

Multiferroic Properties of κ -Al₂O₃-Type GaFeO₃ Epitaxial Thin Films

In this study, high-quality Ga_xFe_{2-x}O₃ ($x = 0-1$) epitaxial films were fabricated and their properties were systematically investigated. X-ray magnetic circular dichroism revealed that the large magnetization at $x = 0.6$ is derived from Fe³⁺ ($3d^5$) at octahedral sites. The controllable range of the electric coercive field, magnetic coercive field, and saturated magnetization values at room temperature (400–800 kV/cm, 1–8 kOe, and 0.2–0.6 μ B/f.u., respectively) is very wide and differs from those of well-known multiferroic BiFeO₃. Furthermore, the Ga_xFe_{2-x}O₃ films exhibit room-temperature magnetocapacitance effects, indicating that adjusting the Curie temperature (T_C) near room temperature is useful to achieve large room-temperature magnetocapacitance behavior.

κ -Al₂O₃-type structured Ga_xFe_{2-x}O₃ has attracted much attention due to the coexistence of ferroelectric and ferrimagnetism at room temperature. The κ -Al₂O₃-type structure consists of three oxygen octahedral sites and one tetrahedral site. The origin of ferroelectricity is a non-centrosymmetric displacement of cation and oxygen along the c -axis direction. The origin of ferrimagnetism is a different magnetic moment from oxygen octahedral and tetrahedral sites. Although the existence of ferroelectricity depends on their space group (the space group of κ -Al₂O₃ is $Pna2_1$), the magnetic moment strongly depends on their constituent cations in octahedral and tetrahedral sites. Therefore it is very important for understanding magnetic properties to investigate the cation conditions such as valence, coordination number and occupancy in each site. In this study, we systematically investigated the detailed crystal structure and multiferroic properties of Ga_xFe_{2-x}O₃ epitaxial thin films [1].

The relation between the magnetic properties and cation sites was investigated using X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements. For the measurements, the $x = 0.6$ film was used because of its high magnetization. **Figure 1(a)** shows the Fe L -edge XAS spectrum of the $x = 0.6$ film together with that of α -Fe₂O₃ as a reference of O_h Fe³⁺ [2]. The spectrum of the film shows Fe L_3 and L_2 peaks, which have very similar peak shapes

and positions as those of α -Fe₂O₃, confirming the trivalent state of Fe in the $x = 0.6$ film. In the Fe L_3 peak, two peaks are observed at 708.7 and 710.2 eV. Because the peak at 708.7 eV is due to O_h Fe³⁺ sites [3], it is suggested that the Fe ions are mainly located at O_h sites in the film. Notably, the film has three O_h sites (Fe1, Fe2, and Ga2) and one T_d site (Ga1) [Fig. 1(c)]. **Figure 1(b)** shows the XMCD spectrum of the $x = 0.6$ film. At the Fe L_3 -edge, there are sharp negative (A), positive (B), and negative (C) peaks at 708.6, 709.6, and 710.4 eV, respectively. The A and C peaks are derived from Fe³⁺ at O_h sites, while the B peak is due to Fe³⁺ at the T_d site [4, 5]. The A and C peaks show negative values, confirming that the inner product between the applied magnetic field and total magnetic moment of Fe at the O_h sites is positive. The B peak is positive, indicating that magnetic moment of Fe at T_d Ga1 sites is antiparallel to the applied magnetic field. This is reasonable because magnetization is represented as $(M_{Fe2} + M_{Ga2} - M_{Fe1}) - M_{Ga1}$. It is noted that the absolute intensity of the B peak is much smaller than those of the A and C peaks, indicating that the Fe ions are mostly located at O_h sites (Fe1, Fe2, and Ga2). This is the main reason why the $x = 0.6$ film exhibits a large magnetization.

We investigated the dielectric and magnetocapacitance (MC) properties of the GFO epitaxial films. **Figure 2(a)** shows the dielectric constants for the $x = 0.8$ film

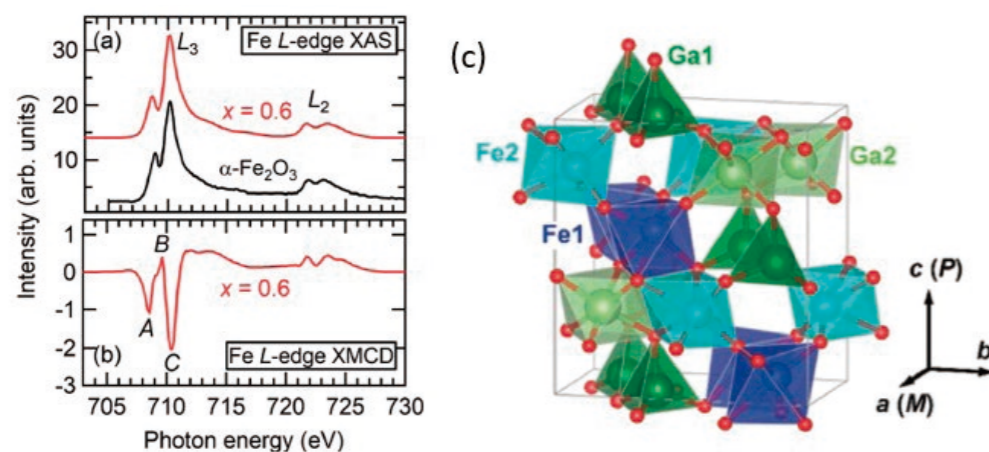


Figure 1: Fe L -edge (a) XAS and (b) XMCD ($\mu_{\uparrow} - \mu_{\downarrow}$) spectra of Ga_{0.6}Fe_{1.4}O₃ thin film measured at 35 K under H of 50 kOe. The XAS spectrum of α -Fe₂O₃ is included for comparison [2] (c) Schematic illustration of GaFeO₃ crystal structure.

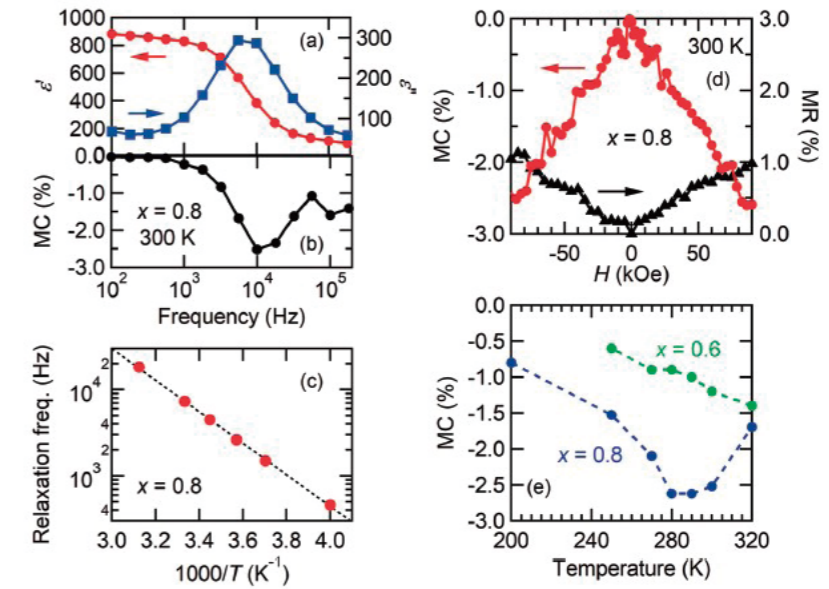


Figure 2: Frequency dependence of (a) real (ϵ' , red circle) and imaginary (ϵ'' , blue square) parts of the dielectric constant, and (b) magnetocapacitance [MC = $\epsilon'(H) - \epsilon'(0 T) / \epsilon'(0 T)$] at $H = 9 T$ for the Ga_{0.8}Fe_{1.2}O₃ film measured at 300 K. (c) Temperature dependence of the relaxation frequencies for the Ga_{0.8}Fe_{1.2}O₃ film. (d) Magnetic field (H) dependence of MC (red circle) and magnetoresistance (MR, black triangle) for the Ga_{0.8}Fe_{1.2}O₃ film at 300 K. H is applied to the in-plane direction. (e) Temperature dependence of the maximum MC value at 90 kOe for the Ga_xFe_{2-x}O₃ ($x = 0.6$ and 0.8) films.

as a function of frequency. The real part of the relative dielectric constant (ϵ') suddenly decreases from 8.3×10^2 to 1.1×10^2 as the frequency increases from 1 to 100 kHz at 300 K, while the imaginary part of the relative dielectric constant (ϵ'') has a peak at 7 kHz, confirming the existence of a relaxation process. **Figure 2(c)** shows the temperature dependence of the relaxation frequencies for the film. The relaxation frequency increases with temperature according to the Arrhenius plot with an activation energy (E_a) of 0.36 eV. Since both Ga and Fe vacancies have negligible mobility at such low temperatures, the relaxation process probably originates from oxygen ion related defects such as oxygen vacancies. Taking into account that oxygen-vacant BaTiO_{3- δ} films exhibit dielectric relaxation via oxygen vacancies at a few kHz near room temperature with E_a of 0.39 eV [6], the relaxation in this study is attributed to dielectric relaxation through oxygen vacancies, which is coupled with Fe²⁺ ions.

The GFO films exhibit MC behaviors at room temperature. **Figure 2(b)** shows the frequency dependence of the MC values at 300 K, where MC is calculated to be $(\epsilon'(H = 9 T) - \epsilon'(0 T)) / \epsilon'(0 T)$ and H is applied to the in-plane direction. MC strongly depends on frequency. It has a negative peak near the relaxation frequency and becomes smaller when $\tan \delta$ ($= \epsilon'' / \epsilon'$) is small. **Figure 2(d)** shows MC and the magnetoresistance (MR) for the $x = 0.8$ film measured at 300 K as a function of H . As the absolute value of H increases, MC decreases while MR increases almost linearly (i.e., the film exhibits negative MC and positive MR behaviors). The positive MR value suggests that the antiferromagnetic interaction between Fe³⁺ ions decreases electron transfer

between the ions. Considering that ϵ'' is affected more strongly by the transport property when $\tan \delta$ is larger, these results indicate that the negative MC effect in the GFO films is mainly derived from the positive MR behavior. **Figure 2(e)** shows the temperature dependence of the MC values for the $x = 0.6$ and 0.8 films. For the $x = 0.8$ film, the absolute value of MC has a maximum at the magnetic phase transition temperature ($T_C = 290 K$), indicating that adjusting T_C near room temperature is useful to achieve a large room-temperature MC behavior.

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