-situ, leads to low temperature sintering of MgTiO$_3$. When this phase lacks, densification is not enhanced. Lower densification kinetics with eutectic additives (for equivalent Bi$_2$O$_3$/MgTiO$_3$ ratio) is probably due to the fact that both the formation of bismuth titanate and its action as a sintering aid occur in the same temperature range. This densifying effect occurs at a temperature lower than the melting temperature of Bi$_4$Ti$_3$O$_{12}$: it is thus not due to the appearance of a liquid phase, but probably to the improvement of diffusion mechanisms as the secondary phase is to melt. This is supported by the fact that most MgTiO$_3$ grains are equiaxed while those close to empty triple points have a needle-like shape : these triple points could be the result of the leaving of the second phase, so grains could have grown as needles at the contact of bismuth titanate which strongly reminds phenomena like liquid or viscous phase sintering.

The formation of bismuth titanate seems very favourable in air. The added Bi$_2$O$_3$-B$_2$O$_3$ eutectic is supposed to melt around 622°C. But, if this happens, it does not lead to shrinkage as shown on dilatometric curves : shrinkage only begins around 830°C, temperature which is close to the one observed with bismuth titanate additives. Bismuth titanate is detected after sintering on eutectic containing compositions and we have not observed the presence of any

boron glass in the samples. This strongly suggests that, even if the eutectic melts, it is very transitive and its stability is competitive with the reaction of Bi_2O_3 and $MgTiO_3$ to form bismuth titanate. Maybe it is also possible that only the melting behaviour of Bi_2O_3-B_2O_3 additives allows or enhances this reaction.

Bismuth titanate appears to be particularly sensitive to atmosphere. It does not form under neutral or slightly reducing atmosphere and, if previously synthesized, it disappears from the system. It is not very clear whether this vanishment is due to decomposition or migration to surface and evaporation. The decomposition hypothesis does not seem to be valid as nor Bi_2O_3 nor TiO_2 are found in the samples after sintering. But also, if migration/evaporation occurs, why is it not the case in air, what is the role of atmosphere in this process ? Maybe because both processes are combined, decomposition (or non-formation) of bismuth titanate coming first. Further investigations are needed to clarify this point.

Dielectric properties are close to those of pure $MgTiO_3$ for every compositions and are typical of type I capacitors. The chosen additives are thus not detrimental. The obtained samples are even less sensitive to hygrometry than those containing lithium salts.

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