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Conference Report

3RD INTERNATIONAL JOINT MEETING ON ELECTRICAL AND MAGNETIC CERAMICS AT NOORDWIJKERHOUT, THE NETHERLANDS 17th–18th November, 1977.

This was an International Conference with participants from 15 countries; the majority being from West Germany and Holland.

The major topics were ferrites, dielectrics, positive temperature coefficient (PTC), barium titanate resistors, voltage dependent resistors (VDRs) made from zinc oxide, and the various forms of piezoelectric lead titanate zirconate.

PTC barium titanate has recently been the subject of a series of papers from the Philips Aachen laboratories which have established a model based on the formation of vacant sites during sintering, their diffusion during cooling from sintering and their subsequent functioning as sources and traps for current carriers under normal room temperature conditions. This explains most of the phenomena associated with the preparation and use of PTC devices. It was the basis of the many papers at the present meeting and indicated the continued interest by Siemens and Philips. The existence of practical problems was indicated by a Siemen's paper describing the mechanical failure of devices used to control the switching surge in motor windings. The damage was thought to be associated with thermal stresses.

Zinc oxide VDRs are likely competitors with silicon diodes and spark gaps for the protection of integrated circuits from transients. They are an appreciable advance on the present VDRs based on silicon carbide and may be less expensive than silicon diodes at higher voltages. Their raw materials are cheap and they are made by the familiar powder pressing and sintering process. It is not entirely clear how they work so that the manufacturing details are highly empirical but there may be a considerable market for them in, for instance, telephone systems.

There appears to be quite a bit of effort going into the development of low cost high dielectric constant ceramic chip capacitors with the elimination of platinum and palladium from the electrodes as a primary objective. One paper described a dielectric with a K of about 1000 and a sintering temperature compatible with the use of silver. The theoretical model referred to above for PTC resistors also explains the way manganese oxide protects barium titanate from the action of hydrogen and so enables it to be sintered along with a nickel electrode system to give an insulating dielectric (K = 3000). In this connection the BME chip capacitors with nickel electrodes advertised by Globe Union a year ago offer the best properties I have yet seen (K = 5000: leakage about 2000 sec. at 20°C). There is also the Truman Rutt process where a low melting alloy is injected into porous layers between the dielectric layers in air-fired monolithic structures. Little has been heard of this in the past 2–3 years: it may have run into practical problems.

There is a modest revival of interest in very low loss and very low temperature coefficient ceramics for microwave cavities. There are several possible systems and the present concentration on the higher titanates of barium seems rather arbitrary (a matter of following the Bell lead) but it could be a system in which the properties are less sensitive to small compositional changes than most.

The piezoelectric papers reflect current interest in optically active materials but largely consist of dotting the i's in the Sandia work. AEG-Telefunken seem to be developing a similar material to ours for pyroelectric detectors. One paper on a PZT type ceramic for SAW devices indicates that this approach may still be of interest.

Below is a complete list of the papers given in the field of PTC and Varistor Ceramics, Dielectric Ceramics and Piezoelectric Ceramics. A few notes on papers of particular interest are appended. All the papers given at the meeting will be published in a special issue of *Berichte der Deutschen Keramischen Gesellschaft* which is due to appear in July, 1978.

PTC and Varistor Ceramics

Heterogeneous microstructure of donor-doped $BaTiO_3$ by B. Hoffmann and A. S. Janitzki, Institute of Technology, Karlsruhe.

An attempt to explain the properties of positive temperature coefficient (PTC) barium titanate by postulating other phases in the grain boundaries.

The PTC effect of semiconducting $BaTiO_3$ ceramics as a function of the titanium excess by H. Ihrig, Philips, Aachen.
The PTC effect shows a maximum for a 5 atom % excess of Ti. However, the effects of a grain boundary phase are supposed to be due solely to its influencing the surface states of the conducting $BaTiO_3$ grains.

The shock resistance of 'cold conductors' (PTC resistors) by K. Lubitz, Siemens.
PTC resistors in series with motor windings tend to crack during the heating up period in switching on, i.e. after about 0.5 sec. As at this point about 1 kW is being dissipated in an 18 mm diameter 7 mm thick piece of ceramic, high thermal stresses are clearly possible.

Behaviour of ZnO varistors at low temperature by L. M. Levinsen and H. R. Phillipp, G. E. Schenectady.
3.5° to 300°K measurements confirm the usefulness of a model in which conducting grains of zinc oxide are immersed in a semiconducting matrix.

The preparation and properties of ZnO varistors by B. Knecht and H. P. Klein, Brown Beveri & Co.
There was nothing on preparation but a model was introduced in which the interstitial material was merely given the role of controlling the surface states of the ZnO grains. This led to an appreciation of the effect of grain size on properties.

Doping effects in metal oxide-varistors by R. Einzinger, Siemens.
The author ascribes the behaviour to oxygen deficiencies in the ZnO lattice. These can be rendered unstable by the presence of Mn^{4+} ions. Mn^{4+} can be replaced by Co^{2+} which gives stable material. Co is therefore the really essential doping ion, the others controlling such parameters as grain size. On this model the function of the intergranular phase becomes insignificant.

Direct determination of barrier voltage in ZnO varistors by J. T. C. van Kemenade and R. K. Eijnthoven, Philips, Eindhoven.
Quite definite potential barriers can be measured at grain boundaries averaging about 3.5 V. Other values (down to 2 V) were claimed during discussion but the great significance of grain boundaries seemed to be firmly established experimentally.

Dielectric Ceramics

Ceramic and dielectric properties of selected compositions in the $BaO-TiO_2-NCl_2O_3$ system by D. Kolar, Z. Stadler, S. Gaberšček and D. Suvorov, J. Stefan Institute, Univ. of Ljubljana.
A systematic phase diagram investigation yielding low loss ceramics, but with temperature coefficients of permittivity greater than −50 ppm/°C. Any lower t.c.c. is strongly composition dependent.

Effects of chemical treatment on loss quality of microwave dielectric ceramics by H. M. O'Bryan Jr., J. Thomson and J. K. Plourde, Bell Laboratories.
A very low temperature coefficient of permittivity has been found for the material $Ba_2Ti_9O_{20}$ and the value is not acutely dependent upon composition.

Interaction between metallic films and dielectric ceramic substrates during sintering of the ceramics by A. Peigniez, M. Marchal and N. Gérard, University of Dijon and Thomson C. S. F.
This was concerned with chip capacitors and the way in which thin metal layers break up into globules during sintering. Thus a 1.5 micron thick layer of Pd will give 90% coverage of a surface after sintering at 1400°C while a 1.0 micron layer only gives 20% coverage. This is all part of the problem of economising in precious metal.

Electrical properties of acceptor doped $BaTiO_3$ ceramic by H.-J. Hagemann, Philips, Aachen.
A model which explains why capacitors can be made with base metal electrodes. The objective is cheaper chip capacitors.

The influence of microstructure on the electrical properties of intergranular capacitors by R. Wernicke, Philips, Aachen.
A model for barrier layer capacitors which operate in the 10 V region.

Liquid phase sintering of barium titanate by D. Hennings, Philips, Aachen.
The objective is to reduce the sintering temperature of barium titanate to a level where silver might be substituted as electrode material in chip capacitors. It appears difficult to control crystal growth using the method discussed.

Low sintering ceramic dielectrics by H. Hoppert and H. G. Hoffmann, Dralovic Electronic GmbH.
Again the objective is to reduce the sintering temperature of barium titanate and this is done by using a relatively large proportion of a glassy phase. Chip capacitors with silver electrodes with permittivities of 1000 have been made.

Piezoelectric Ceramics

The influence of the geometry of piezoelectric ceramic plates on the properties of bending mode oscillation by J. Deckert. AEG-Telefunken.

A very specialised paper on mechanical oscillation for 10 to 100 kHz filters.

Grain growth in PLZT ceramics by G. Wolfram, Siemens.

An optical examination of the small signal response of 90° domain walls in transparent PLZT-ceramics, by P. Gerthelm and R. Send, Karlsruhe University.

An explanation of 90° domain wall motion in fine grained PLZT ceramic.

Ageing phenomena in reduced PLZT ceramics by J. Gentner, Karlsruhe University.

Gives a model for ageing effects based on the diffusion of oxygen vacancies.

Dielectric properties of rare earth (III) substituted lead titanate ceramics by K. Keizer and A. J. Burggraft, Twente University of Technology.

The permittivity is calculated as a function of temperature with some success (below the Curie point).

Ternary systems based on P6 (Ti, Zr)O_3 for pyroelectric applications by R. R. Zeyfang and R. M. Henson, AEG-Telefunken.

A preferred system is established for pyroelectric elements, namely Pb(Zr, Ti ($Fe_{1/2}Ta_{1/2}$))O_3

Piezoelectric ceramics for surface wave elements by W. Christoffens, E. Eckert and H. Schichl, SEL-Research Centre.

Permittivities of less than 300 and frequency constant temperature coefficients of about 30 ppm/°C are claimed for compositions rather similar to those discussed by Zeyfang and Henson.

Relaxation phenomena connected with the pyroelectric effect in the paraelectric phase of barium titanate by P. Sasko. Material and Electrotechnical Institute, RWTH, Aachen.

Largely a confirmation of the established model.

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The Plessey Co Ltd
Allen Clark Research Centre
Caswell
Northants
U.K.