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Effects of acceptor and donor additives on the properties of $MgTiO_3$ ceramics sintered under reducing atmosphere

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Abstract

Sintered in reducing atmospheres, $MgTiO_3$ ceramics are known to own ionised oxygen vacancies and conduction electrons which give rise to very poor insulation resistance. Prompted by the example of $BaTiO_3$ ceramics where acceptor doping agents can trap the conduction electrons and donor doping agents compensate the acceptors in place of oxygen vacancies (Hagemann, H. and Hennings, D., Reversible weight change of acceptor-doped $BaTiO_3$. *J. Am. Ceram. Soc.,* 1981, **64,** 590–594), we have investigated on the effects of Mn acceptor and W donor doping agents on the properties of $MgTiO_3$ ceramics sintered under a reducing atmosphere of moist N_2–1%H_2. Resistivities higher than 10^5 MΩ.cm have effectively been obtained in these doped ceramics and dielectric constant of pure $MgTiO_3$ was proved not to be modified by the presence of doping agents. In order to study the possibility of employing these materials in the production of type-I ceramic multilayer capacitors with base-metal electrodes, co-sintering tests with nickel were investigated.

Keywords: Base metal electrodes multilayer capacitors; Capacitors; Dielectric properties

1. Introduction

Magnesium titanate based dielectric materials are classically used for producing type-I ceramic multilayer capacitors. Being sintered at a temperature higher than 1350°C, precious metal electrodes are to be used. In order to reduce the ceramic multilayer capacitors cost, one way is to replace the expensive noble metals by cheaper ones as nickel[2] or copper. This solution implies to sinter the capacitors in atmospheres such as N_2/H_2 or CO/CO_2. But 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. $BaTiO_3$ ceramics containing Mn acceptors and Mo, W or Nb donors were proved to show a high insulation resistance when fired in reducing atmosphere.[1] It has been shown that the conduction electrons can be trapped by incorporation of Mn^{2+} acceptor ions in the perovskite lattice and that the acceptors can be compensated in place of oxygen vacancies by donor ions like W^{6+}. Then it is assumed that donors and acceptors form complexes which mobility in the electric field is extremely low:[3]

$$\left(Mn_{Ti}^{2+}\right)'' + \left(W_{Ti}^{6+}\right)^{\cdot\cdot} \rightleftarrows \left\{\left(Mn_{Ti}^{2+}\right)''\left(W_{Ti}^{6+}\right)^{\cdot\cdot}\right\}$$

Prompted by these results, we have investigated on the effects of Mn acceptor and W donor doping agents on the properties of ilmenite $MgTiO_3$ ceramics sintered under a reducing atmosphere of moist N_2-1%H_2.

The experimental procedure followed is first described. The efficiency of the donor and acceptor doping agents on the electric properties of $MgTiO_3$ sintered under a reducing atmosphere was demonstrated and the possibility of co-sintering such ceramics with nickel investigated.

2. Experimental procedure

The studied ceramic materials have the following general composition:

$$Mg\left(Ti_{1-x}Mn_{x/2}W_{x/2}\right)O_{3-z}$$

with $0 \leqslant x \leqslant 0.02$ and z close to zero.

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MgO, TiO_2 and dopant oxides MnO_2 and WO_3 were weighed and milled together for 1 h in alcohol, using 2 mm in diameter zircon balls. Three compositions were prepared corresponding to $x = 0.005$; 0.01 and 0.02 and labelled M_1, M_2 and M_3, respectively. Calcination temperatures were estimated thanks to dilatometric measurements, which were performed in air on a TMA92 SETARAM dilatometer, and using a heating rate of 300°C h^{-1} and a cooling rate of 900°C h^{-1}. The dilatometric curves are shown Fig. 1. The phase formation begins around 800°C and finishes between 1100 and 1200°C, temperatures for which densification takes place. Three series of M_i, $i = 1$, 2 or 3, so-called $M_i(900)$, $M_i(1000)$ and $M_i(1200)$ were finally prepared, after one-hour calcination at 900, 1000 and 1200°C, respectively.

The calcined materials were systematically analysed by X-ray diffraction. The diffraction patterns were collected using a SIEMENS 5005 diffractometer with CuK_α ($\lambda = 1.5405$ Å), in the range 15–75°C (2θ). All of them show a single phase with ilmenite structure (space group R(-3); structure shown Fig. 2). As an example, Fig. 3 shows the diffraction pattern obtained for $M_2(1000)$. After calcination, new dilatometric measurements were performed on the different samples in order to estimate the firing temperature. The shrinkage curves recorded

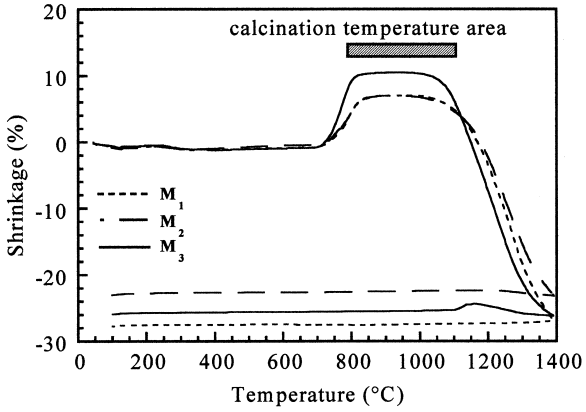

Fig. 1. Dilatometric curves before calcination for samples M_1, M_2 and M_3.

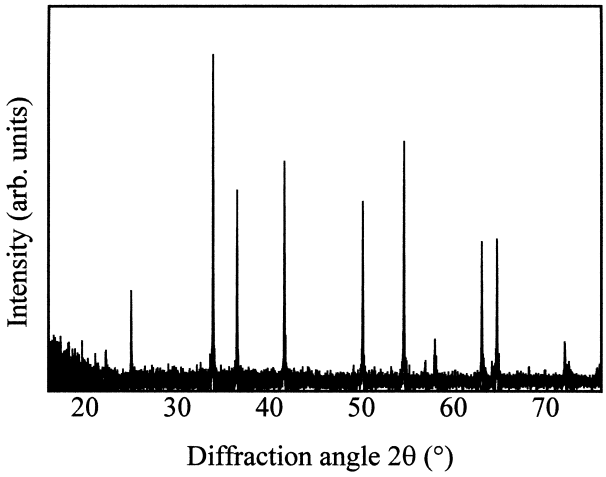

Fig. 3. X-ray diffraction pattern of $M_2(1000)$. The diffraction peaks correspond to a single phase with ilmenite structure.

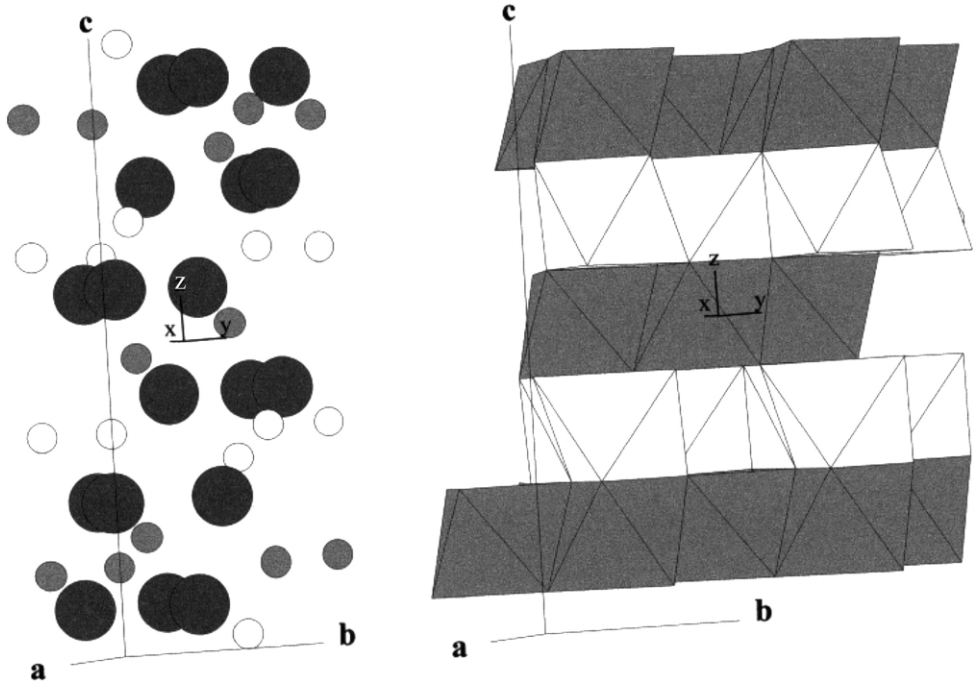

Fig. 2. Ilmenite structure. On the left are represented the different atoms: (i) the oxygen atoms in dark grey; (ii) the titanium atoms in clear grey and (iii) the magnesium atoms in white. The octahedral coordination polyhedrons of titanium (in clear grey) and magnesium (in white) are represented on the right of the figure.

on the samples $M_1(900)$, $M_1(1000)$ and $M_1(1200)$ are reported in Fig. 4. Shrinkage value decreases when the calcination temperature increases, while the temperatures corresponding to the beginning of the shrinkage are very close to each other, i.e. $\approx 1050°C$. For the three samples, the rate of shrinkage slows down beyond approximately 1200°C and sintering process seems finished at 1350°C. The same behaviour was observed for M_2 and M_3, so that the firing temperature was chosen at 1350°C.

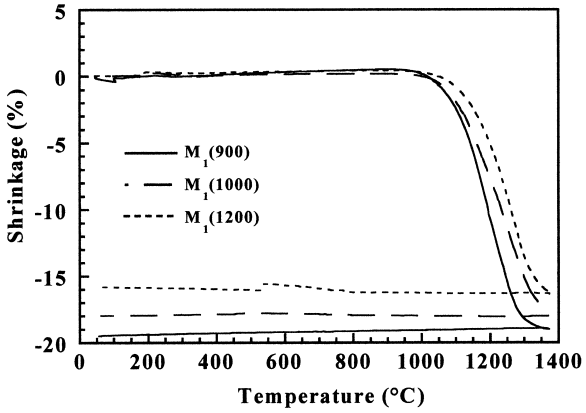

Fig. 4. Dilatometric curves of M_1 after calcination at 900, 1000 or 1200°C.

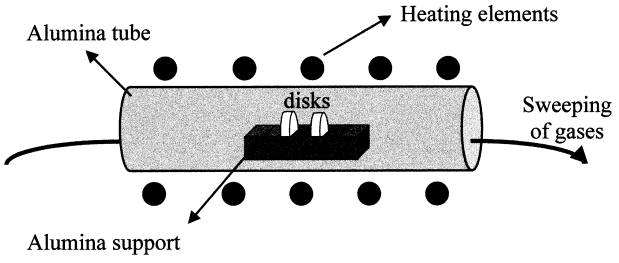

Fig. 5. Positioning of the disks in the tubular furnace.

All the calcined mixtures were pressed at 2000 kg cm^{-2} to obtain disks 15 mm in diameter and around 2 mm in thickness. The disks were then fired in a reducing atmosphere of moist N_2-1%H_2, with heating and cooling rates of 150°C h^{-1} and different soak-times ranging from 1 to 5 h at 1350°C. The position of the disks in the tubular furnace is described in Fig. 5. X-ray diffraction analysis of the fired disks confirmed all the ceramics to be single phased with ilmenite structure.

The microstructures of the sintered samples were observed with a scanning electron microscope HITACHI S-2460-N. The dielectric constant ε_r and the dielectric losses tanδ of the disks were measured at 1 kHz and the electric properties were recorded by applying a 1 kV DC bias at room temperature. The density of the samples was estimated using a helium Micromeritics Accu-Pyc1330 pycnometer.

3. Results

The first evidence is the efficiency of the doping agents Mn^{4+} and W^{6+} on the insulation resistance of $MgTiO_3$ sintered in a reducing atmosphere. Indeed, high insulation

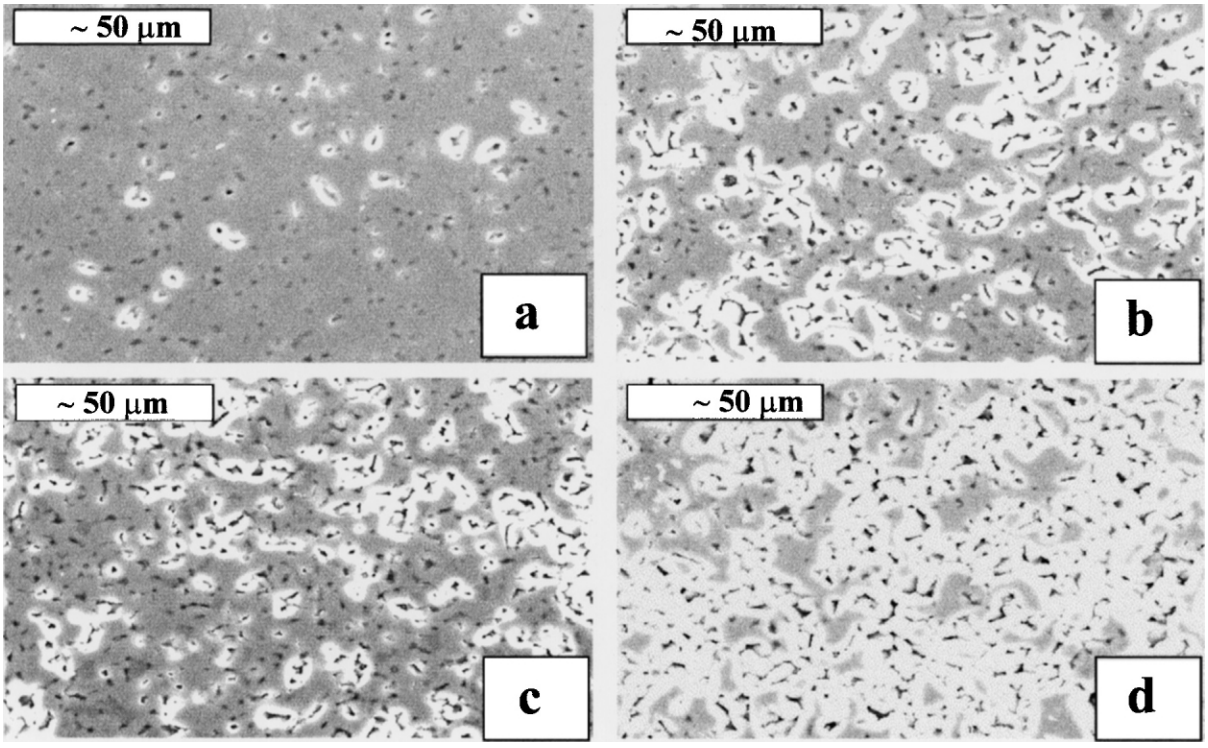

Fig. 6. Microstructures observed for (a) $MgTiO_3$, (b) $M_1(1000)$, (c) $M_2(1000)$ and (d) $M_3(1000)$.

Table 1
Samples characteristics after 1 h sintering at 1350°C under a reducing atmosphere of moist N_2-1%H_2

	Shrinkage (%)	Percentage of theoretical density	Electric resistivity (MΩ cm)	Tanδ (%)	Dielectric constant ε_r
$MgTiO_3$	18.5	96.7	Conductor	387	4.87e+05
M_1(1000)	18.3	93.3	1.85e+06	0.3	46.9
M_2(1000)	17.8	93.5	1.52e+05	3.4	32.9
M_3(1000)	15.3	94.7	3.44e+05	0.7	44.8

resistances (higher than 10^3 MΩ cm) were obtained with the different doped ceramics quoted before, whatever the x value (0.005; 0.01 or 0.02) and the calcination temperature (900, 1000 or 1200°C) are. On the other hand, pure $MgTiO_3$ was confirmed to be highly conductive.

The second evidence is that the presence of doping agents in $MgTiO_3$ gives rise to shrinkages and densities values smaller than the one observed with pure manganese titanate, related to a more important porosity. These parameters are still to be improved. As an illustration, microstructures of $MgTiO_3$, M_1(1000), M_2(1000) and M_3(1000) are compared in Fig. 6.

Then, it was shown that doping agents did not modify the dielectric constant of pure $MgTiO_3$, so that doped ceramics can be used as type-I capacitors. Low dielectric losses could finally be obtained, typically lower than 1%.

The best results after 1 h sintering in a reducing atmosphere at 1350°C were obtained for the samples calcined at 1000°C during 1 h. They are summarised Table 1. The percentage of theoretical density was obtained making the ratio of the measured density on the theoretical density of $MgTiO_3$ (d=3,894 g cm^{-3}). We can see in Table 1 that remarkable high resistivities could be obtained for these doped samples, since higher than 10^5 MΩ cm.

These materials are to be co-sintered with base-metal electrodes in multilayer capacitors. So, co-sintering tests of the ceramics with nickel were then carried out. Disks made up of a layer of nickel intercalated between two layers of ceramics were elaborated and then sintered at 1350°C during one hour in a reducing atmosphere. Fig. 7 represents the interface between nickel (on the right) and the M_2(1000) ceramic (on the left) after sintering. One can see that nickel diffused in the ceramic into an approximately 25 μm zone, which makes impossible the realisation of multilayer capacitors with such ceramics and metal.

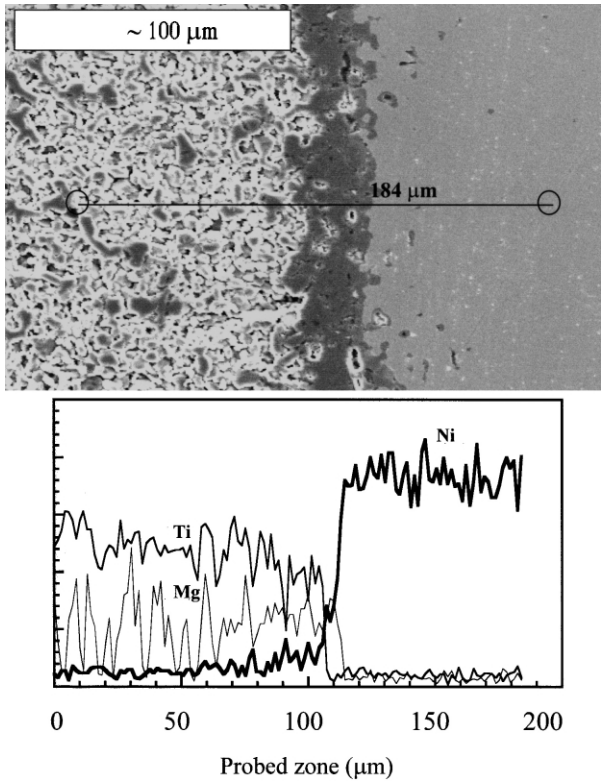

Fig. 7. Photograph and X-ray analysis of the transverse section of the M_2(1000) ceramic co-sintered with nickel.

4. Conclusion

Like in $BaTiO_3$,[1] the presence of Mn acceptor and W donor doping agents in $MgTiO_3$ allowed to obtain ceramics with high resistivities (higher than 10^5 MΩ cm) after sintering under a reducing atmosphere of moist N_2-1%H_2. Furthermore, it was shown that introducing these doping agents in the titanate magnesium ilmenite structure did not modify the dielectric constant. But it was proved that these doped ceramics could not be employed in the production of type-I ceramic multilayer capacitors with nickel electrodes, since this metal diffuses in the ceramic during sintering.

Within the framework of our collaboration with the TEKELEC-TEMEX society, we are actually studying the possibility of realising such type-I ceramic multilayer capacitors with copper electrodes. Using such metal requires to work at lower temperature (<1000°C), so that the role of different compounds as sintering aids is being investigated.

Acknowledgements

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