

Effect of grain boundary on resistive magnetodielectric property of polycrystalline γ -Fe₂O₃

T. Bonaedy · Y.S. Koo · K.D. Sung · K.M. Song ·
N. Hur · J.H. Jung

Received: 14 March 2008 / Accepted: 16 June 2008 / Published online: 6 July 2008
© Springer-Verlag 2008

Abstract We have investigated the role of the grain boundary on the resistive magnetodielectric property of polycrystalline γ -Fe₂O₃ through impedance spectroscopy measurements. Depending on the sample preparation temperature, the dielectric constant of γ -Fe₂O₃ is significantly different especially at low frequencies ($<10^4$ Hz) and high temperatures (>200 K). The value of the magnetodielectric effect at a specific frequency and the resonance frequency for the maximized magnetodielectric effect are different, although polycrystalline γ -Fe₂O₃ samples show a quite similar magnetoresistance. Through the experimentally obtained resistance ratio between the grain and the grain boundary, we can reproduce the magnetodielectric curves based on the Maxwell–Wagner model and the measured magnetoresistance.

PACS 75.50.Gg · 75.80.+q · 77.22.Ch

1 Introduction

The control of electrical properties of multiferroic materials, where more than two ferroic order parameters can co-exist and are coupled, by using an external magnetic field, or vice versa, has drawn great attention due to its scientific interest and technological importance [1–3]. For the change of polarization (magnetoelectric effect) and dielectric constant (magnetodielectric effect) upon a magnetic field, there

have been lots of theoretical and experimental works on the detailed mechanisms, such as the strong coupling between piezoelectricity and magnetostriction [4, 5].

On the other hand, recently, Catalan reported that the magnetodielectric effect can occur through a combination of the Maxwell–Wagner effect and magnetoresistance, called the resistive magnetodielectric effect, in single crystals with large charge depleted interfacial layers, superlattices, and polycrystalline samples, even without the magnetoelectric coupling [6, 7]. Such an extrinsic origin of the magnetodielectric effect could be practically useful due to the scarcity of magnetoelectric multiferroic single crystals [8, 9]. By choosing a material with large magnetoresistance, several experimental works have reported a large magnetodielectric effect near room temperature [10, 11]. However, there are few experimental works on the effect of the grain boundary in the Maxwell–Wagner model for the resistive magnetodielectric property in polycrystalline samples.

In this paper, we investigate the effect of the grain boundary on the resistive magnetodielectric property of polycrystalline γ -Fe₂O₃ samples through impedance spectroscopy measurements. Although the value of magnetoresistance is quite similar, we have found that the value of the magnetodielectric effect and the resonance frequency for the maximum magnetodielectric effect depend on the resistance ratio between the grain and the grain boundary of the samples. This work suggests that the control of the grain boundary is one of the simplest ways to maximize the resistive magnetodielectric effect for possible applications.

2 Experiments

High-quality polycrystalline γ -Fe₂O₃ samples were prepared through the conventional sonochemical method and

T. Bonaedy · Y.S. Koo · K.D. Sung · K.M. Song · N. Hur ·
J.H. Jung (✉)
Department of Physics, Inha University, Incheon 402-751, South
Korea
e-mail: jhjung@inha.ac.kr

subsequent heat treatment, as described elsewhere [12]. The obtained powders were hydrostatically pressed (~ 200 MPa) into a disk shape and fired at 200 and 250°C for 24 h in atmosphere. Hereafter, we call γ -Fe₂O₃ fired at 200 and 250°C γ -Fe₂O₃ (I) and γ -Fe₂O₃ (II), respectively. By using X-ray diffraction and optical absorption measurements, we have confirmed the single phase of both samples. (Below 150°C and above 350°C of the firing temperature, we could find some Fe₃O₄ and α -Fe₂O₃ impurity phases, respectively.) Based on Scherrer's formula for the X-ray diffraction (311) peak and independent transmission electron microscope measurements, we found that the grain sizes of both γ -Fe₂O₃ (I) and γ -Fe₂O₃ (II) were quite similar at ~ 25 nm.

The complex dielectric constant ($\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$) and impedance ($\tilde{Z} = Z_1 + iZ_2$) were obtained by an LCR meter in the frequency range of 20 Hz to 1 MHz and an applied voltage of 1 V. For these measurements, the samples were cut into the form of a thin plate with a thickness of ~ 1 mm. Silver electrodes with an area of ~ 14 mm² were evaporated on both sides of the sample. By using a conventional four-probe method, direct current resistivity was obtained. For magnetoresistance and magnetodielectric measurements, we applied an external magnetic field up to 9 T, by a superconducting magnet. Irrespective of a separate set of γ -Fe₂O₃ (I) and γ -Fe₂O₃ (II), we obtained quite reproducible experimental data shown below.

3 Results and discussion

Figure 1 shows the frequency-dependent dielectric constant (ε_1) of γ -Fe₂O₃ (I) (a solid line) and γ -Fe₂O₃ (II) (a dashed line) at 293 K. The values of ε_1 show strong frequency as well as temperature (see the inset of Fig. 1) dependences.

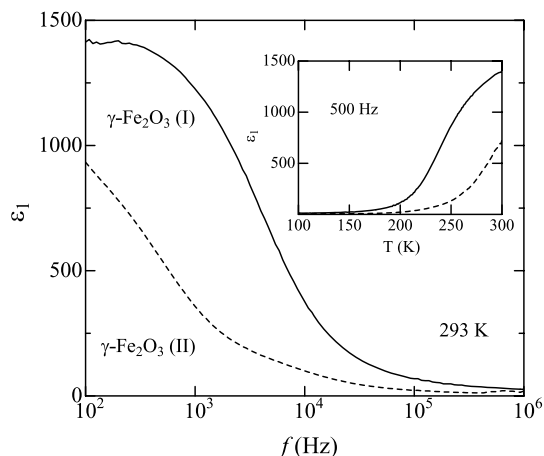


Fig. 1 The frequency-dependent dielectric constants of γ -Fe₂O₃ (I) (solid line) and γ -Fe₂O₃ (II) (dashed line) at 293 K. In the inset, temperature-dependent dielectric constants at 500 Hz are also shown

For example, the ratio of ε_1 between 10² and 10⁶ Hz is estimated to be ~ 60 for a γ -Fe₂O₃ (I) sample. While the values of ε_1 at low frequencies ($< 10^4$ Hz) and high temperatures (> 200 K) are quite different for the two samples, these values are quite similar at high frequencies and low temperatures.

Such a large value of ε_1 even in non-ferroelectric γ -Fe₂O₃, and its strong frequency as well as temperature dependences, have been explained by a possible Maxwell–Wagner two-capacitor model [12, 13] as similar to CaCu₃Ti₄O₁₂ [14]. Due to the polycrystalline nature of our γ -Fe₂O₃, the resistance and capacitance of the grain and grain boundary could be different and depend on the sample preparation temperature. According to the Maxwell–Wagner model [13], the complex dielectric constant can be written as

$$\varepsilon_1 = \frac{1}{C_0(R_G + R_{GB})} \frac{\tau_G + \tau_{GB} - \tau + \omega^2 \tau_G \tau_{GB} \tau}{1 + \omega^2 \tau^2}, \quad (1)$$

$$\varepsilon_2 = \frac{1}{\omega C_0(R_G + R_{GB})} \frac{1 - \omega^2 \tau_G \tau_{GB} + \omega^2 \tau (\tau_G + \tau_{GB})}{1 + \omega^2 \tau^2}, \quad (2)$$

where sub-indexes G and GB refer to the grain and the grain boundary, respectively. Also, R = resistance, C = capacitance, ω = ac frequency, $\tau_G = R_G C_G$, $\tau_{GB} = R_{GB} C_{GB}$, $\tau = (\tau_G R_{GB} + \tau_{GB} R_G) / (R_G + R_{GB})$, and C_0 = capacitance of vacuum. Especially, ε_1 can be approximated at low and high frequencies, respectively, as

$$\varepsilon_1(\omega \rightarrow 0) = \frac{R_G^2 C_G + R_{GB}^2 C_{GB}}{C_0(R_G + R_{GB})^2}, \quad (3)$$

$$\varepsilon_1(\omega \rightarrow \infty) = \frac{C_G C_{GB}}{C_0(C_G + C_{GB})}.$$

From (3), it is quite clear that the dielectric constant at low frequency should depend on R_G and R_{GB} , while that at high frequency is just the sum of C_G and C_{GB} in parallel. Therefore, the dielectric constant of the two γ -Fe₂O₃ samples at low frequency could be different, depending on the values of R_G and R_{GB} even with the same values of C_G and C_{GB} .

To estimate the values of R_G , R_{GB} , C_G , and C_{GB} of our γ -Fe₂O₃, we have performed an impedance spectroscopy analysis.¹ Figure 2 shows the complex impedance plot (Z_2 vs Z_1) of γ -Fe₂O₃ (I) (open circles) and γ -Fe₂O₃ (II) (open squares) at 293 K. For the frequency range of our measurement, i.e. 20 Hz to 1 MHz, the impedance plot clearly shows the two semicircles for both samples. The value of Z_1 at 20 Hz for γ -Fe₂O₃ (II) is around two times larger than that

¹Complex impedance and complex dielectric constant are interrelated as $\tilde{Z} = 1/(i\omega C_0 \tilde{\varepsilon})$.

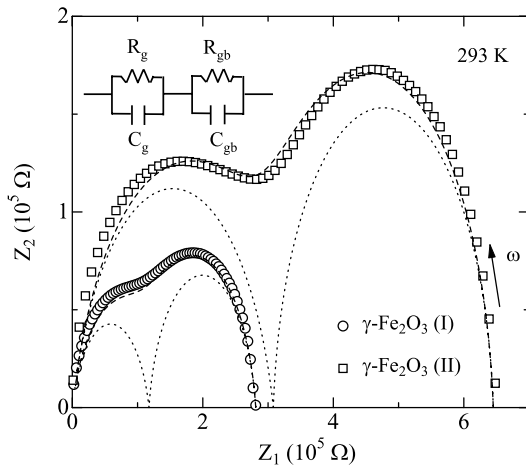


Fig. 2 Complex impedance spectroscopy plots of γ -Fe₂O₃ (I) (open circles) and γ -Fe₂O₃ (II) (open squares) at 293 K. Note that the scales of Z_1 and Z_2 axes are different. The dotted and dashed lines represent the contributions of each semicircle and the sum of two semicircles, respectively. In the inset, an equivalent circuit is schematically shown

for γ -Fe₂O₃ (I), and that at 10^6 Hz is nearly zero for both samples.

For the Maxwell–Wagner model, the impedance of a material has been modeled by two leaky capacitors in series, as schematically shown in the inset of Fig. 2. According to the general expression for impedance analysis [15], the semicircle on the left (at high frequency) is assigned as the contribution of the grain, while the semicircle on the right (at low frequency) is the result of the grain boundary. Also, the intercept of the semicircles on the real axis gives the resistance of the corresponding component contributing to the impedance of the sample.

Based on this approach, we fit the experimental data and obtain the values of R_G (R_{GB}) as ~ 1.17 M Ω (~ 1.64 M Ω) for γ -Fe₂O₃ (I) and ~ 3.03 M Ω (~ 3.42 M Ω) for γ -Fe₂O₃ (II). Note that the centers of the two semicircles of our γ -Fe₂O₃ are on axes down below the real Z_1 axis. Therefore, instead of the relation of $\omega R_G C_G = \omega R_{GB} C_{GB} = 1$ for the peak positions of two semicircles, we obtain the values of C_G and C_{GB} from the values of R_G and R_{GB} in (1), and also by fitting the magnetodielectric curves (see below), i.e. C_G (C_{GB}) as ~ 4.6 pF (~ 6 pF) for both samples. (For a separate set of γ -Fe₂O₃ (I) and γ -Fe₂O₃ (II), we have obtained nearly the same values of R_G , R_{GB} , C_G , and C_{GB} within 5% error bar.)

Figures 3a and b show magnetodielectric ($\Delta\varepsilon_1/\varepsilon_1 = \{\varepsilon_1(H) - \varepsilon_1(0)\}/\varepsilon_1(0)$) and magnetoresistance ($\Delta R/R = \{R(H) - R(0)\}/R(0)$) curves, respectively, for γ -Fe₂O₃ (I) (open circles) and γ -Fe₂O₃ (II) (open squares) at 293 K. While the resistance decreases with the increase of the external magnetic field, i.e. negative magnetoresistance, the dielectric constant increases with the increase of the external magnetic field, i.e. positive magnetodielectric effect. How-

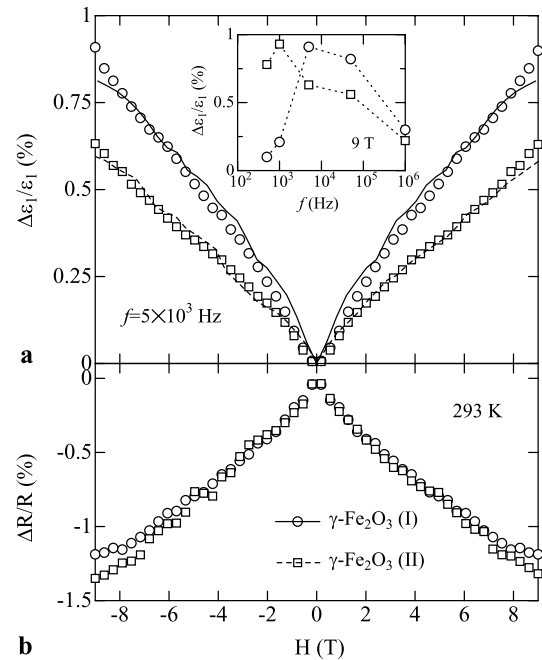


Fig. 3 (a) Measured (open dots) and calculated (solid lines) magnetodielectric curves at 5×10^3 Hz and (b) magnetoresistance of γ -Fe₂O₃ (I) (open circles) and γ -Fe₂O₃ (II) (open squares) at 293 K. In the inset of (a), we also show the values of the magnetodielectric effect at 9 T for selected frequencies

ever, one may clearly notice that while the values of the magnetoresistance are similar for the two samples, i.e. $\sim -1.3\%$ at 9 T, those of the magnetodielectric effect are different, i.e. $\sim 0.91\%$ for γ -Fe₂O₃ (I) and $\sim 0.63\%$ for γ -Fe₂O₃ (II) at 5×10^3 Hz. As shown in the inset of Fig. 3a, the magnetodielectric effect at 9 T seems to be maximized near 5×10^3 Hz for γ -Fe₂O₃ (I), while it is maximized near 1×10^3 Hz for γ -Fe₂O₃ (II).

The main reason for the deviation of the magnetodielectric curves for the two γ -Fe₂O₃ samples, even with the quite similar values of magnetoresistance and capacitance, should come from the different values of the resistance ratio between the grain and the grain boundary, i.e. $R_{GB}/R_G \sim 1.40$ for γ -Fe₂O₃ (I) and $R_{GB}/R_G \sim 1.13$ for γ -Fe₂O₃ (II). According to (1), the value of $\Delta\varepsilon_1/\varepsilon_1$ should depend on the values of $\Delta R/R$, R_{GB}/R_G , and C_{GB}/C_G . To directly show the effect of R_{GB}/R_G in our γ -Fe₂O₃, we calculated the magnetodielectric curves by inserting the experimentally obtained $\Delta R/R$,² R_{GB}/R_G , and C_{GB}/C_G in (1). As shown clearly in Fig. 3a, the calculated $\Delta\varepsilon_1/\varepsilon_1$ (a solid line for γ -Fe₂O₃ (I) and a dashed line for γ -Fe₂O₃ (II)) fit the experimental $\Delta\varepsilon_1/\varepsilon_1$ curves well for both samples.

²We assumed that magnetoresistance should occur only in the grain, since it is difficult for tunneling magnetoresistance through the grain boundary to occur at high temperatures like 293 K.

Enhancement of the magnetodielectric effect through the increase of the resistance ratio between the grain and grain boundary in γ -Fe₂O₃ might imply the possible tunability of the resistive magnetodielectric effect through grain boundary control. It is well known that the resistance of the grain boundary is easily controlled by changing the annealing temperature and/or environment [16]. Therefore, we may infer that polycrystalline ferromagnetic insulators with large resistance ratio between the grain and the grain boundary, besides large magnetoresistance, could be one of the good candidates for the possible device application by using the resistive magnetodielectric effect.

4 Summary

In summary, we showed that the resistance ratio between the grain and the grain boundary is one of the key factors to control the magnetodielectric effect in polycrystalline γ -Fe₂O₃ samples through impedance spectroscopy measurements. Our result suggests that the control of the grain boundary through the annealing environment and/or temperature should be quite useful for possible magnetodielectric devices.

Acknowledgements This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-070-C00053) and (KRF-2006-331-C00092).

References

1. T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, *Nature (Lond.)* **426**, 55 (2003)
2. N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha, S.-W. Cheong, *Nature (Lond.)* **429**, 392 (2004)
3. M. Gajek, M. Bibes, S. Fusil, K. Bouzehouane, J. Fontcuberta, A. Barthélémy, A. Fert, *Nat. Mater.* **6**, 296 (2007)
4. H. Zheng, J. Wang, S.E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S.R. Shinde, S.B. Ogale, F. Bai, D. Viehland, Y. Jia, D.G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, *Science* **303**, 661 (2004)
5. C.-W. Nan, G. Liu, Y.-H. Lin, H. Chen, *Phys. Rev. Lett.* **94**, 197203 (2005)
6. G. Catalan, *Appl. Phys. Lett.* **88**, 102902 (2006)
7. G. Catalan, J.F. Scott, *Nature (Lond.)* **448**, E4 (2007)
8. G. Lawes, R. Tackett, O. Masala, B. Adhikary, R. Naik, R. Sehadri, *Appl. Phys. Lett.* **88**, 242903 (2006)
9. Y.S. Koo, T. Bonaedy, K.D. Sung, J.H. Jung, J.B. Yoon, Y.H. Jo, M.H. Jung, H.J. Lee, T.Y. Koo, Y.H. Jeong, *Appl. Phys. Lett.* **91**, 212903 (2007)
10. J. Rivas, J. Mira, B. Rivas-Murias, A. Fondado, J. Dec, W. Kleemann, M.A. Señaris-Rodríguez, *Appl. Phys. Lett.* **88**, 242906 (2006)
11. J. Cao, R.C. Rai, S. Brown, J.L. Musfeldt, R. Tackett, G. Lawes, Y.J. Wang, X. Wei, M. Apostu, R. Suryanarayanan, A. Revcolevschi, *Appl. Phys. Lett.* **91**, 021913 (2007)
12. T. Bonaedy, Y.S. Koo, K.D. Sung, J.H. Jung, *Appl. Phys. Lett.* **91**, 132901 (2007)
13. A. von Hippel, *Dielectrics and Waves* (Artech House, London, 1995)
14. D.C. Sinclair, T.B. Adams, F.D. Morrison, A.R. West, *Appl. Phys. Lett.* **80**, 2153 (2002)
15. E. Barsoukov, J.R. Macdonald, *Impedance Spectroscopy* (Wiley, New York, 2005)
16. A.J. Moulson, J.M. Herbert, *Electroceramics: Materials, Properties and Applications* (Chapman and Hall, London, 1990)