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研究課題名（和文）マルチフェロイック物質の高異方性構造擾乱による磁性と磁気電気結合の増大

研究課題名（英文）Enhancement of magnetism and magneto-electric coupling in multiferroic structures with geometrical frustration caused by high tetragonality phases

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研究成果の概要（和文）：本課 題は、強誘電性と強磁性を共有しかつ相互作用する結晶についての研究である。(i)強誘電性は永 久電気双極子、つまり正と負に帯電した結晶内原子の電荷中心が場所的にずれて存在することで生じ、また(ii)強磁性は、結 晶内原子に局在する電子のスピンの磁気双極子が互いに打ち消し合わずに一定の方向に揃うことによって生じる。我々はBiFe03系材料に注目 し、電気分極に直接関係する単位格子内原子配位を、磁気分極を発現するFeの電子殻軌道 のつめ方を変えて、調べた。理論計算の結果、いくつかの新しい結晶対称性が作製条件をうまく選べば、室温で強誘電性と強磁性を同時に 存在し相互作用もあることがわかった。

研究成果の概要（英文）：The research project has investigated crystalline materials in which two important properties coexist: ferroelectricity (centers of positive and negative atomic charges are always separated, creating permanent electric dipoles or polarization that can be controlled by external electric field) and ferromagnetism (electrons of certain atoms in the crystal arrange themselves so that their magnetic dipole of spin are uncompensated and aligned). We have studied crystals in the family of BiFe03. Our atomistic calculations have shown that we can control the atomic displacements (that yield a large/small polarization) by changing the way we fill up the electronic shells of Fe (thus creating a large/small magnetization). Our research revealed that for obtaining large magnetism and ferroelectricity, coupled to each other at room temperature, some exotic crystal symmetries or BiFe03 (that are normally difficult to stabilize) should be promoted by careful selection of the fabrication conditions.

研究分野：物理学

キーワード：マルチフェロイック　第1原理計算　BiFe03　強誘電性　強磁性

１．研究開始当初の背景

The beginning of the 21-st century has seen a strong revival of the research in the field of magnetoelectric multiferroics, with the hope that the advances in technology and computing power will bring about progress into a topic that used to be pursued entirely for scientific curiosity purposes. Nowadays, while the chemistry and physics of materials that favor both ferroelectric displacements and magnetic ordering remain exotic enough to attract the interest of scientists from a broad spectrum of research topics, additional interest has been aroused from the viewpoint of novel practical applications to multiple-state memories and spintronics.

Because of the distinct natures of ferroelectric and ferromagnetic ordering, it has proved difficult to find a single phase room-temperature multiferroic material with large polarization, large magnetization, and robust magnetoelectric coupling. The focus of most research is on materials in the family of bismuth ferrite (BFO), which is one of the few multiferroics with room temperature ferroelectricity and magnetism. However, while BFO is a ferroelectric with large spontaneous polarization, it is antiferromagnetic and therefore its magnetization and magnetoelectric coupling are invariably much smaller than would be useful for applications. Most current multiferroic devices are based on nanocomposites and multiferroic heterostructures, making use of the coupling of ferroelectric and magnetism to strain for obtaining robust magnetoelectric coupling.

Although many experimental and theoretical investigations on such heterostructures are made in Japan and overseas, there are still challenges on how to select the proper material combinations and how to predict the properties that are likely to result from such combinations of nanoscale stoichiometry and restricted geometry.

２．研究の目的

This project has focused on using first-principles calculations to explore novel BFO-based structures, aiming to address the shortcomings of this material related to its small magnetization and weak magneto-electric coupling at room temperature.

The inspiration for this research stemmed from our earlier contributions (experimental and theoretical) to highlighting the unique properties of BFO: a giant polarization of 150 $\mu C/cm^2$ and the possibility to fabricate hybrid BFO thin films where a phase with large c/a of ~ 1.25 (super-tetragonal, ST) coexists with a small c/a (pseudo-cubic, PC) phase.

３．研究の方法

We have performed first-principles calculations on materials in the BFO family with various compositions, crystal symmetries and magnetic ordering, with the ultimate purpose to investigate how the presence of mixed pseudo-cubic and super-tetragonal phases in a BFO-based compound impacts on its ferroelectric and ferromagnetic properties. Careful testing of calculation parameters has been done for materials in the $BiFeO_3$-$BiCoO_3$ (BFO-BCO) family, comparing the results of single unit cell calculations of BFO and BCO with conventional and unconventional crystal symmetry with the results reported in literature. Additionally, the testing of LDA+U first-principles implementation for the exchange and correlation of localized electrons as well as the spin-orbit coupling have been done by calculations of conventional perovskite $SrTiO_3$.

All first-principles calculations have been done using the density functional theory, under the spin-polarized local density approximation including the correction for the strongly correlated 3d electrons of Fe and Co, as implemented in the ABINIT package. For all chemical elements we have used projected-augmented wave pseudo-potentials, which allowed faster calculations than using regular pseudo-potentials.

４．研究成果

First we have examined BFO-BCO as a prototype for a system with mixed tetragonality, particularly examining the distribution of structural features (the tetragonality ratio c/a, the off-centering ratios corresponding to Fe/Co-O and Bi-O bond lengths and an estimation for the local spontaneous polarization derived from a point-charge model) inside a given BFCO supercell, in presence of various types of antiferromagnetic (AFM) orderings.

Upon geometry optimization of supercells with rhombohedral and tetragonal symmetry, comparison of the total energy calculated from first-principles allowed us to conclude that the most stable structure of BFO doped with 12.5% Co has rhombohedral symmetry and G-type AFM ordering, while BFO doped with 50% Co has tetragonal symmetry and C-type AFM ordering. Further, it has been revealed

that the spatial distribution of the tetragonality ratio in a BFCO supercell doped with 12.5% Co exhibits similar features with the Bi-O off-centering distribution. On the other hand, the spontaneous polarization distribution depends mainly on the Fe/Co-O off-centering rather than on the Bi-O off-centering, with the tetragonality ratio appearing to have only secondary importance for deciding the spontaneous polarization value. The tetragonality ratio itself does not vary significantly when the AFM ordering of the BFCO tetragonal supercell is changed from A-type to C-type, while the G-type AFM ordering provides the smallest c/a from the analyzed tetragonal BFCO12 supercells.

With respect to the magnetoelectric properties, our first-principles calculations revealed that the Co doping can be an effective method to enhance the magnetization of (nominally antiferromagnetic) BFO, from 20 emu/cm^3 in case of BFCO doped with 12.5% Co to 80 emu/cm^3 in case of BFCO doped with 50% Co. On one hand this was caused by the onset of ferrimagnetic ordering in the BFCO supercells used for calculations, which have incomplete spin compensation due to unequal local magnetic moments at Fe and Co sites. Additionally, while having little influence on the macroscopic magnetization, the type of AFM ordering impacts on the values of the average spontaneous polarization in the supercell, thus proving that the magnetic and electric interactions in BFCO are intrinsically coupled.

Subsequently, we have studied the impact of various electronic configurations (high-spin HS, low-spin LS, intermediate-spin IS) of Co^{3+} ion on crystal structure, ferroelectricity and magnetism of such systems. Assuming a HS electronic configuration for the Co^{3+} ion in tetragonal Co-doped BFO, an increase in Co doping level enhances the magnetization proportionally with the number of uncompensated magnetic moments of Fe–Co pairs present in the analyzed supercell. However it does not significantly affect how the phase stability depends on the type of antiferromagnetic ordering or the values of tetragonality ratio c/a (the latter being approximately proportional to the spontaneous polarization).

On the other hand, by imposing LS and IS electronic configurations for Co while keeping Fe in its HS state, we have detected significant changes of the tetragonality ratio when the type of antiferromagnetic ordering and the electronic configuration of Co changes. This should result in strong magneto-electric coupling in such Co-doped BFO compounds.

Furthermore, we have found an additional route to enhance the magnetization of tetragonal BFCO compounds with IS-Co^{3+}, while remaining coupled to ferroelectric degrees of freedom, namely by inducing a ferrimagnetic-to-ferromagnetic phase transition in 50%-doped Co-BFO with A-type antiferromagnetic ordering.

The undertaken first-principles calculations suggest that exploiting the complex interplay between the crystal symmetries, antiferromagnetic ordering and local spin configurations in Co-doped bismuth ferrite might be helpful in solving the enduring problem of robust magneto-electric coupling for materials at room temperature. Specifically, fabricating BFCO thin films where the Co^{3+} ion is stabilized in a low spin or intermediate spin electronic configuration might be a promising approach to realize the full potential of these materials.

After that, we have used first-principles calculations carried out under the density functional theory for probing ways to enhance the magnetization of undoped BFO, while preserving robust ferroelectricity. Our calculations revealed the existence of BFO phases with monoclinic and tetragonal symmetries, in addition to the rhombohedral one corresponding to its ground state structure, with dramatic changes in lattice constants when passing from one phase to another. This rich crystal phase portrait allows the existence of several spin configurations of Fe in BFO, with ab-initio-calculated total energies generally higher (within 0.5 eV/formula unit) than that corresponding to conventional high-spin (HS) state of Fe.

We have identified two different low-spin (LS) and intermediate-spin (IS) configurations of the Fe^{3+} ion in the tetragonal structure of BFO, which impact on the c/a ratio, atomic displacements and on the spontaneous polarization according to the way how the majority and minority t_{2g} and e_g orbitals are filled. A key finding is that only one of the identified LS configurations of Fe strongly reduces the tetragonality ratio of BFO, while the structures with IS-Fe maintain values of c/a similar to that of BFO with HS-Fe. On the other hand, the magnetic moment of BFO doped with IS-Fe^{3+} can become as large as 2 μB/supercell, and it can even increase to 4 μB/supercell in case of BFO doped with LS-Fe^{3+}.

Furthermore, the total energy, atomic displacements, the distribution of tetragonality ratio and magnetization were examined for different BFO geometries with mixed spin configurations of Fe^{3+}, including the effect of

external constraint parameters such as biaxial stress and pressure. We observed that the tetragonality ratio and Fe-O bond lengths along the polar axis are virtually homogeneous in superlattices with LS and IS Fe^{3+} having unpaired electrons in t_{2g} orbitals.

Under hydrostatic pressure, stable state of Fe^{3+} in tetragonal BFO changes from HS to LS with paired electrons, while it has proven impossible to stabilize LS and IS states of Fe^{3+} with unpaired electrons. This proves that a possibility to enhance the magnetization of tetragonal BFO would be through manipulation of the unit cell volume using external hydrostatic pressure.

A similar change in volume, with impact on the stability of Fe^{3+} spin configuration, could be achieved by biaxial tensile and compressive stresses (such as those induced by in-plane misfit between BFO films and substrates they grow on). Our calculations revealed that, in tetragonal BFO, tensile (compressive) stresses can stabilize IS states of Fe^{3+} with unpaired (paired) electrons, respectively. Also, tetragonal BFO superlattices containing IS-Fe^{3+} with unpaired electrons are less sensitive to external tensile stresses.

We have also analyzed the possibility of stabilizing superlattices with mixed large and small c/a in a monoclinic supercell. The calculations have shown that supercells with distributed tetragonality are more stable than tetragonal ones, and that HS-Fe^{3+} electronic configuration continues to be the most favorable one in absence of external constrains such as pressure or biaxial strains.

On experimental side, BFO thin films have been prepared by magnetic-field-assisted pulse laser deposition (PLD) in which ablated species react vigorously with the substrate under strong magnetic field. The fabricated films have revealed a columnar structure, attributed to modification of atomic species' spiral trajectories by the magnetic field during the deposition. The ferroelectric hysteresis loops of the BFO films prepared using magnetic-field-assisted PLD have been improved and the magnetization is slightly enhanced.

Furthermore, we have simulated the piling up effect of atomic species, considering the incident angle dependence of the movement trajectory under the applied magnetic field. We have shown that the lateral growth of the film is controlled by the effect of the shadow of the growing grain, which determines the structure to become columnar.

As for the BFCO thin film fabricated by magnetic field-assisted PLD, it has been shown that its magnetization slightly increases from the case of BFO, from measurements of magnetic hysteresis, in qualitative agreement with the results of our first-principles calculations.

The research performed during these three years has revealed that it is worth looking beyond the conventional monoclinic structure of BFO with HS electronic configuration of Fe^{3+}. Our results revealed that many metastable phases exist, with tetragonal symmetry as well as with coexisting tetragonal-like and rhombohedral-like symmetries, where the spin of Fe can vary as dictated by external constraints. The large polarization of BFO can be maintained in such unconventional material, and the magnetization as well as the magnetoelectric coupling can be enhanced. Our future research will concentrate more on using the knowledge acquired during these years for controlling the metal-insulator phase transition behavior of BFO (bandgap tuning), which is highly relevant for solar energy conversion applications.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

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