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자성산화물의 자기저항에 의한 자기유전성질에 관한 연구

Resistive Magnetodielectric Property of Magnetic Oxide

2009년 2월

인하대학교 대학원
물리학과(이론 및 물성물리 전공)

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이 논문을 석사학위 논문으로 제출함

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Abstract

Recent theory paper [G. Catalan Appl. Phys. Lett. 88, 102902 (2006)] had shown that magnetoresistance and Maxwell-Wagner model can yield magnetocapacitance (magnetodielectric) effect. Catalan also argued that the sign of magnetodielectric effect depends on whether the negative magnetoresistance takes place at the grain or grain boundary. This thesis is focused on investigating resistive magnetodielectric effect in polycrystalline $\gamma$-Fe$_2$O$_3$ and ferroelectric-ferromagnetic composites samples.

The dielectric constants of $\gamma$-Fe$_2$O$_3$ have strong temperature and frequency dependences. That seems to follow Maxwell-Wagner model. Positive magnetodielectric effect is observed with negative magnetoresistance. The value of magnetodielectric effect of polycrystalline $\gamma$-Fe$_2$O$_3$ is maximized at specific frequency, which is inversely proportional to resistivity. The role of grain boundary on the resistive magnetodielectric property of polycrystalline $\gamma$-Fe$_2$O$_3$ is investigated through the impedance spectroscopy measurement. We have found that, the resistance ratio between grain and grain-boundary could affect the value of magnetodielectric effect. By using polycrystalline $\gamma$-Fe$_2$O$_3$, we are able to prove that resistive magnetodielectric effect can be originated from Maxwell-Wagner model, and magnetoresistance, and its value depends on the resistance ratio between the grain and the grain boundary.

In order to understand resistive magnetodielectric effect more deeply, the sign of magnetodielectric effect is studied in ferroelectric-ferromagnetic i.e. Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-La$_{0.7}$Ca$_{0.3}$MnO$_3$ composites. Positive magnetodielectric effect is maximized at 270 K, while that is negatively maximized near 10 K. The negative magnetoresistance of La$_{0.7}$Ca$_{0.3}$MnO$_3$ grain can be responsible for the positive magnetodielectric effect at 270 K. On the other hand, negative magnetodielectric effect at 10 K may be due to intrinsic magnetoelectric through strain not the negative magnetoresistance from grain-boundaries.

Key words: magnetoresistance, magnetodielectric property, ferroelectric-ferromagnetic composites, magnetoelectric property
국문요약

최근 이론 관련 논문에서 [G. Catalan Appl. Phys. Lett. 88, 102902 (2006)] 맥스웰-와그너 모델과 자기저항이 자기유전성질을 유도할 수 있다는 것을 보여왔다. Catalan은 자기유전성질의 부호가 grain 과 grain boundary 의 자기저항에 의존한다고 언급했다. 이러한 개념은 polycrystalline $\gamma$-Fe$_2$O$_3$ 와 강유전성-강자성이 혼합된 물질의 자기저항, 자기유전성질의 연구에 적용된다. $\gamma$-Fe$_2$O$_3$의 유전 상수는 온도의 변화와 주파수에 크게 의존된다. 이것은 마치 맥스웰-와그너 모델을 따르는 것처럼 보인다. 양(陽)의 자기유전성질은 음(陰)의 자기저항성질을 보인다. Polycrystalline $\gamma$-Fe$_2$O$_3$의 자기유전성질 값은 특정한 주파수에서 저항에 비례하는 최대값을 가진다. Polycrystalline $\gamma$-Fe$_2$O$_3$의 자기유전성질에서 grain boundary 의 성질은 임피던스 스펙트로스코프로 측정되었다. 우리는 여기서 grain과 grain boundary 의 저항의 비는 자기유전성질 값에 영향을 줄 수 있다는 것을 발견했다. Polycrystalline $\gamma$-Fe$_2$O$_3$에서, 자기유전성질은 맥스웰-와그너 모델, 자기저항으로부터 설명될 수 있고, 그것의 값은 grain과 grain boundary 의 저항의 비에 의존한다.

자기유전성질을 좀 더 잘 이해하기 위해, Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-La$_{0.7}$Ca$_{0.3}$MnO$_3$ 혼합물에서의 자기유전성질을 연구하였다. 양(陽)의 자기유전성질은 270K에서 최대가 되었고, 10K에서 최소가 되었다. La$_{0.7}$Ca$_{0.3}$MnO$_3$의 음(陰)의 자기저항성질은 270K에서 양(陽)의 자기유전성질을 유도할 수 있다. 다른 한편, 10K에서 음(陰)의 자기유전성질은 grain boundary 의 자기저항에 의한 것이 아니라, strain에 의한 고유한 자기유전성질이다.
Chapter 1
Introduction

1.1 Multiferroics

Recently, multiferroics materials become the hot issue that many people study in due to their unique property. Materials are called multiferroics, sometimes called magnetoelectric, when two or more of the primary ferroic properties (ferroelectric, ferromagnetic, and ferroelastic) are united in the same phase [1]. The definition of a ferroic was motivated by the desire to categorize materials and effects that allow the formation of switchable domains [2]. Since domains can be formed in the case of ferroelectric, ferromagnetic, ferrotoroidic or ferroelastic ordering, primary ferroics are compounds exhibiting a form of ordering from this group.

Ferromagnetic ferroelectric multiferroics are particularly appealing not only because they have the properties of both parent compounds, but also because interactions between the magnetic and electric polarizations lead to additional functionalities. For example, the magnetoelectric effect (the induction of a magnetization by an electric field or of a polarization by a magnetic field) could yield entirely new device paradigms [3].

In magnetoelectric multiferroics, magnetic order is coupled to polarization and also dielectric constant. The change of dielectric constant by applied magnetic field of magnetoelectric multiferroics is called magnetocapacitance (or magnetodielectric). This effect has been reported in many single materials such as TbMnO₃ [4], TbMn₂O₅ [5], DyMnO₃ [6], DyMn₂O₅ [7], BiMnO₃ [8], CdCr₂S₄ [9], La₂NiMnO₆ [10].

Besides in magnetoelectric multiferroics single crystal, multiferroic composites which are composed of ferroelectric materials with large electric polarization and ferromagnetic ones with large magnetization are also intensively studied. Multiferroics composites formed by ferroelectric and ferromagnetic material such as combination of piezoelectric ceramic (e.g. BaTiO₃) and magnetostrictive materials (e.g. CoFe₂O₄) exhibit a large magnetoelectric response at room temperature [11]. The mechanism of
magnetoelectric behavior is depending on their microstructure and the coupling interaction across the ferroelectric-ferromagnetic interface [12].

Coupling between ferroelectricity and ferromagnetism would be applicable for multistate memory, or memories with dual read-write mechanism [13]. Especially, materials with the tunable change of dielectric constant (magnetodielectric effect) and/or polarization (magnetoelectric effect) by using low magnetic field near room temperature are highly required for technological application.
Figure 1.1: Magnetodielectric effect of BiMnO$_3$ [8]

Figure 1.2: (a). Change of dielectric constant vs magnetic field of DyMn$_2$O$_5$, (b). Change of the electric polarization by magnetic field of DyMn$_2$O$_5$ [7]
1.2 Resistive Magnetodielectric Effect

There is another way to produce magnetodielectric effect instead of magnetoelectric coupling. Magnetoresistance combine with Maxwell-Wagner effect can also produce large magnetodielectric effect [14]. Such an extrinsic origin of magnetodielectric effect i.e. resistive magnetodielectric effect could be practically useful due to the scarcity of magnetoelectric multiferroics single crystal [15,16].

In resistive magnetodielectric effect, three features are noteworthy. Magnetoresistance can yield magnetocapacitance. The sign of magnetocapacitance (magnetodielectric) depends on whether the magnetoresistace takes place whether at the grain or the grain boundary (see figure 1.3). And also, the magnetoresistance directly affect the dielectric loss [14].

Resistive magnetodielectric effect has been reported in manganites [16], ferrite nanoparticles [15]. According to G.Lawes et. al. result’s on $\gamma$-Fe$_2$O$_3$, this material showed a field dependent dielectric constant above blocking temperature (200 K and 300 K) and a peak in dielectric loss at the magnetic blocking temperature [15]. Unfortunately, clear experimental works are rare for the combined role of the Maxwell-Wagner effect and magnetoresistance.
Figure 1.3: Calculated magnetocapacitance and magnetolosses of magnetoresistive material when the magnetoresistance is core-based and interfaced-based [14].

Figure 1.4: Calculated relative dielectric constant and dielectric losses as a function of frequency [14].
1.3 Outline of Thesis

In this thesis, the author investigated resistive magnetodielectric effect that exists in polycrystalline $\gamma$-Fe$_2$O$_3$ and ferroelectric-ferromagnetic composites i.e. Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-La$_{0.7}$Ca$_{0.3}$MnO$_3$. In chapter 2, the theoretical backgrounds such as, Maxwell-Wagner effect and impedance spectroscopy analysis are discussed. Chapter 3 presents experimental details for sample preparation and electric and magnetic property measurement of the sample. In chapter 4, systematical experiment results are shown and discussed. The summary of the thesis is presented in chapter 5.
Chapter 2
Theoretical Backgrounds

2.1 Maxwell-Wagner Effect

For the dielectric constant to be measured in a multiferroics system, a capacitor structure has to be made so that an ac electric field can be applied to it. The response to the electric field will contain at least one capacitive (dielectric) term and resistive (leakage) term. The heterogeneous nature of sample (the grain and the grain boundary) can be described by the Maxwell-Wagner capacitor model.

Maxwell-Wagner capacitor model is originated from Maxwell-Wagner two-layer condenser. The dielectric consists of two parallel sheets of material (1) and (2), characterized by their dielectric constant, conductivity, and thickness \((\varepsilon_1', \sigma_1, d_1)\) and \((\varepsilon_2', \sigma_2, d_2)\), respectively. When a d-c field is suddenly applied, the initial field distribution corresponds to the electrostatic requirement of constant flux density [18].

\[
D_1 = D_2
\]

or

\[
\frac{E_1}{E_2} = \frac{\varepsilon_2'}{\varepsilon_1'} \tag{2.1}
\]

Whereas the final distribution follows from the condition of current continuity

\[
J_1 = J_2
\]

Or

\[
\frac{E_1}{E_2} = \frac{\sigma_2}{\sigma_1} \tag{2.2}
\]
This Maxwell-Wagner two layer condenser can be derived into the equivalent circuit as shown in figure 2.2.

\[ V = V_1 + V_2 \]  \hspace{1cm} (2.3)

\[ I = C_1 \frac{dV_1}{dt} + \frac{V_1}{R_1} = C_2 \frac{dV_2}{dt} + \frac{V_2}{R_2} \]

\[ C_1 = \frac{A}{d_1} \epsilon'_1 \quad C_2 = \frac{A}{d_2} \epsilon'_2 \]  \hspace{1cm} (2.4)

\[ R_1 = \frac{d_1}{A \sigma_1} \quad R_2 = \frac{d_2}{A \sigma_2} \]

(where \( \sigma \) is the conductivity)

\( A \) is the surface area of the plate capacitor.

For \( V_1 \) and \( V_2 \), we obtain

\[ V_1 = V \frac{R_1}{R_1 + R_2} \left[ 1 - \left( 1 - \frac{C_2 R_2}{\tau} \right) e^{-t/\tau} \right] \]

\[ V_2 = V \frac{R_2}{R_1 + R_2} \left[ 1 - \left( 1 - \frac{C_1 R_1}{\tau} \right) e^{-t/\tau} \right] \]  \hspace{1cm} (2.5)

where relaxation time (\( \tau \))

\[ \tau = \frac{R_1 R_2 (C_1 + C_2)}{R_1 + R_2} \]
The steady-state solution, when an a-c voltage $V = V_0 e^{i\omega t}$ is applied, can be derived from the admittance of the circuit

$$ Y = \frac{I}{V} = \frac{Y_1 Y_2}{Y_1 + Y_2} \quad (2.6) $$

where

$$ Y_1 = \frac{1}{R_1} + i\omega C_1 = \frac{1 + i\omega \tau_1}{R_1} \quad (\tau_1 = R_1 C_1), $$

$$ Y_2 = \frac{1}{R_2} + i\omega C_2 = \frac{1 + i\omega \tau_2}{R_2} \quad (\tau_2 = R_2 C_2). $$

The admittance may be rewritten as

$$ Y = \frac{1}{R_1 + R_2} \frac{(1 + i\omega \tau_1)(1 + i\omega \tau_2)}{1 + i\omega \tau}. $$

$$ (2.7) $$

The admittance determines the complex permittivity (dielectric constant) of the capacitor as

$$ Y = i\omega \tilde{\kappa} C_0, \quad \tilde{\kappa} = \frac{\varepsilon}{\varepsilon_0} $$

$$ (2.8) $$

where $C_0 = \frac{A\varepsilon_0}{d}$, $d = d_1 + d_2$. 

Figure 2.2: Maxwell-Wagner equivalent circuit of two-layer condenser
Material (1) and material (2) can be referred to grain-boundary (gb) layer and grain (g) layer, respectively. The real and imaginary parts of dielectric constant of two layers condenser are

\[
\varepsilon_1(\omega) = \frac{1}{C_0(R_{gb} + R_g)} \frac{\tau_{gb} + \tau_g - \tau + \omega^2 \tau_{gb} \tau_g \tau}{1 + \omega^2 \tau^2} \quad (2.9)
\]

\[
\varepsilon_2(\omega) = \frac{1}{\omega C_0(R_{gb} + R_g)} \frac{1 - \omega^2 \tau_{gb} \tau_g + \omega^2 \tau(\tau_{gb} + \tau_g)}{1 + \omega^2 \tau^2} \quad (2.10)
\]

Where, \(\omega = \text{ac frequency} R = \text{resistance}, C = \text{capacitance}, \tau_{gb} = R_{gb}C_{gb}, \tau_g = R_gC_g, \tau = (\tau_{gb}R_g + \tau_gR_{gb})/(R_g + R_{gb}),\) and \(C_0 = \text{capacitance of vacuum.}\) Especially, \(\varepsilon_1\) can be approximated at low and high frequencies, respectively, as

\[
\varepsilon_1(\omega \rightarrow 0) = \frac{R_g^2C_g + R_{gb}^2C_{gb}}{C_0(R_g + R_{gb})^2}, \quad (2.11)
\]

\[
\varepsilon_1(\omega \rightarrow \infty) = \frac{C_gC_{gb}}{C_0(C_g + C_{gb})}. \quad (2.12)
\]

### 2.2 Impedance Spectroscopy Analysis

The ac impedance spectroscopy is widely used to analyze electric respond of electrical materials. There are four possible complex formalisms that can be analyzed such as the impedance \((\tilde{Z})\), the electric modulus \((\tilde{M})\), the admittance \((\tilde{Y})\), and the permittivity \((\tilde{\varepsilon})\)[19]. These are related each other:

\[
\tilde{M} = i\omega C_0 \tilde{Z}, \quad (2.13)
\]

\[
\tilde{\varepsilon} = (\tilde{M})^{-1}, \quad (2.14)
\]

\[
\tilde{Y} = (\tilde{Z})^{-1}, \quad (2.15)
\]

\[
\tilde{Y} = i\omega C_0 \tilde{\varepsilon}, \quad (2.16)
\]

where \(\omega\) is the angular frequency \(2\pi f\).

In order to analyze and interpret experimental data, it is need to have a model equivalent circuit that provides a realistic representation of electrical properties. The circuit as shown in figure 2.3 is widely used to represent grain and grain-boundary
phenomena in polycrystalline materials, especially in cases, where the grain boundary impedance is the dominant impedance of the sample.

By using a series circuit such as given in figure 2.2, it is desired to separate each of the parallel RC elements and measure their component R and C values. Each parallel RC element gives rise to a semicircle in the complex impedance (Z’’ vs Z’) [20]. We can see it from the equation for the impedance of this circuit:

\[
\tilde{Z} = \left( \frac{1}{R_1} + i\omega C_1 \right)^{-1} + \left( \frac{1}{R_2} + i\omega C_2 \right)^{-1}
\]

\[
\tilde{Z} = Z’ - i\omega Z’’,
\]

where

\[
Z’ = \frac{R_1}{1 + (\omega R_1 C_1)^2} + \frac{R_2}{1 + (\omega R_2 C_2)^2}, \tag{2.17}
\]

and

\[
Z’’ = R_1 \left( \frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2} \right) + R_2 \left( \frac{\omega R_2 C_2}{1 + (\omega R_2 C_2)^2} \right). \tag{2.18}
\]

The response of this circuit in the two semicircles is shown in figure 2.3. Here, we attribute R_1 as the resistance grain boundary (R_{gb}) and R_2 as the resistance of grain (R_g), same explanation for the capacitance. The frequency of peak maxima in Z’’ spectroscopic plot is given by the relation \(2\pi fRC = 1\). These two semicircles will give us information of the role of grain boundary and grain conduction of the sample. The first semicircle at lower frequency belongs to grain boundary respond the electric field, while the other semicircle at higher frequency is the result of grain. The intercept of the semicircles on the real axis gives the resistance of the corresponding component contributing to the impedance of the sample.
Figure 2.3: Complex impedance for the circuit shown

- $C_1 = 4 \times 10^9 \text{F}$
- $C_2 = 1 \times 10^{10} \text{F}$
- $R_1 = 4 \times 10^5 \Omega$
- $R_2 = 3 \times 10^5 \Omega$
Chapter 3
Experimental Details

3.1 Experimental Details of Polycrystalline $\gamma$-Fe$_2$O$_3$

Polycrystalline $\gamma$-Fe$_2$O$_3$ samples were made by sonochemical method [21]. First, two kinds of solution were prepared before sonochemical reaction is started. The first solution was made from FeCl$_2$.4H$_2$O and CH$_3$COOH in 500 ml distilled water. The other solution was made from CH$_3$COONH$_4$, NH$_4$OH, and NaNO$_2$ in 500 ml distilled water. Lines and peristaltic pump with flow rate 3.0 ml/min were used to flow these two solutions into a reaction vessel. The ultrasound wave (70 W, 10 kHz) is applied for 2 hours into the reaction vessel and kept it at 70 $^\circ$C. Reacted solutions were filtered and dried at 110 $^\circ$C. The obtained powders were hydrostatically pressed (~200 MPa) into disk shape and fired at 250 $^\circ$C for 24 hours in atmosphere. The quality of our sample is observed by using x-ray diffraction (RIGAKU DMAX 2500) and optical absorption measurements. Grain size of polycrystalline $\gamma$-Fe$_2$O$_3$ is analyzed by using field-effect transmission electron microscope.

Direct current resistivity was measured by using a standard four-probe method and current source measure unit (KEITHLEY model 236). Complex dielectric constant and complex impedance were measured by using a standard two-probe measurement and LCR meter (Agilent 4284A Precision) in the frequency range from 20 Hz to 1MHz and an applied voltage of 1 V. For those measurements, the samples were cut into the form of a thin plate with a thickness of ~1mm, and silver paste electrodes with area of ~4mm$^2$ were evaporated on both sides of the samples. Physical property measurement system (PPMS from Quantum Design) is used to measure magnetoresistance and magnetodielectric effect of $\gamma$-Fe$_2$O$_3$ samples.
Figure 3.1: Schematic diagram of sample preparation of polycrystalline $\gamma$-Fe$_2$O$_3$
3.2 Microstructure of Polycrystalline $\gamma$-Fe$_2$O$_3$

Figure 3.2 shows the x-ray diffraction pattern of polycrystalline $\gamma$-Fe$_2$O$_3$ with several sintering temperatures. From the XRD pattern can be seen that below 350 °C sintering temperature, single phase $\gamma$-Fe$_2$O$_3$ exists in the sample. Some impurities like $\alpha$-Fe$_2$O$_3$ phase appear in the sample above 350 °C sintering temperature e.g. 400 °C. This impurity is detected at the angle (hkl), such as 33.16° (104), 40.8° (113), 49.5° (024) of x-ray diffraction result.

Transmission electron microscope measurement is used to analyze the grain size of polycrystalline $\gamma$-Fe$_2$O$_3$. As shown in figure 3.3, the grain size of polycrystalline $\gamma$-Fe$_2$O$_3$ is ~25 nm. This is agree with the x-ray diffraction result in which there is no broadening peak that usually appear for quiet small grain size (<10 nm).
Figure 3.2: X-ray diffraction pattern of polycrystalline $\gamma$-Fe$_2$O$_3$
Figure 3.3: TEM result of polycrystalline $\gamma$-Fe$_2$O$_3$
3.3 Experimental Details of Polycrystalline $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3-\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Composites

$(1-x)\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3-(x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($x = 0$, 0.05, 0.1, and 0.15) composites were prepared through a conventional double sintering process. The $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BSTO) phase was made of commercial $\text{BaCO}_3$, $\text{TiO}_2$, and $\text{SrCO}_3$ in stochiometric proportion while the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) phase was synthesized by mixing the commercial $\text{La}_2\text{O}_3$, $\text{CaCO}_3$, and $\text{MnO}_2$. The samples were sintered at 1300 °C and 1350 °C, respectively. Separately prepared pellets were crushed into powders and mixed with appropriate volume fraction. Mixed powders were hydrostatically pressed (~200 MPa) into disk shapes and sintered at 1100 °C for 10 hours in air. We measured x-ray diffraction to analyze sample quality of our composites samples.

Complex dielectric constant and electrical polarization were examined by an LCR meter (Agilent 4284A Precision) with applied voltage of 1 V and a home-built Sawyer-Tower circuit, respectively. For these measurements, the samples were cut into the form of thin plate with thickness of ~0.3 mm, and silver electrodes with areas of ~4.7 mm² were evaporated on both sides of the samples. Direct current (dc) resistivity was measured by a standard four-probe method and current source measure unit (KEITHLEY model 236). Physical property measurement system (PPMS from Quantum Design) is used to measure magnetoresistance and magnetodielectric effect of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3-\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ composites samples.
Figure 3.4: Schematic diagram of sample preparation of polycrystalline (1-x) Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ - (x) La$_{0.7}$Ca$_{0.3}$MnO$_3$ composites
3.4 X-Ray Diffraction Result of Polycrystalline Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-La$_{0.7}$Ca$_{0.3}$MnO$_3$ Composites

The identification phase of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BSTO)-La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) composites is based on Joint Committee on Powder Diffraction Standards-The International Center for Diffraction Data (JCPDS-ICDD). Figure 3.5 shows the x-ray diffraction result of 0.85BSTO-0.15LCMO (in volume %) samples and for comparison XRD pattern of BSTO and LCMO. According to the result, all the x-ray diffraction peaks belong to the parent phase (BSTO and LCMO).
Figure 3.5: Powder x-ray diffraction patterns of polycrystalline $0.85\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$-$0.15\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ composites, $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$, and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. 
Chapter 4
Results and Discussion

4.1 Studies of Polycrystalline $\gamma$-Fe$_2$O$_3$

4.1.1 Dielectric Properties of Polycrystalline $\gamma$-Fe$_2$O$_3$

Figure 4.1 and 4.2 show the temperature dependent of dielectric constant $\varepsilon_1$ and loss tan $\delta$ of $\gamma$-Fe$_2$O$_3$ at selected frequencies i.e. 1 kΩ, 10 kΩ, 100 kΩ, and 1 MΩ. The dielectric constant and dielectric loss show strong temperature dependence, especially above 100 K and frequency dependence at below $10^5$ Hz. The dielectric constant, in case $10^3$ Hz, at room temperature (300 K) approximately around three times larger than 100 K. While at high frequency (1 MΩ) the dielectric constants show quiet small temperature dependences. This large value of dielectric constant and the reduction of dielectric constant with the increase of frequency may be due to the artifact of carrier migration.

Figure 4.3 shows Cole-Cole plot, i.e. the plot between $\varepsilon_1$ and $\varepsilon_2$, at 20 K. Cole-Cole plot shows linear behavior. It suggests that the dielectric property of $\gamma$-Fe$_2$O$_3$ sample is lossy and more than two relaxation mechanisms play a role [18].

This polycrystalline $\gamma$-Fe$_2$O$_3$ sample is highly insulating material. As seen in figure 4.4 the resistivity of $\gamma$-Fe$_2$O$_3$ is increase as the temperature decrease. This insulating ferromagnetic behavior of the $\gamma$-Fe$_2$O$_3$ sample is possible to treat as two capacitors with different conductivities, i.e. one for grain and the other for grain boundary and should be well described by using Maxwell-Wagner series capacitor model [18].
Figure 4.1: Dielectric constant as function of temperature and frequency of \( \gamma\text{-Fe}_2\text{O}_3 \)

Figure 4.2: Dielectric loss as function of temperature and frequency of \( \gamma\text{-Fe}_2\text{O}_3 \)
Figure 4.3: Cole-Cole Plot at 20K

Figure 4.4: Temperature Dependent of Resistivity
4.1.2 Magnetic Properties of Polycrystalline $\gamma$-Fe$_2$O$_3$

Negative magnetoresistance, i.e. the decrease of resistance with applied magnetic field of $\gamma$-Fe$_2$O$_3$ is shown in figure 4.5. Due to high resistivity of the $\gamma$-Fe$_2$O$_3$ sample, the magnetoresistance below 180 K is difficult to measure. Absolute value of magnetoresistance is increase as the temperature decrease (solid circle in the figure 4.7).

Figure 4.6 shows the magnetodielectric effect ($\Delta\varepsilon/\varepsilon_1$) at $5 \times 10^3$ Hz of $\gamma$-Fe$_2$O$_3$. The polycrystalline $\gamma$-Fe$_2$O$_3$ has positive magnetodielectric effect i.e. the increase of dielectric constant with magnetic field. As reported before by Lawes et.al, above 40 K the value of magnetodielectric effect of $\gamma$-Fe$_2$O$_3$ is increase and shows maximum value (~0.4%) at 200 K. In contrary, there is no magnetic field dependence of dielectric constant below 40 K [15]. From figure 4.7, we can see that the value of magnetodielectric effect is decreasing below 200 K and reaches to ~0.2% at 20 K, this is almost same with the G.Lawes’ result.

This positive magnetodielectric effect could be related with magnetoresistance. Magnetodielectric effect can occur through combination of Maxwell-Wagner effect and magnetoresistance, called the resistive magnetodielectric effect. The sign of magnetodielectric effect depends on whether the (negative) magnetoresistance takes place at the grain boundary or at the grain [14].

The magnetodielectric effect is calculated in order to understand the origin of magnetodielectric effect of the $\gamma$-Fe$_2$O$_3$ sample. Through the combination of equation (2.9) and (2.10) and magnetoresistance, the calculation result is shown in figure 4.6 (solid line). The calculation of magnetodielectric effect also needs experimental value of resistivity and magnetoresistance, and assume the magnetoresistance only in grain. By adjusting the value of capacitance of grain and grain boundary and the ratio between resistance of grain and grain boundary as fitting parameter can reproduce the sign of magnetodielectric effect as shown in figure 4.6 for some selected temperatures, such as 200 °C, 250 °C, 290 °C.
Figure 4.5: Magnetoresistance of $\gamma$-Fe$_2$O$_3$ at selected temperature.
Figure 4.6: Measured (closed dots) and calculated (solid lines) of magnetodielectric curves at $5 \times 10^3$ Hz of $\gamma$-Fe$_2$O$_3$. 
Figure 4.7: The values of magnetodielectric effect (solid squares) and absolute value of magnetoresistance (solid circles) at 1 Tesla.
4.1.3 Frequency Dependent Dielectric Constant Ratio of Polycrystalline γ-Fe₂O₃

Figure 4.8 shows the frequency dependence of dielectric constant ratio between 1T and 0T, i.e. $\varepsilon_1(1T)/\varepsilon_1(0T)$ at 290 K, 200 K, 150 K. The frequency for maximum magnetodielectric effect $f_{\text{max}}$ significantly increases with temperature, as marked as solid circle. At 150 K, positive magnetodielectric effect is significantly increased below $10^4$ Hz (see figure 4.8) and shows a maximum peak near 200 Hz.

Since the charge carriers in grain and/or grain boundary will respond to an external electric field in low frequency region (see figure 4.9), hence, the magnetodielectric effect should show frequency dependence. Relaxor like behavior of the maximum magnetodielectric effect can also be explained by the conductivity cutoff, i.e., the frequency dependent magnetodielectric effect should show a peak when measured frequency nearly coincides with $1/RC$ [14].
Figure 4.8: Frequency dependent dielectric constant ratio \([\varepsilon_1(1T)/\varepsilon_1(0T)]\) for 150 K, 200 K, and 290 K. The frequencies for maximum magnetodielectric effect \(f_{\text{max}}\) are marked as solid circles.
Figure 4.9: Frequency dependence dielectric constant at 0T (solid line) and 1T (dashed line)
4.1.4 The Role of Grain Boundary on Resistive Magnetodielectric Effect of Polycrystalline $\gamma$-Fe$_2$O$_3$

In order to investigate the effect of the grain boundary on the resistive magnetodielectric effect of polycrystalline $\gamma$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$ samples are made by varying the sintering temperature. The $\gamma$-Fe$_2$O$_3$ (I) sintered at 200 $^\circ$C while the $\gamma$-Fe$_2$O$_3$ (II) sintered at 250 $^\circ$C. Figure 4.10 shows the frequency-dependent dielectric constant ($\varepsilon_1$) of $\gamma$-Fe$_2$O$_3$ (I) (solid line) and $\gamma$-Fe$_2$O$_3$ (II) (dashed line) at 293 K. The values of $\varepsilon_1$ show strong frequency as well as temperature (figure 4.11) dependences. For example, the ratio of $\varepsilon_1$ between $10^2$ and $10^6$ Hz is estimated to be $\sim$60 for $\gamma$-Fe$_2$O$_3$ (I) sample. While the values of $\varepsilon_1$ at low frequencies ($<$10$^4$ Hz) and high temperature ($>$200 K) are quite different for the two samples, these values are quite similar at high frequencies and low temperatures.

Such large value of $\varepsilon_1$ even in non-ferroelectric $\gamma$-Fe$_2$O$_3$, and its strong frequency as well as temperature dependences have been explained by possible Maxwell-Wagner two-capacitor model [22, 19] as similar to CaCu$_3$Ti$_4$O$_{12}$ [23]. Due to polycrystalline nature of the $\gamma$-Fe$_2$O$_3$ sample, the resistance and capacitance of grain and grain boundary could be different and depend on sample preparation temperature.
Figure 4.10: The temperature-dependent dielectric constant of $\gamma$-Fe$_2$O$_3$ (I) (solid line) and $\gamma$-Fe$_2$O$_3$ (II) (dashed line) at 500 Hz
Figure 4.11: The frequency-dependent dielectric constant of $\gamma$-Fe$_2$O$_3$ (I) (solid line) and $\gamma$-Fe$_2$O$_3$ (II) (dashed line) at 293 K.
4.1.5 Impedance Spectroscopy Analysis of Polycrystalline $\gamma$-Fe$_2$O$_3$

Figure 4.12 shows the complex impedance plot ($Z_2$ vs $Z_1$) of $\gamma$-Fe$_2$O$_3$ (I) (open circles) and $\gamma$-Fe$_2$O$_3$ (II) (open squares) at 293 K. The complex impedance plot, for the frequency range from 20 Hz to 1MHz, shows clearly two semicircles for both samples. Impedance spectroscopy analysis is used to analyze the complex impedance result. From fitting the experimental data through equation (2.17) and (2.18), the values of $R_g$ ($R_{gb}$) are ~1.17 MΩ (~1.64 MΩ) for $\gamma$-Fe$_2$O$_3$ (I) and ~3.03 MΩ (~3.42 MΩ) for $\gamma$-Fe$_2$O$_3$ (II). The values of $C_g$ and $C_{gb}$ are obtained from the values $R_g$ and $R_{gb}$ in the Maxwell-Wagner model [18] and also by fitting the magnetodielectric curve. The obtained values of $C_g$ and $C_{gb}$ are ~4.6pF and 6pF for both samples.
Figure 4.12: Complex impedance spectroscopy of $\gamma$-Fe$_2$O$_3$ (I) (open circles) and $\gamma$-Fe$_2$O$_3$ (II) (open squares) at 293 K.
4.1.6 Magnetoresistance and Magnetodielectric Property of $\gamma$-Fe$_2$O$_3$ (I) and $\gamma$-Fe$_2$O$_3$ (II) at 293 K

Magnetoresistance of the two $\gamma$-Fe$_2$O$_3$ at 293 K is shown in figure 4.13. Like the previous result of magnetoresistance of $\gamma$-Fe$_2$O$_3$, at this samples also have negative magnetoresistance. The value of magnetoresistance is quiet similar for $\gamma$-Fe$_2$O$_3$ (I) (open circles) and $\gamma$-Fe$_2$O$_3$ (II) (open squares), i.e. $\sim$1.3% at 9 Tesla.

Figure 4.14 shows magnetodielectric effect of $\gamma$-Fe$_2$O$_3$ (I) and $\gamma$-Fe$_2$O$_3$ (II). The magnetodielectric effect has different value for the two samples such as $\sim$0.91% for $\gamma$-Fe$_2$O$_3$ (I) and $\sim$0.63% for $\gamma$-Fe$_2$O$_3$ (II). From the plot of frequency dependence of magnetodielectric effect at 9 T (figure 4.15), the magnetodielectric value maximize near $5 \times 10^3$ Hz for $\gamma$-Fe$_2$O$_3$ (I) while for $\gamma$-Fe$_2$O$_3$ (II) maximize near $1 \times 10^3$ Hz.

The main reason for the deviation of magnetodielectric curves for two $\gamma$-Fe$_2$O$_3$ samples, even with the quite similar values of magnetoresistance and capacitance should come from the different values of resistance ratio between grain and grain boundary, i.e., $R_{gb}/R_g \sim$1.40 for $\gamma$-Fe$_2$O$_3$ (I) and $R_{gb}/R_g \sim$1.13 for $\gamma$-Fe$_2$O$_3$ (II). According to equation (2.9), the value of $\Delta \varepsilon_1/\varepsilon_1$ should depend on the values of $\Delta R/R$, $R_{gb}/R_g$, and $C_{gb}/C_g$. The calculated $\Delta \varepsilon_1/\varepsilon_1$ (a solid line for $\gamma$-Fe$_2$O$_3$ (I) and a dashed line for $\gamma$-Fe$_2$O$_3$ (II)) fit the experimental $\Delta \varepsilon_1/\varepsilon_1$ curves well for both samples [24].
Figure 4.13: Magnetoresistance of $\gamma$-Fe$_2$O$_3$ (I) (open circles) and $\gamma$-Fe$_2$O$_3$ (II) (open squares) at 293 K.
Figure 4.14: Measured (open dots) and calculated (lines) of magnetodielectric curves at $5 \times 10^3$ Hz and 293 K of $\gamma$-Fe$_2$O$_3$ (I) (open circles) and $\gamma$-Fe$_2$O$_3$ (II) (open squares).
Figure 4.15: The value of magnetodielectric effect at 9 Tesla for selected frequencies.
4.2 Studies of of Ba_{0.6}Sr_{0.4}TiO_{3}-La_{0.7}Ca_{0.3}MnO_{3} Composites

4.2.1 Electric and Magnetic Properties of Each Ba_{0.6}Sr_{0.4}TiO_{3} and La_{0.7}Ca_{0.3}MnO_{3}

Figure 4.16 shows the dielectric constant of BSTO at 1 kHz and dc resistivity of LCMO. As consistent with the previous report [25], the BSTO sample shows a typical dielectric anomaly, accompanying a paraelectric-ferroelectric transition at T_{CE} ~275 K. The LCMO sample (figure 4.16) shows a typical insulator-metal transition, accompanying a paramagnetic-ferromagnetic transition at T_{CM} ~270 K [26]. Paramagnetic and ferromagnetic phases at 300 K and 10 K, respectively, are clearly verified by magnetization versus applied magnetic field (M-H) curve (figure 4.17).

Figure 4.18 shows the magnetoresistance curves, \( \Delta \rho/\rho = [(\rho(H) - \rho(0))/\rho(0)] \), of LCMO at selected temperatures. The value of magnetoresistance becomes maximized near T_{CM} and increases again below 100 K with decreasing temperature (inset in figure 4.18). The magnetoresistance curve at 270 K (~ T_{CM}) continuously decreases, while the curve at 10 K becomes saturated above 1 Tesla. Such magnetoresistance behaviors may be consistent with the double-exchange origin in LCMO grain near T_{CM} and with the tunneling origin in LCMO grain-boundary at low temperature [26].
Figure 4.16: Temperature-dependent dielectric constant of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (solid line) at 1 kHz and dc resistivity of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (dashed line).
Figure 4.17: Magnetic hysteresis loops at 10 K and 300 K of La$_{0.7}$Ca$_{0.3}$MnO$_3$. 
Figure 4.18: Magnetoresistance of LCMO at selected temperature. In the inset, magnetoresistance values at 3 T.
4.2.2 Dielectric Properties of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-La$_{0.7}$Ca$_{0.3}$MnO$_3$ Composites

The temperature-dependent dielectric constant $\varepsilon_1 (T)$ curves of (1-x)BSTO-(x)LCMO (x = 0, 0.05, 0.1, and 0.15) composites is shown in figure 4.19. For clarity, the values of x = 0 and 0.05 are divided by 2. With increasing x, the value of dielectric constant becomes reduced and the dielectric anomaly near $T_{CE}$ becomes unclear. In addition, the loss ($\tan\delta = \varepsilon_2 / \varepsilon_1$) becomes larger with x as shown in the inset of figure 4.19. Therefore, overall dielectric features should be related to the increase of metallic LCMO; i.e., (1-x)BSTO-(x)LCMO becomes leaky with x. Since the x = 0.05 sample shows a rather clear $T_{CE}$ with a quite small loss, then the investigation of magnetoelectric coupling among (1-x)BSTO-(x)LCMO composites concentrates only on this sample.
Figure 4.19: Dielectric constant curves of (1-x)BSTO-(x)LCMO composites for cooling run. The values of x = 0 and 0.05 are divided by 2 for clarity. In the inset, the values of tanδ versus x are shown at 300 K.
4.2.3 Magnetoelectric Coupling of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$-$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Composites

In order to examine possible magnetoelectric coupling in BSTO-LCMO composites is urged to investigate the magnetic field dependence of electrical polarization (magnetoelectric property). Figure 4.20 shows the curves of electrical polarization versus applied electric field (P-E) at selected magnetic fields of 0.95BSTO-0.05LCMO at 270 K. Due to the limitation of applied electric field, the P-E curve of a composite does not follow the canonical behavior of ferroelectric materials. However, a clear hysteresis with coercive field (~1.3 kV/cm) and remnant polarization (~0.25 μC/cm²) confirm the ferroelectric nature of 0.95BSTO-0.05LCMO in the measured temperature range. When we increase the magnetic field, the P-E curve becomes more rounded and the polarization at maximum electric field ($P_s$) becomes reduced (the upper inset of figure 4.20). While, the P-E curve at 10 K does not show any magnetic field dependences (the lower inset of figure 4.20).

The rounded P-E curve and reduction of $P_s$ with increasing magnetic field at 270 K might be related to the negative magnetoresistance of LCMO [27, 28]. As shown in figure 4.18, the LCMO becomes more conducting with applied magnetic field; therefore, the free carrier in the LCMO grain will more effectively screen the electric polarization of the adjacent BSTO grain. On the other hand, the negligible magnetic field dependence of the PE curve at 10 K might be related with the fact that there is no channel to make LCMO more conducting by applying external magnetic field. LCMO grain is already highly conducting at 10 K, therefore, the grain should show little magnetoresistance, as already proved by the magnetic field dependence of LCMO single crystals [26]. In 0.95BSTO-0.05LCMO composite, in addition, only 5% volume fraction of LCMO grain is embedded in 95% volume fraction of BSTO grain. Therefore, the LCMO grain should be well-isolated; hence there should be little tunneling-type magnetoresistance through the grain-boundaries among adjacent LCMO grains.
Figure 4.20: Polarization-electric field (P-E) curves of 0.95BSTO-0.05LCMO at 270 K for 0 T (solid line) and 3 T (dash-dot line). For comparison, P-E curves at 10 K are shown for 0 T and 3 T in the lower inset. In the upper inset, the magnetic field-dependent $P_s$ at 270 K (solid dots) obtained at $E=6$ kV/cm and at 10 K (open dots) obtained at $E=16$ kV/cm are shown.
4.2.4 Magnetodielectric Property of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$-$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Composites

Figure 4.21 shows magnetodielectric curves $\Delta \varepsilon_i/\varepsilon_i = [(\varepsilon_i(H)-\varepsilon_i(0))/\varepsilon_i(0)]$, of 0.95BSTO-0.05LCMO composite at selected temperatures. Distinctly, the value of magnetodielectric effect at 3 T is maximized near 270 K at which magnetoresistance at grain is maximized, while that is negatively maximized near 10 K at which magnetoresistance at grain-boundary is maximized (figure 4.18). In addition, the dielectric constant increases as the magnetic field increases with strong frequency dependences at 270 K, and the dielectric constant decreases as the magnetic field increases without strong frequency dependences at 10 K (figure 4.22).

Incorporating the result of the magnetic field-dependent P-E curve at 270 K, the negative magnetoresistance of LCMO may be responsible for the positive magnetodielectric effect at 270 K in 0.95BSTO-0.05LCMO. In fact, Catalan recently argued that the magnetodielectric effect could be originated from the Maxwell-Wagner effect and magnetoresistance, and could be positive (negative) sign when the magnetoresistance took place at the grain (grain-boundary) [14, 29]. In addition, Catalan predicted the strong frequency dependences of the magnetodielectric effect due to the conductivity cut-off of the free carrier [14, 29]. The positive magnetodielectric behavior and its strong frequency dependence at 270 K in insulating BSTO and metallic LCMO composite seem to be consistent with the Catalan’s argument. Negative magnetoresistance of LCMO grain will play a similar role as the reduction of dielectric thickness, hence the increase of dielectric constant, and will generate conducting free carrier which will respond up to a certain frequency, hence the strong frequency dependence of magnetodielectric curves.
Figure 4.21: Magnetodielectric curves of 0.95BSTO-0.05LCMO at selected temperatures.
On the other hand, negative magnetodielectric behavior at 10 K does not seem to be related to tunneling-type magnetoresistance. As we discussed earlier, well-isolated LCMO grain in BSTO matrix may not have channels for magnetoresistance through the grain boundary. In addition, we cannot observe any clear frequency dependences of magnetodielectric value, at least, in our measured frequency range (10^3-10^6 Hz). Possibility for the observed negative magnetodielectric effect at 10 K is due to the intrinsic magnetoelectric coupling through strain, as similar to titanates-manganites multilayer [30, 31]. Application of a magnetic field will cause a stress in the LCMO grain through magnetostriction. The stress will be transferred to piezoelectric BSTO; hence the dielectric constant of BSTO-LCMO composite can be changed. The other possibility is the antiferromagnetic spin correlations near the surface of LCMO grain. According to a simple phenomenological model [32], magnetodielectric effect should be proportional to spin-pair correlation of neighboring spins, and be negative (positive) sign for antiferromagnetic (ferromagnetic) spin ordering. Since antiferromagnetic spin correlation should be increased near the surface of isolated LCMO grain due to the reduced exchange energy, the sign of magnetodielectric effect at 10 K might be negative[33]. However, further studies are highly required to clarify this scenario. With increasing temperature, the magnetodielectric effect due to the magnetoresistance of LCMO grain starts to increase and hence the sign change could occur near 100 K.
Figure 4.22: The frequency-dependent dielectric constant ratio, $\varepsilon_1(3T)/\varepsilon_1(0T)$, for 270 K (dashed line) and 10 K (dash-dotted line).
Chapter 5
Summary

In summary, the magnetodielectric effect has been investigated in polycrystalline $\gamma$-Fe$_2$O$_3$. The strong dependence of magnetodielectric effect on magnetoresistance and frequency, and the relaxor like behavior of the maximum magnetodielectric clearly shows that the observed magnetodielectric effect in polycrystalline $\gamma$-Fe$_2$O$_3$ should originate from the combined Maxwell-Wagner effect and magnetoresistance. The resistance ratio between the grain and the grain boundary is one of the key factors to control the magnetodielectric effect in polycrystalline $\gamma$-Fe$_2$O$_3$ through impedance spectroscopy analysis measurement.

In order to understand resistive magnetodielectric effect more deeply, the sign of magnetodielectric effect is studied in ferroelectric-ferromagnetic i.e. Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-La$_{0.7}$Ca$_{0.3}$MnO$_3$ composites, in which the constituent Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ have similar Curie temperatures. The value of dielectric constant is sharply reduced and the dielectric anomalies near 275 K become unclear above $x \geq 0.1$, probably due to the increase of metallic La$_{0.7}$Ca$_{0.3}$MnO$_3$ volume fraction. The electric polarization of $x=0.05$ decreases with applied magnetic field, and the dielectric constant increases with strong frequency dependence at 270 K. On the other hand, at 10 K, the polarization does not show any magnetic field dependence, and the dielectric constant decreases without frequency dependence. The negative magnetoresistance of La$_{0.7}$Ca$_{0.3}$MnO$_3$ grain can be responsible for the positive magnetodielectric effect at 270 K. On the other hand, negative magnetodielectric effect at 10 K may be due to intrinsic magnetoelastic through strain not the negative magnetoresistance from grain-boundaries.
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Acknowledgement

Author would like to thank to people who help for completion this thesis. First of all, I want to express my gratitude to my supervisor Prof. Jung Jong-Hoon for giving opportunity to work and study in his groups, Quantum Functional Material Lab, Department of Physics, INHA University. Under his guidance, I have learned to operate many instruments and to publish my work in international journal. His teaching also furthered my knowledge in the field of solid state physics. Next, I would like to thank to Prof. Hur Nam-Jung and Prof Lee Jae-II for helpful discussion and comments on my thesis. Their guides and suggestion have helped me to understand much more about my research.

I would like to thank my lab mates; Koo Yong-Sung who have helped me since I first came to Korea, and taught me to synthesize and to measure the sample; Sung Kil-Dong, Song Ki-Myung, Won Chung-Jae, Park Young-An, Lee Seung-Min, Lee Kyung-Dong, thank for your help during my master study in INHA University and my live in Korea.

I would like to thank my Indonesian friend, Eko, Sujandi, Ni Luh Karina, Nazarudin, Rostineu, Aminullah, Freddy, Ardy who always help me during I live in Korea.

And finally, I would thank my parents and my sisters for their support and pray for me so that I can finish my master study in INHA University, Korea. I also thank my betrothed for your encourage and support for me. May GOD always bless all of you.