Study of magnetic dynamics of LuFe$_2$O$_4$

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Abstract. A detailed study of the magnetic properties has been carried out for the LuFe$_2$O$_4$ system. Room temperature X-ray diffraction indicated single phase of the polycrystalline powder. The dc magnetization reveals the magnetic transition near 225 K. The ac susceptibility showed a peak corresponding to the magnetic transition; however, the peak is found to be frequency-dependent. With increasing frequency, the peak-temperature of the real part of the ac susceptibility ($\chi'$) increases and the respective susceptibility values are decreased. The imaginary part of the ac susceptibility ($\chi''$) increases with increasing frequency and so as the magnetic peak-temperature. The dynamic scaling of the ac susceptibility reveals the spin glass nature of this phase. The unusual glassy nature of the magnetic transition seems to be related to the presence of fractional disorder of the Fe$^{2+}$ and Fe$^{3+}$ ions resulted from the oxygen nonstoichiometry.

1. Introduction

Since last few decades multifunctional elements have attracted a lot of attention due to the simultaneous control of different order parameters led to the advancement of modern electronic devices [1]. Among these, LuFe$_2$O$_4$ has been an unique one because of its electronic ferroelectricity arising from the charge ordering (near 330 K) making it a new generation multiferroic for microelectronics [2]. LuFe$_2$O$_4$ is a member of RFe$_2$O$_4$, consist of two layers, one is the hexagonal double layer of Fe ions having average ionic radii +2.5 sandwiched by a R$_2$O$_3$ layer. These structural features led to behave this material as a charge-spin frustrated system. In LuFe$_2$O$_4$, coupling between the localized Fe moments give rise to ferrimagnetic ordering below the Néel temperature $T_N$ around 240 K. In addition to this, they exhibit electrical polarization around magnetic ordering temperature and giant room temperature magnetodielectric property [3]. Apart from their multifunctional behaviors, the magnetism of this material itself demands much attention. In RFe$_2$O$_4$ family, the physical characteristics of the materials strongly depend on the oxygen stoichiometry. For example, nearly stoichiometric and the nonstoichiometric YFe$_2$O$_4$, respectively show the three dimensional (3D) and two dimensional (2D) magnetic ordering [4]. For LuFe$_2$O$_4$, 2D charge correlation is observed below 500 K, while below 320 K 3D charge order is established [5]. It has been suggested from the neutron scattering that the ferrimagnetic nature of LuFe$_2$O$_4$ is 2D in nature [6]. Recent study has shown the presence of reentrant spin glass nature and possibilities based on the oxygen stoichiometry has been discussed [7]. The strong sample dependent properties in the members of RFe$_2$O$_4$ suggests that more attention should be paid on the LuFe$_2$O$_4$ depending on its oxygen stoichiometry.

In the present work we have studied the effect of variation of oxygen content on the magnetic properties of LuFe$_2$O$_4$ system. The magnetic dynamics of as prepared and oxygen
annealed LuFe$_2$O$_4$ samples have been compared by dc magnetization and frequency-dependent ac susceptibility studies.

2. Experimental

Polycrystalline LuFe$_2$O$_4$ sample has been prepared by solid state reaction method. The high purity (99.9%) Lu$_2$O$_3$ and Fe$_2$O$_3$ powders were annealed at 1200°C for 24 hours in a CO$_2$-CO gas flow and quenched to room temperature. The phase purity of the sample was investigated by X-ray diffraction using a D5000 (Siemens) with CuK$_\alpha$. To vary the oxygen content the sample was further annealed in O$_2$ atmosphere at 800°C for 6 hours. The dc and ac magnetic susceptibilities were carried out by quantum design MPMS-XL7 SQUID magnetometer.

![X-ray diffraction pattern of LuFe$_2$O$_4$ powder at 300 K.](image)

3. Results and Discussion

The X-ray pattern of LuFe$_2$O$_4$ taken at room temperature is shown in Fig. 1. The peaks are consistent showing the single phase behavior of the sample with no impurity phase. Figure 2 (a) shows the temperature dependence of the zero field cooled (ZFC) and field-cooled (FC) magnetization curves within the temperature range 5-300 K. The applied field has been selected to be 1000 Oe. The behavior of the magnetization is almost identical to earlier reports [8]. The ZFC curve shows a steady increase with temperature and then falls sharply showing a maxima near 225K. The value of $T_N$ has been determined taking the derivative of the FC data and its value comes out to be nearly 227K. The value is comparable to those of nearly stoichiometric LuFe$_2$O$_4$ [7]. Previous report has revealed the presence of spin glass transition in LuFe$_2$O$_4$ very close to the ferrimagnetic transition temperature. In order to investigate that, both real ($\chi'$) and imaginary ($\chi''$) parts of the magnetic susceptibility data has been measured with varying temperature. Figure 3 shows the temperature-dependent $\chi'$ and $\chi''$ for four different frequencies. The ac magnetic field has been kept as 1 Oe. The peak near 225 K corresponds to the magnetic ordering already found from the dc magnetization data. Interestingly this peak monotonically shifts towards the higher temperature and the maximum susceptibility value is going down with increasing frequency. It is known that for a long-range ordered system the ac susceptibility does not show any frequency-dependent shift. This indicates that the magnetic ordering in the present system is associated to short range ordering which leads to distributed sizes of magnetically ordered small regions. The peak temperature of the real part of the ac susceptibility, $T_f$, can be modeled with critical slowing down

$$\tau_{\text{max}} = \tau_o (T_f / T_g - 1)^{-z\nu}$$

where $T_g$ is the spin glass temperature, $z\nu$ is the dynamical exponent, $\tau_o$ is the microscopic
flipping time of the spins and $\tau_{\text{max}} = \frac{2\pi}{\omega}$ ($\omega$ is the driving frequency of the ac magnetic field). The best fit to Eq. 1 is observed (see inset of Fig. 3) for $T_g = 223.4$ K, $z\nu = 4.2$ and $\tau_0 \sim 10^{-12}$. The value of $z\nu$ is similar to conventional spin glass [9]. This indicates that in the present system the magnetic transition is associated to frustration whose frequency dependence resembles to that of a spin glass. The appearance of spin glass-like state in such a charge order system is itself a mystery as the average valence of Fe in the sample is +2.5 and therefore there exists equal amount of Fe$^{2+}$ and Fe$^{3+}$ making it a charge order system. It suggest the presence of even small amount of oxygen nonstoichimetry making the ratio of Fe$^{2+}$ and Fe$^{3+}$ unequal and induce disorder in the exchange interaction. Previously magnetic dynamics study on the similar system revealed that the system showed a ferrimagnetic transition at $T = 234$ K which is followed by a spin glass transition at around 228 K [7]. This is in contrast to our result where long range and short ordering simultaneously present at the same temperature. We suggest that the different oxygen content may be reason for this dissimilar result. The amount of oxygen content is not easy to control in such system however it is a crucial factor and even a small change can effect the physical properties largely.

To study the effect of O$_2$ content we have further annealed the as prepared sample in an oxygen atmosphere at 800°C for 6 hours to have excess oxygen content in the system. The room temperature XRD has been done and interestingly a completely new phase is observed.
for this sample. The temperature dependent magnetization has been measured under a similar condition mentioned above. The magnetization value is found to increase by 20 times compared to the as prepared sample and no clear transition is evident. This proves that the oxygen content can change the scenario of the system drastically and therefore an important factor to take into account.

4. Conclusion

To conclude, we have studied the magnetic properties of the polycrystalline LuFe$_2$O$_4$ system. The ac susceptibility shows the simultaneous presence of the long and short range (spin glass) magnetic ordering at the same temperature. The presence of spin glass phase indicates the presence of unequal Fe$^{2+}$ and Fe$^{3+}$ (Fe$^{2+}$/Fe$^{3+}$ ≠ 1) might be resulted from the oxygen nonstoichiometry. The oxygen content is found to control the behavior largely in such LuFe$_2$O$_4$ system.

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