Dielectric Properties of the Charge Ordered Oxyborate Fe_2OBO_3

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In this work we present a detailed investigation of the dielectric properties of the oxyborate Fe_2OBO_3. This compound exhibits a high dielectric constant at room temperature ($\varepsilon_r' > 10^3$) for frequencies up to 10^4 Hz. An impedance spectroscopy analysis of the data reveals an important extrinsic contribution to these high ε_r' values. In order to eliminate the extrinsic contribution, we have sandwiched the sample in-between two mica layers, obtaining relatively high values of ε_r' at room temperature for this kind of oxides ($\varepsilon_r' \sim 45$). The temperature dependence of the remaining intrinsic contribution shows a jump, that at high frequencies occurs at the temperature at which a rearrangement of the charge-order pattern takes place and at low frequencies occurs at temperatures close to the onset of the antiferromagnetic long-range order. This suggests a certain coupling between the electronic, magnetic and dielectric properties in this compound.

***Index Terms*—Dielectric materials, dielectric measurements, magnetic transitions, Maxwell–Wagner effects, oxyborates.**

I. INTRODUCTION

THE search of new dielectric materials has given a turn short ago, with increasing efforts in the exploration of alternative strategies to achieve electronic polarization out of the typical structural approach (i.e., to design materials in which the centers of positive charges in the crystalline lattice do not coincide with those of negative charges).

Ours has been to focus on systems with charge condensation, after the finding of a high capacitive behavior in $Pr_{0.67}Ca_{0.33}MnO_3$ when approaching and entering its CO regime [1], [2]. This circumstance is, for us, an evidence of the relationship of the electronic state and the increase of the dielectric response, even in a non-ferroelectric material.

In this line, Ikeda *et al.* [3] have found in $LuFe_2O_4$ electronic ferroelectricity due to the charge-order of the divalent and trivalent Fe ions. Its charge distribution allows the presence of a local electrical polarization, since the centers of Fe^{2+} and Fe^{3+} do not coincide in the superstructure unit cell. Their result points to the possibility of ferroelectricity originating from the electron density modulation without a dipole cation-anion, a new way to induce ferroelectric state. Also, it has the advantage that it is possible to obtain ferroelectricity due to this electronic mechanism at room temperature, a very important aspect for the potential applications of these materials.

Another iron mixed valent compound for which charge ordering has been reported is the oxyborate Fe_2OBO_3 [4]. This compound crystallizes in the warwickite structure, in which the Fe^{2+} and Fe^{3+} cations show an octahedral coordination and the $[FeO_6]$ groups share edges to form ribbons of four infinite chains linked by corner sharing and the trigonal planar BO_3 groups [5].

According to the initial studies performed on a polycrystalline sample, this compound experiences an electrostatically driven charge ordering below 317 K [4] and orders antiferromagnetically below $T_N = 155$ K [6].

On the basis of further studies a revised and more complex electronic phase diagram for this compound was proposed [7], that includes the presence of a spatially inhomogeneous short-range charge-order sate below 317 K that becomes truly long range only below the Néel temperature.

More recently, Angst *et al.* [8], [9] have carried out detailed studies on Fe_2OBO_3 single crystals, observing the structural transition traditionally associated to the charge ordering process (from orthorhombic to monoclinic symmetry) at slightly higher temperatures: 340 K. Very interestingly, they detected and described an intermediate phase between 280–340 K characterized by coexisting mobile and immobile carriers and by incommensurate modulations due to a geometrical charge frustration [9]. Below 280 K the CO superstructure changes again and it is described by two types of micro-domains, where the four-chain ribbons present different diagonal order [9].

These electronic features make this compound an attractive candidate to present interesting and novel dielectric properties and for this reason we are exploring them in the present paper. To our knowledge it is the first time the dielectric characterization of this compound is been reported. Moreover, if the values of dielectric constant were high enough, the presence of an antiferromagnetic phase transition would give the opportunity of looking for potential variations of the dielectric properties at T_N. If such variations were found, the material would be a candidate to exhibit magnetoelectric effect.

II. EXPERIMENTAL DETAILS

Polycrystalline Fe_2OBO_3 was synthesized following the method reported in [7].

The complex dielectric permittivity was measured with a parallel-plate capacitor coupled to a precision LCR meter Agilent 4284 A, capable to measure in frequencies ranging from 20 to 10^6 Hz. The capacitor was mounted in an aluminium box refrigerated with liquid nitrogen, incorporating a mechanism to control the temperature. The samples in form of pellets with an

Digital Object Identifier 10.1109/TMAG.2008.2002585

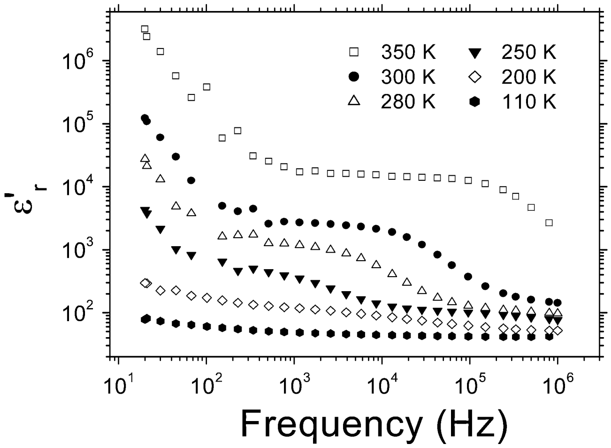

Fig. 1. AC dielectric dispersion of polycrystalline Fe_2OBO_3 at different temperatures, showing the high values of the dielectric constant.

area of 10 mm^2 and thickness of 0.9 mm were prepared to fit in the capacitor, and gold was sputtered on their surfaces to ensure good electrical contact with the plates of the capacitor.

Additional measurements were carried out by preparing a multilayer mica-oxyborate-mica system. For this purpose the oxyborate was sandwiched in between two mica layers, that were sputtered with gold on its external faces prior to the insertion of this system in-between the plates of the capacitor.

Complex plane analysis of the obtained impedance data was performed using the computer program LEVM [10].

III. RESULTS AND DISCUSSION

A. Dielectric Measurements

The behavior of the dielectric constant of Fe_2OBO_3 as a function of frequency is shown in Fig. 1. As it can be seen, the values are very high. After a general initial decrease at low frequencies, probably due to diffusion processes, this high dielectric constant keeps a constant value for a certain frequency range giving rise to a plateau, and then it decreases in a step-like manner as frequency gets higher. It is also interesting to note that the dielectric constant values markedly increase with temperature. The plateau extends over larger frequency ranges as temperature gets higher, so that for T= 350 K these high ε'_r values ($\varepsilon'_r \sim 10^4$) are retained up to 10^5 Hz.

This means that there is a significant increase of the dielectric constant above certain temperatures, reaching very high values at room temperature. The temperatures at which this increase takes place markedly shift to higher values as the measuring frequency increases.

These results are qualitatively similar to those shown by other CO mixed oxides such as $La_{1.5}Sr_{0.5}NiO_4$ [11], $Ca_{2-x}Pr_xMnO_4$ [12], [13], or $CaMn_7O_{12}$ [14]. In adittion, they also bear a strong parallelism with the behavior observed in $LuFe_2O_4$ [3] and also with the very high values of dielectric constant for $CaCu_3Ti_4O_{12}$ ($\varepsilon'_r > 80000$ at temperatures as high as 250 K and frequencies up to 1 MHz [15]).

Specially this latter gigantic ε'_r values gave rise to a fruitful debate and controversy about the question of whether really intrinsic colossal dielectric constant can exist [16], [17]. It was demonstrated the necessity of making the difference between bulk intrinsic contributions and extrinsic factors, coming from space-charge or Maxwell-Wagner polarization [18] occurring in electrical inhomogeneous systems (that can give rise to very high apparent dielectric constants), in order to correctly interpret the dielectric behavior of these colossal dielectric constant materials.

Therefore, in view of the high ε'_r values of Fe_2OBO_3 we suspected of the presence of Maxwell-Wagner effects in this material.

In this context, it is known that when an electric current passes through interfaces between two different dielectric media, because of their different conductivities surface charges pile up at the interfaces. Then, the system shows a Debye-like relaxation process under an external alternating field, even in absence of dipole relaxation, the so-called Maxwell–Wagner relaxation [19].

Such Debye-like relaxation can be expressed as [19]:

$$\varepsilon'_r = \varepsilon'_\infty + (\varepsilon\prime_s - \varepsilon'_\infty/1 + \omega^2\tau^2) \qquad (1)$$

where ε'_∞ is the value of the dielectric constant at high frequency, ε'_s is the value of dielectric constant at low frequency, ω is the angular frequency and τ is the relaxation time with $\tau = \tau_0 \exp(E_a/k_B T)(E_a = \text{activation energy})$.

In this case the calculated data fit only partially the ε'_r (T) data and the Maxwell-Wagner expression can simulate only the increase that takes place at high temperatures.

B. Impedance Spectroscopy Analysis

In order to understand better the dielectric behavior of Fe_2OBO_3 an impedance spectroscopy (IS) analysis was carried out. This kind of analysis allows to distinguish the intrinsic part of the dielectric constant from the extrinsic part. And we find, in fact, different behaviors as a function of temperature (Fig. 2).

For temperatures $T \leq 200$ K the complex plane plots show a single arc that intercepts the origin (Fig. 2(a)), whereas for higher temperatures $200 < T(K) \leq 300$ a second smaller arc appears in the low frequency range [Fig. 2(b)]; and for $T > 300$ K a single arc is again present (Fig. 2(c)). The large arc observed for $T \leq 300$ K can be modeled by a resistance (R_1), a capacitance (C_1), and a frequency-dependent distributed element (DE) connected in parallel. As this large arc intercepts zero, it seems to be associated with the material bulk response [20], as corroborated by the fact that the order of magnitude of the its associated capacitance is of pF/cm, typical of bulk response.

On the other hand, the second smaller arc can be modeled as a single RC connected in series with the circuit that describes the bulk arc. This small arc is associated to extrinsic contributions (such as Schottky barriers) as it does not intercept the origin [20] and its associated capacitance is of the order of nF/cm. For $T > 300$ K, the presence of the single arc that does not intercept the origin indicates that only extrinsic factors are being observed in this region. It can be modeled as a single RC connected in series with a R in order to consider the resistance of the non-observed bulk.

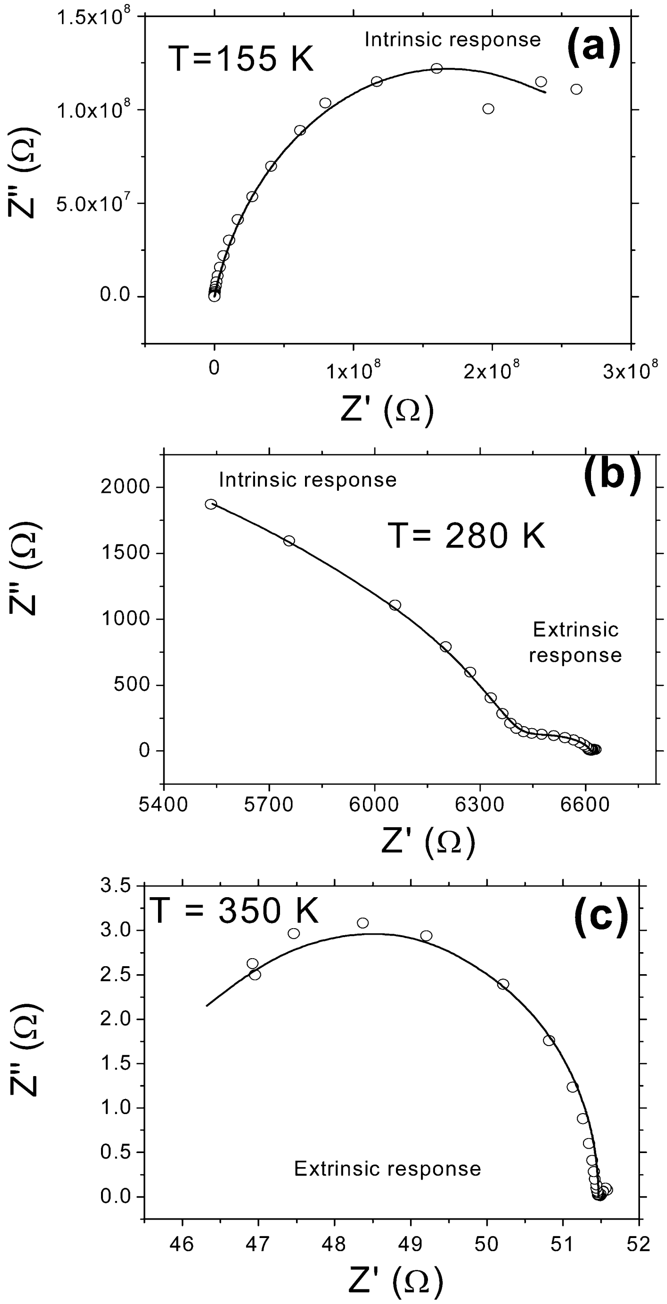

Fig. 2. Impedance complex plane plots and corresponding fits for Fe_2OBO_3, illustrating the different regimes of dielectric behavior: (a) low temperature region ($T \leq 200$ K), (b) intermediate temperature region $200 < T(K) \leq 300$, and (c) high temperature region $T > 300$ K. The open circles represent the experimental data and the solid line the corresponding fits.

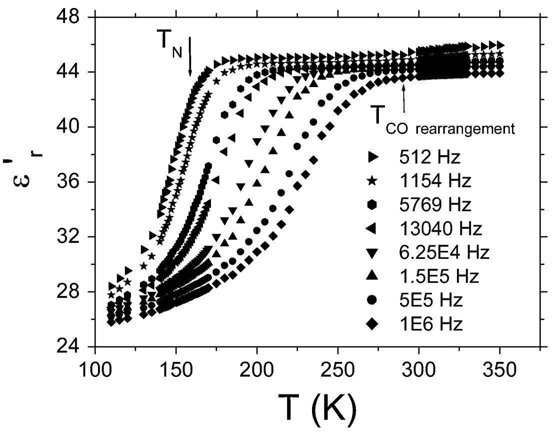

Fig. 3. AC dielectric constant of the multilayer system mica-oxyborate-mica as a function of temperature measured at different frequencies.

With all these results we can conclude that, for $T \leq 200$ K, the dielectric response is intrinsic to the material.

In the temperature range $200 < T(K) \leq 300$ [Fig. 2(b)], the dielectric response is due to intrinsic (at high frequencies) and to extrinsic factors (at low frequencies). At $T > 300$ K, the dielectric response is mainly extrinsic and it can be described by the Maxwell–Wagner model.

In order to avoid the possible formation of Schottky barriers at the contact-sample interface and directly observe the intrinsic response up to higher temperatures, we have performed additional studies sandwiching the pelletized sample in between two mica layers prior to its introduction in the capacitor. The dielectric behavior of this sandwiched and pelletized sample is shown in Fig. 3.

The first general remark is the large decrease in the value of the dielectric constant with respect to that of the single material. This is the expected result for a situation in which the extrinsic contributions are removed and only the intrinsic response is observed.

Also, the value of the dielectric constant does not change very much with frequency both at low and high temperatures. Meanwhile, for intermediate temperatures it is strongly dependent (see Fig. 3).

The behavior of the dielectric constant as a function of temperature is particularly interesting: ε_r', that at room temperature shows a value of ≈ 45, experiences a marked jump at lower temperatures converging to values of $\varepsilon_r' \approx 25$ at the lowest available temperatures ($T = 110$ K). For low measuring frequencies such jump takes place close to the onset of the antiferromagnetic long-range order. The higher the measuring frequency, the broader becomes the jump. Along our available range (up to 1 MHz) it seems to approach 280 K, temperature at which a rearrangement of the charge-order pattern takes place [9].

The sensitivity of the dielectric constant to the magnetic order points to a certain coupling between the electronic, magnetic and dielectric properties in this compound, that deserves further investigation.

Moreover, we think that a parallelism can be established between these results and those of $LuFe_2O_4$. On the basis of what is reported here it is very possible that the high values reported for the a.c. dielectric dispersion of $LuFe_2O_4$, which reach values around $\varepsilon_r' = 5000$ [3], had also important extrinsic contributions as in the case of Fe_2OBO_3. An IS analysis should be done to clarify this point.

In any case, in the here reported Fe-oxyborate material once the extrinsic contribution is removed, the intrinsic dielectric constant measured at room temperature $\varepsilon_r' \approx 45$ is higher than expected (ε_r' is typically of the order 1–10 for conventional dielectric oxides [19]). As in $LuFe_2O_4$, this enhancement could be related to the breaking in the inversion symmetry that occurs by charge ordering.

IV. CONCLUSION

It is found that Fe_2OBO_3 shows a high dielectric constant caused by interfacial polarization effects. This contribution might be tailored by controlling the interfaces of the sample.

Once this extrinsic contribution is removed, the system shows a rather high intrinsic dielectric constant ($\varepsilon_r' \approx 45$). This intrinsic dielectric constant shows a very revealing anomaly as a function of temperature: a marked jump at low measuring frequencies around the magnetic ordering point of the system. These results point to a certain coupling between the electronic, magnetic and dielectric properties of this compound, and to a certain contribution of the former to the enhanced values of its intrinsic dielectric constant.

ACKNOWLEDGMENT

This work was supported by the Spanish Ministerio de Educación y Ciencia (MEC) and UE under Projects FEDER-MAT 2004-05130 and FEDER-MAT 2007-66696.

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