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Low sintering temperature of $MgTiO_3$ for type I capacitors

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Abstract

Magnesium titanate $MgTiO_3$ is a well-known compound for type I multilayer ceramic capacitors. Nevertheless, the sintering temperature of the pure ilmenite $MgTiO_3$ 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 implies that $MgTiO_3$-based MLCC include palladium-rich inner electrodes. The high level of variation of both the costs of Pd and Ag justifies research 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 into the use of fluorine containing additives for the reducing of the sintering temperature of magnesium titanate, showing 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 has been devoted to the production of type II multilayer ceramic capacitors with non-noble metals electrodes[1–4] for more than 30 years, only few reports have been published related to the solving of the same problem with type I capacitors. Yet, the economic problems due to the high and variable 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 thus 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, which makes the sintering temperature to be much lower than 1000 °C.

Magnesium titanate $MgTiO_3$, with its 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 N_2 + 1 vol.% H_2) when Ti^{4+} in the B site of the ilmenite structure was substituted with equal at% amounts of W^{6+} and Mn^{2+} acting as the couple donor/acceptor in the same way as previously stated for type II $BaTiO_3$-based compositions.[5,6]

This temperature is quite compatible with the use of nickel electrodes, but is totally inadequate for the use of copper electrodes. Furthermore, when $MgTiO_3$ is co-sintered with nickel, the EDX analysis performed at the Ni/$MgTiO_3$ interface shows that some reaction occurs between these two materials.[6] 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 $BaTiO_3$ and the ilmenite $MgTiO_3$ 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 $SrTiO_3$, the relaxors PMN/PFN or titanium oxide at temperatures lower than 1000 °C.[7]

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Particularly in the case of $BaTiO_3$, lithium compounds additions, preferably LiF or $BaLiF_3$, 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 Li^+, thanks to its ionic radius, can easily substitute Ti^{4+} with the consequence of anionic vacancies in the "BO_3" network that lead to the formation of extended defects such as the elimination of oxygen rows in the $\langle 1\,1\,0 \rangle$ direction or along $\langle 1\,0\,0 \rangle$ and the formation of 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 $Ba(Ti_{1-x}Li_x)O_{3-3x/2}$.

The second one is to be considered only when lithium is introduced together with fluorine: Li^+ ions substitute Ti^{4+} and F^- ions O^{--} in the perovskite cell, leading to the formation of a solid solution between $BaTiO_3$ and $BaLiF_3$ that can be expressed as $BaTi_{1-x}Li_xO_{3-3x}F_{3x}$. $BaLiF_3$ melts incongruently at 750 °C, and thus the solid solution can densify at a low temperature.

Yet the structure of the ilmenite $MgTiO_3$ is quite different to that of the $BaTiO_3$ perovskite. In both structures, Ti^{4+} ions are 6-coordinated. For the A site of the two structures, large Ba^{2+} ions possess a 12 coordinence while the smaller Mg^{2+} ions are 6-coordinated. Furthermore, although the $MgLiF_3$ 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 (Ti^{4+} = 0.605 Å, Mg^{2+} = 0.72 Å and Li^+ = 0.74 Å).

2. Experimental procedure

The $MgTiO_3$ powders were synthesized by the classical solid-state route. The starting powders (MgO, TiO_2) were mixed together for 1 h in water by attrition milling (Dyno Mill KDLA, BACHOFEN, Switzerland) using 0.8 mm diameter yttried stabilized zircon balls (YTZ grinding media TOSOH). The powders were then calcined in air at 1000 °C during 1 h 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 Cu Kα (λ = 1.5405 Å), in the range 15–85° (2θ)). After calcination fluorine compounds was added and the powders were milled in a planetary agitator (Pulverisette FRITCH with agate bawl and balls). Densification behavior was studied by dilatometric measurements performed only in air on a TMA92 SETARAM dilatometer, with heating and cooling rates of 300 °C h^{-1}.

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 a moist $N_2 - 1\%\ H_2$ reducing atmosphere, with heating and cooling rates of 150 °C h^{-1} and dwell time of 1 h.

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 μm^{-1} DC bias (Sefelec (SIM 1000 A) megohmeter). 1 kHz dielectric characterizations (*C* and tan δ) were realized 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. Sintering of $MgTiO_3$ + Li compounds addition

We have discussed earlier the sintering of $MgTiO_3$ with different lithium sources[8] Fig. 1 is an illustration of the sintering behavior of such compositions. Whatever the lithium source is, densification is easier than with pure $MgTiO_3$. It seems also that are exist two different behaviors: that of the lithium "oxides" with a dramatic lowering of the shrinkage rate close to 1100 °C, and that of the lithium halides characterized by a densification behavior without any accident. Yet, only LiF permits the densification of the ceramic at a temperature much lower than 1000 °C with a high dependence on the stoichiometry: the densification is all the easier if there is an excess of magnesium in the initial ilmenite phase.

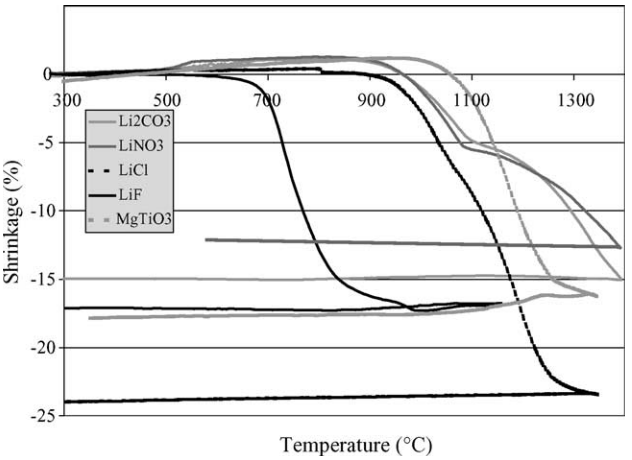
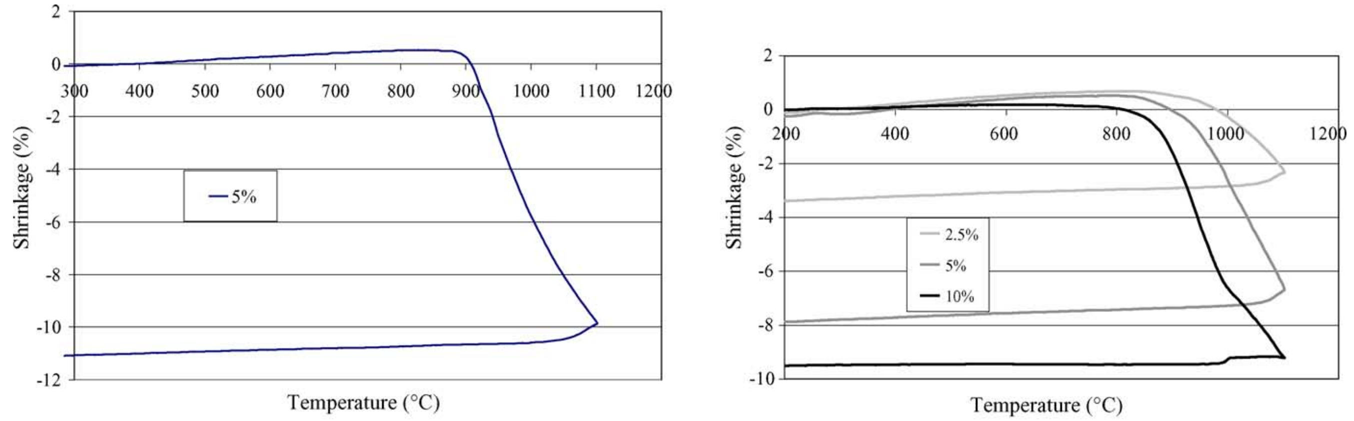


Fig. 1. sintering behavior of $MgTiO_3$ with Mg/Ti = 1.025 sintered with # lithium sources, lithium amount equal to 8.24 at%.

X-ray diffraction analysis points out the existence of a secondary phase for which only two diffraction peaks are visible (d_{hkl} = 0.878 and 1.466 Å) 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



(a) $MgTiO_3$ + 5 wt% CaF_2/MgF_2 binary eutectic

(b) $MgTiO_3$ + 2.5, 5 and 10 wt% BaF_2/MgF_2 eutectic

Fig. 2. Sintering behavior of stoichiometric $MgTiO_3$ with binary eutectics additions.

analysis of this phase pointed out that it contained magnesium but not any titanium.

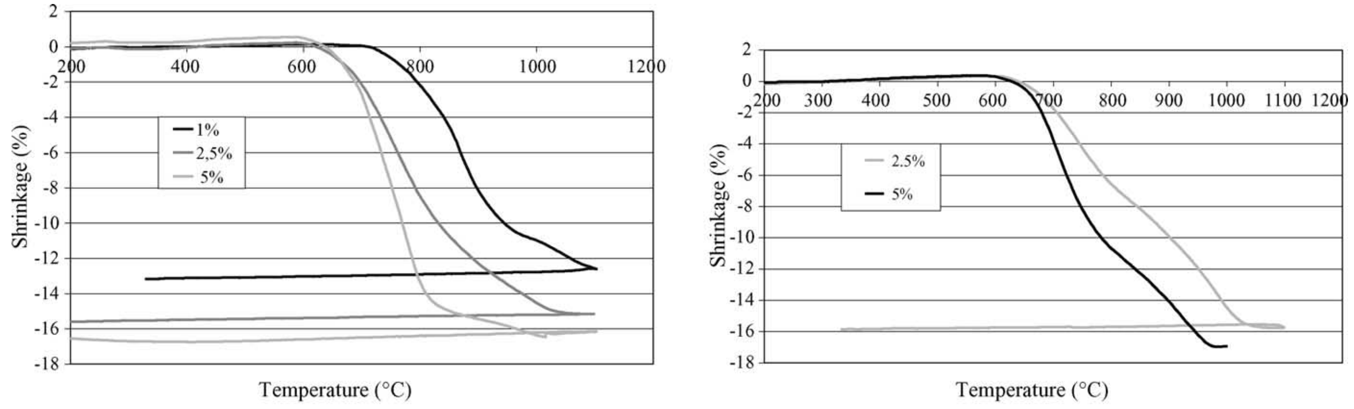
In every case, the dielectric measurements of ceramics sintered in wet ($N_2 + 1\%\ H_2$) are characteristic of $MgTiO_3$ dielectric materials. All resistivities at room temperature are higher than $10^{12}\ \Omega$ cm. Yet, these characteristics slightly degrade when lithium "oxides" are used, evidencing some conduction in the material although these ceramics possess much better insulation characteristics than pure $MgTiO_3$ sintered in oxygen at 1350 °C and heated again together with them in a reducing atmosphere.

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 effect of fluorine compounds addition.

3.2. *Sintering of $MgTiO_3$ + fluorine compounds addition*

Phase diagrams of either the binary systems MgF_2–BaF_2 or MgF_2–CaF_2 and the ternary systems MgF_2–BaF_2–LiF or MgF_2–CaF_2–LiF show binary eutectics and large domains of compositions with low-melting temperatures.[9] Binary eutectic composition composed of 43 at% CaF_2 and 57 at% MgF_2 melts at 980° and the one composed of 60 at% BaF_2 and 40 at% MgF_2 at 912 °C (with, in this last diagram, the incongruent melting of Mg_2BaF_6 at 942 °C). Ternary eutectic composition $0.12CaF_2/0.28MgF_2/0.6LiF$ melts at 672 °C. Two ternary eutectics are observed in the composition diagram $BaF_2/MgF_2/LiF$ respectively at 748 and 654 °C (this last one corresponding to the composition $0.256MgF_2/0.222BaF_2/0.522LiF$) together with a ternary peritectic at 741 °C. Addition of such compounds to $MgTiO_3$ is 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 CaF_2/MgF_2 or the BaF_2/MgF_2 eutectic (Fig. 2) shows effectively that densification is easier and occurs at a lower temperature than pure $MgTiO_3$. Although the dielectric characteristics and the value



(a) $MgTiO_3$ +x wt% CaF_2/MgF_2/LiF ternary eutectic

(b) $MgTiO_3$ + x wt% BaF_2/MgF_2/LiF ternary eutectic

Fig. 3. Sintering behavior of stoichiometric $MgTiO_3$ with ternary eutectics addition.

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 some conduction and thus reduction of the material when it was sintered in wet $N_2 + 1\%\ H_2$. 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.

The lower melting temperatures of the ternary eutectics compared to the equivalent binary eutectics (without LiF) are consistent with the densification occurring now at very low temperatures. It is noteworthy that only magnesium titanate, either stoechiometric or with an excess of magnesium, can be easily densified unlike to titanium excess compositions. The lowest densification temperatures, 840 °C for stoechiometric $MgTiO_3$ and 800 °C for Mg excess $MgTiO_3$, were observed with 5 wt% addition of the $CaF_2/MgF_2/LiF$ eutectic (Fig. 3). This easier densification when $CaF_2/MgF_2/LiF$ eutectic is added may appear surprising as its melting temperature (672 °C) is intermediate between the melting temperature of the $BaF_2/MgF_2/LiF$ eutectic (654 °C) we attempted to add to $MgTiO_3$ 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 an already mentioned unidentified phase present when $MgTiO_3$ was sintered with either LiF or LiCl is also detected often together with MgO.

The dielectric characteristics of ceramics from both systems sintered in a reducing wet N_2/H_2 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 $10^{13}\ \Omega$ cm. Yet, the compositions including the $BaF_2/MgF_2/LiF$ eutectic seem less attractive as the ceramics are characterized 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 behavior may be an indication of a slight electrical conduction in this case.

4. Discussion and conclusion

All these observations point out the evidence that the addition of some at% of an halide lithium compound, either chlorine or, better, fluorine, helps the densification at a low temperature of $MgTiO_3$ 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 consistent 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 in the densification as it 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 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 BaF_2–MgF_2 or CaF_2–MgF_2. The lower the eutectic melting temperature is, the lower the densification temperature is. Yet, as now no acceptor substitutes in the lattice, the insulation resistance is poor when the ceramic is sintered in a reducing atmosphere.

The sintering behavior appears as completely different when lithium is present together with a halide, either Cl^- or, better, F^-. First, it seems that the lithium halide reacts with $MgTiO_3$ with the consequence of the appearance of a new phase with two reticular distances respectively $d_{hkl} = 0.878$ and 1.466 Å. This phase seems to have a structure very close to that of 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 for magnesium and then act as an acceptor. It was shown that, after sintering, the ratio Mg/Ti was significantly lower to the one analyzed by EDS on the ilmenite grains before sintering or on ceramics sintered without lithium.[10] Furthermore, in order to keep the electrical neutrality of the material, titanium Ti^{3+} reduces to Ti^{3+} that, thanks to its ionic radius, goes together with 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 then be described by the following formula: $(Mg_{1-2x}{}^{2+}Li_x{}^{+}Ti_x{}^{3+})Ti^{4+}O_3$.

When Ca^{2+} is present, another substitution may occur: in the case of the addition of $CaTiO_3$ to $BaTiO_3$, it was demonstrated by D. Smyth and co-authors that, either the ionic radii were far to be the same, some amounts of Ca^{2+} ions substituted Ti^{4+} in the B site of the perovskite.[11] We can thus consider the hypothesis that, in the present case as well, Ca^{2+} substitutes Ti^{4+}, acting there as an acceptor. Thanks to the large ionic radii gap ($Ca^{2+} = 1$ Å 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 $CaF_2/MgF_2/LiF$ eutectic added ceramics compared to the $BaF_2/MgF_2/LiF$ eutectic added one when sintered in a reducing atmosphere.

Acknowledgments

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