

Magnetodielectric response in the charge ordered oxyborate Fe_2OBO_3

S. Yáñez-Vilar,¹ M. Sánchez-Andújar,¹ J. Mira,^{2,a)} S. Castro-García,¹ J. Rivas,² and M. A. Señaris-Rodríguez¹

¹Dpto. Química Fundamental, Universidade da Coruña, 15071 A Coruña, Spain

²Dpto. Física Aplicada, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

(Received 18 May 2010; accepted 24 July 2010; published online 14 October 2010)

We present a detailed investigation on the magnetodielectric properties of Fe_2OBO_3 , where we have found a magnetodielectric effect around 150% at room temperature and $\nu=2$ kHz, that cannot solely arise from magnetoresistive extrinsic contributions. In addition, we find a crossover of the magnetodielectric response around T_N , that we attribute to changes in the electronic microstructure of this compound that take place at that temperature. For $T < T_N$ the dielectric constant experiences a jump at a temperature dependent critical field that we relate to a partial melting of the charge ordering state. © 2010 American Institute of Physics. [doi:10.1063/1.3481661]

I. INTRODUCTION

Multiferroic materials, where two important and basic properties like ferromagnetism and ferroelectricity are coupled within one phase, are being the object of an intensive research. The obvious reason is that they are the direct candidates to exhibit the useful ability of changing their dielectric constant under the application of an external magnetic field and vice versa. Unfortunately, multiferroics are a rare gift of nature because the classical ferroelectric (Ti-based) compounds contain transition metal ions with empty d shells and therefore do not bear magnetic moment. The nice exceptions are some geometric multiferroics such as YMnO_3 (Ref. 1) materials combining A-site (lone pair) ferroelectricity with B-site magnetic ordering, e.g., BiMO_3 ($M = \text{Cr}, \text{Mn}, \text{Fe}$) (Refs. 2 and 3) or highly frustrated spin systems, such as TbMnO_3 , TbMn_2O_5 ,⁴ etc. In these latter compounds (better candidates to exhibit large magnetoelectric effects) the electric polarization emerges due to the magnetic order; consequently, the onset of the ferroelectric (FE) state takes place around the corresponding magnetic transition. To obtain the FE state, the magnetic structure must break the inversion symmetry, a condition usually observed in noncollinear magnets.

Unfortunately, noncollinear magnetism usually takes place at low temperatures (typically $T < 50$ K), which is an inconvenience for practical applications.

This has led to the search of high magnetodielectric effects by other mechanisms, which in turn implied looking for alternative ways to find materials with high dielectric constant, i.e., going beyond a structural origin of electric polarization.

One of these strategies has been to focus on systems with charge condensation, starting with charge-ordered manganese perovskites.^{5–7} In this context, our report of the high capacitive behavior in $\text{Pr}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ just below its charge ordering temperature, $T_{\text{CO}}=250$ K,^{5,6} points to a link between the electronic state and the increase in the dielectric response.

In this line, Ikeda *et al.*⁸ have found electronic ferroelectricity in LuFe_2O_4 due to the charge-order of the iron ions that gives rise to 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 FE state even at room temperature, a very important aspect for the potential applications of these materials. Moreover, they also found evidence of a certain coupling between magnetization and electric polarization, result that they rationalized on the basis that it is also the coherent arrangement of spins on the Fe ions what is giving rise to polarization.⁸ Short after this, Subramanian *et al.*⁹ reported that LuFe_2O_4 shows a rather large magnetodielectric effect (-25%) at room temperature under the modest field of 0.1 T.

In this work we explore the possibility of finding magnetodielectric effects in the isostructural Fe_2OBO_3 , another mixed valence iron compound that also shows charge, magnetic, and orbital ordering. This compound crystallizes in the warwickite structure, in which the Fe^{2+} and Fe^{3+} cations show an octahedral coordination and the $[\text{FeO}_6]$ groups share edges to form ribbons of four infinite chains linked by corner sharing and the trigonal planar BO_3 groups.¹⁰

According to the initial studies performed on a polycrystalline sample, this compound experiences an electrostatically driven charge ordering below 317 K (Ref. 11) and orders antiferromagnetically below $T_N=155$ K.¹²

II. EXPERIMENTAL

Fe_2OBO_3 was synthesized by heating pressed pellets of a stoichiometric mixture of FeBO_3 , Fe_2O_3 , and Fe in a sealed evacuated silica tube at 800 °C for 110 h with intermediate grindings. FeBO_3 had been previously obtained by firing Fe_2O_3 and H_3BO_3 in air at 700 °C, following the method reported in Ref. 13.

The complex dielectric permittivity of this compound 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

^{a)}Electronic mail: jorge.mira@usc.es.

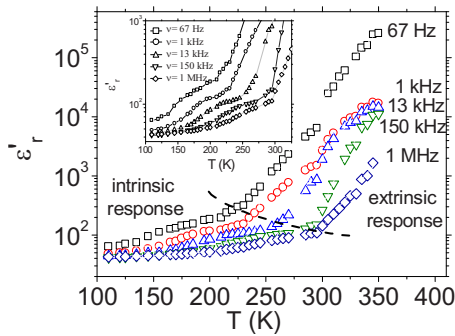


FIG. 1. (Color online) ϵ' vs temperature at different frequencies with gold contacts for Fe-oxyborate, indicating regions of pure intrinsic and extrinsic dielectric response. Inset: detail of the curve around T_N .

mounted in an aluminum box refrigerated with liquid nitrogen. The samples in form of pellets with an area of 10 mm² 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.

In addition dielectric measurements under a magnetic field up to 14 T were performed in a precision *LCR*-meter Quadtech model 1920 in frequencies ranging from 20 to 10⁶ Hz and in the temperature interval [$80 \leq T(\text{K}) \leq 300$].

III. RESULTS AND DISCUSSION

The behavior of the dielectric constant of Fe₂OBO₃ as a function of frequency was already reported in Ref. 14. After a general initial decrease at low frequencies, probably due to diffusion processes, the dielectric constant keeps a very high value, constant for a certain frequency range giving rise to a plateau, and then it decreases in a steplike manner as frequency gets higher.

As shown in Fig. 1, above the Neel temperature, there is a significant increase in the dielectric constant which depends on frequency and reaches very high values at room temperature ($\epsilon'_r \sim 3000$ at $\nu = 10^4$ Hz). These results are qualitatively similar to those shown by other CO mixed oxides such as La_{1.5}Sr_{0.5}NiO₄,¹⁵ Ca_{2-x}Pr_xMnO₄,¹⁶ or CaMn₇O₁₂ (Ref. 17) and they have a strong parallelism with the results obtained in LuFe₂O₄ (Refs. 8 and 9) and also with the very high values of dielectric constant reported in recent times, like, for example, in CaCu₃Ti₄O₁₂.¹⁸ These figures gave rise to a fruitful debate and controversy about the origin of these high dielectric constant^{19,20} and demonstrated the necessity of differentiating between bulk intrinsic contributions and extrinsic factors coming from space-charge or Maxwell-Wagner polarization²¹ occurring in electrical inhomogeneous systems to correctly interpret the dielectric behavior of these colossal ϵ'_r materials.

With this aim, in a previous work¹⁴ we studied this compound by impedance spectroscopy (IS) using the computer program LEVM (Ref. 22) and we found different behaviors as a function of temperature.

For temperatures $T < 200$ K the IS analysis showed a purely intrinsic response. Meanwhile, in the temperature range $200 < T(\text{K}) < 300$, the dielectric response was due to both the bulk (at high frequencies) and to extrinsic factors (at

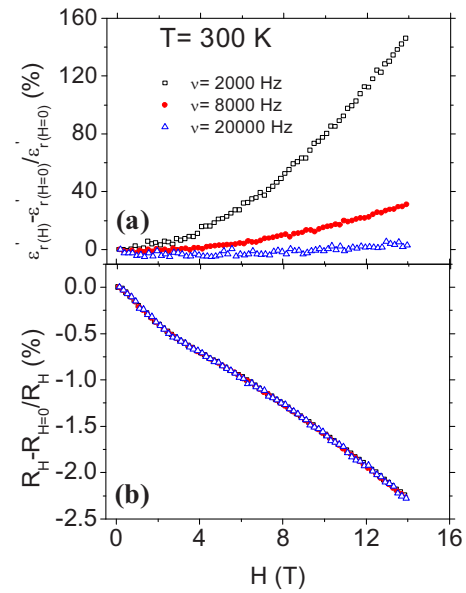


FIG. 2. (Color online) Variation in (a) the dielectric constant and (b) the resistance with magnetic field at 300 K.

low frequencies). Meanwhile, for $T > 300$ K, the dielectric response was mainly extrinsic and described by the Maxwell-Wagner model.

In addition, in order to eliminate the extrinsic contribution, we have also performed experiments by sandwiching the sample in-between two mica layers, obtaining relatively high values of ϵ'_r at room temperature for this kind of oxides ($\epsilon'_r \sim 45$).¹⁴ Most interestingly, the temperature dependence of the remaining intrinsic contribution showed 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 result suggests a certain coupling between the electronic, magnetic, and dielectric properties in this compound.

When applying a magnetic field, we found a very noticeable variation in the dielectric constant. Figure 2(a) shows its variation at room temperature: as it can be seen, ϵ'_r experiences a relevant increase as the magnetic field increases from 0 to 14 T, especially at low frequencies.

Certainly, this high magnetodielectric effect could arise from the extrinsic contribution to the dielectric constant, which is a term dependent on the electrical resistivity. Nevertheless, the value of the magnetoresistance at 300 K is very small, around about 2 % [Fig. 2(b)], while the observed positive magnetodielectric effect is quite large (for example, at 2 kHz it is around 150% and at 8 kHz it is around 30%). This result suggests that the origin of this room-temperature magnetodielectric effect cannot merely be the magnetoresistive extrinsic contribution, as it also occurs in the case of LuFe₂O₄.⁹

We have also measured the magnetodielectric effect at lower temperatures [$80 < T(\text{K}) < 300$]. The magnetodielectric effect is reduced when lowering temperature and, at around T_N , it exhibits a crossover: whereas for $T > T_N$ the magnetodielectric effect is positive, for $T < T_N$ it becomes

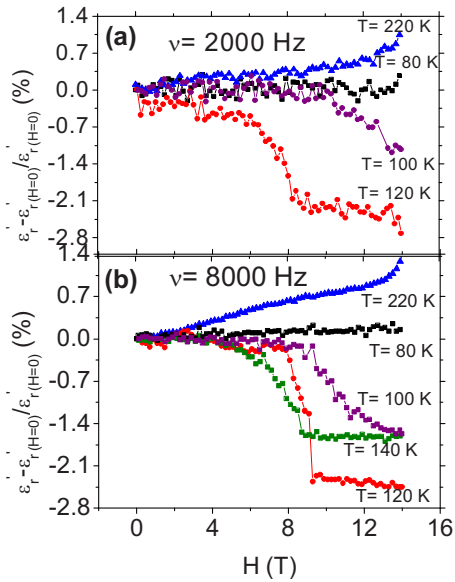


FIG. 3. (Color online) Variation in the magnetodielectric effect with the applied magnetic field at (a) $\nu = 2000$ Hz and (b) $\nu = 8000$ Hz measured at different temperatures.

negative. Moreover, it is worth noting that for $T < T_N$ the dielectric constant experiences a jump at a temperature dependent critical magnetic field, H_c , (Fig. 3).

Such critical field, that increases as temperature gets lower, is reachable with our experimental available magnetic field for $125 < T(K) < 140$ but it becomes too high, and out of our measuring window, for lower temperatures. As a consequence, for $T = 80$ K the dielectric constant is not seen to change upon application of the maximum available field ($H_{\max} = 14$ T) (Fig. 3).

In addition, in this latter temperature range the magnetodielectric response is seen to increase again as temperature decreases further down to 125 K, where the maximum effect is observed MD $\sim -2.5\%$ at $\nu = 8$ kHz (Fig. 3).

In order to interpret these observations it is unavoidable to establish a comparison with LuFe_2O_4 . As anticipated in the introduction, in that compound the origin of the enhanced dielectric constant is the breaking of the inversion symmetry by charge ordering: a spontaneous electric polarization appears below 330 K, in coincidence with the charge ordering of the Fe^{2+} and Fe^{3+} cations. In addition, an increase in the electric polarization is observed around 250 K, the ferrimagnetic ordering temperature.

In principle, one could expect that a similar process would be taking place in the Fe-oxyborate, but in fact in this compound the situation is more complex and slightly different. In this context some of us have found that the electronic phase diagram of this compound includes the presence of a spatially inhomogeneous short-range charge-order state below 317 K that becomes truly long-range only below the Néel temperature.¹⁴

This agrees with the conclusion taken from dielectric data: in Fe_2OBO_3 we find at room temperature and down to T_N a dielectric constant that is very high and is greatly enhanced by extrinsic contributions (detected by the IS

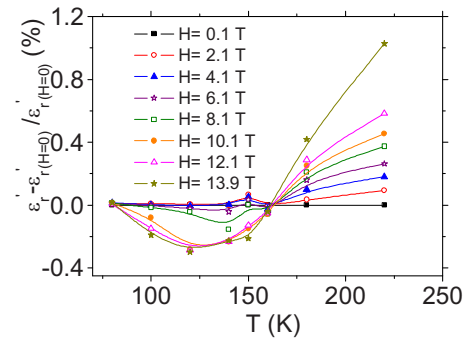


FIG. 4. (Color online) Variation in the magnetodielectric effect with temperature at different magnetic fields measured at $\nu = 8000$ Hz.

results¹⁴). On the other hand, and as indicated in our previous paper, no dielectric anomalies are detected around 317 K.

This is probably due to the fact that from 155 to 317 K the coexistence of antiferromagnetic/charge ordered (AFM/CO) regions embedded in a charge delocalized paramagnetic matrix are greatly enhancing the dielectric constant by means of the space-charge or interfacial polarization produced between the segregated insulator and the metallic regions. As the effect is more pronounced as temperature gets higher, and at 317 K the conductivity of the sample increases further, the truly intrinsic behavior of the Fe_2OBO_3 compound is almost completely covered by the other contribution and cannot be observed in this temperature range.

On the other hand, as temperature decreases below 155 K, the AFM/CO regions percolate, the system becomes antiferromagnetic and the charge ordering becomes long range, which leads to a suppression of charge carriers and therefore to the elimination of this interfacial polarization and its associated enhancement of the dielectric response.

The global result is a decrease in the measured dielectric constant below T_N , and the observation of the purely intrinsic dielectric response of the material, coming from the AFM/CO phase, without the interference of extrinsic factors that show up above T_N . In fact, we relate the observed crossover of the magnetodielectric response close to T_N (Fig. 4) to the change in the electronic microstructure of this compound from short range CO/AFM regions embedded in a paramagnetic matrix to a long-ranged CO and AFM phase.

The step in the dielectric constant at a critical field in a temperature window below T_N [Figs. 3(a) and 3(b)] is suggesting a melting of the CO state, with the subsequent decrease in dielectric constant. It could be partial, as observed in other CO Mn-perovskites,⁶ leading to a short-range CO, that could be the responsible of interfacial polarization effects. Would this be so, it would support our previously suggested idea of the dependence of the dielectric behavior on the characteristics and changes occurring in these complex CO states.

In summary, we have studied the influence of the external magnetic field in the dielectric constant of Fe_2OBO_3 . We have found a magnetodielectric effect around 150% at room temperature and $\nu = 2$ kHz, that cannot solely arise from magnetoresistive extrinsic contributions, that are indeed present and enhancing the observed effect. Very interestingly, we find a crossover of the magnetodielectric response around

T_N , that we attribute to changes that take place in the electronic microstructure of this compound at that temperature. For $T < T_N$ the maximum MD effect seen is -2% .

Also, for $T < T_N$ the dielectric constant experienced a jump at a temperature dependent critical field, H_c , that we relate to a partial melting of the CO state that leads to a short-range CO.

ACKNOWLEDGMENTS

We wish to acknowledge the financial support from Spanish Ministerio de Educación y Ciencia (MEC) and UE under Project FEDER-MAT 2007-66696-C02.

- ¹B. B. Van Aken, T. T. M. Palstra, A. Filippetti, and N. A. Spaldin, *Nature Mater.* **3**, 164 (2004).
- ²J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wutting, and R. Ramesh, *Science* **299**, 1719 (2003).
- ³T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, and Y. Tokura, *Phys. Rev. B* **67**, 180401 (2003).
- ⁴G. R. Blake, L. C. Chapon, P. G. Radaelli, S. Park, N. Hur, S. W. Cheong, and J. Rodríguez-Carvajal, *Phys. Rev. B* **71**, 214402 (2005).
- ⁵C. Jardón, F. Rivadulla, L. E. Hueso, A. Fondado, M. A. López-Quintela, J. Rivas, R. Zysler, M. T. Causa, and R. D. Sánchez, *J. Magn. Magn. Mater.* **196–197**, 475 (1999).
- ⁶F. Rivadulla, L. E. Hueso, A. Fondado, M. A. López-Quintela, J. Rivas, R. Zysler, M. T. Causa, and R. D. Sánchez, *Solid State Commun.* **110**, 179 (1999).
- ⁷G. Catalan, *Appl. Phys. Lett.* **88**, 102902 (2006).
- ⁸N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kito, *Nature (London)* **436**, 1136 (2005).
- ⁹M. A. Subramanian, T. He, J. Chen, N. S. Rogado, T. G. Calvarese, and A. W. Sleight, *Adv. Mater. (Weinheim, Ger.)* **18**, 1737 (2006).
- ¹⁰Y. Takéuchi, T. Watanabe, and T. Ito, *Acta Crystallogr.* **3**, 98 (1950).
- ¹¹J. P. Attfield, A. M. T. Bell, L. M. Rodríguez-Martínez, J. M. Greneche, R. J. Cernik, J. F. Clarke, and D. A. Perkins, *Nature (London)* **396**, 655 (1998).
- ¹²J. P. Attfield, J. F. Clarke, and D. A. Perkins, *Physica B* **581**, 180 (1992).
- ¹³B. Rivas-Murias, F. Rivadulla, M. Sánchez-Andújar, A. Castro-Couceiro, M. A. Señarís-Rodríguez, and J. Rivas, *Chem. Mater.* **18**, 4547 (2006).
- ¹⁴M. Sanchez-Andujar, J. Mira, B. Rivas-Murias, S. Yáñez-Vilar, N. Biskup, J. Rivas, and M. A. Senaris-Rodriguez, *IEEE Trans. Magn.* **44**, 2989 (2008).
- ¹⁵J. Rivas, B. Rivas-Murias, A. Fondado, J. Mira, and M. A. Señarís Rodríguez, *Appl. Phys. Lett.* **85**, 6224 (2004).
- ¹⁶A. Castro-Couceiro, M. Sánchez-Andújar, B. Rivas-Murias, J. Mira, J. Rivas, and M. A. Señarís-Rodríguez, *Solid State Sci.* **7**, 905 (2005).
- ¹⁷S. Yáñez-Vilar, A. Castro-Couceiro, B. Rivas-Murias, A. Fondado, J. Mira, J. Rivas, and M. A. Señarís-Rodríguez, *Z. Anorg. Allg. Chem.* **631**, 2192 (2005).
- ¹⁸C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, and A. P. Ramírez, *Science* **293**, 673 (2001).
- ¹⁹P. Lunkenheimer, V. Bobnar, A. V. Pronin, A. I. Ritus, A. A. Volkov, and A. Loidl, *Phys. Rev. B* **66**, 052105 (2002).
- ²⁰D. C. Sinclair, T. B. Adams, F. D. Morrison, and A. R. West, *Appl. Phys. Lett.* **80**, 2153 (2002).
- ²¹J. Clerk Maxwell, *A Treatise on Electricity and Magnetism* (Clarendon, Oxford, 1892).
- ²²J. R. Macdonald, LEVM version 8.0 Complex Nonlinear Squares Fitting Program, 2003.