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$MgTiO_3$ for Cu base metal multilayer ceramic capacitors

J. Bernard*, D. Houivet, J. El Fallah, J.M. Haussonne

Laboratoire Universitaire des Sciences Appliquées de Cherbourg (Université de Caen Basse Normandie) Site Universitaire de Cherbourg, BP 78-50130 Octeville, France

Abstract

The evolution of the cost of palladium justifies studies devoted to the use of cheap base metals as electrodes for multilayer ceramic capacitors. In a precedent [*J. Eur. Ceram. Soc.*10–11(2001) 1681] work we investigated on Mn acceptor together with W donor additions on the properties of $MgTiO_3$ ceramics sintered at 1350 °C under a reducing atmosphere (wet N_2-1%H_2). As in acceptor/donor [Proceedings K1; 1206 CIMTEF, Florence (1998) 88] codoped $BaTiO_3$ the insulating character of $MgTiO_3$ was conserved. In order to employ these materials in the production of type-I multilayer ceramic capacitors with Copper inner electrodes we investigate now on the possibility of sintering magnesium titanate at low temperature. We have studied the densification behavior of different $MgTiO_3$ compositions with lithium salts additions, considering particularly the effect of the non-stoechiometry expressed as the Mg/Ti ratio. Full densification appears below 1000 °C. The obtained ceramics, that have been co-sintered in a multilayer structure with Cu electrodes, are characterised by a resistivity higher than 10^{13} ohm cm together with a NPO dielectric constant ranging from 14 to 16 depending on the exact composition together with losses lower than 0.2%.

Keywords: $BaTiO_3$ and titanates; Capacitors; Copper electrodes; Dielectric properties; MgO

1. Introduction

Magnesium titanate based dielectric materials are classically used in the production of type-I ceramic multilayer capacitors. As sintering temperature is classically higher than 1350 °C, costly precious metal electrodes as Pd/Ag alloys are to be used. In order to reduce the ceramic multilayer capacitors cost, one way is to replace them by cheaper metals as nickel or copper. This solution implies to sinter the capacitors in atmospheres such as N_2/H_2 or CO/CO_2. In such reducing atmospheres $MgTiO_3$ as $BaTiO_3$ based dielectric ceramics are known to get large numbers of ionised oxygen vacancies and conduction electrons, giving rise to very poor insulation resistance. A solution proposed by Herbert in 1963[3] was to introduce acceptors dopants such as Mn^{2+} on Ti sites of $BaTiO_3$. Unfortunately, such materials present very rapid degradation behavior under electric fields. The problem was solved by Hennings 30 years later,[2,3] by codoping $BaTiO_3$ together with acceptors and donors substituted to Ti in the B site of the pérovskite cell. These compositions were proved to get a high insulation resistance when fired in a reducing atmosphere and very good life stability. Similar results were obtained[1] with the codoped in B site acceptor/donor ilmenite $MgTiO_3$. These materials seem to be good candidates for co-sintering with Ni but not with Cu due to their high sintering temperature. Sintering at lower temperatures can lead to cheaper components. Furthermore, Ni does not own a very high electrical conductivity, and capacitors with Ni electrodes cannot reach very high frequency applications. Moreover, Ni owns magnetic properties incompatible with some particular applications of the capacitors. Copper seems much more attractive, but cannot be used when sintering occurs at temperatures higher than 1000 °C.

In the case of $BaTiO_3$ a few sintering agent are known to reduce densification temperature. Previous works[4] have been devoted to the influence of LiF additions on the sintering behaviour of $BaTiO_3$. Li^+ ions are supposed to substitute Ti^{4+} and F^- ions O^- in the perovskite cell, leading both to the formation of extended anionic defects and of a solid solution with $BaLiF_3$. Both phenomena allow sintering at low temperatures, lower than 1000 °C.

Prompted by these models, we have investigated on the effects of lithium salt additions on the $MgTiO_3$

* Corresponding author. Tel.: +33-02-33-01-42-33; fax: +33-02-33-01-41-35.
E-mail address: bernard@chbg.unicaen.fr (J. Bernard).

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densification behaviour and on the properties of ceramics sintered under a reducing atmosphere of moist N_2-1%H_2.

2. Experimental procedure

The $MgTiO_3$ powders were synthesised by the classical solid-state route. The starting powders (MgO, TiO_2, MnO_2 and WO_3) were mixed together for 1 h in water by attrition milling (Dyno Mill KDLA, BACHOFEN, Switzerland) using 0.8 mm diameter yttried stabilised zircon balls (YTZ grinding media TOSOH). The powders were then calcined in air at 1000 °C during one hour[1] 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_α ($\lambda = 1.5405$ Å), in the range 15–85° (2θ). After calcination lithium salt was added and the powders were milled in a planetary agitator (Pulverisette FRITCH with agate bawl and balls). Densification temperatures were then estimated according to dilatometric measurements performed only in air on 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 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 microstructures of the sintered samples were observed with a SEM HITACHI S-2460-N and elementary analysis performed by EDS (OXFORD LINK ISIS). Both surface and bulk of the disks were analysed by X-ray diffraction. 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). 1kHz dielectric characterizations (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. Compositions with Mn and W

In order to investigate on the influence of lithium fluoride and non stoechiometry (A/B ratio) on the densification behavior of the codoped acceptor/donor $MgTiO_3$ and accepting that, as supposed in the previous studies, both Mn and W are located on the B site of the ilmenite cell, we have realised the following compositions:

- $Mg_{0,975}Ti_{0,99}Mn_{0,005}W_{0,005}O_3$, noted Mg/(Ti + Mn + W) = 0,975;
- $MgTi_{0.99}Mn_{0.005}W_{0.005}O_3$ noted Mg/(Ti + Mn + W) = 1; and
- $MgTi_{0.965}Mn_{0.005}W_{0.005}O_3$ noted Mg/(Ti + Mn + W) = 1.025.

The dilatometric studies of these compositions doped with 1 w% LiF (4.12 mole%) highlight the efficiency of LiF on the densification of $MgTiO_3$ (Fig. 1). These curves show that shrinkage begins around 700 °C as opposed to 1100 °C for the same compositions without LiF. It seems evident that these materials are not full dense and that some shrinkage may be due to some material flow. Yet, we can notice the influence of the A/B ratio on shrinkage phenomena.

The amount of lithium salt also influences the densification behavior. Only the composition 1.025 is fully densified at 1000 °C (Fig. 2) if the amount of LiF is equal to 8.24 mol%, contrariwise to the others compositions (0.975 and 1).

After sintering 1 h at 1000 °C under moist N_2/1%H_2 this composition gives rise to a resistivity $> 10^{11}$ ohm cm with dielectric properties close to the one of pure $MgTiO_3$. The obtained characteristics are a dielectric constant close to 15 and losses $< 0.2\%$ stable in temperature.

Furthermore, as well as Mn or W, Li^+ owns the ability to be located either in A or in B site of the ilmenite cell, and can acts as well as Mn as an acceptor. So, in order to understand the effect of lithium salt addition, we have investigated on the same compositions without Mn and W.

3.2. Compositions without Mn and W

As in the previous case, we investigated on the A/B ratio = Mg/Ti ratio (Mg/Ti = 0.975;1;1.025), with only a LiF amount equal to 8.24 mol%. As shown on the dilatometric curves (Fig. 3), we observe as well the efficiency of lithium fluoride on densification. The

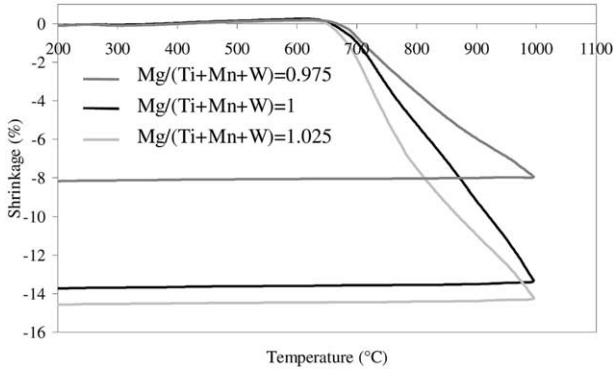

Fig. 1. Dilatometric curves of Mg/(Ti + Mn + W) = 0.975;1;1.025 with 4.12 mol% LiF.

dilatometric analyses highlight also the importance of non stoechiometry on the densification behaviour. As in $BaTiO_3$[4] best results have been obtained with a deficit of Ti in the ilmenite structure.

The choice of the nature of the lithium salt leads to quite different densification behaviors, lithium fluoride seems to be the most efficient sintering agent (Fig. 4) illustrates the difference of densification observed for the same amount in Li (8.24 mol%) introduced as LiCl, $LiNO_3$, Li_2CO_3 and LiF on the 1.025 composition. With LiF, densification begins around 700 °C instead of 1000 °C with the others Li salts, and complete densification occurs at 1000 °C contrariwise to the other salts that promote full densification only at higher temperatures. That shows unambiguously a particular role for the fluorine, together or in addition with the one of the lithium.

X-ray diffraction analysis made on bulk of the sintered disks showed only the $MgTiO_3$ non-distorted phase. Contrariwise, diffractograms of disks surfaces reveal (Fig. 5) the presence of a new phase that is not referenced in the JCPDF database. This phase is only observed on the surfaces of the samples when using a halide as lithium salt addition, and does not depend of the stoechiometry of the ilmenite or of the nature of sintering atmosphere (oxidizing or reducing). When this phase is the only one detected by X-ray diffraction (that is to say when its thickness is important enough for the X-ray not to attain the $MgTiO_3$ bulk), EDS analysis reveal the presence of only magnesium cation.

Prompted by all these correlations, we have investigated on the binary phase diagrams of compounds containing only magnesium and lithium as cations. It appears that there exist solid solutions of magnesium

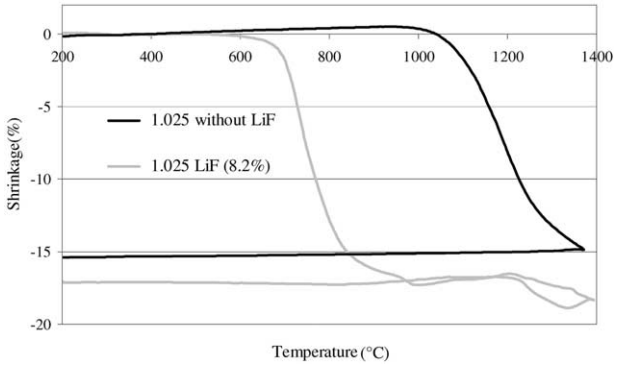

Fig. 2. Dilatometric curves of Mg/(Ti + Mn + W) = 1.025 without and with 8.24 mol% LiF.

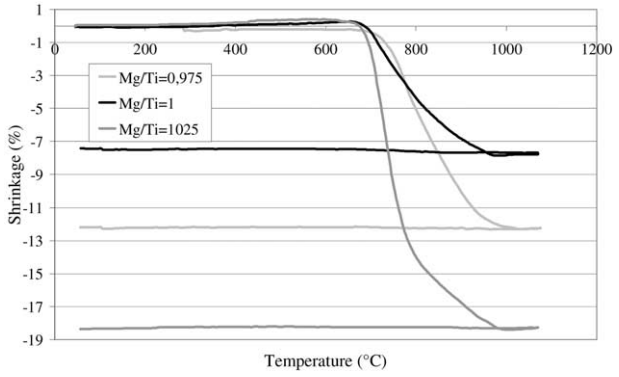

Fig. 3. Dilatometric analysis of compositions Mg/Ti = 0.975 ; 1; and 1.025 with 8.24 mol% LiF.

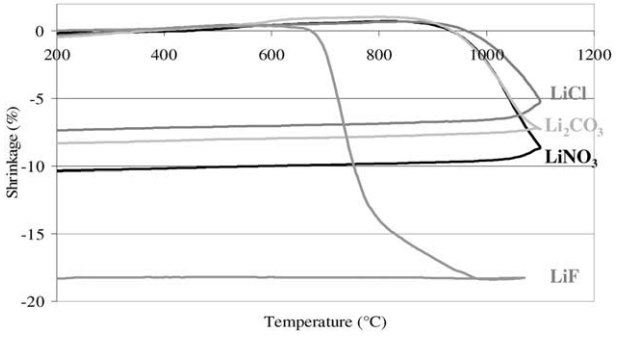

Fig. 4. Effects fo different lithium salts (Li amount equal to 8.24 mol%) on densficatiuon behaviour of the Mg/Ti = 1.025 composition.

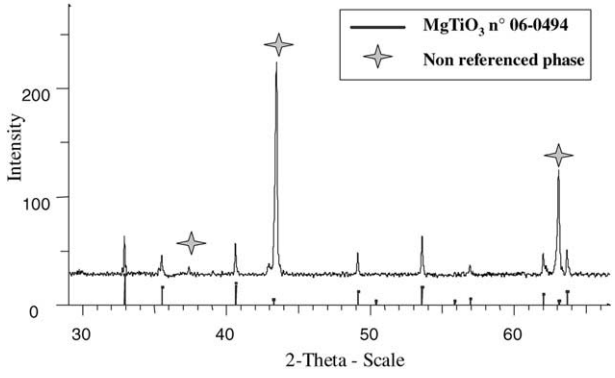

Fig. 5. Diffractogram of the surface of MgTiO3 Mg/Ti = 1.025 sintered with 8.24 mol% LiF addition.

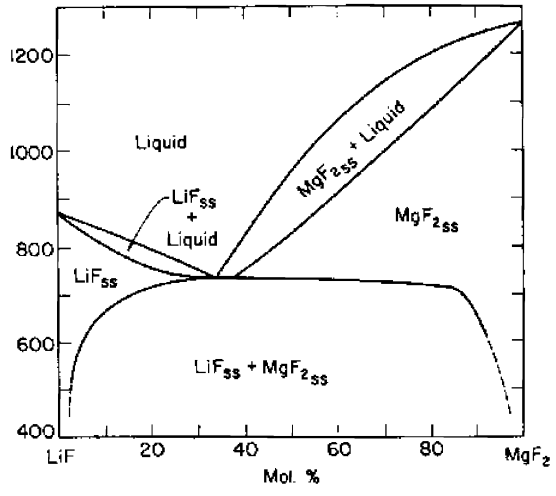

Fig. 6. Phase diagram of the system MgF2/LiF.

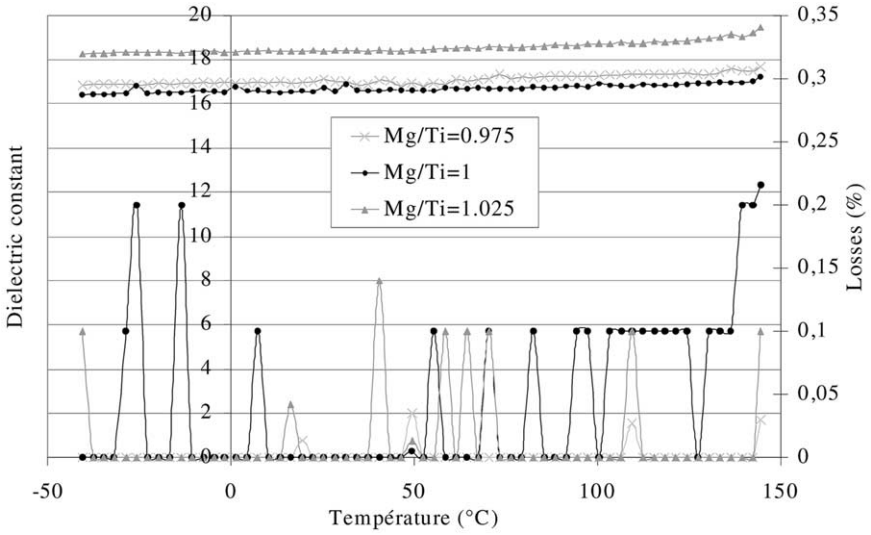

Fig. 7. Dielectric properties of MgTiO3 Mg/Ti = 0.975, 1, 1.025 + 8.24 mol% LiF vs temperature sintered at 1000 °C for 1 h under moist N2/1%H2 flow.

halides with all halide lithium salts, for example MgF_2/LiF[5] (Fig. 6) or $MgCl_2$/LiCl,[6] that all lead to an eutectic at very low temperature.

This point suggests that Li should enter the ilmenite cell in place of Mg. In the case of LiF, the fluorine can react with the expelled Mg, leading to MgF_2 that can form a solid solution with the remaining LiF. The formation of this solid solution can then explain the low temperature densification behaviour when $MgTiO_3$ is sintered with LiF, the phase diagram showing that such a solid solution can melt between 730 (eutectic temperature) and 880 °C (LiF melting temperature). This hypothesis is confirmed by a crystallographic simulation of Mg insertion in LiF structure, leading to a calculated X-ray diffractogram, which peaks correspond to the one of the unknown phase when the Mg amount is 0.1

So, in this hypothesis, contrariwise to $BaTiO_3$, lithium cations seem to be located at least in A site of the illmenite cell. We have thus to consider now the hypothesis of its acceptor behavior concerning the ability of the obtaining of a highly resistive material when sintered in a reducing atmosphere.

Even if the Mg/Ti = 0.975 and 1 compositions are less densified when sintered at 1000 °C under wet $N_2/1\%H_2$ than the 1.025 one, the electrical and dielectric properties of all the compositions are compatible with type I dielectric applications.

Resistivities are all higher to 2.10^{13} ohm cm. Dielectric constant $\varepsilon = 17$–18 and losses $tg\delta < 0.2\%$, stable in temperature (Fig. 7). These characteristics let us think that the material is not reduced during the sintering cycle. This may be explained with two complementary hypotheses:

- The sintering temperature is too low to permit the development of reducing mechanism in the wet $N_2/1\%H_2$ atmosphere;
- The acceptor character of Li^+ in site A of the illmenite structure leads to prevent the reduction behavior, according to Herbert model.

The first hypothesis can be prompted by the following observation: pure $MgTiO_3$ sintered at 1300 °C in an oxidizing atmosphere present a 1.10^{14} ohm cm resistivity together with dielectric losses $tg\delta < 0.2\%$, and, when annealed at 1000 °C in wet $N_2/1\%H_2$ atmosphere, a $0{,}8.10^{14}$ resistivity together with dielectric losses always lower than 0.2%. Annealed at higher temperatures in the same atmosphere, this ceramic presents lower resistivity characteristics. The second hypothesis can be prompted by a similar work devoted to barium titanate densification at low temperature with LiF additions,[7]

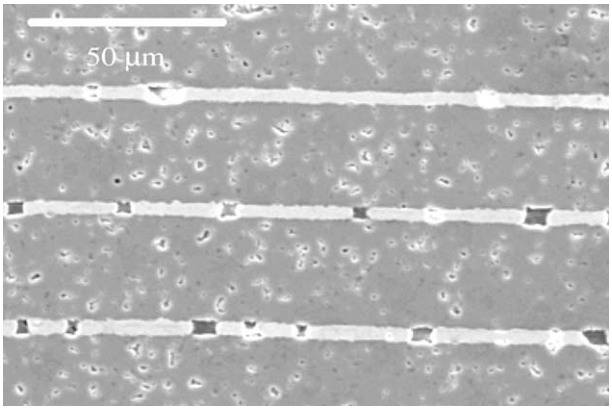

Fig. 8. SEM observation of MLCC (MgTi0.975O3 + 8.24 mol% LiF) with Cu electrodes sintered at 1000 °C under wet (N2/1%H2) gas flow.

this leading as well to high insulation resistances when sintered at 1000 °C in wet $N_2/1\%H_2$ atmosphere contrariwise to pure insulating $BaTiO_3$ annealed at 1000 °C in the same atmosphere.

4. Conclusion

This study shows the possibility of sintering $MgTiO_3$ at 1000 °C (compatible with Cu electrode) and the influence of the stoechiometry on the sintering behavior when $MgTiO_3$ is sintered with Lithium fluoride. The obtained electric and dielectric properties after sintering under a reducing atmosphere are compatible with type I application ($R > 2.10^{13}$, $\varepsilon = 17$–18, $\mathrm{tg}\delta < 0.2\%$). The insulation resistance values of the acceptor (Mn)/donor (W) codoped $MgTiO_3$ sintered with LiF are lower than the one without Mn and W. So contrary as in $BaTiO_3$ the Mn/W doping seems to be useless probably due to the acceptor character of Li^+ if lithium enters the ilmenite cell and also to the low sintering temperature, which don't permit the development of reducing mechanisms in $MgTiO_3$. Considering all these results, the composition $MgTi_{0.975}O_3 + 8.24$ mol% LiF was chosen to realize ceramic multilayer capacitors with Cu inner electrodes. The Fig. 8 shows the obtained multilayer structure after sintering at 1000 °C under moist $N_2/1\%H_2$. The electrical properties of these multilayers capacitors are to be characterized so the results will be publish in a next paper.

Acknowledgements

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