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Magnetoelectric effect in rare earth ferrites, $LnFe_2O_4$

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Dielectric and magnetic properties of selected rare earth ferrites, $LnFe_2O_4$ (Ln=Y, Er, Yb), have been investigated. All these materials show ferroelectricity near the ferrimagnetic transition temperature around 250 K. More importantly, they exhibit a change in the dielectric behavior on the application of magnetic fields. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2946455]

Rare earth ferrites of the general formula $LnFe_2O_4$ (Ln =Dy to Lu, or Y) crystallize in rhombohedral structures with the space group $R-3m$.[1] They possess a layered structure consisting of alternating stacking of the two-dimensional triangular lattices of the rare earth, iron, and oxygen ions along the *c* direction. The Fe ions are in a mixed valent state with equal amounts of Fe^{2+} and Fe^{3+}. Electrostatic interaction between Fe^{2+} and the Fe^{3+} ions and antiferromagnetic superexchange interaction between the nearest neighbor spins on the triangular net are responsible for some of their interesting properties. In the low-temperature phase, both the charges and the spins of the iron ions form ordered structures. All the rare earth ferrites show ferrimagnetic ordering around 250 K due to the strong magnetic interactions between the localized Fe moments.[2–5] Electron hopping expected between Fe^{2+} and the Fe^{3+} ions within the layer leads to high electrical conductivity and competing interactions between the charges of nearest and next nearest neighbor ions on the triangular lattice gives rise to charge ordering.[6–8] Many of the ferrites exhibit a Verwey-type phase transition due to the ordering of Fe^{2+} and Fe^{3+} ions.[9] Neutron diffraction studies of $LuFe_2O_4$ have shown that it undergoes successive phase transitions from a disordered state to a two-dimensional charge density wave state and then to a three-dimensional charge density wave state.[10,11] *In situ* cooling transmission electron microscopy observations on $LuFe_2O_4$ show that the charges in the ground state are well crystallized in a charge-stripe phase and that charge concentration in this charge-stripe phase can be characterized by a nonsinusoidal charge density wave which gives rise to an electric polarization.[12] Ferroelectricity has been observed in some of these ferrites as evidenced by the low-frequency dielectric dispersion.[4,5,13] The superstructure formed by Fe^{2+} and Fe^{3+} ions supports electric polarization consisting of distributed electrons of polar symmetry since the centers of Fe^{2+} and Fe^{3+} ions do not coincide.[13–15] The dielectric dispersion of $LnFe_2O_4$ can be understood qualitatively on the basis of the charge frustration of the iron ions in the two-dimensional triangular lattice, where the electrons hop between Fe^{2+} and Fe^{3+} ions[16–18] and the origin of ferroelectricity is basically related to the charge-ordering transition arising from strong electron correlation.[18,19] Magnetodielectric response was recently reported in $LuFe_2O_4$ at room temperature indicating a coupling between the spins and electric dipoles.[20] The magnetocapacitance effect in $LuFe_2O_4$ at room temperature is considered to be due to charge fluctuations arising from the interconversion between the two types of charge order, which are hindered by an applied magnetic field.[21] We have been investigating properties of members of the $LnFe_2O_4$ family and have found that many of them besides $LuFe_2O_4$ show magnetoelectric effect.

Polycrystalline $Lu_{0.5}Y_{0.5}Fe_2O_4$ and $YbFe_2O_4$ were prepared starting with a mixture of high purity (Sigma-Aldrich 99.9%) Ln_2O_3, Fe_2O_3, and Fe metal powder taken in stoichiometric quantities. The mixtures were ground thoroughly in an agate mortar and pelletized. The pellets were heated in an evacuated quartz tube at 1100 °C for 24 h and quenched into liquid nitrogen. YFe_2O_4 and $ErFe_2O_4$ were prepared from a stoichiometric mixture of Ln_2O_3 and Fe_2O_3, which were thoroughly mixed, pelletized, and heated in a reducing atmosphere with a controlled oxygen partial pressure of CO_2/H_2 gas mixtures at 1200 °C for 24 h and rapidly cooled to room temperature. Powder x-ray diffraction measurements using Cu $K\alpha$ radiation confirmed the formation of the single phases of the ferrites. Magnetization measurements were carried out using the physical property measurement system (PPMS) (Quantum Design) magnetometer. Dielectric measurements were performed using precision impedance analyzer (Agilent 4294 A) in the frequency range of 100 Hz–1 MHz.

In Fig. 1, we show the magnetization data of YFe_2O_4 and $Lu_{0.5}Y_{0.5}Fe_2O_4$ to show typical magnetic behavior of these ferrites. We observe the occurrence of ferrimagnetism around 250 K. Frequency and the temperature dependent dielectric constant data of YFe_2O_4 are shown in Fig. 2(a). Dielectric constant data for $Lu_{0.5}Y_{0.5}Fe_2O_4$ are shown in Fig. 2(b). We notice a marked increase in the dielectric constant near the magnetic transition temperature in these ferrites. As strong correlation exists between the spin and the charge orderings of the Fe ions, we would expect the dielectric

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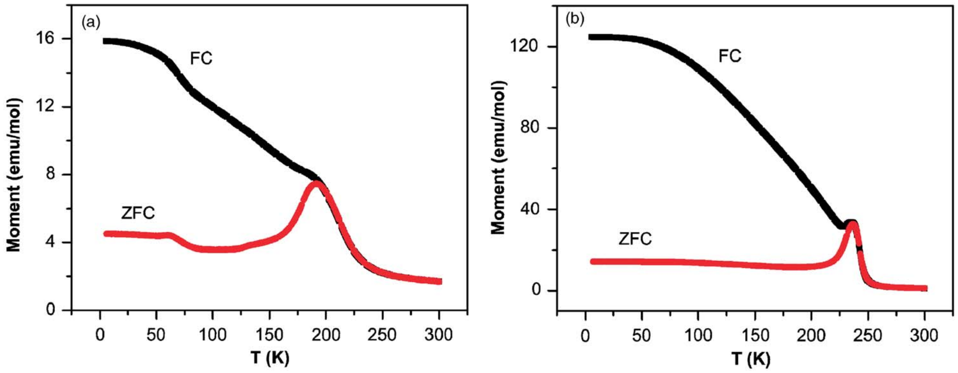

FIG. 1. (Color online) Temperature dependence of magnetization for (a) YFe_2O_4 and (b) $Lu_{0.5}Y_{0.5}Fe_2O_4$ at 100 Oe. The black squares are the field cooled (FC) and the red circles are the zero field cooled (ZFC) data.

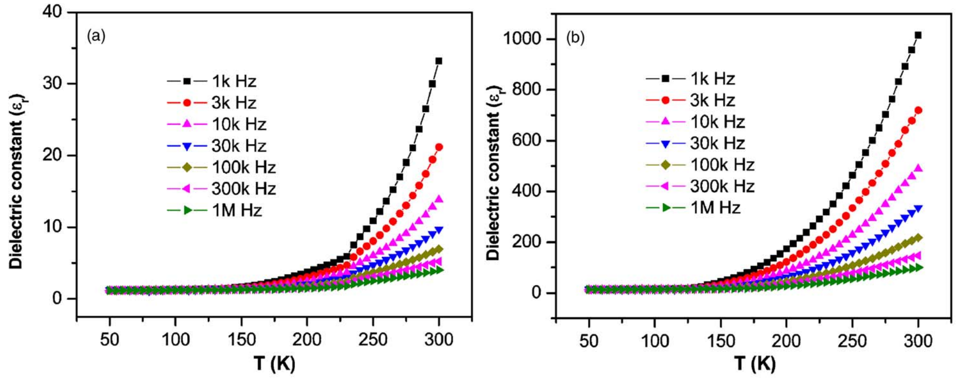

FIG. 2. (Color online) Dielectric constant (ε) plotted against the temperature for (a) YFe_2O_4 and (b) $Lu_{0.5}Y_{0.5}Fe_2O_4$ for different frequencies.

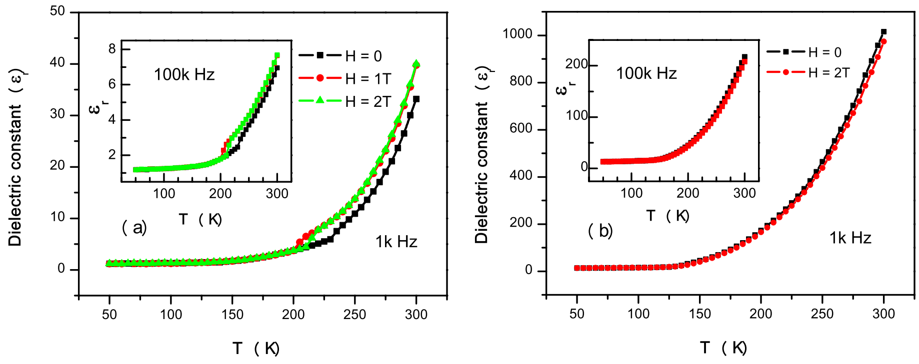

FIG. 3. (Color online) (a) Dielectric constant vs temperature of YFe_2O_4 measured at 0, 1, and 2 T for the frequency 1 kHz. The inset shows the data for 100 kHz. (b) Dielectric constant vs temperature of $Lu_{0.5}Y_{0.5}Fe_2O_4$ measured at 0 and 2 T for 1 kHz. The inset shows the data for 100 kHz.

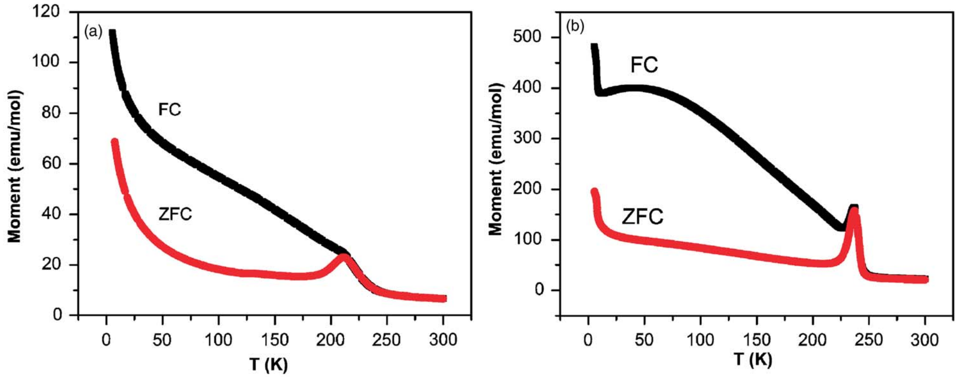

FIG. 4. (Color online) Temperature dependence of magnetization for (a) $ErFe_2O_4$ and (b) $YbFe_2O_4$ at 100 Oe. The black squares are the FC and the red circles are the ZFC data.

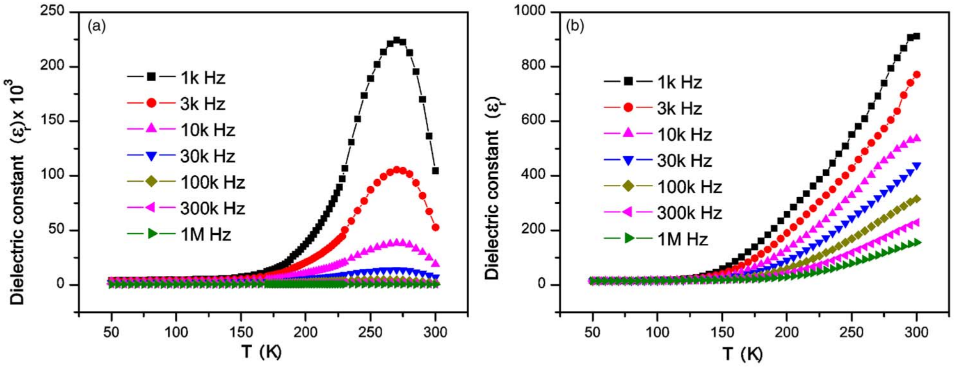

FIG. 5. (Color online) Dielectric constant (ε) plotted against the temperature for (a) $ErFe_2O_4$ and (b) $YbFe_2O_4$ for different frequencies.

properties to change at the magnetic transition.

Figure 3(a) demonstrates the magnetocapacitance behavior of the YFe_2O_4. From the figure, we notice that YFe_2O_4 shows a positive magnetocapacitive effect around the magnetic transition temperature. Figure 3(b) shows the weak negative magnetocapacitance in $Lu_{0.5}Y_{0.5}Fe_2O_4$. This may be because of the fact that $LuFe_2O_4$ shows a significant negative magnetocapacitance effect while YFe_2O_4 shows a positive one. Thus the behavior of $Lu_{0.5}Y_{0.5}Fe_2O_4$ falls between the two extreme compositions.

We show the magnetization data of $ErFe_2O_4$ and $YbFe_2O_4$ as a function of temperature in Fig. 4. Figures 5(a) and 5(b) show the temperature variation of the dielectric constant at different frequencies in $ErFe_2O_4$ and $YbFe_2O_4$, respectively. A large dielectric relaxation, of the order of 10^4, is observed in the magnetically ordered state in $ErFe_2O_4$. The large value of the dielectric constant is consistent with the existence of spontaneous polarization in the magnetic phase of $ErFe_2O_4$. In the case of $YbFe_2O_4$, the dielectric behavior is slightly different and there is large dispersion.[2] We observe a definitive dielectric constant maximum near the magnetic transition temperature (T_N) in the case of $ErFe_2O_4$, as can be seen in Fig. 5(a). The very high dielectric constant of this ferrite at T_N is noteworthy. The difference in dielectric behavior of the ferrites with different rare earth ions may be attributed to the change in the ionic size and related polyhedral distortions.

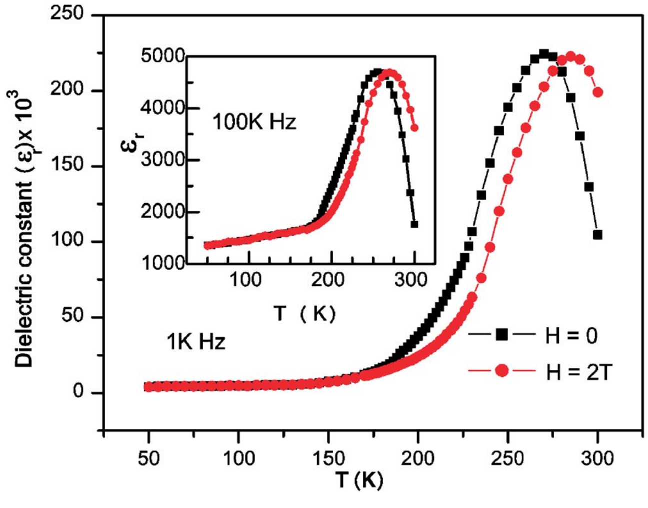

FIG. 6. (Color online) Dielectric constant vs temperature of $ErFe_2O_4$ measured at 0 and 2 T for the frequency 1 kHz. The inset shows the data for 100 kHz.

In the case of $ErFe_2O_4$, the position of the dielectric maximum at T_N shifts to higher temperatures on the application of magnetic fields, as shown in Fig. 6. Accordingly, $ErFe_2O_4$ shows negative magnetocapacitive effect at $T < T_N$ and a positive magnetocapacitance effect above T_N.

In conclusion, we have been able to demonstrate that several members of the rare earth ferrite family are magnetoelectric because of the presence of charge ordering. The coupling between the electric and magnetic order parameters may be useful in device applications.

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