Study on dielectric and magnetodielectric properties of Lu$_3$Fe$_5$O$_{12}$ ceramics

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Polycrystalline Lu$_3$Fe$_5$O$_{12}$ ceramics with garnet structure were prepared by a solid-state reaction method. A dielectric relaxor behavior at low temperature was observed which may come from the dipolar effects associated with the charge carrier hopping between Fe^{2+} and Fe^{3+}. It is noticeable that their magnetodielectric (MD) properties are excellent since the applied small magnetic fields can dramatically change the dielectric constants of Lu$_3$Fe$_5$O$_{12}$ ceramics. The origin of the MD effect is discussed. © *2009 American Institute of Physics*. [doi:10.1063/1.3259651]

Multiferroic materials have drawn an increasing amount of interest due to their potential applications in many multifunctional devices.[1–3] After the first experimental realization of magnetoelectric coupling in Cr$_2$O$_3$,[4] similar effects have been observed at low temperatures in DyPO$_4$,[5] BaMnF$_4$,[6] YMnO$_3$,[7] etc. For the ferromagnetic insulators, a large magnetodielectric (MD) coupling near the ferromagnetic Curie temperatures was found in BiMnO$_3$ at 100 K (Ref. 8) and in La$_2$NiMnO$_6$ at 285 K.[9]

However, from the practical application point of view, room-temperature MD effect is necessary, whereas, there are few reports yet. Recently, the dielectric anomalies and magnetoelectric properties of some rare earth iron garnets (RIG) have been investigated[10,11] and a MD coupling ($\Delta\varepsilon/\varepsilon \sim 3\%$) at remarkably low magnetic fields (H$<$2 kOe) was observed in terbium iron garnet (Tb$_3$Fe$_5$O$_{12}$) single crystals.[12] The RIG with the general chemical formula of RE$_3$Fe$_5$O$_{12}$ (RE represents rare earth) has a cubic structure with the space group of $Ia3d$. The spins of Fe at the tetrahedral site are antiparallel to those at the octahedral site, and the moments of RE (except Y and Lu) at the dodecahedral site are aligned antiparallel to the net moment of Fe. The spins of Fe in the iron garnets are ordered in a ferrimagnetic arrangement along the [111] direction.[12] In this letter, we report the synthesis of Lu$_3$Fe$_5$O$_{12}$ RIG polycrystalline ceramic with high Curie temperatures ($T_c \sim 539$ K). Its dielectric and MD properties were carefully studied and discussed.

Lu$_3$Fe$_5$O$_{12}$ ceramics were prepared by a solid-state reaction process from the raw powders of Lu$_2$O$_3$ (99.9%) and Fe$_2$O$_3$ (99.99%). The mixed powders were calcined at 1473 K for 5 h in air, and then pressed into pellets (10 mm in diameter and 1–2 mm in thickness) under a uniaxial pressure of 35 MPa. Finally, the dense Lu$_3$Fe$_5$O$_{12}$ ceramics were obtained by sintering at 1673 K for 5 h in air. Silver electrodes were sputtered for electrical measurements. The structural characterizations of the samples were carried out using a Rigaku (D/MAX-rB) x-ray diffractometer equipped with

Cu Ka radiation. The magnetic properties were measured by vibrating sample magnetometer (EV7, ADE, USA). The dielectric properties were evaluated using HP4194A impedance analyzer in the frequency range from 100 Hz to 1 MHz and in the temperature range from 110 to 525 K. The combination states of Fe 2p electron in Lu$_3$Fe$_5$O$_{12}$ ceramics were examined by x-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250).

The x-ray diffraction (XRD) pattern as shown in Fig. 1 gives that the sample has a polycrystalline structure and no additional or intermediate phases are observed. Figure 2 presents a magnetization-field (M-H) curve of the polycrystalline Lu$_3$Fe$_5$O$_{12}$ pellets measured at room temperature. The sample exhibits a well-defined magnetic hysteresis loop with a saturation magnetization (M_s) of 14 emu/g for a relatively low applied magnetic field of 2 kOe. Despite RIG is a ferrimagnetic, an interesting phenomenon is that the synthesized Lu$_3$Fe$_5$O$_{12}$ ceramics exhibits ferromagnetic characteristics.

Materials with large dielectric constant within a wide range of temperature are extremely attractive for their potential applications in the miniaturization of electronic devices. Figures 3(a) and 3(b) give the temperature dependence of dielectric constant (ε) and loss factor (tan δ) of Lu$_3$Fe$_5$O$_{12}$ ceramics measured at various frequencies, respectively. The Lu$_3$Fe$_5$O$_{12}$ ceramic exhibits a typical relaxor behavior at low temperature range. As shown in Fig. 3(a), a dielectric

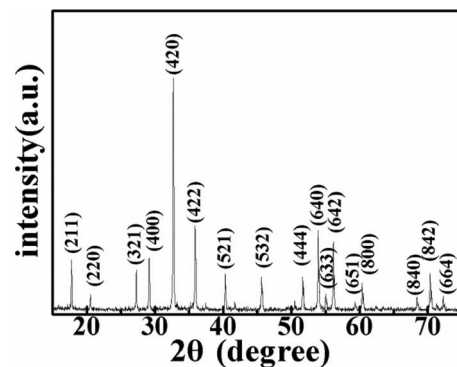
FIG. 1. XRD patterns of Lu$_3$Fe$_5$O$_{12}$ ceramics.

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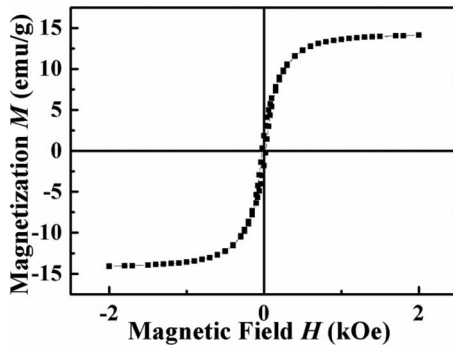FIG. 2. The magnetization-field (*M*-*H*) curve of $Lu_3Fe_5O_{12}$ ceramics measured at room temperature.

FIG. 4. (Color online) X-ray photoelectron spectrum of the Fe $2p$ lines for the binding energy between 706 and 730 eV. Inset shows the Lorentzian dividing of the Fe $2p_{3/2}$ core level for a $Le_3Fe_5O_{12}$ ceramic.

anomaly followed by a large dielectric constant plateau appears at 120–300 K. Meanwhile, the low dielectric loss (<0.2) above the room temperature could be observed in Fig. 3(b). Apparently, there is a dielectric relaxation peak corresponding to the step-increase of dielectric constant as a function of temperature, and its position shifts toward higher temperature side with the increasing frequency. The temperature variation of the characteristic frequency can be described by the Arrhenius relation,

$$\tau = \tau_0 \exp(E_a/k_B T) \quad (1)$$

$$\omega\tau = 1, \quad (2)$$

where T is the peak temperature, τ_0 is the relaxation time, k_B is the Boltzmann constant, and E_a is the activation energy. As the peak will appear when $\omega = 2\pi f$, we can get
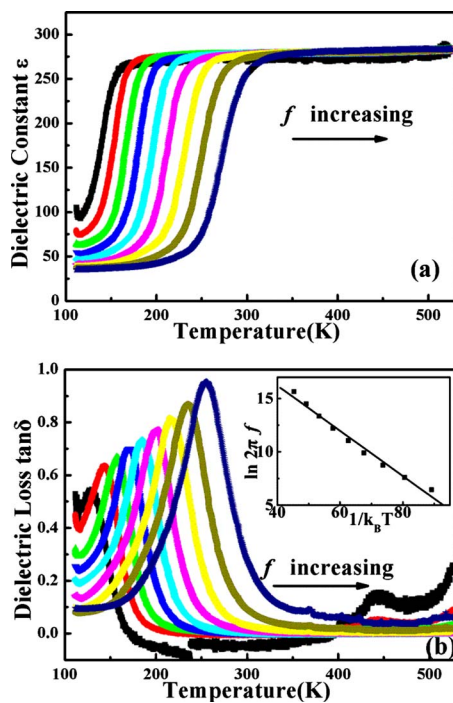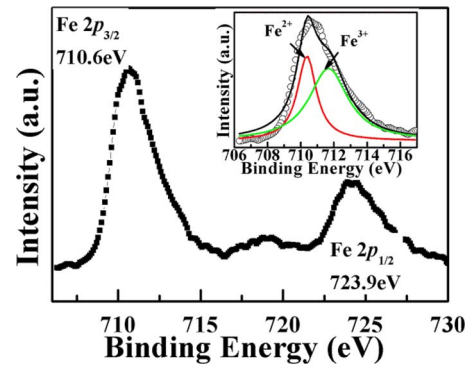

FIG. 3. (Color online) Temperature dependence of (a) dielectric constant and (b) dielectric loss for $Lu_3Fe_5O_{12}$ ceramics measured at various frequencies of 10^2, $10^{2.5}$, 10^3, $10^{3.5}$, 10^4, $10^{4.5}$, 10^5, $10^{5.5}$, and 10^6 Hz. Inset in Fig. 3(b) gives the Arrhenius fitting (solid line) for the peak temperature of tan δ (filled squares).

$$\ln(2\pi f) = -\ln \tau_0 - E_a/k_B T \quad (3)$$

The inset of Fig. 3(b) shows the peak temperature as a function of frequency. The activation energy E_a was calculated to be 0.22 eV from the slope of the fitted straight line. This value is close to the activation energy of a two-site polaron hopping process of charge transfer between Fe^{2+} and Fe^{3+} [$E_a \sim 0.29$ eV].[13] Therefore, the dielectric relaxation may origin from the dipolar effects associated with the charge carrier hopping between Fe^{2+} and Fe^{3+}.

Figure 4 shows a representative XPS scan of the Fe $2p$ lines. The Fe $2p_{3/2}$ peak was reported to occur at 709.5 eV for Fe^{2+} and at 711.0 eV for Fe^{3+}.[14] However, the XPS spectrum shows that the $2p_{3/2}$ peaks for Fe^{2+} and Fe^{3+} are not separated from each other but are positioned between these two values as a mixed peak. Using the standard Lorentzian fitting method, the mixed peak can be fitted by two peaks, corresponding to Fe^{2+} and Fe^{3+} states,[15] respectively (the inset of Fig. 4). The estimated ratio of $Fe^{2+}:Fe^{3+}$ is 35:65. Thus, we could infer that the Fe ions in the compound are in mixed valence states, and the trivalent states is dominant. It is reasonable since Fe^{2+} will be produced through the reduction reaction during the high temperature annealing process.[16] This result could also explain the origin of the dielectric relaxation behavior as shown in Fig. 3(b).

The variations of the dielectric constant and loss factor in $Lu_3Fe_5O_{12}$ ceramics with different magnetic fields at room temperature are shown in Fig. 5. It is well known that MD materials can be classified into the two following categories: (1) $HoMnO_3$ (Ref. 17) which exhibits a large and abrupt change of ε in high magnetic fields ($H > 10$ kOe), usually associated with a phase transition or switching of the polar-
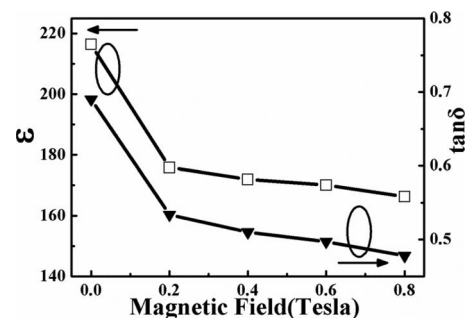

FIG. 5. The variation of dielectric constant and dielectric loss with magnetic field at room temperature at 100 kHz.

ization direction; (2) BiMnO$_3$ (Ref. [8]) which shows a relatively small MD effect ($\Delta\varepsilon/\varepsilon < 1\%$ for $H \sim 90$ kOe) typically proportional to M^2. In both cases, the MD effect occurs only at high H. Hur *et al.*[12] reported a MD effect in a reasonably low field ($\Delta\varepsilon/\varepsilon \sim 3\%$ at 2 kOe) in Tb$_3$Fe$_5$O$_{12}$, but this MD effect occurs at low T (< 159 K) only. In our case, as shown in Fig. 5, the capacitance of Lu$_3$Fe$_5$O$_{12}$ at room temperature is very sensitive to the magnetic fields even at low magnetic fields, and the effect is reversible. The applied magnetic field of 2 kOe leads to an 18% change in capacitance at room temperature. Such a dramatic change can even be easily sensed by low-precision bridges.

Coming back to the XPS results as shown in Fig. 4, the oxidation state of Fe ions in our ceramics were confirmed to be the coexistence of both Fe^{3+} and Fe^{2+} states, which would possibly cause a double exchange interaction between Fe^{2+} and Fe^{3+} ions through oxygen. This kind of interaction can result in the enhancement of ferromagnetism.[18] The existence of Fe^{2+} can induce a charged regions with cation ordered,[19] which will initiate local dipoles of Fe^{2+} and Fe^{3+}. When a magnetic field is applied, the spin reorientation can affect the interaction between dipoles. Thus, the coupling between the dielectric constant and the magnetic field will take place as has been observed for the MD effects. Simultaneously, the complex structure of iron garnet leads to the lower conduction despite there is partial local itinerant electrons in our sample. To demonstrate our hypothesis, the resistivity of the Lu$_3$Fe$_5$O$_{12}$ ceramic is measured under different magnetic fields. It can be found that the resistivity ($\sim 10^7$ Ωm) is considerable and it changes a little ($\sim 0.4\%$) with the magnetic fields changing from -0.8 to 0.8 T (which is not shown here). This result indicates that the MD effect has been slightly impacted by the conduction. Furthermore, as shown in Fig. 5, the magnitude of both ε and tan δ decreases with increasing magnetic field, which suggests that the variation is not due to the magnetoresistance of Lu$_3$Fe$_5$O$_{12}$ or the Lu$_3$Fe$_5$O$_{12}$-electrode interface.[2] Further investigation is still needed to reveal the real physical natures of the MD effects in the compounds.

In summary, polycrystalline Lu$_3$Fe$_5$O$_{12}$ ceramics with garnet structure have been prepared by solid-state reaction method. The sample shows a large dielectric constant with low dielectric loss above room temperature and a dielectric relaxor behavior at low temperature range was observed. The possible reason for the relaxor behavior of the ceramic is considered to be the dipolar effects associated with the charge carrier hopping between Fe^{2+} and Fe^{3+}. At the same time, a large change ($\Delta\varepsilon/\varepsilon \sim 18\%$) in the dielectric constant at room temperature upon the application of small magnetic fields (H ~ 2 kOe) has been observed. The possible origin of MD effect is discussed.

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