Surface resistance and sensitivity to hygrometry of various ceramic compositions for multilayer capacitors

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Abstract: When developing new dielectric compositions for multilayer ceramic capacitors, we have observed an influence of hygrometry on the insulation resistance behavior of some of them. The swiftness of the phenomenon let us suppose a surface mechanism. Prompted by these observations, we have investigated on the sensitivity to hygrometry of various conventional ceramic compositions by measuring their surface resistance versus the moisture rate in air. The studied materials are formulations for type I and type II ceramic capacitors. In order to understand some breakdown phenomena in ceramic multilayer capacitors, we have also investigated on the influence of the screen printed electrodes composition.

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

1. Introduction

Dielectric formulation used in multilayer ceramics capacitors must be no sensitive to the moisture rate in air. One aspect of the sensitivity to the humidity is the decrease of insulation resistance of the dielectric with the increasing rate of hygrometry. This sensibility to hygrometry can lead to major degradation when capacitors work under electric field particularly during the humid heat test. During this test breakdown phenomena, such as matter transport can take place into the dielectric. This transport of matter can come from the dielectric but also from the electrodes. In that case short circuit can occur between electrodes leading so to the final degradation of the component. This point out the importance of the electrode nature.

When developing new dielectric composition for ceramics multilayer capacitors we have observed a very rapid evolution of the insulation resistance correlated to variation of hygrometry. In order to know if our dielectric is too much sensitive to humidity, we have compared the sensitivity of our dielectric to those of commercial composition.

2. Experimental procedure

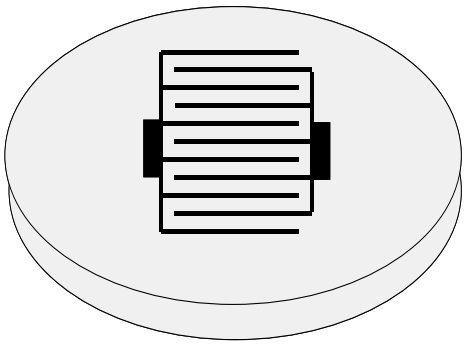
The dielectric studied materials are NPO for the type I and X7R for the type II the detail of their composition is given in the table 1.

Reference	Sintering Temperature	Dielectric Constant	Main constituent	Minor constituents present after sintering
I-1900nl	1100°C	110	$BaTiO_3$	Pb, Bi, Nd
I-2 cl900	1100°C	80	$BaTiO_3$	Pb, Bi, Nd, Ca
I-3 220B	960°C	20	$ZnTiO_3$	Mg, Ca, Ba
I-4	950°C	17	$MgTiO_3$ "Li doped"	-
II-1 302l	1100°C	3000	$BaTiO_3$	-
II-2 262 l	1140°C	2500	$BaTiO_3$	Pb, Bi, B
II-3 212L	1115°C	2000	$BaTiO_3$	Unidentified

All these compositions are commercial and reliable dielectrique only the I-4 composition was synthesize by us. The $MgTiO_3$ powders were synthesised by the classical solid-state route. The starting powders (MgO, TiO_2) were mixed together for one hour 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 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 CuKα (λ = 1.5405Å), in the range 15-85° (2θ)). After calcination lithium fluoride was added and the powders were milled in a planetary agitator (Pulverisette FRITCH with agate bawl and balls). Densification behavior were studied by 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 50 mm in diameter and around 1 mm thick. The disks were fired in air, with heating and cooling rates of $150°C.h^{-1}$ and dwell time of one hour at the temperature given by the manufacturer (see table n°1 for detail).

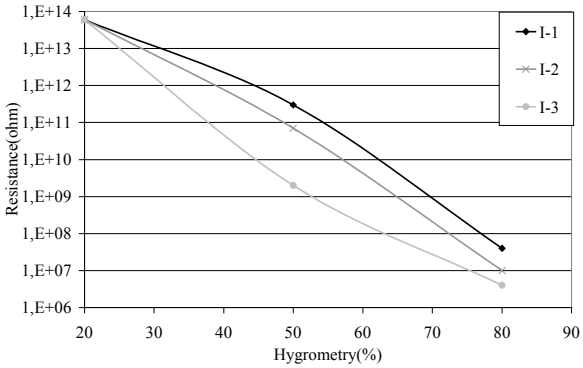
After sintering a motif was silk-screen printed on the surface of the samples in order to obtain the following outline.

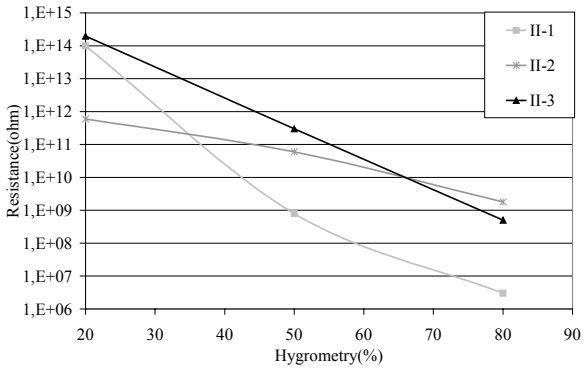


The length of the electrodes is 16 mm for 1 mm width, the space between two electrodes 1 mm. Two metals were used, gold and silver. After screen-printing, the sample were calcined at 850°C during 15 minute with heating and cooling rate of 300°C/H in air. This geometry of inter digitated electrode allows to divide the surface resistance. It correspond at 10 resistances in parallel and so the equivalent resistance is divided. The insulation resistances were measured under various hygrometry rates with a Sefelec (SIM 1000 A) megohmeter. Temperature and hygrometry were regulated with a SECASI hot/cold oven. Measurement were done with the same equilibrium time for each rate of hygrometry: 15 minutes.

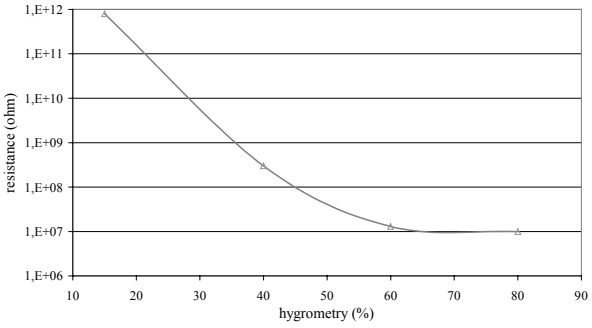
3. Results

As shown on figure 1 and 2 the surface resistances of all dielectric compositions(type I and II) fall down with the increasing of humidity rate. Even if these results are given in resistance and no in resistivity, the design of the electrode is the same for each samples, so results can be compared.





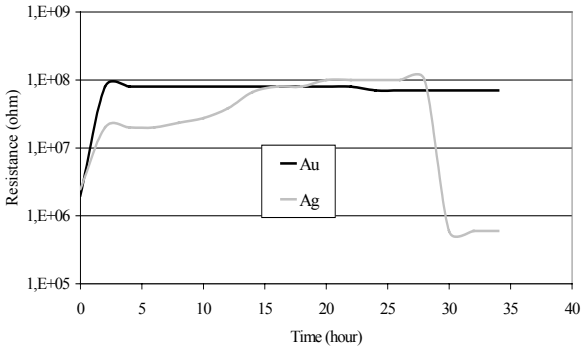
No differences between type I and II can be observed, for all composition surface resistances fall down for 10^{14} ohm to around 10^{8} ohm. Only one compositions don't reach the 10^{14} ohm in dry atmosphere. These measurements don't mean that all studied dielectric composition have the behavior towards hygrometry because response time can be different but are not studied here but it show that most of all dielectric ceramics are sensitive to hygrometry. This phenomenon also occurs on the formulation based on $MgTiO_3$ with lithium salt developed by us.



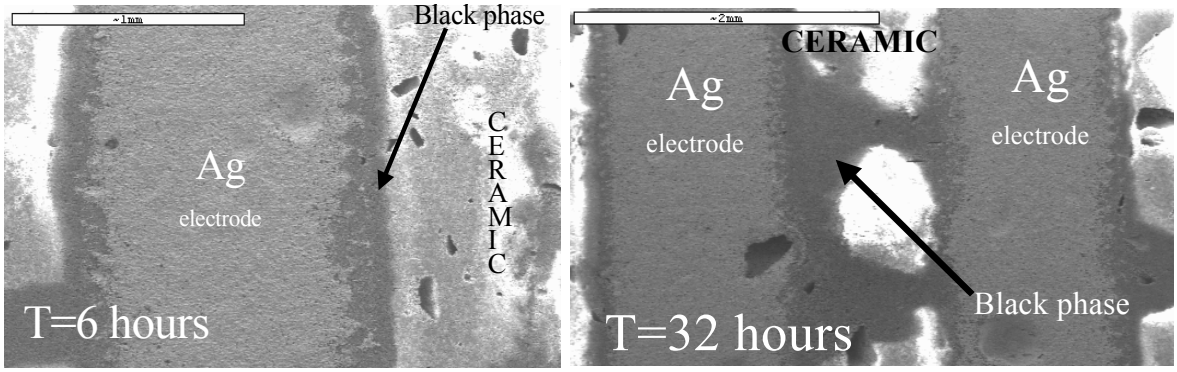
This point is not surprising if we consider the mechanisms of water adsorption on oxides exposed by Traversa[1].

The influence of electrode can be neglected if we try to understand the degradation during the humid heat test. Some oxidation phenomena can occur and migration inside the ceramics can take place[2]. Today ceramic capacitors industry trend to use pure silver inner electrode. However silver is well known to diffuse under electric field. This diffusion can be modified during humid heat test by oxidation phenomena. In order to investigate the electrode nature effect we have screen play the interdigitated electrodes with two different metal: gold and silver on the I-3 dielectric.

We have recorded the insulation resistance under 40°C and 80% of relative hygrometry during 34h. It appears that fist resitance increase for both electrodes silver and gold. During 30 hours the insulation resistance keep quite constant, but suddently the resistance of the sample with silver electrodes fall down 10^9 ohm to 6.10^5 ohm. The sample with gold electrodes dont present the same phenomenon.



The positive electrode of the silver sample is black and seem to diffuse at the surface of the ceramic. The same experiment was done once again and SEM invastigation were realise during the experiment. These investigations shows clearly the blackish phase extention in the ceramic.



When the fall down of insulation resistance take place, blackish phase is continuous between the electrodes. EDS analysis put in evidence that this phase contain silver.

4. Discussion and conclusion

We can exclude that the black phase is silver metal because in that case the sample will be in short circuit and insulation resitance mesured will be lower than the one we have measured (10^5 ohm). The phase aspect, and the polarity of the electrode (+) where phenomenon start let us think to silver oxyde. This point is correlated by the fact that the electrodes don't turn black when the same experiment is done in dry atmosphere (5% of relative hygrometry). So, even if in multilayers ceramics capacitors inner electrodes are not exposed directly to humidity, pure silver seem to be to easily oxidable to pass the humid heat test. We have try to used not pure silver anymore but an alloy of silver and paladium. The phenomenon of oxydation seem to occur once-again but not so quickly as for pure silver. It's possible that for a long time of exposure under heat and humidity the same break-down phenomena occurs than for pure silver. So it's seem more reasonable to introduce some paladium in silver electrode considering the humid heat test.

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[1] E.Traversa. « Ceramic sensors for humidity detection : the state of the art and future developments» Sensors and actuators B, 23, 1995, 135-156.

[2] Wenmin Qu «Effect of electrode materials on the sensitive properties of the thick-film ceramic humidity sensor», *Solid State Ionics, Vol 83, Issues 3-4, 1996, 257-262*