Raman scattering study of multiferroic $Ho_3Fe_5O_{12}$ thin films

# Raman scattering study of multiferroic Ho$_3$Fe$_5$O$_{12}$ thin films

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**Abstract**

Ho$_3$Fe$_5$O$_{12}$ crystallizes in a body-centered cubic lattice and shows no ferroelectricity because of its highly symmetric (centrosymmetric) crystal structure. However, in heteroepitaxially grown thin films, Ho$_3$Fe$_5$O$_{12}$ may exhibit ferroelectricity because of lattice strains induced by the substrate. In this work, heteroepitaxial films of Ho$_3$Fe$_5$O$_{12}$ were grown with different thicknesses of 50–160 nm and studied by x-ray diffraction and Raman scattering. The results were compared with those of bulk polycrystals to characterize residual strains. At room temperature, Raman spectra of films revealed a phonon frequency shift from those of bulk samples, showing lattice distortion. There was a difference in the lattice distortion scheme between the thinner and thicker films. Results of x-ray diffraction were well correlated with the Raman data. Raman measurements at 300–800 K showed the existence of lattice strain up to $\sim$650 K. This suggests a remanent-polarization character of Ho$_3$Fe$_5$O$_{12}$ films up to this temperature. Closeness between the magnetic ordering temperature $T_N = 567$ K and $T_C \sim 650$ K may bring us the ideal multiferroic material with an enhanced magnetoelectric effect at room temperature.

## 1. Introduction

There has been increasing interest in so-called multiferroics, showing ferroelectric properties as well as ferromagnetic or ferroelastic properties. The coexistence of ferroelectricity and ferromagnetism may yield a magnetoelectric effect, in which the magnetization is controlled by the applied electric field. Although multiferroic materials are good candidates for fabricating future innovative electronic devices, such materials working at room temperature are scarce [1].

Although rare-earth iron garnets show ferromagnetism or ferrimagnetism with relatively high $T_N \sim 560$ K [2–4], they show no ferroelectricity because of their highly symmetric (centrosymmetric) crystal structures. However, if they are distorted by lattice strains in heteroepitaxial films, they may show ferroelectricity [5] and can be a good candidate for multiferroics. In this study, we prepared Ho$_3$Fe$_5$O$_{12}$ epitaxial films with different thicknesses as well as bulk polycrystals

for comparison. They were observed by Raman scattering for phonon spectra for the first time. Observed phonon frequencies in Ho$_3$Fe$_5$O$_{12}$ films were shifted from those of bulk samples, suggesting lattice distortions. X-ray diffraction analysis supported the Raman results. Raman measurements at high temperatures showed the existence of lattice strains up to $\sim$650 K. This suggests a remanent-polarization character of Ho$_3$Fe$_5$O$_{12}$ films up to this temperature.

## 2. Experiment

As for all other garnets, Ho$_3$Fe$_5$O$_{12}$ crystallizes in a body-centered cubic lattice (*Ia3d* or O$_h^{10}$ space group). The unit cell contains as many as eight formula units of Ho$_3$Fe$_5$O$_{12}$, which explains the rather large lattice constant, $a = 12.376$ Å. Figure 1 shows the crystal structure of Ho$_3$Fe$_5$O$_{12}$. Ho$^{3+}$ ions occupy eightfold oxygen-coordinated

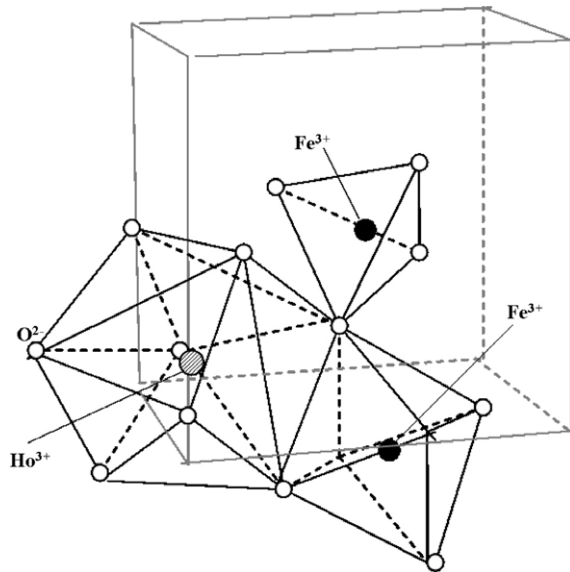**Figure 1.** Crystal structure of $Ho_3Fe_5O_{12}$.

(dodecahedral) lattice sites, while the $Fe^{3+}$ ions occupy sixfold (octahedral) or fourfold oxygen-coordinated (tetrahedral) sites with the ratio of 2:3. Magnetic ordering arises from indirect antiferromagnetic exchange ($Fe^{3+}$–$O^{2-}$–$Fe^{3+}$ superexchange) between nearest-neighbor octahedral and tetrahedral $Fe^{3+}$ ions. Because the electronic ground state of $Fe^{3+}$ is $^6S$, each ferric ion carries a magnetic moment of five Bohr magnetons [6]. The $Fe^{3+}$ magnetic moments in the octahedral and tetrahedral sites align antiparallel in the magnetically ordered phase below $T_N = 567$ K [2].

The $Ho_3Fe_5O_{12}$ epitaxial films were grown by pulsed laser deposition (PLD) on the (100) plane of a $(Gd_{2.7}Ca_{0.3})(Ga_{4.0}Mg_{0.32}Zr_{0.65}Ca_{0.03})O_{12}$ (SGGG) substrate with thickness (#a) 50 nm, (#b) 70 nm and (#c) 160 nm. Bulk polycrystal specimens observed in the Raman study were also used as the PLD target. The lattice constant of $Ho_3Fe_5O_{12}$ is $a = 12.376$ Å, while that of SGGG (which also has a garnet structure) is $a = 12.499$ Å, yielding a lattice mismatch of 0.98%. Therefore, $Ho_3Fe_5O_{12}$ epitaxial films on SGGG are expected to be tensile strained in the growth plane.

The variations of lattice constants of the film samples with thickness were analyzed by x-ray diffraction (XRD) and are plotted in figure 2. Here, the lattice constants in the growth plane (a) and along the growth direction (b) were separately evaluated. The dotted lines give lattice constants of the substrate SGGG and bulk $Ho_3Fe_5O_{12}$ for comparison. Epitaxial growth of the film samples is confirmed in figure 2(a) by the agreement in the lattice constants between the film samples and the SGGG substrate. Comparison of the lattice constants between the $Ho_3Fe_5O_{12}$ films and bulk samples shows that the films #a and #b are tensile strained in the growth plane (figure 2(a)), but compressively strained in the growth direction (figure 2(b)) to break the cubic symmetry. The film #c is, in contrast, tensile strained in both directions. Thus, the breaking of cubic symmetry is relaxed.

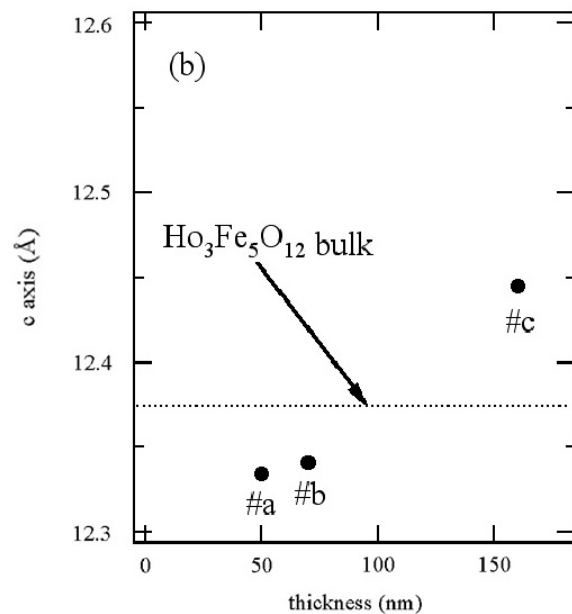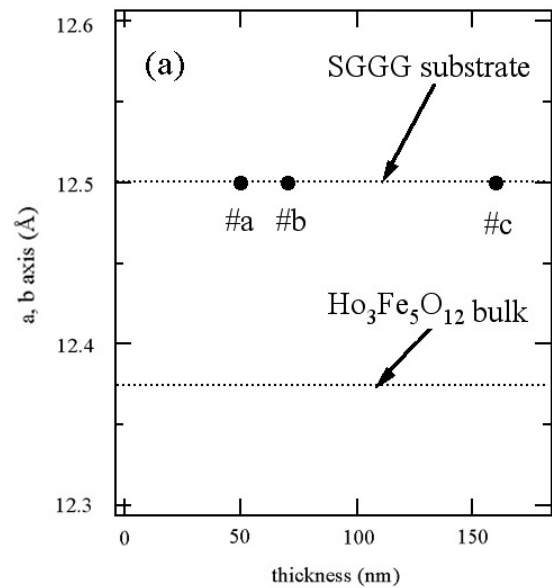Figure 3 shows $P$–$E$ (polarization–electric field) hysteresis curves of the $Ho_3Fe_5O_{12}$ films in the growth plane at room



**Figure 2.** Lattice constants of $Ho_3Fe_5O_{12}$ films analyzed by x-ray diffraction. Dotted lines give lattice constants of the $Ho_3Fe_5O_{12}$ bulk polycrystal and the substrate (SGGG).

temperature. The remnant polarization in the growth plane was observed in the thinner films #a and #b, but not in the thicker one #c. It means that the film thickness is a key factor for generating remnant polarization in $Ho_3Fe_5O_{12}$ films. The findings of XRD for the anisotropic strains as seen in figure 2 are consistent with the $P$–$E$ hysteresis results.

The Raman measurement was conducted at 300–800 K: the samples were placed in an electric furnace (Linkam Scientific Instruments) placed on the stage of a Raman microscope. An $Ar^+$ laser at 488.0 nm was used for the excitation source. The laser beam was linearly polarized and focused by an objective lens on the sample surface. The scattered light was collected in the backscattering geometry by the same objective lens, fed to a double monochromator of
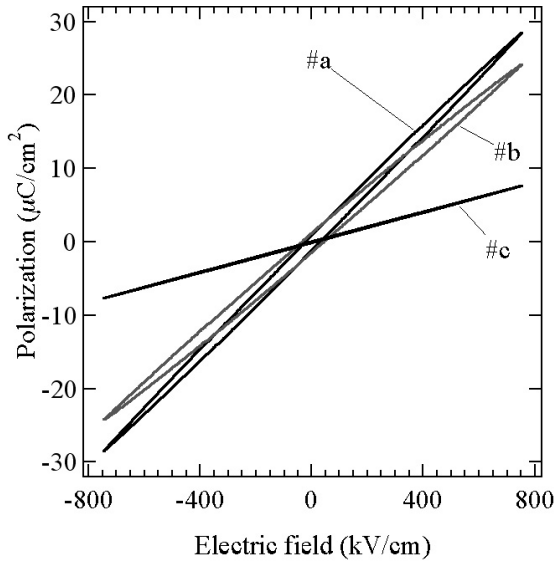
**Figure 3.** $P$–$E$ hysteresis curves of the $Ho_3Fe_5O_{12}$ films with thicknesses #a (50 nm), #b (70 nm) and #c (160 nm) in the growth plane.

focal length 85 cm (SPEX 1403) for dispersion, and the spectra were detected by a liquid-nitrogen-cooled charge-coupled-device (CCD) camera.

## 3. Results and discussion

Figure 4 shows Raman spectra of the $Ho_3Fe_5O_{12}$ films observed at room temperature with the results of the SGGG substrate and the $Ho_3Fe_5O_{12}$ bulk polycrystal for comparison. The inset shows polarized spectra of the film sample #c. Here, the Raman scattering geometry is described by Porto's notation [7] with directions defined as $x \parallel [001]$, $y \parallel [010]$, $z \parallel [100]$, $x' \parallel [011]$ and $y' \parallel [0\bar{1}1]$: $z(x', x')\bar{z}$ means, for example, that the incident light propagates along $z$ with the polarization vector along $x'$ and the scattered light propagates along $\bar{z}$ with the polarization vector along $x'$.

A group theoretical analysis predicts 25 Raman-active phonon modes at the $\Gamma$ point; $\Gamma_{Raman} = 3A_{1g} + 8E_g + 14T_{2g}$ [8]. In the present Raman scattering set-up, these modes can be observed in the following geometries;

$$z(x, x)\bar{z} \rightarrow A_{1g}, E_g$$

$$z(x, y)\bar{z} \rightarrow T_{2g}$$

$$z(x', x')\bar{z} \rightarrow A_{1g}, E_g, T_{2g}$$

$$z(x', y')\bar{z} \rightarrow E_g.$$

In the present experiment, a total of 17 phonon peaks of $Ho_3Fe_5O_{12}$ were clearly observed in bulk polycrystals. In contrast, the film spectra are mainly dominated by the SGGG substrate signals as marked by asterisks because the probe laser easily penetrates the thin epitaxial layers with thicknesses 50–160 nm and excites the substrate. However, careful comparison
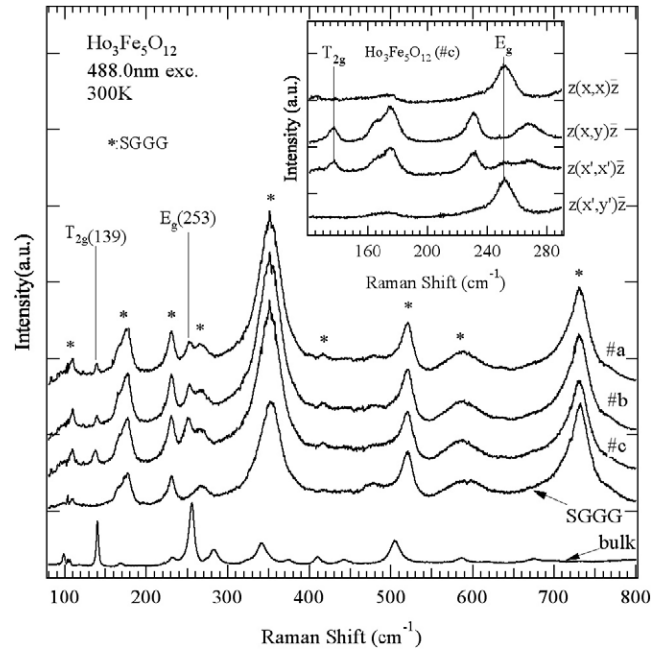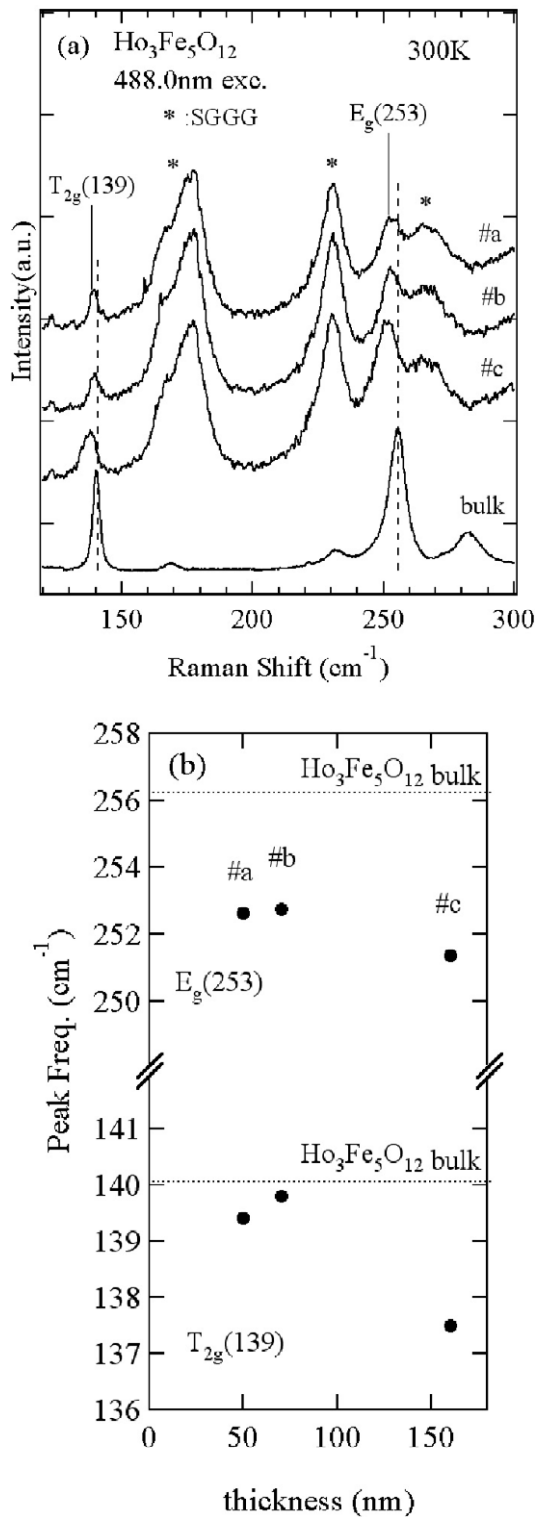


**Figure 4.** Raman spectra of $Ho_3Fe_5O_{12}$ films at room temperature. Spectra of the substrate (SGGG) and $Ho_3Fe_5O_{12}$ bulk polycrystal are also shown for comparison. Asterisks in film spectra show the substrate signal. The inset shows polarized Raman spectra of #c.

between the film and substrate spectra indicates two weak intrinsic signals of $Ho_3Fe_5O_{12}$ at 139 and 253 $cm^{-1}$. In the bulk polycrystal spectrum, these peaks give intense signals. The polarized Raman analysis in the inset shows that the 139 and 253 $cm^{-1}$ peaks are assigned to $T_{2g}$ and $E_g$ modes, respectively.
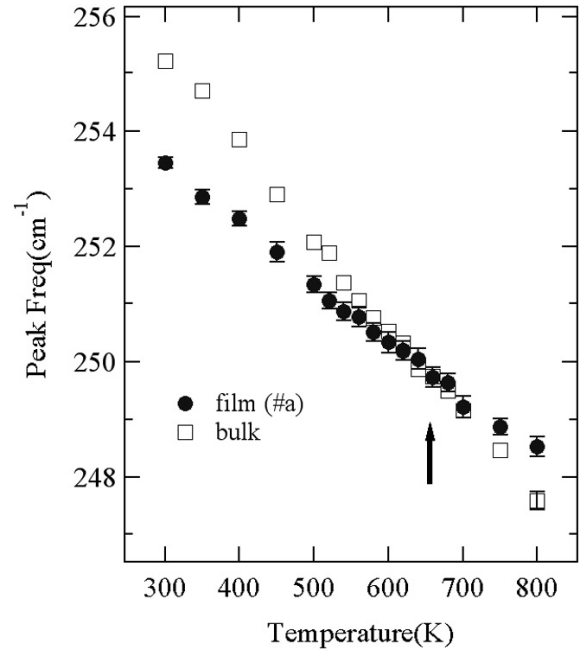
Figure 5(a) shows enlarged spectra of the low-frequency region in figure 4. The $T_{2g}$ (193 $cm^{-1}$) and $E_g$ (253 $cm^{-1}$) modes of the $Ho_3Fe_5O_{12}$ films are shifted in frequency from those of the bulk samples, suggesting lattice distortion in the films. As plotted in figure 5(b), the thickest sample (#c) shows much greater frequency shifts than the thinner ones, #a and #b, from the corresponding bulk frequencies. These anomalies are consistent with the results of XRD (figure 2) and our experiment for $P$–$E$ hysteresis (figure 3).

We have compared the frequency variation of the $E_g$ phonon mode of $Ho_3Fe_5O_{12}$ at ~253 $cm^{-1}$ (300 K) between the thinnest film (#a) and the bulk sample. Figure 6 shows the result obtained from the Raman measurement at higher temperatures. Both the bulk (open square) and film (filled circle) samples show monotonic decreases in frequency with increasing temperature. Since the bulk sample shows a larger slope, the frequency difference at room temperature (~2 $cm^{-1}$) is reduced at higher temperatures, diminishing at ~650 K. This suggests that the remanent-polarization character of the film induced by lattice distortion may remain up to $T_C \sim$ 650 K. This value is relatively close to the magnetic ordering temperature of $Ho_3Fe_5O_{12}$, $T_N = 567$ K, when compared with those for other multiferroic candidates already reported, such as $BiFeO_3$ ($T_C = 1103$ K, $T_N = 643$ K) [9, 10] and $YMnO_3$ ($T_C \sim 900$ K, $T_N = 80$ K) [11, 12]. The hybridization effect in multiferroics between magnetic ordering and ferroelectricity,

**Figure 6.** Temperature variation of $E_g$ phonon mode in $Ho_3Fe_5O_{12}$ film (#a) in comparison to $Ho_3Fe_5O_{12}$ bulk polycrystal data.

## 4. Conclusion

Heteroepitaxial films of $Ho_3Fe_5O_{12}$ with different thicknesses of 50–160 nm were grown and studied by x-ray diffraction and Raman scattering. The results were compared with those of bulk polycrystals. At room temperature, we have observed a total of 17 phonon modes in Raman spectra of bulk samples while only two phonon peaks were confirmed in the films, which were classified as $T_{2g}$ and $E_g$ modes. These phonon frequencies are shifted from those of bulk samples, showing lattice distortion in the film. Raman scattering suggested different lattice distortion schemes between the thinner and thicker films. The results of x-ray diffraction are well correlated with the Raman data. Raman measurements at higher temperatures showed the existence of lattice strain up to ∼650 K. We may expect, then, the remanent-polarization character of $Ho_3Fe_5O_{12}$ films up to this temperature. The closeness between the magnetic ordering temperature $T_N = 567$ K and $T_C \sim 650$ K may bring us an enhanced magnetoelectric effect at room temperature.

**Figure 5.** (a) Enlarged Raman spectra of $Ho_3Fe_5O_{12}$ films at room temperature. The $Ho_3Fe_5O_{12}$ bulk spectrum is also shown for comparison. Asterisks show the substrate signal. (b) Frequencies of $E_g$ (upper) and $T_{2g}$ (lower) phonon modes are plotted against the thickness. Dotted lines give phonon frequencies in the bulk.

the so-called magnetoelectric effect, is enhanced if the critical temperatures are about the same [13–15]. From this viewpoint, we may expect a large magnetoelectric effect in $Ho_3Fe_5O_{12}$ films.

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