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Magnetodielectric effect of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film under an ultra-low magnetic field

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Abstract

Good-quality and fine-grain $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ magnetic ferroelectric films with single-phase layered perovskite structure have been prepared successfully via the metal organic decomposition (MOD) method. The results of low-temperature magnetocapacitance measurements reveal that an ultra-low magnetic field of 10 Oe can produce a non-trivial magnetodielectric response in zero-field cooling conditions, and the relative variation of dielectric constants in a magnetic field is positive, i.e. $[\varepsilon_r(H) - \varepsilon_r(0)]/\varepsilon_r(0) = 0.05$, when $T < 55$ K, but negative with a maximum of $[\varepsilon_r(H) - \varepsilon_r(0)]/\varepsilon_r(0) = -0.14$ when $55 \text{ K} < T < 190 \text{ K}$. The magnetodielectric effect shows a sign change at 55 K, which is due to a transition from an antiferromagnetic to a weak ferromagnetic, and vanishes abruptly at around 190 K, which is thought to be associated with an order–disorder transition of iron ions at the B site of perovskite structures. Our results allow the expectation of low-cost applications of detectors and switches for extremely weak magnetic fields over a wide temperature range of 55–190 K.

1. Introduction

Magnetoelectric materials, which possess at least magnetic and ferroelectric ordering over a certain range of temperature and therefore promise applications of smarter multifunctional devices, have entered the spotlight of the scientific community [1]. Quite a few researchers have been interested in the combination of the high permittivity of ferroelectrics with the magnetic degree of freedom of manipulation, which has potential applications in the non-contact control of dielectricity in insulating devices [1]. The magnetodielectric (MD) effect means the relative variation in dielectric constant before and after applying magnetic fields, i.e. $\Delta = [\varepsilon_r(H) - \varepsilon_r(0)]/\varepsilon_r(0)$ [2]. A significant MD effect, such as giant magnetocapacitance

with a peak $\Delta = 5$ and colossal magnetocapacitance also with a peak $\Delta = 5$, has recently been discovered in DyMnO_3 [2] and CdCr_2S_4 [3] single crystals, respectively. Usually, rather high magnetic fields, with $H > 1 \times 10^4$ Oe, are inevitably needed for high MD effects [2]. Remarkably low fields, e.g. of the magnitude of 10^3 Oe, induced a maximum $\Delta = 0.03$ in bulk terbium iron garnet [4]. Hybrid films have been attempted and exhibit sensible maximum MD responses even under quite a low magnetic field of 50 Oe [5], but one may find that their origins are non-intrinsic or indirect, such as magnetoelastic or magnetotransport effects over a small length scale, rather than direct coupling between the magnetic field and polarizability [6]. Since sensible intrinsic magnetodielectric effects under ultra-low magnetic fields have not yet been reported, our efforts have been devoted to the study of the magnetodielectric behaviour of thin films of appropriate multiferroic materials under an ultra-low magnetic field.

The bismuth-layered structure ferroelectric family has a general formula $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$, where $M = \text{Bi}$ or rare earths and $R = \text{Fe/Ti}$ [7]. In this paper, $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ magnetic ferroelectric film is used. Bismuth-layered magnetoelectrics doped with iron have been proved to be novel in multiferroic output [8], since bismuth-layered structures suggest excellent ferroelectricity [9] and magnetic ordering forms easily after introducing iron ions partially on pseudoperovskite B sites [10]. So it was decided to study the coexistence of ferroelectrics and magnetism in bismuth-layered titanate via iron substitution. To synthesize thin films, the metal organic decomposition (MOD) method was chosen because it has couples of merits for depositing oxide coatings, i.e. lower temperature, non-vacuum and, especially, low cost and extensive tailorability [11].

2. Experimental details

As for the wet chemistry method, the precursor is evidently crucial to the structure of the final film [11]. In order to synthesize the precursor of the $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film, hydrated bismuth nitrate with 10 mol% Bi excess (to compensate for its volatility at high temperature when annealing) and stoichiometrical hydrated iron nitrate were first put into 2-methoxyethanol, with glacial acetic acid as an organic ligand agent and ethylene glycol to crosslink the metal–organic molecules [12], and then stoichiometrical tetrabutyl titanate was put into this solution. It is noteworthy that the molar weights of acetic acid and ethylene glycol are equal to that of nitric ion and half that of the aggregate metal molar weight, respectively. The specific steps are drawn schematically in figure 1. It is worth emphasizing ageing of the mixture, because of its non-trivial effect on the micro-morphology and electric properties of the films [13].

For experimental convenience, an N-type Si wafer with (111) orientation and a thickness of $500 \mu\text{m}$ was cut into pieces with a size of around $1.2 \times 1.2 \text{ cm}^2$. After a series of cleaning and oxidation procedures [14], a layer of amorphous platinum with a thickness of about 100 nm was sputtered onto the Si/SiO₂ substrate, then the Pt bottom electrode was crystallized at 400°C for 1 h in ambient atmosphere before the deposition of metal–organic sol.

The samples were obtained by spin coating and rapid thermal processing [15]. The spinning parameters were set at 4000 rpm for 30 s. Wet films were subsequently placed onto hot plates with temperatures set at $160\text{--}180^\circ\text{C}$ for 1 min to vaporize solvent and other volatiles, and at $400\text{--}500^\circ\text{C}$ for 10 min to nucleate the Bi-layered structure, respectively [16]. Usually, we repeated the above steps four times to obtain the final multilayer film with a thickness of hundreds of nanometers. Ultimately, the multilayer films were subject to a furnace at $650\text{--}750^\circ\text{C}$ for 60 min to grow the grain sizes [16]. Before electric characterizations, each sample also needed to have a thin platinum layer (30–100 nm) deposited as the top electrode via mask technology, where the round electrode areas were confined to the range $0.04\text{--}1 \text{ mm}^2$.

An optical microscope and a scanning electron microscope (SEM) were used to diagnose morphology. Thicknesses were also estimated by SEM. X-ray diffraction (XRD) using $\text{Cu K}\alpha$

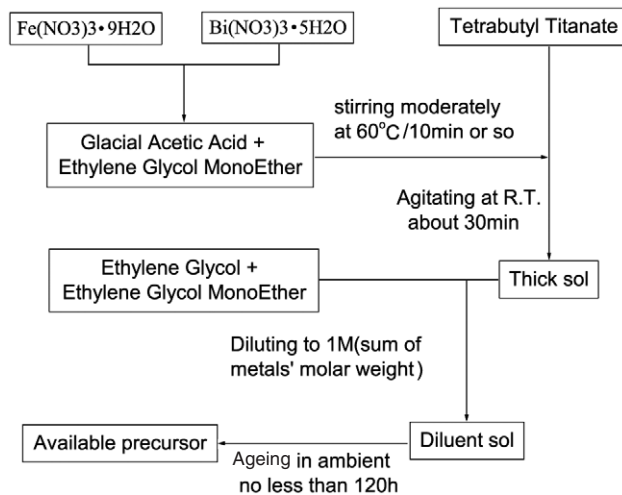


Figure 1. Schematic illustration of sol processing.

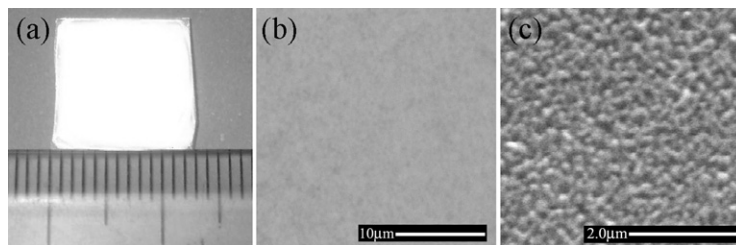


Figure 2. Morphology and structure of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film in a macroscopic view (a), low magnification under optical microscopy (b), and high magnification under SEM (c).

radiation acted as our major means to reveal crystallograms. The installation of our facility for dielectric measurements was according to the Sawyer–Tower circuit [17], where the signal applied to films was a 1 kHz sine wave, and a 10 nF standard capacitor in series with the sample was used to measure charges. In addition, during testing, the samples were placed in a Cryogen Free Superconducting Magnet & VTI System produced by CRYOGENIC, where the direction of the magnetic field was perpendicularly out from the films.

3. Results and discussion

The $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ films that were obtained have good quality, as shown in figure 2. The whole surface, with a size of $13 \times 13 \text{ mm}^2$, is smooth, as shown in figures 2(a) and (b). Figure 2(c) indicates that the film with a grain size of about 150 nm is crack-free and pinhole-free.

The structure of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film is revealed, in comparison to powder derived from the corresponding sol and with the same treatment conditions as those of films, as shown in figure 3. Figure 3(a) is the XRD pattern of the $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film and figure 3(b) is that of the powder. Figure 3(c) is the XRD pattern of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder, which is cited from JCPDS file 35-0795 and suggests its single-phase nature. Comparing figure 3(a) with figures 3(b) and (c), it is understandable that the $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film possesses single-phase structure similar to

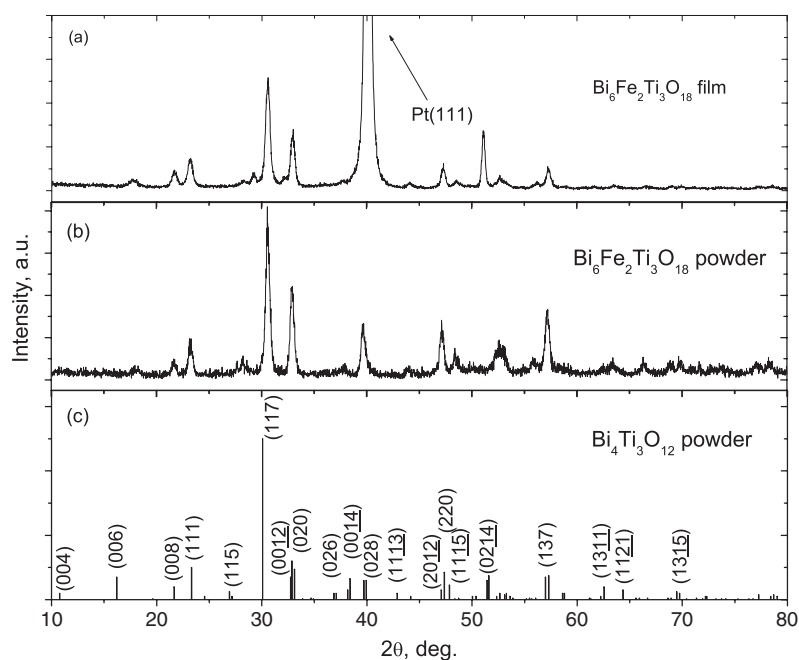


Figure 3. XRD patterns of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film (a), $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ powder derived from the same sol as the film (b), and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder from JCPDS, which is single phase (c).

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$, since the reflection positions agree well with those of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders. The difference in intensities may be attributed to disorder at the Fe/Ti site [10].

The results of magnetodielectric measurements are presented in figure 4. Figure 4(a) shows the dielectric constant during warming and cooling without a magnetic field, i.e. $\varepsilon_r(0)$, and that during warming in a magnetic field of 10 Oe after zero-field cooling, i.e. $\varepsilon_r(H)$. Judging from figure 4(a), we find that $\varepsilon_r(H)$ during warming in a magnetic field of 10 Oe is evidently different from $\varepsilon_r(0)$ during warming without a magnetic field. It is worth noting that the magnitude of the presented dielectric constants without a magnetic field is comparable to the bulk bismuth titanate in single crystals and polycrystals [18]. Therefore, it is reasonable to exclude the extrinsic contributions from the Schottky barriers at electrical contacts [19].

Figure 4(b) is the relative variation in dielectric constant, i.e. $\Delta = [\varepsilon_r(H) - \varepsilon_r(0)]/\varepsilon_r(0)$, which is calculated from figure 4(a), versus warming temperature. There are two major features in our MD findings, as shown in figure 4(b), i.e. a change in sign of magnetodielectric responses takes place at 55 K, and an abrupt attenuation of magnetodielectric effects at around 190 K. Experiments showed that there was a magnetic transition from antiferromagnetism (AFM) to weak ferromagnetism at 65 K for $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ ceramics [8]. We have scanned the magnetodielectric properties at around 55 K several times in a back and forth protocol, and this transition reappeared with high reproducibility. Therefore, a sign change in MD at 55 K should be due to the magnetic transition from antiferromagnetism to ferromagnetism, and the difference in this transition point between film at 55 K and bulk at 65 K may be explained by the constraining effect from the substrate [20].

It should be not unexpected that a second conversion takes place at around 190 K in figure 4(b) and we make some detailed discussions here. Bear in mind that room-temperature disorderliness exists at the B site in iron-modified bismuth titanate, where iron ions partially

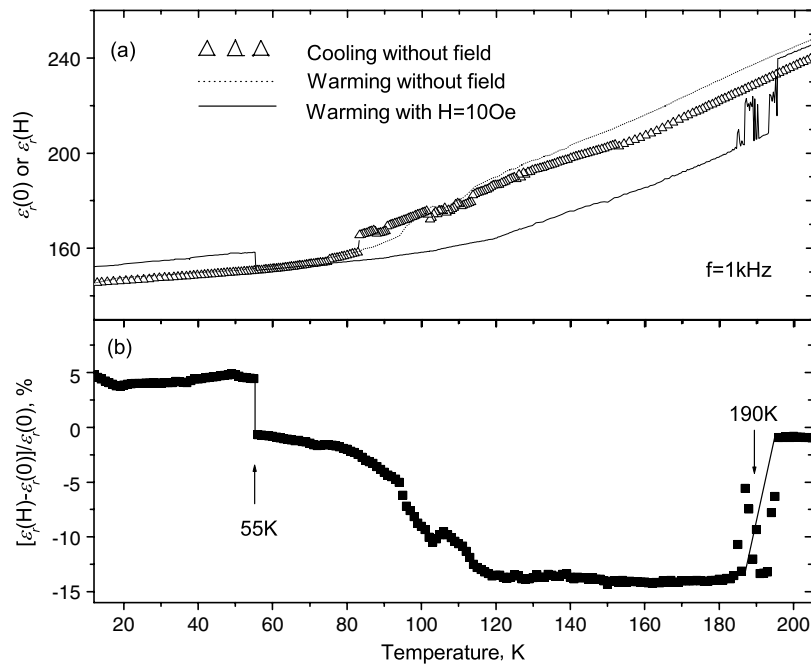


Figure 4. Dielectric constants (a) and the relative variation in dielectric constants in a magnetic field of 10 Oe, i.e. $[\varepsilon_r(H) - \varepsilon_r(0)]/\varepsilon_r(0)$ (b) of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film versus temperature. Open triangles denote cooling without a field, dotted lines denote warming without a field, and fine solid lines denote warming in a magnetic field of 10 Oe.

substitute Ti^{4+} [10]. On the other hand, the presence of local orderliness with a kind of short-range interaction is understandable when temperature gets sufficiently low. It is true that, for the systems of iron-substituted perovskite, an order–disorder transition can be observed in the χ – T curves during cooling without a magnetic field [21]. For $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ bulk materials, an order–disorder transition of iron ions at the perovskite B site occurred at around 170–190 K and produced a peak at around 170–190 K in the plot of magnetic-induced electric polarization output versus temperature [8]. Hemberger *et al* also suggested that the colossal magnetodielectric effects of CdCr_2S_4 , found at low temperature, arise from the coupling between relaxor ferroelectrics and magnetic fields where the long-range order losses and local order differ substantially from global symmetry [3]. For $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ films, similar to the bulk materials, there is also an order–disorder transition of iron ions at the perovskite B site at around 170–190 K. As a consequence, the abrupt diminution of the magnetodielectric effect at around 190 K in figure 4(b) should be due to the order–disorder transition of iron ions at the perovskite B site of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ films.

Intriguing questions may be raised regarding the sign of the magnetodielectric effects. Conventionally, negative magnetodielectric responses occur because magnetic fields suppress the excitation from a singly occupied state to another state [22]. The positive magnetodielectric responses below 55 K in figure 4(b) are attributable to the fact that magnetic fields play a role in preventing the low-temperature reduction in dielectric constants when the nearest-neighbour spin correlation increases for antiferromagnetic structures [23].

Magnetodielectric effects with a maximum $\Delta = 0.03$ in low magnetic fields of 1–2 kOe were interpreted by a variation in magnetic domain occupancy, specifically, domain

reorientation accompanied by a huge magnetostriction in $\text{Tb}_3\text{Fe}_5\text{O}_{12}$ [4]. Since, in bulk materials including $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$, so far no observation of the MD effect under a ultra-low magnetic field with a magnitude of 10 Oe has been reported, the results presented in this paper therefore strongly suggest that the uniqueness of thin films can be regarded as reasons for ultra-low-field magnetodielectric behavior, as well as the high sensitivity of a magnetodielectric to composition and structure [24]. A thin film can be considered as a quasi-two-dimensional system and the quantum interference becomes important, where the spin-orbit interaction has only a z -component and magnetic scattering could set in dominantly under very low magnetic fields [25]. When weak magnetic fields are applied perpendicular to the surface of films, time-reversal invariance is broken, because external magnetic fields impose a valid perturbation on the phase coherence of spin to produce large magnetoelectronic responses [26]. Magnetoresistance experiments showed that extremely weak magnetic fields below 100 Oe induced a significant change in resistance in semiconductor films with a thickness of 0.1 to 1 μm [27]. So, it is reasonable to contemplate that magnetodielectric behaviour with a maximum $\Delta = -0.14$ under an ultra-low magnetic field of 10 Oe in the $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ film here originates from the interaction between the weak magnetic field and the phase coherence of the local spin possessed by Fe. A theoretical study has revealed that, in a perovskite-structure $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$, the atom Fe has a contribution to the ferroelectricity [28], which is also a collective behaviour caused by a coherent shift of the centre atoms for perovskite structures. Subsequently, in this case, the polarization of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ films under a weak magnetic field of 10 Oe was changed as a consequence of the interplay between spin coherence and ferroelectric activity at the Fe sites. Detailed work is now ongoing, and the current authors call for further comments on quantitative research.

4. Summary

Good-quality and fine-grain $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$ films can be obtained by metal organic decomposition processes. The film reveals an intrinsic zero-field-cooling magnetodielectric effect under an ultra-low magnetic field of 10 Oe. A change in sign of MD from positive to negative occurs at 55 K due to a transition from antiferromagnetism to weak ferromagnetism. The magnetodielectric effect vanishes abruptly at around 190 K, which is due to an order-disorder transition of iron ions at the perovskite B site. Our findings are expected to be applicable to low-cost detectors and switches for very low magnetic fields in an acceptable temperature range of 55–190 K.

Acknowledgments

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