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Résumé - Les propriétés électriques en courant continu et alternatif des thermistances CTP ont été étudiées dans l'intervalle de température (30-450°C). Le modèle de Heywang seul ne permet pas une interprétation quantitative des résultats. Il est nécessaire de prendre en compte l'hétérogénéité du système.

Abstract - The dc and ac electrical properties of PTC barium titanate ceramics were measured in the temperature range from 30 to 450°C. The Heywang's model alone is not sufficient to perform a quantitative analysis of the results. The heterogeneity of the system is taken into account.

I - Introduction

It is well known that the n-type doped polycrystalline barium titanate ceramics show a particular resistance-temperature curve. They are of low resistance at room temperature and become rapidly insulating above a critical temperature Tc (about 120°C), an example of which is given in Fig.1. For this reason, they are called PTC (Positive Temperature Coefficient) thermistors. It has been clearly proved that the PTC effect is a grain boundary property /1/ and the mechanism of the PTC effect is essentially explained by the Heywang's model /2/. Above Tc, the high resistance stems from the presence of potential barriers at the grain boundaries. The variations of the resistivity with temperature are concomitant to those of the dielectric constant of the material according to the Curie law. At Tc, the para-ferroelectric transition occurs and the spontaneous polarization sets in. Below Tc, this polarization partially compensates for the interface charge associated with the Schottky barriers. The potential barriers at the grain boundaries are strongly lowered. In this paper we present and discuss the dc and ac electrical properties of PTC thermistors. It is concluded that the Heywang's model alone is not sufficient to perform a quantitative analysis. We develop a new approach based on percolation arguments to have a better understanding of the PTC characteristics.

II - Experimental

PTC samples whose final composition was $BaTiO_3$ + 1mol%TiO_2 + 0.2mol%Y_2O_3 + 0.08mol%MnO + 2mol%SiO_2 were prepared by a conventional solid-state reaction process. The mixed powders of $BaCO_3$ and oxides were calcined at 1200°C for 2h, pressed into disks, and sintered at 1350°C for 2h. NiCr films were evaporated on the disks as ohmic electrodes.
The temperature-resistance characteristics were measured on using a dc technique. A dc bias in the ohmic region (<5V) and a heating/cooling rate less than 1K/min were employed for the measurements in the temperature range (30-450°C). The characteristics for heating and cooling were identical within the experimental error.
The ac measurements were conducted as a function of frequency (10mHz<f<1MHz) in the temperature range from 30 to 450°C.
In those conditions, the measured impedance or resistance was essentially

that of the grain boundaries.

III - Results and discussion

It is taken into account in the Heywang's model /2-8/ that the specific electronic structure of the interface is defined by an interface density states Ns(E) and a Fermi level E_{F0} in such a way that the interface is neutral if the states are occupied up to E_{F0}. If E_{F0} is lower in energy than the bulk Fermi level E_F, then conduction electrons migrate from the neighboring grains towards the interface to occupy additional states. A negative charge Q builts up at the interface. According to Poisson's law electric field and potential exist in the depleted regions. The potentia barrier height Vi and grain boundary conductivity σgb are described as follows :

$$Vi = \frac{Q^2}{2qNd\varepsilon_0 \varepsilon} \quad (1) \quad \text{and} \quad \sigma gb = \sigma_0 \exp\left(-\frac{qVi}{kT}\right) \quad (2)$$

where q is the elementary charge, Q is the total interface charge, ε is dielectric constant in the vicinity of the grain boundary, Nd is the don concentration in the adjacent grains. In the paraelectric state, i.e. ab Tc, the dielectric constant obeys the Curie law :

$$\varepsilon = \frac{C}{T - To} \quad (3)$$

where C and To are characteristics of the material. By definition, Q is given by :

$$Q = \int_0^{Eg} \frac{Ns(E)\, dE}{1+\exp[(E+qVi-E_F)/kT]} - \int_0^{Eg} \frac{Ns(E)\, dE}{1+\exp[(E-E_{F0})/kT]} \quad (4)$$

The solution of Eqs.(1) and (4) can be found numerically or graphically depicted in Fig.2. Slightly above Tc, the dielectric constant is high. Tl amount of the interface charge is maximum, i.e. all the interface states occupied, and the potential barrier is low . In those conditions, depict as regime I in Fig.2, the potential barrier increases linearly with temperature. Above a given temperature Tm, however, it goes into regime which is characterized by a decrease of the interface charge. The potent barrier is almost constant and can even decrease.

The variation of Vi with the temperature can be derived from the experimental data on using Eq.(2). The curve obtained for the data plott in Fig.1 is reported in Fig.3. In agreement with the theoretical predictions, a linear behavior can be seen up to 180°C, the slope of whi depends on Qmax and Nd. The latter has been reported to be $3x10^{24} m^{-3}$ in a previous publication /9/ and therefore Qmax is equal to 0.2 Cb/m^2. Abo 260°C, i.e. Tm, a decrease of Vi is observed associated with regime II. Theoretically, the most rapid decrease of Vi(T) is predicted for a very narrow distribution of interface states such as a delta function, Ns(E)= No.δ(E-Eo) if No is the density of states associated with the trap level Then, Vi(T) decreases linearly with the temperature in the region T>>Tm

$$qVi(T) = Eg-Eo - kT \ln(Nc/Nd) \quad (5)$$

where Nc is the conduction band density of states of barium titanate and about $2x10^{27} m^{-3}$ /10/. This equation permits us to have an upper estimate of Nd. The value estimated from Fig.3 is about $2x10^{22}$ m^{-3}, very different from the value already quoted above. It is preliminarily concl from the dc results that the Heywang's model is not entirely satisfactor We propose that the heterogeneity of the microstructure has to be taken account.
In Fig.4, the capacitance versus frequency curves obtained at two differe temperatures show a dispersion of the electrical properties. It will be

justified in a forthcoming full paper that the system can be approximately described as a series of resistance-capacitance cells Zgb along the current lines or percolation paths. The frequency dependent capacitance is then interpreted as due to a statistical distribution of the grain boundary resistances along these paths. Accordingly,

$$Z(w) = \sum^{N} Zgb(w) = \int \frac{R}{1+jwRC} G(\ln R)\, d(\ln R) \qquad (6)$$

with

$$\int G(\ln R)\, d(\ln R) = N \qquad (7)$$

if N is the total number of cells in a line. The distribution function G(lnR) can be approximated by /11/,

$$G(\ln \frac{1}{w}) = - \frac{1}{R} \frac{d(\mathrm{Re}Z(w))}{d(\ln w)} \text{ and } wRC = 1 \qquad (8)$$

where ReZ(w) is the real part of the impedance Z(w). Figure 5 shows the evolution of the distribution function G(ln(1/w)) with temperature.
The resistance R or equivalently the potential barrier Vi depends on several variables, namely the dopant concentration Nd, the Curie temperature To (Tc), and the interface characteristics No,Eo in the case of a δ distribution which will be considered in the following. Their influence on the Vi(T) curve is manyfold. In regime I, which is linear, To affects the onset temperature of the PTC effect, Nd and No the slope of the straight line. In regime II, a linear relationship is also observed but with a negative slope, see Eq.(5). Eo is the extrapolated value of Vi at a temperature of 0 K and the slope is determined once again by Nd. Let us come back to the experimental results presented in Fig.5. Below Tm, the width of the distribution increases only slightly with temperature. It can be concluded that ,in this temperature range, grains which form the current lines, have a relatively high and uniform Nd, the one measured at room temperature /9/ and that the statistical distribution is essentially affected by variations of To. Clearly, above Tm, this is no longer the case. Low doped grains become of importance because the associated potential barriers saturate first and then decrease, see Fig.6. In Fig.5, the distribution resolves into two broad peaks. This is certainly due to a very heterogeneous spatial distribution of the dopant but could also be the consequence of two distinct energy levels Eo.

IV - Conclusion

The dc electrical properties of PTC barium titanate thermistors were measured in the temperature range from 30 to 450°C. The Heywang's model alone does not permit a quantitative analysis of the resistance-temperature curve. We propose that the heterogeneity of the system and in particular the distribution of the dopant is of importance. It was clarified that the electrical microstructure was not identical to the ceramic one, i.e. the current lines change with the temperature. Ac measurements in a wide frequency range (10 mHz-1 MHz) proved to be very useful to elucidate the way this change occurs.

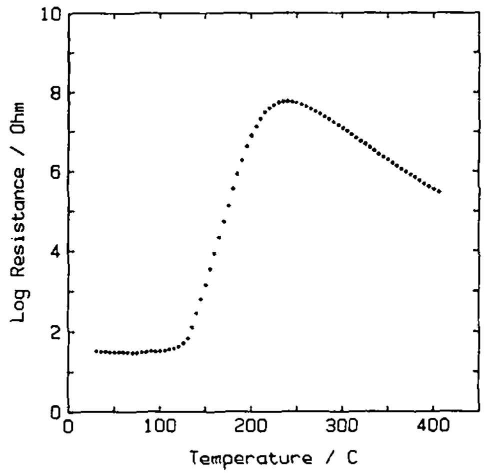

Figure 1 - Resistance versus temperature curve of a PTC thermistor.

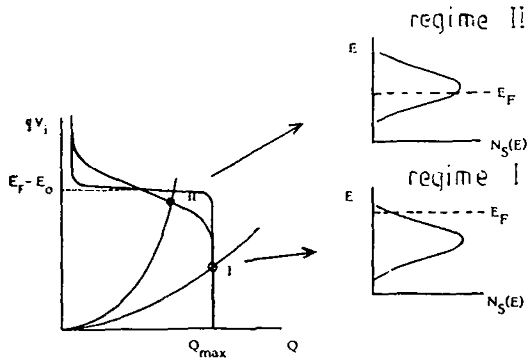

Figure 2 - Graphical solution of Eqs.(1) and (4), see text.

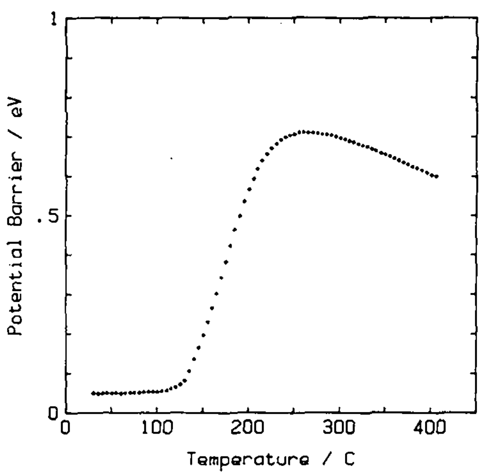

Figure 3 - Potential barrier versus temperature curve calculated on using the data of Fig.1.

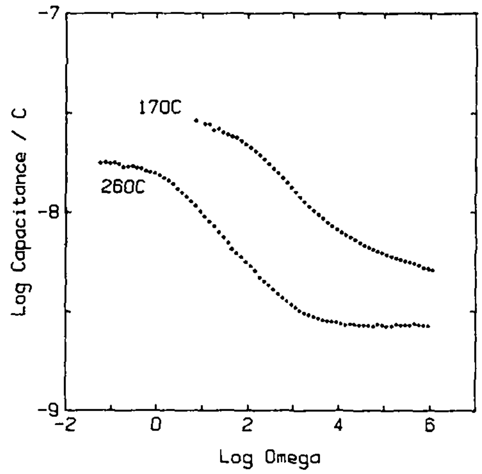

Figure 4 - Capacitance versus frequency (w=2πf) curves for the PTC thermistor of Fig.1.

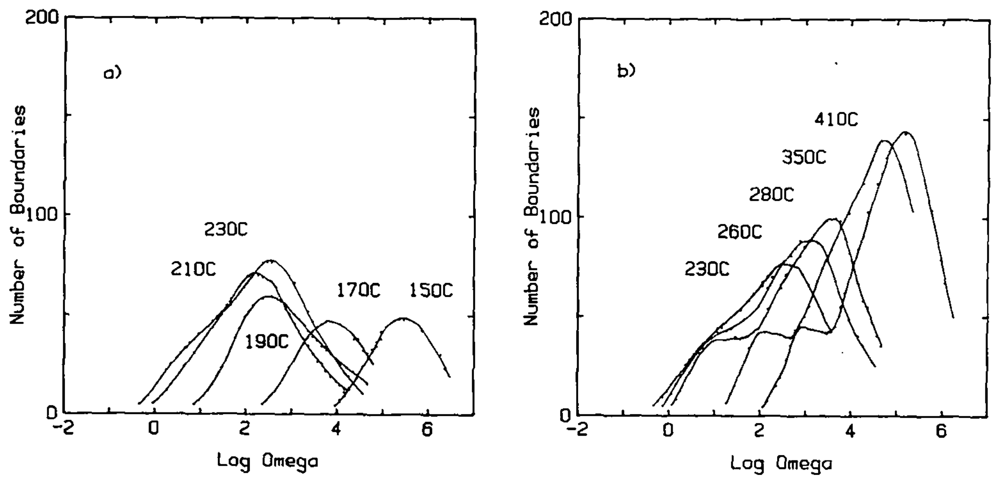

Figure 5 - Plot of the statistical distribution of resistance G(ln R) versus frequency (=1/(RC)) curves on a logarithmic scale and for different temperatures a)<230°C b)>230°C.

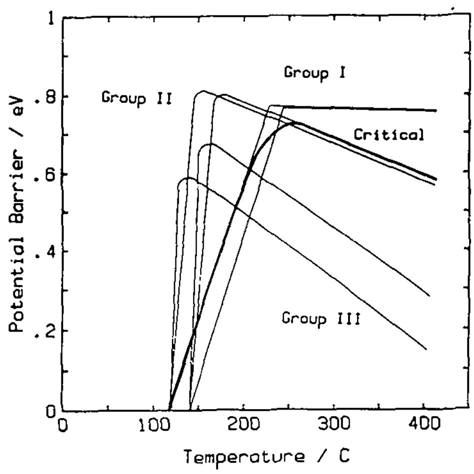

Figure 6 - Proposed interpretation of the potential barrier versus temperature curve (Fig.3).

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