

## **Low sintering temperature of MgTiO<sub>3</sub> with fluorine containing additives for type I capacitors**

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**Abstract:** Magnesium titanate MgTiO<sub>3</sub> is a well known compound for type I multilayer ceramic capacitors. Nevertheless the sintering temperature of the pure ilmenite MgTiO<sub>3</sub> is around 1350°C. Such a high sintering temperature together with the high sensitivity of the dielectric material to reduction when heated in a low-oxygen containing atmosphere involve that MgTiO<sub>3</sub>-based MLCC include palladium-rich inner electrodes. The high level of variation of both the costs of Pd and Ag justifies researches leading to the use of cheaper metals such as silver or base metals such as nickel or copper. When using low-melting temperature metals (silver melts at 960°C and copper at 1085°C), the sintering temperature of the dielectric material has to be lowered. We report here on our investigations on the use of fluorine containing additives for the reducing of the sintering temperature of magnesium titanate, showing so the ability of this material to be sintered at temperatures much lower than 1000°C. Both dielectric and electric properties of such ceramics are compatible with type I capacitors requirements.

**Keywords:** Capacitors, Dielectric properties, Sintering, Titanates, Halides

## **1. Introduction**

Although much R&D have been devoted for now more than thirty years to the production of type II multilayer ceramic capacitors with non noble metals electrodes, only few reports have been published related to the solving of the same problem with type I capacitors. Yet, the economical problem due to the highly variable and high cost of the noble metals, palladium and silver, classically used to form the inner electrodes is exactly the same in both families of capacitors.

Another problem has to be solved together: as many applications of type I MLCC exclude the use of magnetic materials, the use of nickel inner electrodes is then prohibited and copper electrodes have to be considered. Copper electrodes have another advantage: thanks to their high electrical conductivity,

they allow the use of these capacitors at very high frequencies. Yet, an important technological problem remains that is the low melting temperature of copper, 1085°C, that makes the sintering temperature to be much lower than 1000°C.

Magnesium titanate  $\text{MgTiO}_3$ , that owns the ilmenite structure, is one of the materials classically used for the making of noble metal electrodes MLCC. It has been previously demonstrated that it was possible to sinter it at 1350°C in a slightly reducing atmosphere (wet  $\text{N}_2 + 1 \text{ vol}\% \text{ H}_2$ ) when  $\text{Ti}^{4+}$  in the B site of the ilmenite structure was substituted with equal at. amounts of  $\text{W}^{6+}$  and  $\text{Mn}^{2+}$  acting as the couple of donor/acceptor in the same way that previously stated for type II  $\text{BaTiO}_3$ -based compositions<sup>1,2</sup>.

This temperature is quite compatible with the use of nickel electrodes, but is totally inadequate for the use of copper electrodes. Furthermore, when  $\text{MgTiO}_3$  is co-sintered with nickel, the EDX analysis performed at the Ni/ $\text{MgTiO}_3$  interface shows that some reaction occurs between these two materials<sup>2</sup>. It is thus important to be able to lower the sintering temperature of magnesium titanate in order to consider its use together with copper inner electrodes.

Although the structures of the perovskite  $\text{BaTiO}_3$  and the ilmenite  $\text{MgTiO}_3$  are quite different, we were prompted at the beginning of this work by the conclusions of previous studies that concluded to the ability of sintering barium titanate or other compounds such as the perovskite  $\text{SrTiO}_3$ , the relaxors PMN/PFN or titanium oxide at temperatures lower than 1000°C<sup>3</sup>.

Particularly in the case of  $\text{BaTiO}_3$ , lithium compounds additions, preferably LiF or  $\text{BaLiF}_3$ , to barium titanate with a controlled stoichiometry were demonstrated to be particularly efficient. Two different and independent mechanisms have been demonstrated that, acting as well alone or together, allow sintering at low temperatures, lower than 1000°C.

The first one involves only lithium substitutions to titanium. Lithium ion  $\text{Li}^+$ , thanks to its ionic radius, can easily substitute  $\text{Ti}^{4+}$  with the consequence of anionic vacancies in the “ $\text{BO}_3$ ” network that lead to the formation of extended defects such as the elimination of oxygen rows in the  $\langle 110 \rangle$  direction or along  $\langle 100 \rangle$  and the formation of  $\text{TiO}_5$  pyramids. Both types of extended defects are supposed to exist

together, leading to easier diffusion and, thus, lower temperature densification. The formula of the material can then be written  $\text{Ba}(\text{Ti}_{1-x}\text{Li}_x)\text{O}_{3-3x/2}$ .

The second one is to be considered only when lithium is introduced together with fluorine:  $\text{Li}^+$  ions substitute  $\text{Ti}^{4+}$  and  $\text{F}^-$  ions  $\text{O}^-$  in the perovskite cell, leading to the formation of a solid solution between  $\text{BaTiO}_3$  and  $\text{BaLiF}_3$  that can be expressed as  $\text{BaTi}_{1-x}\text{Li}_x\text{O}_{3-3x}\text{F}_{3x}$ .  $\text{BaLiF}_3$  melts incongruently at  $750^\circ\text{C}$ , and, thus, the solid solution can densify at a low temperature.

Yet, the structure of the ilmenite  $\text{MgTiO}_3$  is quite different to the one of the  $\text{BaTiO}_3$  perovskite. In both structures,  $\text{Ti}^{4+}$  ions are 6-coordinated. For the A site of the two structures, large  $\text{Ba}^{2+}$  ions own a 12 coordination while the smaller  $\text{Mg}^{2+}$  ions are 6-coordinated. Furthermore, although the  $\text{MgLiF}_3$  compound is supposed theoretically to exist, it has never been experimentally synthesized and observed. So, the analogy with the previous studies can be only related to the first mechanism, that is to say the possible introduction of Li in either the A or the B site of the ilmenite (but, due to the values of the ionic radius, preferably in the A site by substituting Mg), acting in both cases as an acceptor and, thus, being susceptible to lead to the formation of oxygen vacancies. ( $\text{Ti}^{4+} = 0.605 \text{ \AA}$ ,  $\text{Mg}^{2+} = 0.72 \text{ \AA}$  and  $\text{Li}^+ = 0,74 \text{ \AA}$ ).

## 2. Experimental procedure

The  $\text{MgTiO}_3$  powders were 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, BACHOFEN, Switzerland ) using 0.8 mm diameter yttrium stabilised zircon balls (YTZ grinding media TOSOH). The powders were then calcined in air at  $1000^\circ\text{C}$  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  $\text{CuK}\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ), in the range  $15-85^\circ$  ( $2\theta$ ). After calcination fluorine compounds was added and the powders were milled in a planetary agitator (Pulverisette FRITCH with agate bowl and balls). Densification behavior were studied by dilatometric measurements performed only in air on TMA92 SETARAM dilatometer, with heating and cooling rates of  $300^\circ\text{C}\cdot\text{h}^{-1}$ .

The different compositions were pressed at  $2000 \text{ kg.cm}^{-2}$  to obtain disks 10 mm in diameter and around 1.5 mm thick. The disks were fired in moist  $\text{N}_2\text{-1\%H}_2$  reducing atmosphere, with heating and cooling rates of  $150^\circ\text{C.h}^{-1}$  and dwell time of one hour.

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

### **3. Results**

#### ***3.1 Sintering of $\text{MgTiO}_3$ + Li compounds addition.***

We have discussed earlier on the sintering of  $\text{MgTiO}_3$  with different lithium sources<sup>4</sup> Figure 1 is an illustration of the sintering behavior of such compositions. Whatever the lithium source is, densification is easier than with pure  $\text{MgTiO}_3$ . It seems also that there exist two different behaviors: the one with the lithium “oxides” with a dramatic lowering of the shrinkage rate close to  $1100^\circ\text{C}$ , and the lithium halides’ one characterized by a densification behavior without any accident. Yet, only LiF permits the densification of the ceramic at a temperature much lower than  $1000^\circ\text{C}$  with a high dependance on the stoichiometry: the densification is all the more easier that there is an excess of magnesium in the initial ilmenite phase

X-ray diffraction analysis point out the existence of a secondary phase for which only two diffraction peaks are visible ( $d_{\text{hkl}} = 0.878$  and  $1.466 \text{ \AA}$ ) always present when the material is sintered with a lithium halide addition, either LiF or LiCl, and never when sintered with a lithium “oxide”. The analysis of this phase pointed out that it contained magnesium but not any titanium.

In every case, the dielectric measurements of ceramics sintered in wet ( $\text{N}_2 + 1\% \text{ H}_2$ ) are characteristic of  $\text{MgTiO}_3$  dielectric materials. All resistivities at room temperature are higher than  $10^{12} \Omega.\text{cm}$ . Yet, these characteristics slightly degrade when lithium “oxides” are used, evidencing some conduction in

the material although these ceramics own much better insulation characteristics than pure  $\text{MgTiO}_3$  sintered in oxygen at  $1350^\circ\text{C}$  and heated again together with them in a reducing atmosphere.

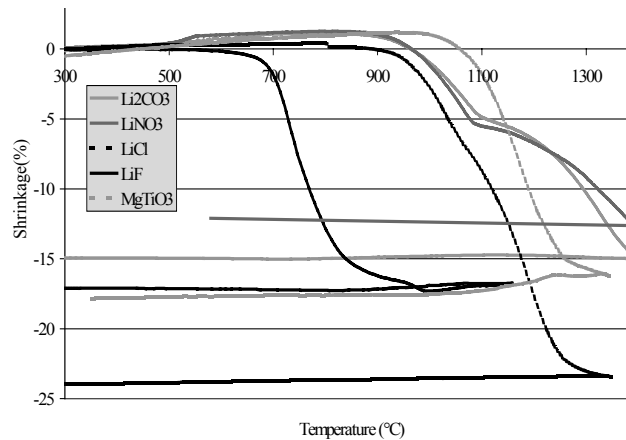


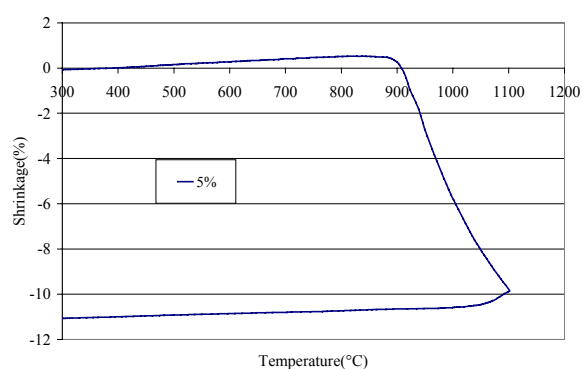
Figure 1: : sintering behavior of  $\text{MgTiO}_3$  with  $\text{Mg}/\text{Ti} = 1.025$  sintered with # lithium sources, lithium amount equal to 8.24 at. %

These observations point out that, although Li alone has a strong effect on the sintering process, the presence of fluorine is necessary for the obtaining of an easy densification at low temperature. We have thus investigated on the effect of fluorine compounds addition.

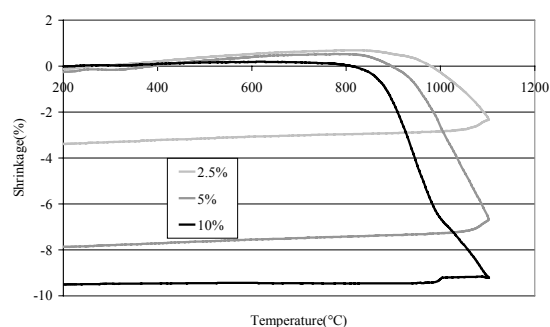
### 3.2 Sintering of $\text{MgTiO}_3$ + fluorine compounds addition

Phase diagrams of either the binary systems  $\text{MgF}_2$ - $\text{BaF}_2$  or  $\text{MgF}_2$ - $\text{CaF}_2$  and the ternary systems  $\text{MgF}_2$ - $\text{BaF}_2$ - $\text{LiF}$  or  $\text{MgF}_2$ - $\text{CaF}_2$ - $\text{LiF}$  show binary eutectics and large domains of compositions with low melting temperatures<sup>5</sup>. Binary eutectic composition composed of 0.43 at%  $\text{CaF}_2$  and 0.57 at%  $\text{MgF}_2$  melts at  $980^\circ$  and the one composed of 0.6 at%  $\text{BaF}_2$  and 0.4 at%  $\text{MgF}_2$  at  $912^\circ\text{C}$  (with, in this last diagram, the incongruent melting of  $\text{Mg}_2\text{BaF}_6$  at  $942^\circ\text{C}$ ). Ternary eutectic composition 0.12 at%  $\text{CaF}_2$  / 0.28 at%  $\text{MgF}_2$  / 0.6 at%  $\text{LiF}$  melts at  $672^\circ\text{C}$ . Two ternary eutectics are observed in the composition diagram  $\text{BaF}_2/\text{MgF}_2/\text{LiF}$  respectively at 748 and  $654^\circ\text{C}$  (this last one corresponding to the composition 0.256 at %  $\text{MgF}_2$  / 0.222  $\text{BaF}_2$  / 0.522 at%  $\text{LiF}$ ) together with a ternary peritectic at  $741^\circ\text{C}$ . Addition of such compounds to  $\text{MgTiO}_3$  are thus attractive as they may allow a lower sintering temperature without any danger of the introduction of species detrimental to the electric and dielectric properties.

Dilatometric analysis of the sintering of stoichiometric magnesium titanate with either the  $\text{CaF}_2/\text{MgF}_2$  or the  $\text{BaF}_2/\text{MgF}_2$  eutectic show effectively that densification is easier and occurs at a lower temperature than pure  $\text{MgTiO}_3$ . Although the dielectric characteristics and the value of the insulation resistance were compatible with the use in dielectric formulations when sintered in an oxidizing atmosphere, both the losses and the insulation resistance values showed of some conduction and, thus, reduction of the material when it was sintered in wet  $\text{N}_2+1\%\text{H}_2$ . It is noteworthy as well that the “unknown phase” appearing when lithium fluorine or chlorine were added alone is never detected in the present case.

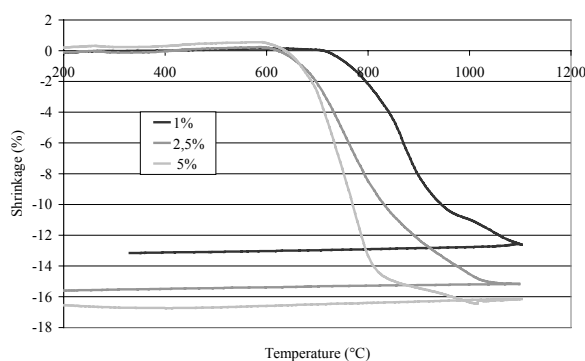


a)  $\text{MgTiO}_3 + 5 \text{ wt}\% \text{ CaF}_2/\text{MgF}_2$  binary eutectic

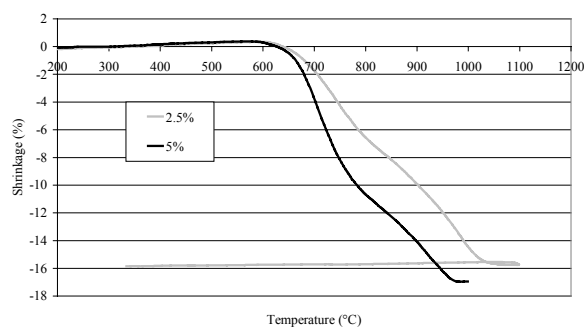


b)  $\text{MgTiO}_3 + 2.5, 5 \text{ and } 10 \text{ wt}\% \text{ BaF}_2/\text{MgF}_2$  eutectic

Figure 2: Sintering behavior of stoichiometric  $\text{MgTiO}_3$  with binary eutectics additions



a)  $\text{MgTiO}_3 + x \text{ wt}\% \text{ CaF}_2/\text{MgF}_2/\text{LiF}$  ternary eutectic



b)  $\text{MgTiO}_3 + x \text{ wt}\% \text{ BaF}_2/\text{MgF}_2/\text{LiF}$  ternary eutectic

Figure 3 Sintering behavior of stoichiometric  $\text{MgTiO}_3$  with ternary eutectics addition

The lower melting temperatures of the ternary eutectics compared to the equivalent binary eutectics (without LiF) are coherent with the densification occurring now at very low temperatures. It is noteworthy that only magnesium titanate either stoichiometric or with an excess of magnesium can be easily densified contrariwise to titanium excess compositions. The lowest densification temperatures,

840°C for stoichiometric MgTiO<sub>3</sub> and 800°C for Mg excess MgTiO<sub>3</sub>, were observed with 5 wt% addition of the CaF<sub>2</sub>/MgF<sub>2</sub>/LiF eutectic. This easier densification when CaF<sub>2</sub>/MgF<sub>2</sub>/LiF eutectic is added may appear as surprising as its melting temperature (672°C) is intermediate between the melting temperature of the BaF<sub>2</sub>/MgF<sub>2</sub>/LiF eutectic (654°C) we attempted to add to MgTiO<sub>3</sub> and the one of the second ternary eutectic of this diagram (748°C).

An important observation is that, whatever the ternary eutectic containing LiF and the Mg/Ti stoichiometry are, the presence of already mentioned unidentified phase present when MgTiO<sub>3</sub> was sintered with either LiF or LiCl is as well detected often together with MgO.

The dielectric characteristics of ceramics from both systems sintered in a reducing wet N<sub>2</sub>/H<sub>2</sub> atmosphere are typical of type I dielectric capacitors with a dielectric constant close to 14 or 15, dielectric losses lower than 0.2 % and insulation resistances higher than 10<sup>13</sup>Ω.cm. Yet, the compositions including the BaF<sub>2</sub>/MgF<sub>2</sub>/LiF eutectic seem less attractive as the ceramics are characterised by a negative temperature coefficient that seems difficult to reduce to 0 value. Furthermore, a careful examination of the losses characteristic versus temperature shows that a slight increase of its value occurs at high temperatures (higher than 120°C). This particular behaviour may be an indication of a slight electrical conduction in this case.

#### **4. Discussion and conclusion**

All these observation point out the evidence that the addition of some at% of an halide lithium compound, either chlorine or, better, fluorine, helps to the densification at a low temperature of MgTiO<sub>3</sub> dielectric compositions. This temperature may be compatible with the co-sintering of the dielectric material with copper electrodes. Furthermore, the presence of both lithium and fluorine and/or chlorine is necessary to the ability for this dielectric composition to be sintered in a reducing atmosphere compatible with copper electrodes. They are coherent with the hypothesis of the following model explaining the densification process and the ability to sinter these materials in a reducing atmosphere.

When lithium is alone, it can introduce in the A site of the ilmenite and substitute magnesium. It helps first to the densification as that leads to the creation of oxygen vacancies to assure the electrical neutrality. Yet, due to the substitution of Mg by Li in the structure, magnesium oxide second phase appears that interferes with the densification process. As  $\text{Li}^+$  acts then as an acceptor, the material can be sintered in a reducing atmosphere without losing its insulation resistance characteristics.

When fluorine is present without lithium, the densification aid comes then from the presence of low melting temperature eutectics, either  $\text{BaF}_2\text{-MgF}_2$  or  $\text{CaF}_2\text{-MgF}_2$ . The lower the eutectic melting temperature is, the lower the densification temperature is. Yet, as now not any acceptor substitutes in the lattice, the insulation resistance is bad when the ceramic is sintered in a reducing atmosphere.

The sintering behaviour appears as completely different when lithium is present together with a halide, either  $\text{Cl}^-$  or, better,  $\text{F}^-$ . First, it seems that the lithium halide reacts with  $\text{MgTiO}_3$  with the consequence of the appearance of a new phase with two reticular distances respectively  $d_{\text{hkl}} = 0.878$  and  $1.466 \text{ \AA}$ . This phase seems to have a structure very close to the one of  $\text{MgO}$  but is quite independent of it as stated when these two compounds can be detected together. The composition of the unknown phase includes magnesium but not titanium. Thus, its appearance has at least two consequences: first, it helps at the evidence the densification at low temperature. Secondly, when it is present, lithium can substitute to magnesium and then act as an acceptor. It was shown that, after sintering, the ratio  $\text{Mg}/\text{Ti}$  was significantly lower to the one analyzed by EDS on the ilmenite grains before sintering or on ceramics sintered without lithium<sup>6</sup>. Furthermore, in order to keep the electrical neutrality of the material, titanium  $\text{Ti}^{3+}$  reduces to  $\text{Ti}^{2+}$  that, thanks to its ionic radius, goes together with  $\text{Li}^+$  on the A site of the ilmenite with as a consequence the creation of acceptor/donor pairs that keep the material from reduction when sintered in a reducing atmosphere. The ilmenite can be then described as the following formula:  $(\text{Mg}_{1-2x}^{2+}\text{Li}_x^+\text{Ti}_x^{3+})\text{Ti}^{4+}\text{O}_3$ .

When  $\text{Ca}^{2+}$  is present, another substitution may occur: in the case of the addition of  $\text{CaTiO}_3$  to  $\text{BaTiO}_3$ , it was demonstrated by D. Smyth & co-workers that, either the ionic radii were far to be the same, some amounts of  $\text{Ca}^{2+}$  ions substituted  $\text{Ti}^{4+}$  in the B site of the perovskite<sup>7</sup>. We can thus consider the hypothesis that, as well in the present case,  $\text{Ca}^{+2}$  substitutes  $\text{Ti}^{4+}$ , acting there as an acceptor. Thanks to



the large ionic radii gap ( $\text{Ca}^{2+} = 1 \text{ \AA}$  when 6-coordinated) that leads to the appearance of some easier diffusion paths in the structure and, thus, to a slightly easier densification. Furthermore, that could explain the better insulation resistance of the  $\text{CaF}_2/\text{MgF}_2/\text{LiF}$  eutectic added ceramics compared to the  $\text{BaF}_2/\text{MgF}_2/\text{LiF}$  eutectic added one when sintered in a reducing atmosphere.

**Acknowledgments:** The results presented here were obtained with the support of TEMEX Company. We thank also the Europe Community for the financial support (FEDER Funds).

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