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Dielectric property studies of multiferroic $GaFeO_3$

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Abstract
Magnetic and dielectric properties of a polycrystalline $GaFeO_3$ sample prepared by a solid-state reaction have been investigated. A ferrimagnetic phase transition T_N of the material was identified at a temperature of 225 K. An anomaly on the permittivity as a function of temperature has been observed near its magnetic transition point T_N, which could be induced by the magnetoelectric coupling between its electric and magnetic orders. At low temperature, $T < T_N$, the permittivity variation $\Delta\varepsilon$ depends on magnetization M and shows clearly a linear relationship between $\Delta\varepsilon$ and M^2, which indicates that a dielectric and magnetic correlation exists in the compound. Furthermore, its dielectric relaxation process is discussed in the temperature interval of 77–300 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Multiferroics combining ferroelectric and magnetic parameters in the same phase have recently attracted much attention due to their fundamental physics and technological applications. [1] Till now, many muliferroics, such as boracites [2], $BaMnF_4$ [3], $SeCuO_3$ [4], $BiFeO_3$ [5], $RMnO_3$ and RMn_2O_5 (R = Rare earth, Y and Bi), etc [6–10], have been reported. However, for most of the materials, the magnetic and ferroelectric transition temperatures are far lower or higher than room temperature, and the coupling between magnetic and ferroelectric order parameters at room temperature is always weak. A material that suits the commercial application has not been found so far. In order to search for the physical mechanism and new multiferroic material, we prepared a $GaFeO_3$ compound and studied its magnetic and dielectric properties. Fe–Ga oxides $Ga_{2-x}Fe_xO_3$ ($0.7 \leqslant x \leqslant 1.4$) have been largely investigated owing to their combination of ferromagnetic and piezoelectric properties and large linear ME effect. Their magnetic transition temperature (200–340 K) is around room temperature [10–18]. These phenomena show that Fe–Ga oxides can be a candidate for multiferroic materials with great technological application. In this report, we studied the magnetic and dielectric properties of polycrystalline $GaFeO_3$, and investigated the possible correlation among the dielectric and magnetic behaviours. A signal of magnetocapacitance related to the coupling between the magnetic and electric order has been observed near the magnetic transition temperature. Below T_N, a linear relationship between $\Delta\varepsilon$ and M^2 was observed which verified the coupling between the polarization and magnetization orders in this compound. Furthermore, a dielectric relaxation process is observed near room temperature at low frequencies.

2. Experimental procedure

A polycrystalline $GaFeO_3$ sample was prepared using a conventional solid-state reaction method. Stoichiometric mixtures of Ga_2O_3 and Fe_2O_3 with purity higher than 99.9 at% were mixed, grounded, pre-calcinated at 1173 K and then 1323 K for 12 h, respectively. Finally, it was sintered at 1493 K for 12 h. Phase identification was performed by the x-ray powder diffraction (XRD) method on a Rigaku D/Max-2400 V powder diffractometer equipped with Cu Kα. Magnetic measurement was carried out on a commercial superconducting quantum interference device magnetometer (MPMS-5) in a 0.1 T magnetic field ranging from 5 to 300 K under a zero-field-cooling condition. Dielectric properties were measured using an Agilent 4294 A precision impedance analyser. Ag paste was used as the electrodes.

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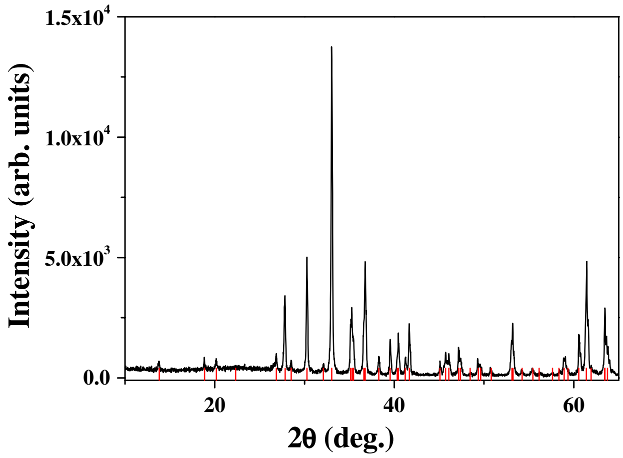

Figure 1. XRD pattern of polycrystalline $GaFeO_3$. The bold vertical lines indicate that the diffraction peaks correspond to the reported data of JCPDS-ICDD 76-1005 for $GaFeO_3$.

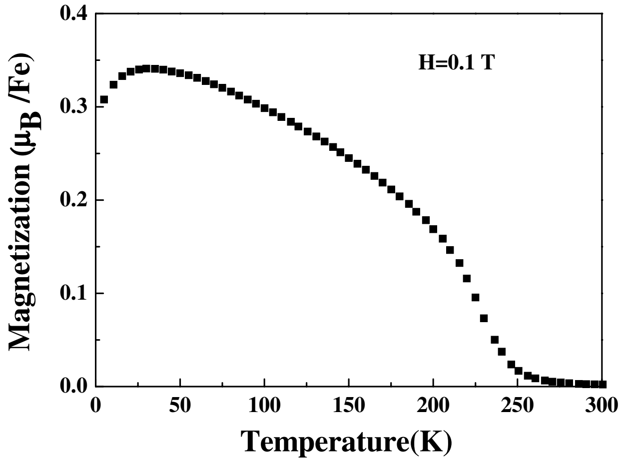

Figure 2. Temperature dependence of magnetization for $GaFeO_3$ in zero field-cooling (ZFC) at an applied magnetic field $H = 0.1$ T(a); temperature derivative of the magnetization (b).

3. Results and discussion

The XRD pattern for $GaFeO_3$ is shown in figure 1. The pattern obtained here showed a clean single-phase pattern similar to the JCPDS-ICDD 76-1005 (the peaks are shown by lines in figure 1) for $GaFeO_3$. All the diffraction peaks can be indexed using the Jade 5.0 program [19] into an orthorhombic unit cell with lattice parameters $a = 8.7467(8)$ Å, $b = 9.394(1)$ Å, $c = 5.0817(6)$ Å. This result is in agreement with the literature data for single-crystal $GaFeO_3$. Then, the polycrystalline sample here has the same space group $Pc2_1n$ as the single-crystal, and has the spontaneous polarization along the b axis, and behaves as ferrimagnetic with the spin moment along the c axis [14, 18].

Magnetization (M) versus temperature (T) at the magnetic field (H) of 0.1 T is shown in figure 2. The M–T behaviour displays a P-type shape characteristic, which is a type of ferrimagnetic material M–T curve [20]. $GaFeO_3$ thus can be considered as a ferrimagnetic compound [13, 14]. According to figure 2, the ferrimagnetic transition temperature (T_N) of $GaFeO_3$ was identified at about 225 K, which is measured by the differential maximum of the M–T (not shown here), and it is different from those reported by previous studies for single crystals [12–14]. This difference in T_N was induced by the different preparation techniques, for the magnetic transition temperature T_N of GaFeO3 significantly depends on the preparation technique [14, 17].

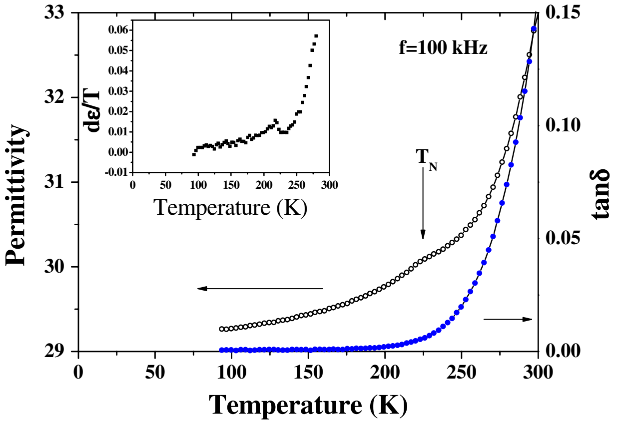

Figure 3. Permittivity (ε) and dielectric loss ($\tan\delta$) as a function of temperature at 100 kHz for $GaFeO_3$; inset shows the differential of ε versus T.

Temperature dependence of permittivity (ε) and dielectric loss ($\tan\delta$) of $GaFeO_3$ at 100 kHz are shown in figure 3. A dielectric anomaly in permittivity is clearly observed around the magnetic transition temperature T_N. Moreover, the first order differential maximum of the ε versus T curve reveals that the anomaly has taken place at about 220 K (shown as inset in figure 3). This dielectric anomaly is very similar to the cusp characteristic of the permittivity–temperature curve of ferroelectric–antiferromagnets $BaNiF_4$ [3], $YMnO_3$ [9] and ferroelectric–ferromagnet $BiMnO_3$ [8], which has contributed to the magnetocapacitance or magnetodielectric effect [8, 9]. In figure 3, the permittivity decreases steeply below T_N. This suggests that the magnetic ordering suppresses the dielectric constant [8]. So, we infer that this kind of dielectric anomaly of $GaFeO_3$ is induced by its ferrimagnetic order and could be attributed to a magnetic ordering from the super-exchange interaction between neighbouring Fe^{3+} ions.

As temperature lower than T_N, $GaFeO_3$ is in ferrimagnetic order state. An associated variation of the dielectric permittivity would then be induced by the hyperfine internal magnetic field. Let us assume that no magnetic transition has taken place at low temperature for $GaFeO_3$; the low temperature permittivity would change with decreasing temperature in the same way as at high temperature (paramagnetic phase). Then, in assuming zero internal magnetic field condition, the low temperature permittivity (ε_0) can be obtained from the extrapolation of the experimental value at high temperature. The difference $\Delta\varepsilon$ between ε_0 and the measurement value ε of permittivity at low temperature is the variation that results from the magnetic order. The permittivity variation $\Delta\varepsilon = \varepsilon_0 - \varepsilon$ could be proportional to the square of magnetization [8, 21]

$$\Delta\varepsilon \sim M^2(T). \tag{1}$$

The permittivity–temperature curve of $GaFeO_3$ and the extrapolation line from paramagnetic phase of $GaFeO_3$ in the temperature interval 100–300 K are shown in figure 4. It reveals

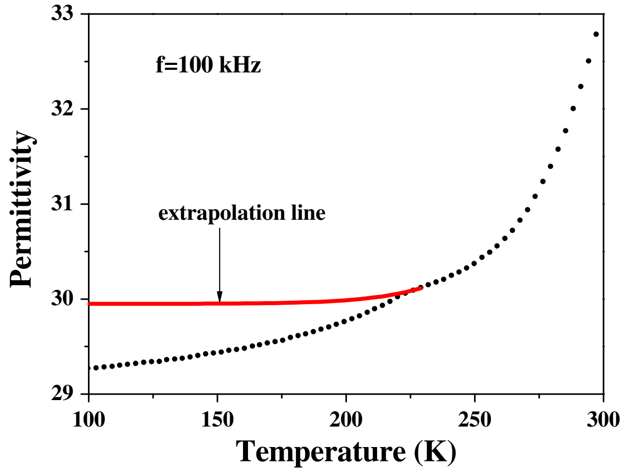

Figure 4. Permittivity for $GaFeO_3$ at 100 kHz (●, experimental points) and its extrapolation from the paramagnetic range (——).

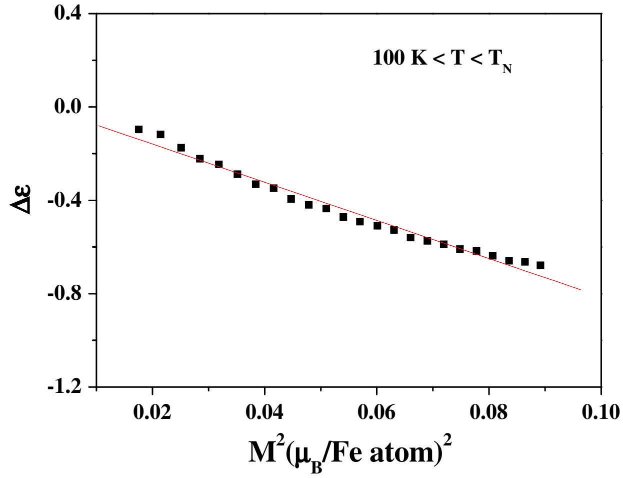

Figure 5. Relation between $\Delta\varepsilon$ and M^2 in the temperature range from 100 K to T_N.

that the magnetic order induces the permittivity decrease as a temperature lower than magnetic order temperature. The difference $\Delta\varepsilon = \varepsilon_0 - \varepsilon$ of both curves as the function of square magnetization M^2 is shown in figure 5. It displays that the $\Delta\varepsilon$ is a linear function of the M^2 in the temperature interval 100–225 K. As a result, the magnetoelectric coupling behaviour of $GaFeO_3$ could be confirmed by the cusp of permittivity on the temperature dependence and the linear relation between $\Delta\varepsilon$ and M^2. For the experimental phenomenon, Smolenskii and co-workers [22, 23] have given it a perfect theoretical description, and it has also been verified in polycrystalline $BiMnO_3$ [8] and single crystal $Pb(Fe_{1/2}Nb_{1/2})O_3$ [21].

Analogous to the dielectric anomaly in $BiMnO_3$ [8], the dielectric cusp in $GaFeO_3$ at T_N might be fully suppressed by a certain applied magnetic field, and then no dielectric cusp will be observed. Thus according to the magnetocapacitance effect calculated by the follow formulation

$$\mathrm{MC} = \frac{\varepsilon(h, T) - \varepsilon(0, T)}{\varepsilon(0, T)}, \qquad (2)$$

where $\varepsilon(h, T)$ represents the permittivity at a certain magnetic field, and $\varepsilon(0, T)$ is the permittivity when the external magnetic field is zero, the MC for $GaFeO_3$ was estimated to be about -0.5%. It is similar for ferromagnetic $BiMnO_3$ whose MC effect at T_C is about -0.6% [8].

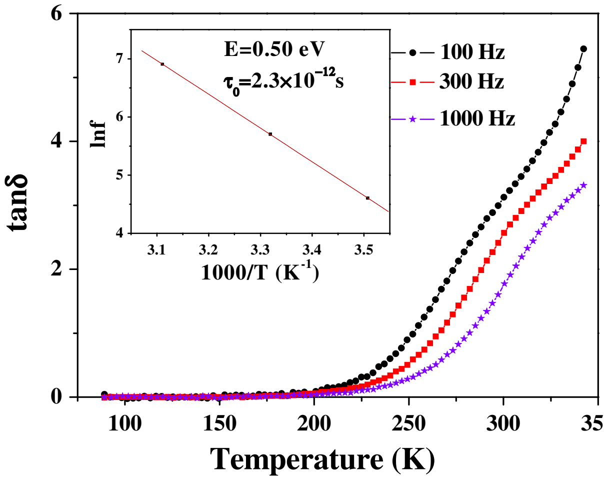

Figure 6. Dependence of dielectric loss (tan δ) on temperature at low frequencies of 100 Hz, 300 Hz and 1 kHz, from top to bottom, respectively. Inset shows the Arrhenius plot for the relaxation peak.

Furthermore, a relaxation process around room temperature at low frequencies is observed as shown in figure 6. For a thermally activated dielectric relaxation process, the corresponding activation energy (E) can be got from the famous Arrhenius law

$$f = f_0 \exp(-E/k_B T_p), \qquad (3)$$

where E is activation energy, f_0 is the characteristic relaxation frequency at infinite temperature, k_B is the Boltzman parameter, and T_p is the peak temperature. The relaxation frequency as a function of inverse peak temperature, obtained from the dielectric loss peaks, is plotted in the inset of figure 6, which indicates that the data are well fitted to the Arrhenius law. The activation energy obtained is $E = 0.50$ eV, and the relaxation time $\tau_0 = 2.3 \times 10^{-12}$ s. As the activation energy is close to the value for oxygen vacancies in $SrBi_2Ta_2O_9$ [24], $SrTiO_3$ [25], YBCO ceramics [26] and BiT [27], this dielectric relaxation process might be associated with the oxygen vacancies.

4. Summary

In summary, we have investigated the temperature dependence of magnetic and dielectric properties of $GaFeO_3$. A ferrimagnetic phase transition is identified at 225 K on the magnetic susceptibility. A dielectric anomaly at the magnetic transition temperature has been observed. At temperatures below T_N, a linear relationship between $\Delta\varepsilon$ and M^2 is confirmed. These distinct features could be associated with the coupling between magnetic and dielectric properties. This implies that $Ga_{2-x}Fe_xO_3$ compounds have potential application as multiferroic materials in future.

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