Phase transitions in ferrimagnetic and ferroelectric ceramics by ac measurements

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Ac conductivity measurements were carried out on polycrystalline samples of a ferrimagnetic spinel ($Zn_{0.44}Mn_{0.56}Fe_2O_4$) and a ferroelectric perovskite ($Sr_{0.25}Bi_4Ti_{3.25}O_{12.75}$), in the temperature range 20–160 and 20–660 °C, respectively, and in the frequency range 5 Hz–13 MHz. The impedance response in both cases could be resolved into two contributions, associated with the bulk (grains) and the grain boundaries. An analysis by means of the ac conductivity power law showed evidence of a critical temperature of 132 and 536 °C, for the ferrimagnetic and the ferroelectric samples, respectively, which corresponds to the Curie temperature for each type of material. These results are interpreted in terms of the disorder increase approaching the phase transition. © *1998 American Institute of Physics.* [S0003-6951(98)04640-3]

Impedance spectroscopy[1] (IS) is a measuring technique which is becoming a powerful characterization methodology for a wide range of materials. In the case of polycrystalline ceramics, the electrical properties of grains can be separated from the other sources of impedance, i.e., grain boundaries and electrodes, by using the complex impedance formalisms and other related formalisms. In ferroelectric materials, ac measurements can, therefore, separate the ferroelectric permittivity and provide an accurate image of polarization phenomena.[2] IS has also been used in polycrystalline ferrites to study the effects of additives,[3] for instance, by analyzing the changes introduced in the grain and grain-boundary impedance response. To our knowledge, however, no direct evidence of the Curie transition has been observed in ac conductivity experiments.

A convenient formalism to investigate the frequency behavior of conductivity in a variety of materials is based on the power relation proposed by Jonscher,[4]

$$\sigma_T(\omega) = \sigma(0) + A\omega^s, \qquad (1)$$

where σ_T is the total conductivity, $\sigma(0)$ is the frequency-independent conductivity, and the coefficient A and exponent s are temperature and material dependent.[5] The term $A\omega^s$ contains the ac dependence and characterizes all dispersion phenomena. The exponent s has been found to behave in a variety of forms:[6–9] a constant, decreasing with temperature, increasing with temperature, etc., but always within $0 < s < 1$.

In this letter, a study of the thermal behavior of the power-law frequency dependence, of Zn–Mn ferrites and Sr–Bi–Ti ferroelectrics is presented. It is found that both the coefficient A and the exponent s exhibit a critical point (a minimum and a maximum, respectively) at the order–disorder (from ferrimagnetic to paramagnetic in the first case, and from ferroelectric to paraelectric, in the second) transition temperature. An interpretation in terms of the disorder involved in the phase change is proposed.

$Zn_xMn_{1-x}Fe_2O_4$ ferrites in the composition $x = 0.44$ were prepared by the usual ceramic methods, from high-purity, reagent-grade (Johnson Matthey GmbH) α-Fe_2O_3, $MnCO_3$, and ZnO. Samples of ferroelectric $Sr_xBi_4Ti_{3+x}O_{12+3x}$, with $x = 0.25$ were prepared also from high-purity, reagent-grade (Johnson Matthey GmbH) $SrTiO_3$ and Bi_2O_3 oxides, by the ceramic technique.

Impedance measurements were carried out in the frequency range 5 Hz–13 MHz in a system including a HP 4192A impedance analyzer controlled by a PC. The measuring software, created in our laboratory, allows the measurement of 94 discrete frequencies in about 3 min.

Initial magnetic permeability as a function of temperature was measured in an apparatus[10,11] where the sample, with a toroidal shape, is used as a transformer core.

We first present the IS results for the MnZn ferrite sample. Complex impedance plots, $Z_i = f(Z_r)$, where Z_i and Z_r are the imaginary and real components of impedance, respectively, showed two well-resolved semicircles over the whole measured temperature range, Fig. 1. These results can

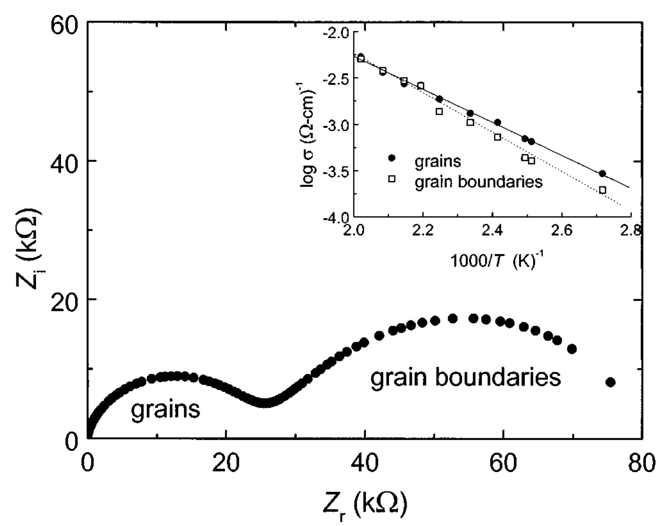

FIG. 1. Complex impedance plot at room temperature. Inset, the Arrhenius plot of grains and grain-boundary conductivity.

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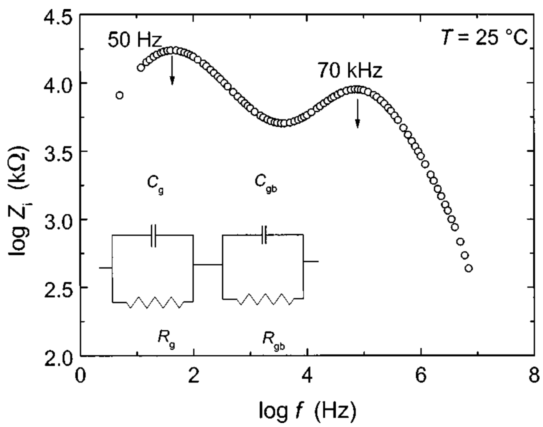

FIG. 2. Dependence of imaginary impedance on frequency. Inset, the equivalent circuit.

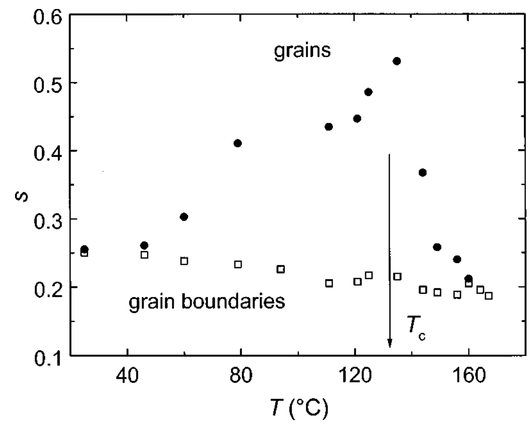

FIG. 4. Thermal behavior of the exponents $s1$ (grains) and $s2$ (grain boundaries) in the modified power relation of Jonscher.

be modeled by an equivalent circuit formed by two *RC* parallel arms in series, inset of Fig. 2. The value of each equivalent resistor can be extracted from the diameter of semicircles. A relaxation frequency is observed for each arm, Fig. 2; at this frequency, the condition $Z_i = Z_r$ occurs and it is possible to calculate the corresponding value of equivalent capacitors from $C = 1/(\omega R)$, where ω is the angular frequency ($\omega = 2\pi f$).

The values of capacitors provide a criterium to relate these semicircles with the pertinent microstructural feature at the origin of specific impedance contribution.[12] One of the arms, $R_g C_g$, is, therefore, associated with the impedance response of the bulk (or grains), and the other one, $R_{gb} C_{gb}$, with the response of grain boundaries. As the measuring temperature increases, R_g and R_{gb} decrease following a variation of Arrhenius type. A linear relationship is observed when these data are plotted in the form log σ vs $1/T$, where σ is the electrical conductivity, as shown in the inset of Fig. 1.

The ac conductivity power law of Eq. (1) can be used to analyze the obtained results. $\sigma_T(\omega)$ is obtained form the real part of admittance Y_r as

$$\sigma_T(\omega) = gY_r = gZ_r/[(Z_r)^2 + (Z_i)^2], \tag{2}$$

where g is the geometrical factor.

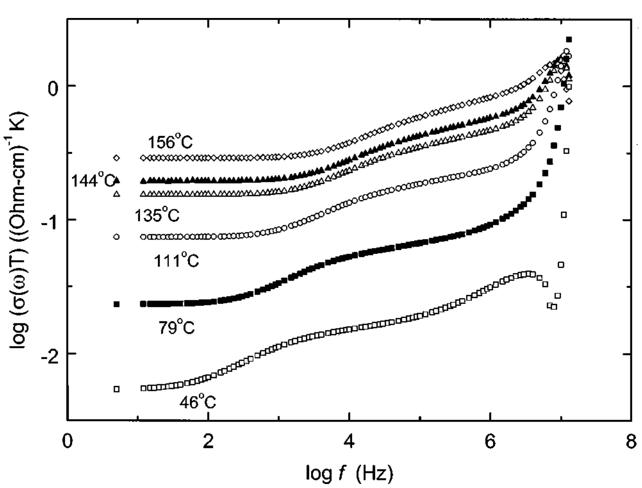

FIG. 3. Dependence of total conductivity $\sigma_T(\omega)$ with frequency for selected temperatures.

The variations of $\sigma_T(\omega)$ with frequency, for selected temperatures, are shown in Fig. 3 in log–log form. A frequency-independent plateau appears for the low-frequency range, associated with the term $\sigma(0)$. As frequency increases, two dispersion regions appear for all temperatures. If the low-frequency dispersion is associated with grain boundaries (since it is associated with the larger capacitance value) and the high-frequency one with grains (smaller capacitance value), Eq. (1) can be modified as[13]

$$\sigma_T(\omega) = \sigma(0) + A_1\omega^{s1} + A_2\omega^{s2}, \tag{3}$$

to describe these different contributions to conductivity. The behaviors of A_1, A_2, $s1$, and $s2$ with temperature appear in Figs. 4 and 5.

The exponents $s1$ and $s2$ exhibit a quite different dependence with temperature, Fig. 4. $s1$, associated with the grain-boundary conductivity, shows a small decrease with temperature, with no particular feature. In contrast, $s2$, which depends on grain (or bulk) conductivity, shows a steep increase and then a maximum at about $T = 132$ °C, followed by a decrease to values close to the room-temperature ones. In the case of the A terms, A_2, which is grain related, exhibits a clear minimum value for the same temperature where $s2$ showed a maximum. A_1, on the other hand, shows a continuous increase, with no special feature for any temperature.

In order to obtain some insight about the critical behavior of the A_2 and $s2$ parameters, the initial magnetic perme-

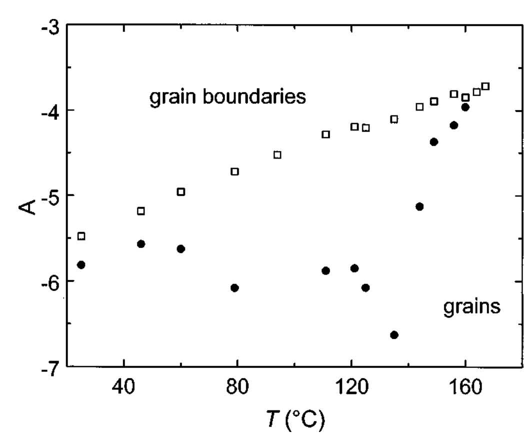

FIG. 5. Thermal variations of the A_1 (grains) and A_2 (grain boundaries) terms in the power relation.

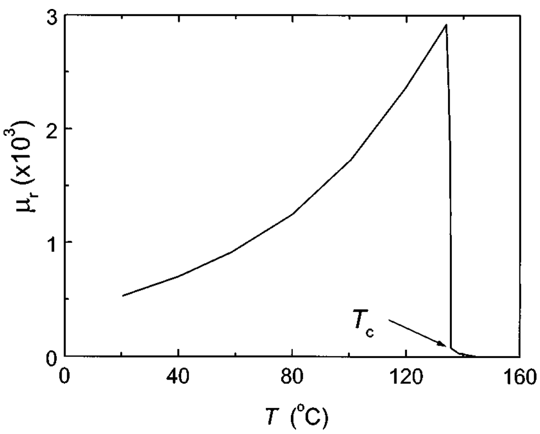

FIG. 6. Thermal variations in the relative initial magnetic permeability of the MnZn ferrite sample.

ability of the ferrite sample was measured as a function of temperature, Fig. 6. This property shows an increase as the temperature increases, and an almost vertical drop at the Curie temperature T_c, where the sample changes from a long-range ordered ferrimagnetic arrangement to a disordered paramagnetic structure. The observed value, Fig. 6, is $T_c = 132\ °C$, which coincides quite well with the maximum in the $s2$ vs T plot (Fig. 4), and the minimum in the thermal variations of A_2, Fig. 5. In other words, the *magnetic* phase change is associated with a critical behavior in the *electrical* conductivity parameters A and s.

In order to verify the generality of these results, a similar methodology was followed on the ferroelectric sample. After frequency measurements, which resulted also in a clear resolution of the bulk and grain-boundary contributions to the impedance, the A and s terms were calculated and are shown in Fig. 7. A similar behavior is observed, with a maximum for the s exponent, and a minimum for the A term, both for the ferroelectric Curie temperature $T_c = 563\ °C$. It, therefore, turns out that the critical behavior of s and A is associated not only with magnetic phase transitions, but also with ferroelectric phase transitions.

The ac conductivity power law seems to be originated by relaxation processes with a wide distribution of time constant; ''parallel'' and ''series'' relaxation processes have been used[9] to propose a general explanation in highly disordered materials such as glasses. While a direct correlation between the observed A and s values is still lacking, some form of disorder seems to be essential for a system to exhibit a power-law behavior. Also, variations in the exponent s can be expected if the polarizability of the involved material depends on the energy barrier for a simple hopping process between two sites.

In the present case, it appears that in the temperature-

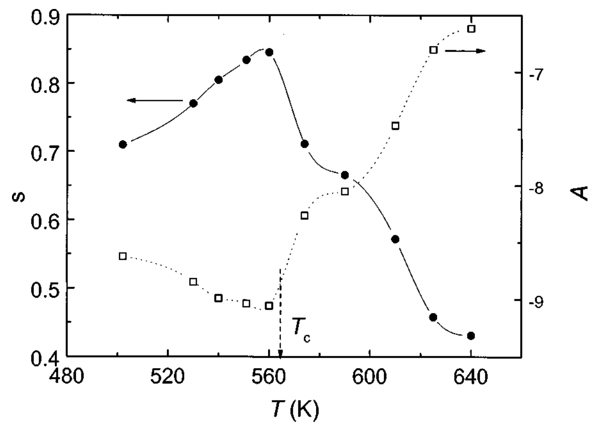

FIG. 7. Exponent s and coefficient A in the case of the ferroelectric sample.

increasing process, the proximity to the phase transition is associated with an increase in disorder. In the case of magnetic transitions, the significant increase in specific heat close to the Curie temperature effectively appears to be consistent with this view. An important point to note is that while most ferroelectric–paraelectric transitions are considered first-order transitions from a thermodynamic point of view, ferrimagnetic–paramagnetic phase changes account for second-order transitions. Our results would, therefore, point to a more general feature of conductivity behavior. Electrically based methods can effectively lead to a detailed characterization of a wide range of materials.

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