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

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Abstract

Developing new dielectric compositions for multilayer ceramic capacitors, the authors of this work 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 the sensitivity of various conventional ceramic compositions to hygrometry 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 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 not be sensitive to the moisture rate in air.[1] One aspect of the sensitivity to 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 to the final degradation of the component. This points out the importance of the electrode nature.

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

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 Table 1.

All these compositions are commercial and reliable dielectrics only the I-4 composition was synthesized by us. The $MgTiO_3$ powders were synthesised 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 stabilised 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 ($\lambda = 1.5405$ Å), 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 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 50 mm in diameter and around 1 mm thick. The disks were fired in air, with heating and cooling rates of

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Table 1
Description of the studied dielectric compositions

Reference	Sintering temperature (°C)	Dielectric constant	Main constituent	Minor constituents present after sintering
I-1	1100	110	$BaTiO_3$	Pb, Bi, Nd
I-2	1100	80	$BaTiO_3$	Pb, Bi, Nd, Ca
I-3	960	20	$ZnTiO_3$	Mg, Ca, Ba
I-4	950	17	$MgTiO_3$ "Li doped"	–
II-1	1100	3000	$BaTiO_3$	–
II-2	1140	2500	$BaTiO_3$	Pb, Bi, B
II-3	1115	2000	$BaTiO_3$	Unidentified

150 °C h^{-1} and dwell time of 1 h at the temperature given by the manufacturer (see Table 1 for details).

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 and the space between two electrodes 1 mm. Two metals were used, gold and silver. After screen-printing, the samples were calcined at 850 °C for 15 min with a heating and cooling rate of 300 °C h^{-1} in air. This geometry of inter digitated electrode allows to divide the surface resistance. It corresponds to 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. Measurements were done with the same equilibrium time for each rate of hygrometry, 15 min.

3. Results

As shown in Figs. 1 and 2 the surface resistances of all dielectric compositions (type I and II) decrease with the increasing of humidity rate. Even if these results are given in resistance and not in resistivity, the design of the electrode is the same for each sample, so results can be compared (Fig. 3).

No differences between type I and II can be observed. For all compositions surface resistances fall down for 10^{14} ohm to around 10^{8} ohm. Only one composition does not reach the 10^{14} ohm in dry atmosphere. These measurements do not mean that all studied dielectric compositions have the same behavior towards hygrometry because response times can be different but are not studied here. However, but it show that most dielectric ceramics are sensitive to hygrometry. This phenomenon also occurs in the formulation based on $MgTiO_3$ with lithium salt developed by us (Fig. 4).

This point is not surprising if we consider the mechanisms of water adsorption on oxides exposed by E.Traversa.[2]

The influence of the electrode can be neglected, if we try to understand the degradation during the humid heat test.

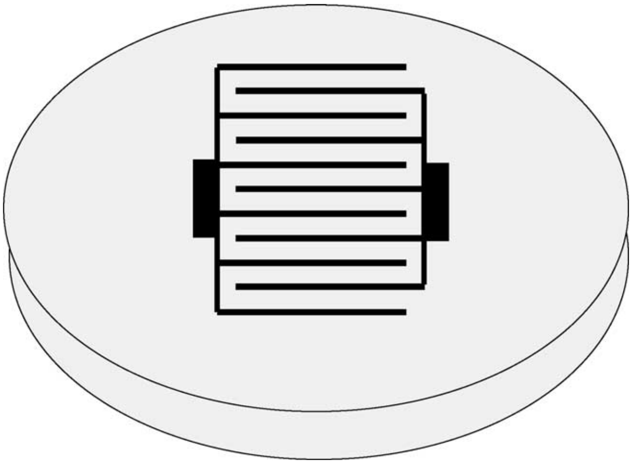

Fig. 1. Scheme of the screenprinted electrodes.

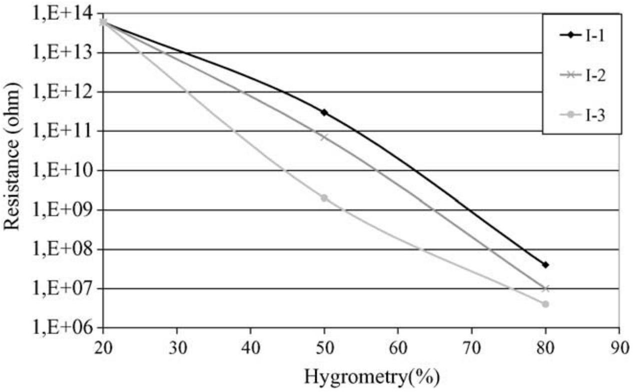

Fig. 2. Insulation resistances of type I dielectric composition vs. moisture rate in air at 25 °C.

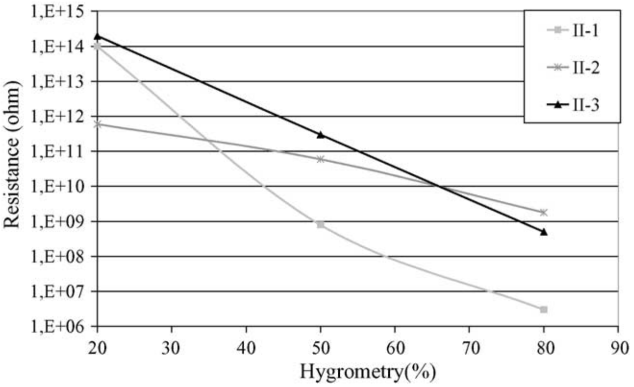

Fig. 3. Insulation resistances of type II dielectric composition vs. moisture rate in air at 25 °C.

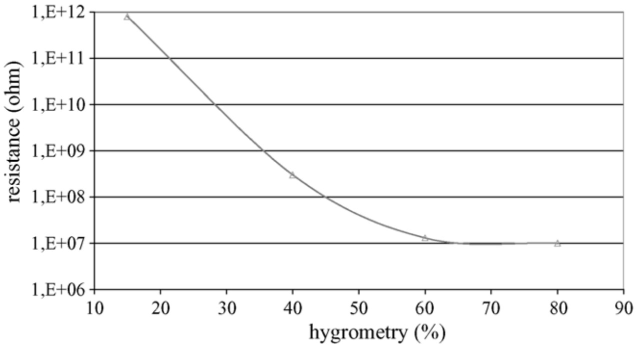

Fig. 4. Insulation resistances of $MgTiO_3 + LiF$ vs. moisture rate in air at 25 °C.

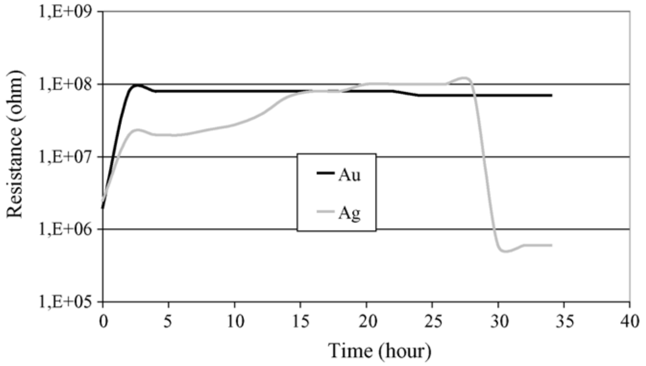

Fig. 5. Evolution of the insulation resistance vs. time at 40 °C and 80% of relative hygrometry.

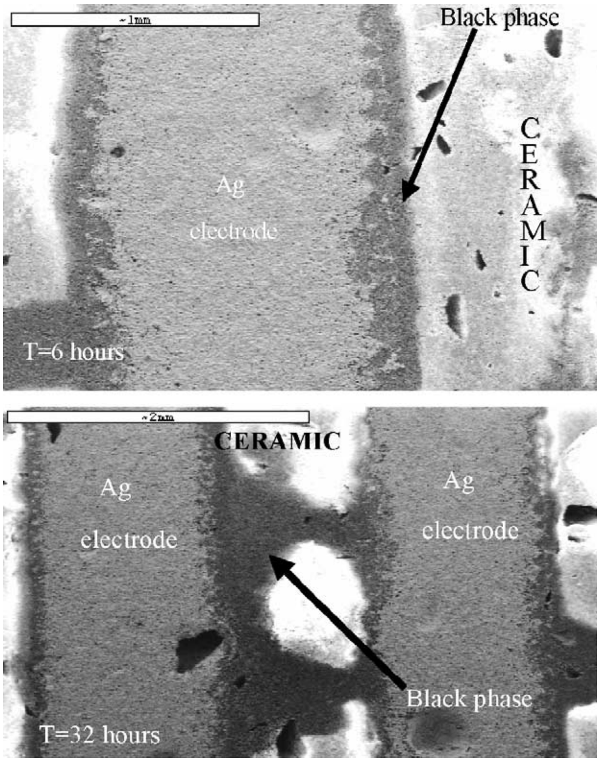

Fig. 6. SEM micrography of the sample with silver electrodes after 6 h and 32 h of test.

Some oxidation phenomena can occur and migration inside the ceramics can take place.[3] Today the ceramic capacitors industry tends to use pure silver inner electrodes. However, silver is well known to diffuse under electric fields. This diffusion can be modified during humid heat tests by oxidation phenomena. In order to investigate the electrode nature effect we have screen play the interdigitated electrodes with two different metals: gold and silver on the I-3 dielectric.

We have recorded the insulation resistance under 40 °C and 80% relative hygrometry during 34 h. It appears that initially resistance increase for both silver and gold electrodes. For 30 h, the insulation resistance keep quite constant, but suddenly the resistance of the sample with silver electrodes falls from 10^9 to 6×10^5 ohm. The sample with gold electrodes does not present the same phenomenon (Fig. 5).

The positive electrode of the silver sample is black and seems to diffuse at the surface of the ceramic. The same experiment was done once again and SEM investigations were realised during the experiment. These investigations show clearly the blackish phase extension in the ceramic (Fig. 6).

When the fall of insulation resistance takes place, blackish phase is continuous between the electrodes. EDS analysis revealed that this phase contains silver.

4. Discussion and conclusions

We can exclude that the black phase is silver metal because in that case the sample will be in short circuit and insulation resistance will be lower than the one we have measured (10^5 ohm). The phase aspect, and the polarity of the electrode (+) where the phenomenon starts lead us to think of silver oxide. This point is correlated by the fact that the electrodes do not turn black when the same experiment is done in dry atmosphere (5% relative hygrometry). So, even if in multilayer ceramic capacitors inner electrodes are not exposed directly to humidity, pure silver seems to be too easily oxidable to pass the humid heat test. We have tried not to use pure silver anymore but an alloy of silver and paladium. The phenomenon of oxidation seems to occur once again but not so quickly as for pure silver. It is possible that for a long time of exposure under heat and humidity the same breakdown phenomena occurs as for pure silver. So it seems more reasonable to introduce some paladium in silver electrodes considering the humid heat test.

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