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# Why Are Garnets Not Ferroelectric? A Theoretical Investigation of $Y_3Fe_5O_{12}$

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Results are presented on the electronic, electric, and magnetic properties of yttrium iron garnet, $Y_3Fe_5O_{12}$ using first-principles calculations. A cubic centrosymmetric structure and a tetragonally strained structure of $Y_3Fe_5O_{12}$ are investigated. Frozen-phonon calculations are performed for both phases. We show, using symmetry arguments and by analyzing the crystal structure, that stoichiometric garnets are unlikely multiferroic materials despite their magnetization at room temperature and above.

## 1. Introduction

Garnet, especially yttrium iron garnet, $Y_3Fe_5O_{12}$, has recently received some renewed interest for various microwave applications.[1−3] The crystal structure of garnet was first described in 1917 by Nishikawa and fully by Menzer in his pioneering work "Die Kristallstruktur der Granate" in 1928.[4,5] A review of recent research on silicate garnets can be found in ref 6. The crystal structure of $Y_3Fe_5O_{12}$, yttrium iron garnet (YIG), was determined by Geller and Gilleo in 1957 and 1959.[7,8]

Most, but not all, garnets belong to the cubic centrosymmetric space group No. 230 ($Ia\bar{3}d$). The cubic unit cell contains 160 atoms which, in the body centered (bcc) unit cell, are reduced to 80. Their general formula is $R_3M^O_2M^T_3O_{12}$, where $R$ is a large cation with dodecahedral coordination, $M^O$ a smaller octahedrally coordinated cation, and $M^T$ the tetrahedrally coordinated cation. In $Y_3Fe_5O_{12}$, the Y ions occupy the 24c Wyckoff sites, $Fe^O$ the 16a sites, and $Fe^T$ the 24d sites. The oxygen site 96 h (which defines the 96 oxygens in the cubic unit cell) has three free $x$, $y$, and $z$ positions, while all cation sites are on special crystallographic positions. YIG is ferrimagnetic with the $Fe^T$ $d^5$ electrons antiferromagnetically coupled to the $Fe^O$ $d^5$ electrons. This leads to a magnetization of 5 $\mu_B$ per formula unit with a ferrimagnetic Curie temperature of 550 K.[9]

Owing to their high Curie temperature, $R_3Fe_5O_{12}$ garnets could be interesting multiferroic materials if it were possible to induce an off-centering and a lowering of the symmetry, which could give rise to ferroelectric behavior.

Recent experimental results hinted at the possibility of in-plane ferroelectricity in lattice-mismatched films of $Ho_3Fe_5O_{12}$ and $Gd_3Fe_5O_{12}$ that were grown epitaxially on $Gd_3Ga_5O_{12}$.[10]

Indeed, the enhancement of ferroelectric behavior by strain has been observed in some materials. $SrTiO_3$ is an incipient ferroelectric showing no spontaneous polarization unless it is somehow perturbed. Haeni et al. grew a thin epitaxial layer of $SrTiO_3$ on $DyScO_3$. The resulting strain caused $SrTiO_3$ to become ferroelectric with a Curie temperature around room temperature.[11] The spontaneous polarization of compressively strained $BaTiO_3$ was increased by Choi et al. by more than 250%, and its ferroelectric $T_C$ increased by nearly 500 K.[12] For other systems (e.g., $BiFeO_3$, $PbTiO_3$, or $LiNbO_3$), the calculated spontaneous polarizations are less strain-dependent.[13]

Ogawa et al. and Takano et al. found experimental evidence for the possibility of ferroelectricity in $Y_3Fe_5O_{12}$ by measuring its magnetoelectric (ME) properties.[14,15] However, when measuring another sample with an electrical conductivity lower by about 3 orders of magnitude than the previous ones, they found this to be due to some spurious effect, probably due to sample contamination.[16] They concluded "that the appearance of the first order ME effect is not due to a phase transition but to freezing of some kind of defects with electric polarization."[16] In 1994 they published another paper, claiming again that they did observe a

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first order magnetoelectric effect in YIG.[17] Later, Patri et al. measured the spontaneous polarization of polycrystalline YIG at room temperature and observed a hysteresis with a remanent polarization of 0.19 $\mu$C/cm$^2$. However, they concluded that their sample was likely to be a leaky dielectric.[18−20]

Using EXAFS spectroscopy, Dong and Lu found that in YIG (and other garnets) up to 10% of the yttrium atoms can be found at the tetrahedral and octahedral sites and vice versa. Such an exchange would lead to a symmetry lowering, but the cation exchange proceeds in a way that the center of inversion is not lost but leads to the centrosymmetric space group $R\bar{3}$.[21] A symmetry lowering to $R\bar{3}$ was also observed by Vandormael et al. using Mössbauer spectroscopy.[22]

This symmetry lowering seems to arise from magnetic anisotropy based on the neutron-diffraction structure refinement of Rodic et al.[23] However, their refinement of the crystal structure in space group $R\bar{3}$ seems to carry large uncertainties on the atomic positions.

In terbium iron garnet, $Tb_3Fe_5O_{12}$, a magnetodielectric effect has been observed, which is due to the appearance of noncollinearity of the spins of the Tb f-electrons below 150 K. This also leads to a rhombohedral symmetry.[24]

There are some observations of first order magnetoelectric effects in garnet thin films that have mixed *R*-site occupancies, for example, $(YBiPrLu)_3(FeGa)_5O_{12}$,[25] $(YBiLaPr)_3(FeGa)_5O_{12}$, and $(YBi)_3(FeGa)_5O_{12}$,[26,27] or second harmonic generation in Bi-doped $Y_3Fe_5O_{12}$[28] and diverse garnets having mixed R sites.[29]

In nature, some birefringent garnets (e.g., some types of grandite or grossular) can be found.[30] These materials are, however, not pure $R_3M^O_2M^T_3O_{12}$ garnets but have different types of ions sharing either the R site or the $M^O$ site.[30] The observed anisotropy is ascribed to a short-range ordering occurring during crystal growth of the mixed systems.

It is not clear from the cited article whether these materials are also polar, as the necessary condition for birefringence is a uniaxial anisotropy; no breaking of the inversion symmetry is required. Allen and Buseck also note that for all but one of the crystals investigated "on heating, an anisotropic garnet becomes increasingly disordered until it loses its birefringence and becomes cubic", meaning that the materials did not crystallize in their structural ground state but only reach it upon annealing.

There are, to the best of our knowledge, only two first-principles band-structure studies that calculated the electronic structure and optical properties of $Y_3Fe_5O_{12}$ by using an orthogonalized linear combination of atomic orbitals.[31,32]

In this study we investigate the electronic and structural properties of $Y_3Fe_5O_{12}$ by performing first-principles electronic structure calculations, particularly to discuss whether instability toward noncentrosymmetric structures is present or not.

In our work, we are only interested in stoichiometric $R_3M^O_2M^T_3O_{12}$ garnets without any doping or fractional occupancies of the ionic sites present. Such exchange might lead to nonreproducible symmetry lowerings and explain some of the observed effects cited above. A systematic substitution of ions would also lead to unit cells of lower symmetry and would be presently a problem of which the solution exceeds the computational capabilities at hand.

## 2. Computational Details

To calculate the structural and electronic properties of yttrium iron garnet, we used density functional theory (DFT), as implemented in the ultrasoft-pseudopotential code STATE and the FLAPW code HiLAPW.[33−36] The electronic structure was described using the local density approximation (LDA). The volume and the ionic positions of garnet were optimized using STATE. The optimal volume was determined by fitting the energy versus volume curve using the Birch−Murnaghan equation of state.[37]

The atomic positions were optimized by minimizing the forces acting on the ions. With STATE, a 4×4×4 *k*-point grid was used for the integration over the Brillouin zone. For calculating the properties of tetragonal garnet using HiLAPW, a 5×5×5 Γ centered *k*-point mesh was used. The cutoff energies used were 25 and 400 Ry with STATE and 15 and 60 Ry with HiLAPW for the wave functions and the charge density, respectively. (For the calculations of $Ia\bar{3}d$ YIG with HiLAPW, a 6×6×6 Γ centered *k*-mesh and cutoff energies of 20 and 120 Ry were used. Other exceptions are mentioned in the text.) Using HiLAPW, the muffin tin radii were set to 1.2, 1.0, and 0.8 Å for Y, Fe, and O, respectively.

As all the YIG structures showed a bandgap already by using the LDA exchange- and correlation-functional, we deemed it unnecessary to use LDA+*U* in order to describe the behavior of the d electrons. For the determination of the symmetries of our

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**Table 1. Calculated and Experimental Structures of Cubic $Y_3Fe_5O_{12}$[a]**

| | WP | $Ia\bar{3}d$ calcd [$x/y/z$] | $Ia\bar{3}d$ exp [$x/y/z$] [7,8] |
|---|---|---|---|
| $a$ [Å] | | 12.178 | 12.376 |
| Y | 24c | $(^1/_8)/0/(^1/_4)$ | $(^1/_8)/0/(^1/_4)$ |
| $Fe^T$ | 24d | $(^3/_8)/0/(^1/_4)$ | $(^3/_8)/0/(^1/_4)$ |
| $Fe^O$ | 16a | 0/0/0 | 0/0/0 |
| O | 96h | 0.9728/0.0574/0.1495 | 0.9726/0.0572/0.1492 |

[a] $a$ is the cubic lattice constant, and WP means the Wyckoff position of the respective ion.

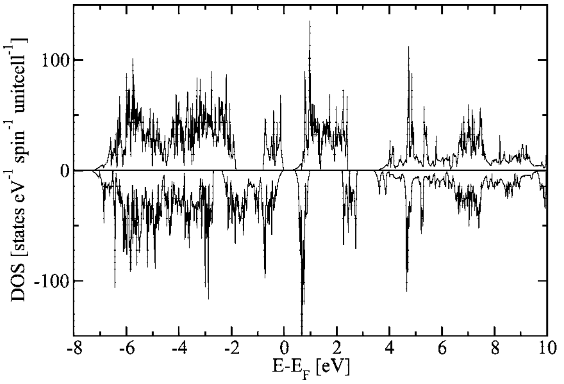

**Figure 1.** Total density of states for cubic ($Ia\bar{3}d$) centrosymmetric $Y_3Fe_5O_{12}$. The valence band maximum is taken at the origin of energy. Upper and lower panels denote the spin-up and spin-down bands, respectively.

materials, we used the FINDSYM code of the ISOTROPY suite for space groups and the Symmetry code for point groups.[38,39]

## 3. Results and Discussion

We began our investigation by relaxing the volume and the atomic positions of cubic centrosymmetric $Y_3Fe_5O_{12}$ using STATE. A lattice constant of 12.178 Å was obtained, which compares with the experimental lattice constant of 12.376 Å[7] to within 1.6%, which is usual for the LDA method. The atomic positions, calculated after the forces acting on them were minimized, also correspond well to the experimentally determined structure (cf. Table 1).[7,8] The $Ia\bar{3}d$ structure is insulating with a bandgap of 0.27 and 0.40 eV for the spin up (↑) and spin down (↓) electrons, respectively. The magnetization is 5 $\mu_B$ per formula unit. The magnetizations (calculated with HiLAPW) inside the muffin tin spheres are $-6.88 \times 10^{-3}$ $\mu_B$ for Y, 3.41 $\mu_B$ for $Fe^O$, $-3.36$ $\mu_B$ for $Fe^T$, and $-8.22 \times 10^{-2}$ $\mu_B$ for O. Figure 1 shows the total density of states (DOS) calculated for cubic ferrimagnetic $Y_3Fe_5O_{12}$. The calculated electronic band structure shows energy gaps both for the spin up and down bands, being consistent with the insulating property.

The symmetry was then lowered to tetragonal with a $c/a$ ratio of 0.987, while the volume was kept constant.[40] The atomic positions were again optimized by minimizing the forces on the atoms. The centrosymmetric tetragonally distorted structure has space group No. 142 ($I4_1/acd$). The Wyckoff positions of the ions are $Y^1$ (16e), $Y^2$ (8b), $Fe^1$ (16c, octahedral), $Fe^2$ (16e, tetrahedral), $Fe^3$ (8a, tetrahedral), $O^1$ (32g), $O^2$ (32g), and $O^3$ (32g). The structural parameters are reproduced in Table 2. There are no significant changes in the band structure or the density of states compared to the centrosymmetric structure.

**Table 2. Calculated Tetragonally Distorted Structure of $Y_3Fe_5O_{12}$[a]**

| | WP | $I4_1/acd$ calcd [$x/y/z$] |
|---|---|---|
| $a = b$, $c$ [Å] | | 12.2311/12.0739 |
| Y | 16e | $0.62475/(^1/_2)/(^3/_4)$ |
| | 8b | $0/(^1/_4)/(^1/_8)$ |
| $Fe^O$ | 16c | 0/0/0 |
| $Fe^T$ | 16e | $0.37452/0/(^1/_4)$ |
| | 8a | $0/(^1/_4)/(^3/_8)$ |
| O | 32g | 0.47257/0.55828/0.64987 |
| | 32g | 0.14948/0.97300/0.05750 |
| | 32g | 0.89921/0.69214/0.22242 |

[a] $a$, $b$, and $c$ are the lattice constants, and WP means the Wyckoff position of the respective ion.

The cubic structure is more stable than the tetragonal one by 54 meV per 80-atom unit cell, meaning that the system will not voluntarily undergo tetragonal symmetry lowering but has to be constrained to tetragonal symmetry (as achieved experimentally by epitaxial growth on a lattice mismatched substrate).

In order to investigate whether a noncentrosymmetric ground-state of the tetragonal garnets could be stabilized by further distortion (be it ferroelectric or nonpolar), we calculated the Γ point phonon frequencies of the cubic ($Ia\bar{3}d$) and the tetragonal ($I4_1/acd$) structures of YIG in a frozen-phonon approach. One atom of each Wyckoff position was displaced by 0.02 Bohr in all six spatial directions ($\pm x$, $\pm y$, and $\pm z$), and the forces on the atoms were calculated for each displacement. The dynamical matrix of the force constants was diagonalized in order to obtain the normal modes. The 15 lowest and six highest frequencies, of the 240 calculated, as well as their symmetry labels are reproduced in Table 3.[41] The calculated phonon densities of states are shown in Figure 2. The spectra have been broadened with a Gaussian with a fwhm of 5 cm$^{-1}$.

The three frequencies of the lowest acoustic modes of both structures (cubic: $T_{1u}$, tetragonal: $E_u$, and $A_{2u}$) are zero within the remaining uncertainties on the ionic positions, calculated forces, and limits of the method used. This absence of any unstable modes (of imaginary frequency) indicates that the centrosymmetric structure is the ground-state structure and that a strained epitaxial thin film of $Y_3Fe_5O_{12}$ will not show any spontaneous polarization.[42]

The lowest few stable (nos. 4−12) modes are polar modes (of ungerade character) for both the cubic and the tetragonal structure.

The eigenvectors of the lowest modes (nos. 4−6) consist mainly of off-centering vibrations of the cations. Phonon modes soften as the lattice constant is increased as the bond lengths increase and the bonds weaken. A freezing in of

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(40) This $c/a$ ratio corresponds to the one a $Ho_3Fe_5O_{12}$ film of about 500 nm thickness epitaxially grown on SGGG adopts.[10,64]

(41) All calculated frequencies and symmetry labels can be found in the Supporting Information.

(42) For our study, we were considering the bcc unit cell containing 80 atoms. Calculating the frozen phonon spectrum for a supercell with a higher number of atoms would be far outside of the capabilities of the computational resources at our disposal

**Table 3. Fifteen Lowest and Six Highest Calculated Frequencies of the Γ Phonons for Cubic and Tetragonal $Y_3Fe_5O_{12}$ and Their Symmetry Labels**

| number | $Ia\bar{3}d$ [cm$^{-1}$] | symmetry | $I4_1/acd$ [cm$^{-1}$] | symmetry |
|---|---|---|---|---|
| 1 | 0.49 *i* | $T_{1u}$ | 0.04 *i* | $E_u$ |
| 2 | 0.49 *i* | $T_{1u}$ | 0.04 *i* | $E_u$ |
| 3 | 0.49 *i* | $T_{1u}$ | 0.03 *i* | $A_{2u}$ |
| 4 | 91.65 | $T_{1u}$ | 91.76 | $E_u$ |
| 5 | 91.65 | $T_{1u}$ | 91.76 | $E_u$ |
| 6 | 91.65 | $T_{1u}$ | 92.53 | $A_{2u}$ |
| 7 | 95.83 | $T_{2u}$ | 96.25 | $B_{2u}$ |
| 8 | 95.83 | $T_{2u}$ | 96.32 | $E_u$ |
| 9 | 95.83 | $T_{2u}$ | 96.32 | $E_u$ |
| 10 | 98.14 | $T_{1u}$ | 98.63 | $A_{2u}$ |
| 11 | 98.14 | $T_{1u}$ | 99.09 | $E_u$ |
| 12 | 98.14 | $T_{1u}$ | 99.09 | $E_u$ |
| 13 | 120.59 | $T_{1g}$ | 120.21 | $E_g$ |
| 14 | 120.59 | $T_{1g}$ | 120.21 | $E_g$ |
| 15 | 120.59 | $T_{1g}$ | 120.80 | $A_{2g}$ |
| 235 | 690.83 | $T_{2g}$ | 682.15 | $A_{1g}$ |
| 236 | 690.83 | $T_{2g}$ | 690.71 | $B_{2g}$ |
| 237 | 690.83 | $T_{2g}$ | 690.95 | $E_g$ |
| 238 | 701.10 | $A_{2g}$ | 690.95 | $E_g$ |
| 239 | 717.09 | $A_{1u}$ | 699.36 | $B_{1g}$ |
| 240 | 793.66 | $A_{1g}$ | 715.52 | $A_{1u}$ |

distortions of the lowest $T_{1u}$ modes in the cubic structure would introduce ferroelectricity into the system as these modes are polar. Such a softening by more than 90 cm$^{-1}$ is not to be expected, as the lattice constant would have to be increased by a larger amount than obtainable by epitaxial strain. Also, upon the application of a tetragonal distortion, the $T_{1u}$ mode splits into two $E_u$ and one $A_{2u}$ mode. The $A_{2u}$ mode hardens as the $z$-axis is compressed (in our calculations it shifts up by about one wavenumber).

The spectrum for the tetragonal YIG is not significantly different from the one of cubic YIG. Some peaks change in their relative intensities and the $A_{1g}$ peak at 794 softens to 682 cm$^{-1}$. Although only consisting of the Γ point vibrations, the rough frequency distribution of the simulated spectrum of cubic YIG compares well to experimental infrared reflectivity data, cf. Figure 5 in ref 43.

To check our result of the frozen phonon calculations against the possibility of ferroelectric displacements in the [100]-direction, we proceeded to off-center all the atoms from their eight Wyckoff positions of $I4_1/acd$ structure by 0.01 times the lattice constant in the [100] direction (corresponding to a displacement of 0.1223 Å). Thereby the inversion symmetry was broken and ferroelectric behavior possible. These structures have space group No. 45 (*Iba*2). The atomic positions of all the eight distorted structures were then relaxed by minimizing the forces acting on the atoms. The calculated positions were then compared to those within $I4_1/acd$. We also simultaneously displaced all the Y (occupying the 16e and the 8b Wyckoff positions) by 0.03 and 0.05 times the lattice constant and then relaxed all ionic positions. If there were any tendency to a symmetry lowering induced via a second-order Jahn−Teller effect, it would evidence itself via the "$d^0$-ness" of Y and thus stabilize their displacement.[44]

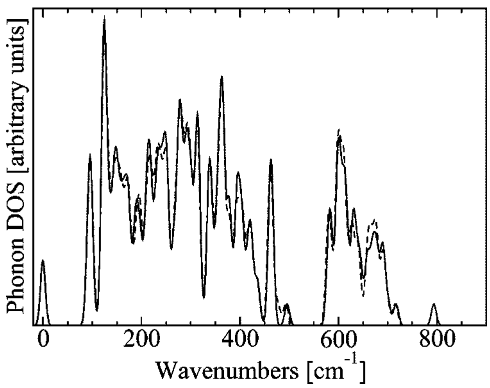

**Figure 2.** Calculated phonon spectra for cubic YIG ($Ia\bar{3}d$), solid line, and tetragonal YIG ($I4_1/acd$), dashed line, at the Γ point. The data have been convoluted with a Gaussian function, $\sigma = 5$ cm$^{-1}$, $\delta = 1$ cm$^{-1}$.

**Table 4. Nearest Neighbor Distances for the Calculated and Experimental $Ia\bar{3}d$ YIG**

| central ion | neighbor | number | calcd *d* [Å] | exp *d* [Å] |
|---|---|---|---|---|
| Y 24c | O | 4 | 2.3284 | 2.3696 |
|  | O | 4 | 2.3875 | 2.4286 |
| $Fe^O$ 16a | O | 6 | 1.9777 | 2.0064 |
| $Fe^T$ 24d | O | 4 | 1.8460 | 1.8752 |

All the distortions that were frozen in relaxed back to their centrosymmetric tetragonal structures. YIG is thus not an incipient ferroelectric, which could result from strain, because the centrosymmetric structure is more stable than the off centered ones.

## 4. Discussion

From the results, there is evidence to suggest that YIG will resist external perturbations to drive it to ferroelectricity. Cubic YIG is clearly nonferroelectric, and even if it is strained, as in the case of a thin film deposited epitaxially on a lattice-mismatched garnet, it will prefer to maintain a centrosymmetric structure.

We now discuss why YIG behaves in this way and whether it is unique for the garnet group or whether there is a possibility to obtain other ferroelectric garnet.

The $YO_8$ unit of cubic YIG is of $D_2$ point symmetry, consisting of two strongly skewed groups of four oxygens at a calculated distance of 2.33 and 2.39 Å from the central ion (cf. Table 4). The individual $O_4$ groups also belong to the point-group $D_2$.

The Fe sites are either fourfold ($Fe^T$) or sixfold ($Fe^O$) coordinated by O. The local symmetries are $D_{2d}$ and $D_{3d}$, respectively. This weak Jahn−Teller like distortion is structural and not electronic, because $d^5$ iron in high-spin configuration is spherical.

The oxygens in $Y_3Fe_5O_{12}$ are coordinated by two Y atoms and one tetrahedral and one octahedral Fe atom with point group $C_1$. Each of the $OM_4$ units has a corresponding unit opposite symmetry center so that total inversion symmetry is conserved. If the material is compressed tetragonally, the point groups of the individual groups of atoms are lowered, but overall inversion symmetry is conserved.

Is it possible to determine what the symmetry of a material will be upon a distortion, whether it loses its center of inversion or stays centrosymmetric?

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In order to address these questions for perovskites and related $ABO_3$-materials, we consider the tolerance factor as defined by Goldschmidt.[45] The tolerance factor is defined as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

where $r_A$, $r_B$, and $r_O$ are the ionic radii of the large A cation, the small B cation, and O, respectively. This equation serves as a first indicator whether a perovskite is more prone to show rotational ($t < 1$) or displacive instability ($t > 1$). For example, one obtains with Shannon and Prewitt ionic radii[46] a tolerance factor of 0.838 for $YFeO_3$. The perovskite is found in the strongly distorted orthoferrite structure (space group *Pnma*), confirming the prediction.[47]

**4.1. Crystal Chemistry in Garnets.** For garnet, a criterion for instability, such as the tolerance-factor for perovskites shown above, cannot be defined. Novak and Gibbs calculated the oxygen coordinates for silicate garnet and found that they could be described using the ionic radii of the cations.[48,46] Hawthorne presented the equations describing the O coordinates for all garnets:[49]

$$x = -0.0278 r_R + 0.0123 r_{M^O} + 0.0482 r_{M^T} + 0.0141$$
$$y = -0.0237 r_R + 0.0200 r_{M^O} + 0.0321 r_{M^T} + 0.0523$$
$$z = -0.0102 r_R + 0.0305 r_{M^O} - 0.0217 r_{M^T} + 0.6519$$

where $r_R$, $r_{M^O}$, and $r_{M^T}$ are the radii of respectively the large, the octahedral, and the tetrahedral cation. Hawthorne obtained the following values for the O-coordinates (atom chosen for comparability with Table 1): $x = 0.9732$, $y = 0.0568$, $z = 0.1505$.[49]

Novak and Gibbs also calculated a field of structural stability based on the radii of the R and the $M^O$ cations for silicates.[48] The same also applies even if the tetrahedrally coordinated cation is not Si but any other atom, but $M^T$ seems to have the smallest influence.[49]

The garnet structure remains stable, if one of the ions is replaced by a Jahn−Teller cation, as shown by Durif for $NaCa_2Cu_2V_3O_{12}$, where $Cu^{2+}$ occupies the octahedral site, and by Mill who synthesized garnets with $Mn^{3+}$ occupying the octahedral site.[50–52] Even incorporation of a "classic" lone-pair ion like $Bi^{3+}$, which is responsible for the off-centering in many perovskites,[44] does not lead to offcentering in garnets. Okuda et al. prepared thin films of $Bi_3Fe_5O_{12}$ garnet on $Sm_3(ScGa)_5O_{12}$.[53] No single crystals of $Bi_3Fe_5O_{12}$ have been made, as it is thermodynamically instable.

If the cubic centrosymmetric ($Pm\bar{3}m$) perovskite is perturbed, it cannot react to the perturbation other than by lowering its space group symmetry (be it in a centrosymmetric or in a noncentrosymmetric way) as it has no structural degrees of freedom. For garnets, however, this is not the case. They can accommodate a wider range of cations and maintain fully cubic symmetry, because the unit cell and the oxygen positions can adjust in order to compensate for different cation sizes and electronic configurations. Due to their structural degrees of freedom, garnets can react to an external disturbance (i.e., electric field, pressure) through correlated rearrangement of the oxygen positions without any symmetry lowering. If the cation sizes deviate too far from an ideal,[48] garnet simply will not crystallize.

**Table 5. Nearest Neighbor Distances for the Calculated $I4_1/acd$ YIG**

| central ion | neighbor | number | *d* [Å] |
|---|---|---|---|
| Y 16e | O | 2 | 2.3312 |
|  | O | 2 | 2.3369 |
|  | O | 2 | 2.3670 |
|  | O | 2 | 2.3916 |
| Y 8b | O | 4 | 2.3269 |
|  | O | 4 | 2.3878 |
| $Fe^O$ 16c | O | 2 | 1.9736 |
|  | O | 2 | 1.9834 |
|  | O | 2 | 1.9855 |
| $Fe^T$ 16e | O | 2 | 1.8461 |
|  | O | 2 | 1.8483 |
| $Fe^T$ 8a | O | 4 | 1.8450 |

This adjustment of the bond lengths also takes place upon the application of epitaxial strain, as can be seen in Tables 4 and 5, where the nearest neighbor distances for the cations of the cubic $Ia\bar{3}d$ structure (both the calculated and the experimental values) and for the calculated tetragonally strained $I4_1/acd$ structure are listed. The Y−O bond lengths increase by up to 0.063 Å, and the Fe−O bonds increase or decrease by smaller but still noticeable amounts, thus minimizing the forces. A further lowering of the symmetry is unfavorable as we showed in the frozen-phonon calculations. The off-centering modes are stable and could not be frozen in easily.

We did not investigate the possibility that certain electronic effects could change the bonding in garnets that contain rare earth elements at the R site. However, we consider it unlikely that any bonding of the low-lying d orbitals with the oxygen p orbitals would induce some kind of noncentrosymmetric symmetry lowering. Oxygen vacancies or a noncubic centrosymmetric exchange of cations could, however, lead to (irreproducible) nonpolar structures and thus allow for the spurious appearance of spontaneous polarization. Careful preparation and prohibition of nonstoichiometricity of the samples are of paramount importance.

We would like to stress the importance of such theoretical considerations, since there is a danger of interpreting measurement artifacts as proof of ferroelectricity (cf. particularly Figure 1 in ref 19).[19,20,54,55]

This can be seen in recent literature, where the ferromagnetic insulating spinel systems $CdCr_2S_4$ and $HgCr_2S_4$ were also being discussed as being possible multiferroic materials.[56−59]

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These claims have however been put into question using theoretical and experimental considerations,[60,61] and explanations have been given as to why spurious hysteresis loops can arise from nonferroelectric materials.[62,63]

## 5. Conclusion

In conclusion, we have shown the properties of centrosymmetric cubic and tetragonally distorted $Y_3Fe_5O_{12}$ using first-principles calculations. From calculated frozen-phonon frequencies, it can be seen that this garnet seems to show no tendency toward a ferroelectric distortion. Using symmetry arguments, we then arrived at the conclusion that garnets are an unlikely class of materials to adopt ferroelectricity, as there is no possibility to define something akin to the tolerance factor for the centrosymmetric high symmetry phase. The material will instead stay within the highly symmetrical space group and accommodate a range of cation radii by adjusting the oxygen positions. If the radii are too far away from the ideal, the material will adopt an alternative structure and not stay in the garnet structure.

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**Supporting Information Available:** Calculated frequencies of the Γ-phonons for cubic and tetragonal $Y_3Fe_5O_{12}$ and their symmetry labels (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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