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Effect of hygrometry on dielectric materials

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Abstract

We have investigated the electrical properties of sintered disks elaborated from different type I and type II dielectric compositions by measurement of their insulation resistance versus the moisture content in air. The insulation resistance of the disks can reach values such as 10^{13} ohm when measured in dry air and 10^{8} ohm when measured in a wet atmosphere. This behaviour may be due to reversible surface reactions occurring at the surface of the dense ceramics.

Keywords: $BaTiO_3$ and titanates; Electrical properties; Humidity

1. Introduction

When studying dielectric materials for ceramic multilayer capacitors, it is currently admitted that an easy way consists of forming disks from powders, and then sinter these disks and study the dielectric and electric behavior of the densified ceramics.

Making such investigations when developing new materials, we noticed a high sensitivity of the measured insulation resistance of such disks on the moisture rate of air. So, we investigated on the insulation resistance of different type I and type II dielectric compositions for multilayer ceramic capacitor measured on disks in various moisture contents in air.

2. Experimental

All studied materials, the characteristics of which are reported in Table 1, except the I-6 one, are ceramic powders developed and effectively used for multilayer ceramic capacitors production. All type I are NPO, and all type II are either X7R or X7P materials. The type I $MgTiO_3$-based material noted I-6 is more precisely described elsewere.[1] Mixed with lithium fluorine, it can be sintered at 1000 °C in a reducing atmosphere together with copper electrodes. Main constituent and minor constituents present in these materials after sintering have been identified both by X-ray diffraction (Siemens D5005 diffractometer) and EDS (SEM HITACHI S-2460-N and OXFORD Link Isis).

Except for the I-6 one, all these materials were pressed into 10 mm diameter and approximately 1.5 mm thick disks and sintered in oxygen at a temperature previously determined by dilatometry. I-6 material was pressed into both a 10 mm diameter and a 50 mm diameter one and sintered at 1000 °C in a wet $N_2+1\%H_2$ atmosphere. After sintering, they were metallized with an In-Ga alloy except the two I-6 disks that was painted with a copper-based ink fired at 900 °C in a wet $N_2+1\%H_2$ atmosphere. Insulating resistance measurements were made in an oven (SECASI hot/cold oven SLH 100/70 with moisture rate regulated from 0 to 100% for temperatures higher than 10 °C), at 25 °C, with the moisture rate in air regulated from 10 to 70% (step of 10%, equilibration time of 30 min). We used a megohmmeter (SEFELEC sim 1000 A) for these measurements with a DC bias varying from 5 to 1500 V. Bias was applied some minutes before every measurement that was carried out only when stabilization occurred.

3. Experimental results

Fig. 1 shows the variation of the resistivity versus moisture rate in air at 25 °C for the different 10 mm

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Table 1
Different studied dielectric materials

Reference	Sintering temperature (°C)	Dielectric constant	Main constituent present after sintering	Minor constituents present after sintering
I-1	1100	35	$BaNd_2Ti_5O_{14}$	$Bi_4Ti_3O_{12}$
I-2	1100	29	$BaNd_2Ti_5O_{14}$	$MgTiO_3$
I-3	1100	20	$BaNd_2Ti_5O_{14}$	$Bi_4Ti_3O_{12}+Nd_2Ti_4O_{11}$
I-4	1350	15	$MgTiO_3$	Mg_2SiO_4
I-5	1125	23	$MgTiO_3$	$CaTiO_3$-
I-6	1000 °C N_2/H_2	17	$MgTiO_3$ "Li doped"	–
II-1	1100	3000	$BaTiO_3$	$BaBi_4Ti_4O_{15}$
II-2	1250	2500	$BaTiO_3$	–
II-3	1100	2500	$BaTiO_3$	Unidentified, Bi-containing

ceramic disks when a 1 V μm^{-1} DC bias is applied. Depending on every composition, resistivities fall down with 10 to the power of 2 to 5 drop values when humidity climbs up from 10 to 70%. For each ceramic disk, this phenomenon seems reproducible and occurs in each composition. Furthermore, all type I materials are characterized by curves which concavity is turned up while all type II materials show curves with their concavity turned down. This is only a simple statement of act, we do not suggest any explanation for this particular behavior.

This phenomenon seems highly fast, as it was impossible for us to estimate any delay between the change of moister content in air and the resistivity measurement. This observation does not allow us to consider any volume transformation of the material but exclusively a surface modification. So, we investigated further the surface behavior of the dielectric ceramics. Classically, when considering a conductor or a resistance screen printed on a surface, the easy concept to calculate the electrical resistance is the resistance by square. Let us consider Fig. 2 the outline of an electrical conductor or resistance with a length L, a width l and a thickness e. If ρ is the electrical resistivity, its resistance can be calculated as

$$R = \rho \frac{L}{l.e} = \frac{\rho}{e} \frac{L}{l}$$

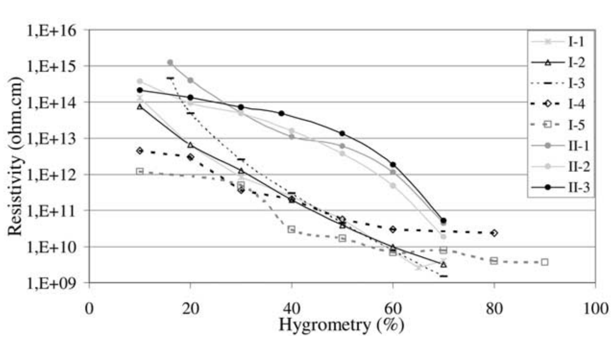

Fig. 1. Resistivity of the different ceramics at room temperature (25 °C) versus moisture content in air, DC bias 1V μm^{-1}.

where $\frac{\rho}{e}$ is called the resistance by square $R/\square$. It is then easy to get directly the value of the resistance of a conductor or an electrical resistance by multiplying $R/\square$ by the number of squares. For example, if the length of the resistance outlined Fig. 2 is twice its width, so two squares can be defined on it. The value of its resistance is thus 2* $R/\square$.

We focused thus our attention to the I-6 material, with the copper electrodes designed as schematized on Fig. 3. With such a geometry, the measured resistance gives directly the $R/\square$ value of the surface resistivity. Fig. 4 shows the measurement made at 25 °C with a DC bias equal to 1 V μm^{-1} between the two electrodes. The behavior is exactly the same as the one of the type I materials reported Fig. 1 related to measurements made on disks with a DC bias equal to 1 V μm^{-1}. This is a second evidence of a surface phenomenon.

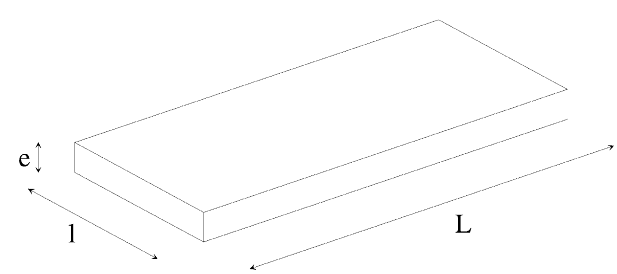

Fig. 2. Outline of a screen-printed resistance or conductor.

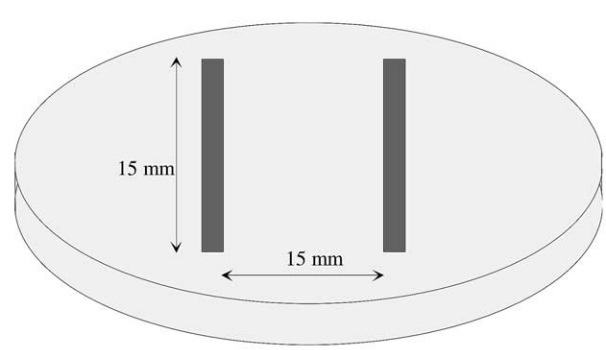

Fig. 3. Schedule of the electrodes screen-printed on the 50 mm disk.

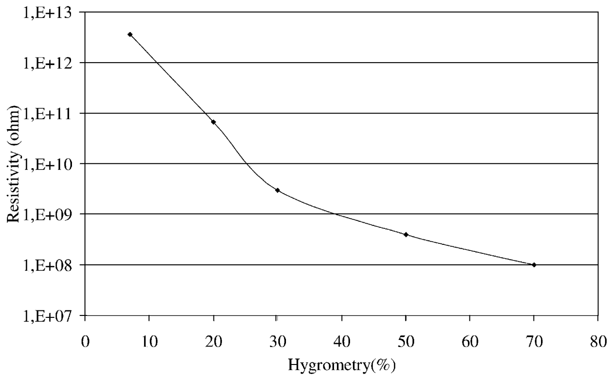

Fig. 4. $R_{/\square}$ versus moisture rate measured on surface of the 50 mm $MgTiO_3$ Li doped disk for a DC bias $=1V\ \mu m^{-1}$.

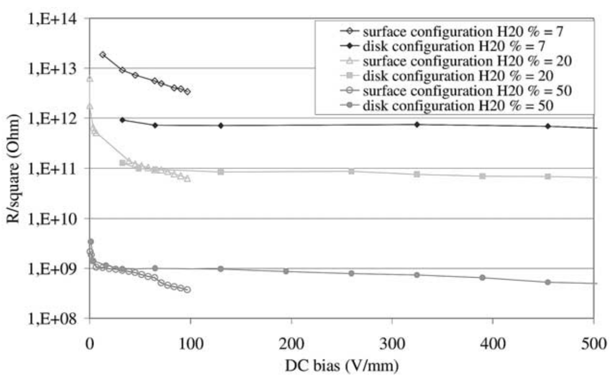

Fig. 5. Resistance by square measured on both disk and surface versus DC bias.

The problem is now to be able to appreciate the bulk resistivity of the material and differentiate it from the surface resistivity. The idea consists of considering (1) the configuration of two electrodes printed on the same surface of a dielectric material that permits the measurement of a pure surface conduction, and (2) the disk configuration that can be assimilated to two resistances in parallel, one consisting of the bulk of the material and the other one of the side of the disk that is a pure surface resistance.

We have made resistance measurements on both the disk configuration and the surface configuration of the same $MgTiO_3$ material and calculated the resistance by square in each case, considering then the disk composed of a perfect isolating material with some surface conduction. Fig. 5 shows, for three different moisture rates, the so calculated $R/\square$ versus the DC bias.

It is noteworthy that, for the two 20 and 50% rates, the behaviors observed on the disk and on the surface configuration are quite similar. For these rates, the value of the surface resistance of the disk is much lower then the bulk resistance, and, thus, the bulk resistance can be neglected. This point is far to be true when the moisture rate is low (<10 Y). In that particular case, surface resistance is high and of the same magnitude of the bulk one. If we admit that, for this paraelectric material, the value of the bulk resistivity is independent of the DC bias, we can deduce the value of the resistance by square of its surface for a 100 V/mm DC bias from the resistance measurement made on the disk. The so calculated $R/\square$ value is $2.24.10^{12}\ \Omega$, that is not far from $3.36.10^{12}\ \Omega$ directly measured with the surface configuration.

4. Conclusion

The surface conduction of dielectric materials seems to be a general behavior, particularly perceptible when characterizing dielectric materials for ceramic multilayer capacitors. Although we have not gone into too much details relatively to the slight difference of behavior observed between the type I and II dielectric materials, it seems evident that the surface conduction is due to adsorption of H_2O molecules on the surface of the dielectric materials.

A first and direct consequence of these observations is that, if insulation resistance measurements of a capacitor are made in a non-dried atmosphere, there is the risk that the measurement does not characterize the dielectric material but only its surface resistance. An estimation of the bulk resistivity can only be made with two measurements carried out in a low moisture containing atmosphere with both disk and surface configurations.

A second consequence of the existence of the surface conduction is that, when an electric field is applied to a ceramic capacitor, some materials transport can occur, especially materials coming from the electrodes of the capacitor, leading to the appearance of an undesirable leakage current. Furthermore, electrolytic processes can occur as well. These diffusion behaviors can be accelerated by temperature and, as we saw it, by moisture rate. This leads naturally to understanding the importance of the life accelerating life test so-called humid heat test.

References

1. Bernard, J., Houivet, D., El Fallah, J. and Haussonne, J-M., $MgTiO_3$ for base metal multilayer ceramic capacitors. *Electroceramics VIII, Rome, 25/28 aout*, 2002.