

# Low temperature sintering of $\text{MgTiO}_3$ with bismuth oxide based additions

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## Abstract

$\text{MgTiO}_3$  is a classical material for type I MLCC. However, its densification temperature is too high to allow co-sintering with copper electrodes. Investigations into low temperature sintering of  $\text{MgTiO}_3$  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  $\text{MgTiO}_3$ /copper MLCC seem to be possible [Bernard, J., Houivet, D., El Fallah, J. and Haussonne, J. M.,  $\text{MgTiO}_3$  for base metal multilayer ceramic capacitors. *J. Eur. Ceram. Soc.*, 2004, **24**, 1877–1881] studies have pointed out several remaining problems such as sensibility to hygrometry [Bernard, J., Houivet, D., El Fallah, J. and Haussonne, J. M., Effect of hygrometry on dielectric materials. *J. Eur. Ceram. Soc.*, 2004, **24**, 1509–1511]. Investigations into low temperature sintering of  $\text{MgTiO}_3$  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  $\text{MgTiO}_3$  sintering temperature without altering its final properties. In this study bismuth titanate is either formed in situ by reaction-sintering of  $\text{Bi}_2\text{O}_3$ – $\text{B}_2\text{O}_3$  additives with  $\text{MgTiO}_3$  or obtained by pre-calcination of  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  powders and then added to  $\text{MgTiO}_3$  prior to sintering. Bismuth titanate appears as a good sintering aid that allows sintering of  $\text{MgTiO}_3$  under 1000 °C. It is however highly sensitive to the nature of the sintering atmosphere, oxidizing or reducing. Dielectric properties of sintered specimens are compatible with type I capacitors applications. © 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Sintering; Dielectric Properties; Capacitors; Titanates

## 1. Introduction

$\text{MgTiO}_3$  is a classical material for type I MLCC. The high and variable and cost of the noble metals, palladium and silver, classically used to form the inner electrodes is a recurrent economic problem. Using non noble metals for these electrodes (for instance copper) could be a solution but would require sintering 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 economic problems, leading to a partial solution, the use of silver electrodes.

Both solutions have in common the same technological problem. Classical sintering temperatures of  $\text{MgTiO}_3$  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  $\text{Ti}^{4+}$  in the B site of the ilmenite structure of  $\text{MgTiO}_3$  was substituted with equal atomic amounts of  $\text{W}^{6+}$  and  $\text{Mn}^{2+}$  acting as a couple donor/acceptor in the same way as previously stated for type II  $\text{BaTiO}_3$ -based compositions.<sup>1,2</sup> 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 cause the sintering temperature to be much lower than 1000 °C. It is thus necessary to investigate on the possibility of lowering the sintering temperature of  $\text{MgTiO}_3$ .

Recent studies have been devoted to the use of lithium compounds as additives.<sup>3–5</sup> These additives allow to sinter  $\text{MgTiO}_3$  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 with hygrometry may remain.<sup>6</sup> The purpose of the present work is to try to find an alternative to this solution by

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using bismuth oxide based additives that seem attractive by their sintering aid capabilities ( $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$  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.<sup>7,9–13</sup>

## 2. Experimental procedure

$\text{MgTiO}_3$  powder was synthesised by the classical solid-state route. The starting powders ( $\text{MgO}$ ,  $\text{TiO}_2$ ) were mixed together for one hour in water by attrition milling (Dyno Mill KDLA, WAB) using 0.8 mm diameter yttrium stabilised zircon balls (YTZ grinding media TOSOH). We used the same material as the one developed in the previous studies ( $\text{MgTiO}_3$  with Mg/Ti atomic ratio = 1.025). The powders were then calcinated 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  $\text{Cu K}\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ), in the range 15–85° ( $2\theta$ ).

Bismuth oxide based additives were prepared by milling a mix of starting powders ( $\text{Bi}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$  or  $\text{TiO}_2$ ) in a planetary agitator (FRITSCH Pulverisette with agate bowl and balls). The first additive was an eutectic composition from the  $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$  phase diagram (80.9 mole%  $\text{Bi}_2\text{O}_3$ /19.1 mole%  $\text{B}_2\text{O}_3$ ). The second additive was a mix of 40 mole%  $\text{Bi}_2\text{O}_3$  and 60 mole%  $\text{TiO}_2$  calcinated in air at 800 °C after milling.

Bismuth oxide based compounds were then added to the pre-calcinated  $\text{MgTiO}_3$  and the powders were milled together in a planetary agitator.

The different compositions were pressed at 2000 kg  $\text{cm}^{-2}$  to obtain disks 10 mm in diameter and around 1.5 mm thick. The disks were fired in air,  $\text{N}_2$  or moist  $\text{N}_2\text{--}1 \text{ vol.}\% \text{ H}_2$  reducing atmosphere, with heating and cooling rates of 150 °C  $\text{h}^{-1}$  and dwell time of 5 h at 960 °C. Densification behavior was studied by dilatometric measurements performed in air or  $\text{N}_2$  on a TMA92 SETARAM dilatometer, with heating and cooling rates of 300 °C  $\text{h}^{-1}$ .

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 1 V  $\mu\text{m}^{-1}$  dc bias (Sefelec (SIM 1000 A) megohmmeter). Dielectric characterizations at 1 kHz ( $C$  and  $\tan \delta$ ) 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. $\text{MgTiO}_3 + \text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$ additives

Fig. 1 compares the dilatometric behaviour of air-sintered samples containing various amounts of additives (1–5 wt.%)

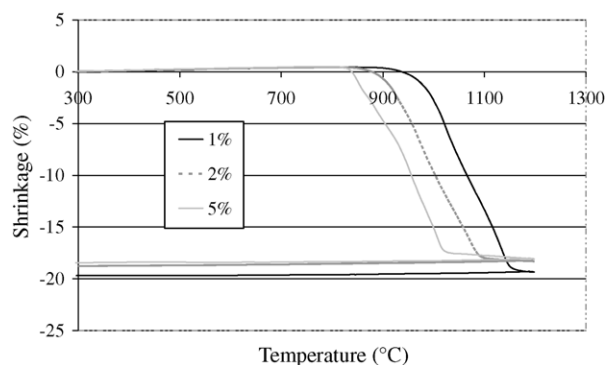


Fig. 1. Dilatometric behaviour of  $\text{MgTiO}_3$  1.025 with eutectic additives.

of the eutectic composition 0.809  $\text{Bi}_2\text{O}_3\text{--}0.191 \text{ B}_2\text{O}_3$  which melts around 622 °C.<sup>8</sup> As the quantity of additives increases shrinkage curves are shifted towards much lower temperatures than the typical sintering temperature of pure  $\text{MgTiO}_3$ . However, the temperature at which shrinkage begins is different for every formulation and diminishes to 830 °C with 5 wt.% additives.

The best composition ( $\text{MgTiO}_3$  1.025 + 5 wt.% eutectic) was sintered in air. XRD measurements of sintered samples reveal that all samples contain  $\text{MgTiO}_3$  and an additional phase which is a complex bismuth titanate, probably  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . Traces of minor bismuth titanates were also detected but no sign indicated the presence of boron within crystalline phases. Sintered samples are not fully dense as indicated by the micrographs on Fig. 2: many small pores, mainly intragranular, together with empty triple points remain though linear shrinkage is estimated at around 15%. Grains of  $\text{MgTiO}_3$  appear in grey, rare white grains are bismuth titanate. Some  $\text{MgTiO}_3$  grains are large, more than 20  $\mu\text{m}$  for an average particle size of 3  $\mu\text{m}$  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  $\text{N}_2$  and moist  $\text{N}_2\text{--}1 \text{ vol.}\% \text{ H}_2$  atmospheres as these conditions could be of great interest for the use of non noble metal electrodes. Samples sintered in moist  $\text{N}_2\text{--}1 \text{ vol.}\% \text{ H}_2$  did not shrink at all.

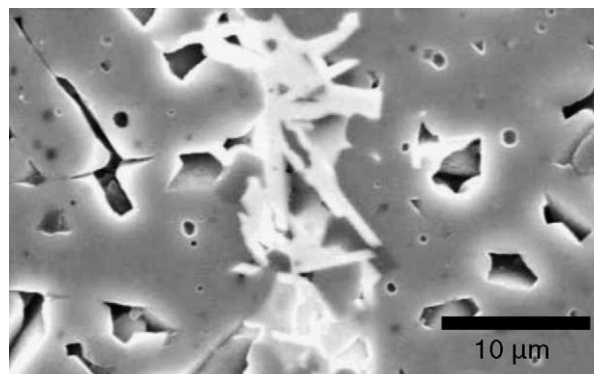


Fig. 2.  $\text{MgTiO}_3$  1.025 + 5 wt.% eutectic sintered in air (960 °C × 5 h).

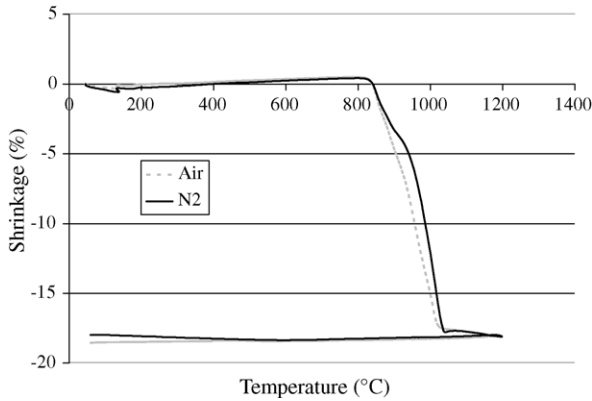


Fig. 3. Effect of atmosphere on dilatometric behaviour of  $\text{MgTiO}_3$  1.025 + 5 wt.% eutectic.

Shrinkage of samples sintered in  $\text{N}_2$  are intermediate between them and those sintered in air. Only little shrinkage occurs and densification is poor. Fig. 3 shows that dilatometric behaviours of  $\text{MgTiO}_3$  1.025 + 5 wt.% eutectic under  $\text{N}_2$  and air atmospheres are quite similar but the shrinkage rate slows down around 900 °C in  $\text{N}_2$ . XRD experiments indicate that bismuth titanate is not present after sintering under  $\text{N}_2$ –1 vol.%  $\text{H}_2$  and is in very limited amounts after sintering in  $\text{N}_2$ .

The electrical resistivity of the samples sintered in air is higher than  $10^{13} \Omega \text{ cm}$  under 5% regulated moisture rate. This value decreases a little but remains higher than  $10^{11} \Omega \text{ cm}$  when hygrometry is shifted to 50%. Dielectric properties, permittivity and losses, are close to those of pure  $\text{MgTiO}_3$ , respectively around 13 and 0.2%.

### 3.2. $\text{MgTiO}_3 + \text{Bi}_4\text{Ti}_3\text{O}_{12}$ additives

Six and 12 wt.% pre-calcinated bismuth titanate are added to  $\text{MgTiO}_3$  1.025. Among these two compositions the first one has exactly the same  $\text{Bi}_2\text{O}_3/\text{MgTiO}_3$  ratio as in  $\text{MgTiO}_3$  1.025 + 5 wt.% eutectic and this ratio is doubled for the second one.

Dilatometric results show Fig. 4 that this additive also lowers the shrinkage temperature of pure excess magnesium

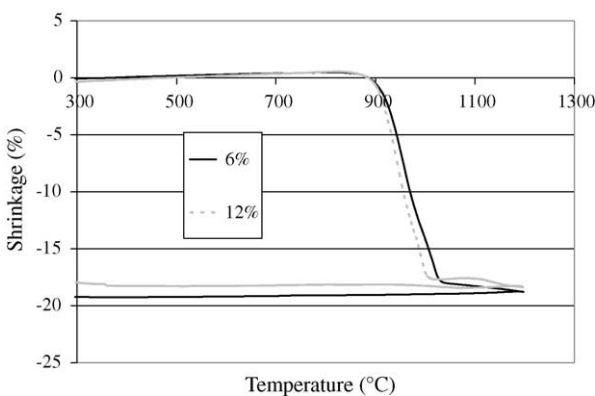


Fig. 4. Dilatometric behaviour of  $\text{MgTiO}_3$  1.025 with  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  additions.

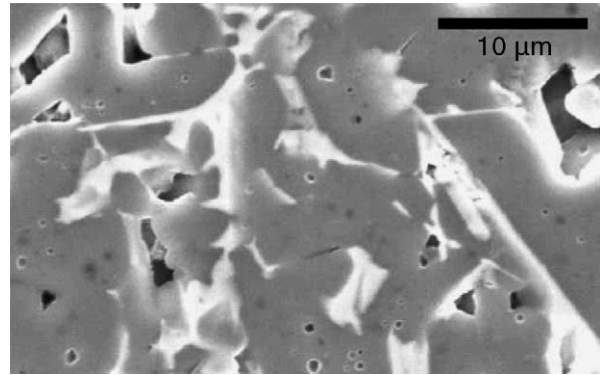


Fig. 5.  $\text{MgTiO}_3$  1.025 + 6 wt.%  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  sintered in air (960 °C × 5 h).

$\text{MgTiO}_3$ . The curves obtained with 6 wt.% bismuth titanate and 5 wt.% 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 12 wt.% titanate, around 30 °C less than with only 6 wt.%.

Some samples have been sintered in air. XRD shows that all samples contain  $\text{MgTiO}_3$ ,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and some traces of other titanates. Densification seems good though the micrograph Fig. 5 shows a large number of intragranular pores. Also many empty triple points contribute to porosity. Some  $\text{MgTiO}_3$  grains are large (even larger than with eutectic additives), especially for 12 wt.% bismuth titanate composition, and many of them have a 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 (white region on the SEM photography Fig. 5) present in higher amounts than with eutectic additives, even for the 6 wt.% composition.

Sintering was performed with the 6 wt.% bismuth titanate composition in  $\text{N}_2$  and  $\text{N}_2$ –1 vol.%  $\text{H}_2$ . Both atmospheres do not lead to any densification. This is illustrated in Fig. 6, which compares shrinkage curves obtained in air and  $\text{N}_2$  for this composition. Under  $\text{N}_2$  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

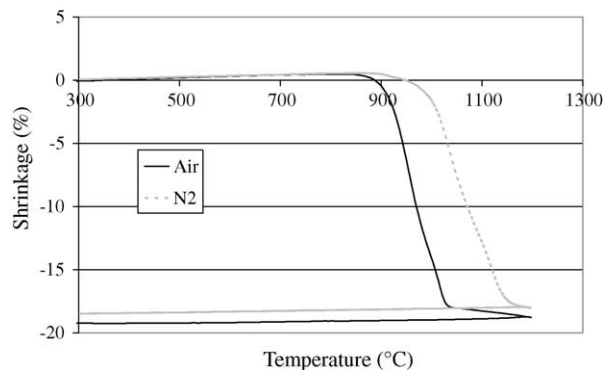


Fig. 6. Effect of atmosphere on dilatometric behaviour of  $\text{MgTiO}_3$  1.025 + 6 wt.%  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ .

instead of 1030 °C. XRD measurements show that the samples sintered in air contain MgTiO<sub>3</sub>, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> plus other titanates while no titanate is present after sintering in N<sub>2</sub>. Pre-calcination of bismuth titanate has been performed in N<sub>2</sub>–1 vol.% H<sub>2</sub>. While in air the calcinated powder is almost pure Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (with traces of excess Bi<sub>2</sub>O<sub>3</sub>), in N<sub>2</sub>–1 vol.% H<sub>2</sub> only traces of Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> are detected with Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> as major phases.

Samples sintered in air have been electrically tested. Resistivities are higher than 10<sup>13</sup> Ω cm under dry atmosphere (5% moisture). These values decrease with hygrometry but remain higher than 10<sup>11</sup> Ω cm in 50% moisture for 12 wt.% bismuth titanate additions: the 6 wt.% 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<sub>3</sub> 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<sub>3</sub>. Boron cannot substitute with Mg or Ti in A or B site because it cannot get the SIX coordinence. Bismuth ion is too large (1.02 Å) when having the 6 coordinence compared to Mg<sup>2+</sup> (0.72 Å) or Ti<sup>4+</sup> (0.605 Å): substitution with bismuth thus seems difficult consider. 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<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, pre-calcinated or formed in situ, leads to low temperature sintering of MgTiO<sub>3</sub>. When this phase is lacking, densification is not enhanced. Lower densification kinetics with eutectic additives (for equivalent Bi<sub>2</sub>O<sub>3</sub>/MgTiO<sub>3</sub> 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<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>: 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<sub>3</sub> 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 recalls phenomena like liquid or viscous phase sintering.

The formation of bismuth titanate seems very favourable in air. The added Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> and MgTiO<sub>3</sub> to form bismuth titanate. It could also be possible that only the melting behaviour of Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> 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 disappearance is due to decomposition or migration to the surface and evaporation. The decomposition hypothesis does not seem to be valid as neither Bi<sub>2</sub>O<sub>3</sub> nor TiO<sub>2</sub> 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? Perhaps because both processes are combined, decomposition (or non-formation) of bismuth titanate comes first. Further investigations are needed to clarify this point.

Dielectric properties are close to those of pure MgTiO<sub>3</sub> for every composition 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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