

## Influence of substrate effects on the properties of multiferroic thin films

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 395901

(<http://iopscience.iop.org/0953-8984/21/39/395901>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 05:28

Please note that [terms and conditions apply](#).

# Influence of substrate effects on the properties of multiferroic thin films

St Kovachev<sup>1</sup> and J M Wesselinowa<sup>2</sup>

<sup>1</sup> Bulgarian Academy of Science, Institute for Nuclear Research and Nuclear Energy, Boulevard Tzarigradsko chaussee 72, 1784 Sofia, Bulgaria

<sup>2</sup> Department of Physics, University of Sofia, Boulevard J Bouchier 5, 1164 Sofia, Bulgaria

Received 16 June 2009, in final form 10 August 2009

Published 1 September 2009

Online at [stacks.iop.org/JPhysCM/21/395901](http://stacks.iop.org/JPhysCM/21/395901)

## Abstract

The influence of substrate effects on the ferroelectric and magnetic properties in multiferroic thin films is studied based on the Heisenberg and transverse Ising model. Green's function technique allows the calculation of static and dynamic properties in the dependence on temperature, film thickness and different substrates. It is demonstrated that the polarization, the magnetization, the critical temperatures and the spin-wave energies are very sensitive to the exchange interaction constants between the surface and the substrate and could be increased or decreased by using different kinds of substrates. The dependence on the film thickness is also discussed. The results are in qualitative accordance with the experimental data.

## 1. Introduction

One of the known ferroelectromagnets is BiFeO<sub>3</sub> (BFO), which exhibits both ferroelectricity and ferromagnetism (i.e. multiferroism), an intrinsic multifunctionality that would ostensibly make it a strong candidate for nanoscale electronics applications. Both its spontaneous polarization and saturation magnetization, however, are disappointingly low when compared to many standard ferroelectrics and ferromagnets. Recently, Wang *et al* [1] reported an enhancement of polarization (almost an order of magnitude higher than that of the bulk) and related properties in epitaxially constrained thin films of BFO on SrTiO<sub>3</sub> (STO). The films also exhibit an enhanced thickness-dependent magnetism compared to the bulk. Enormous strains can exist in thin films when one material is deposited on another, resulting from differences in crystal lattice parameters and thermal expansion behavior between the film and the underlying substrate, or arising from defects formed during deposition. As a result, the properties of thin films can be markedly different than the intrinsic properties of the corresponding unstrained bulk materials. The importance of substrate effects on phase transitions can be seen for example in multiferroic (MF) Ho<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> thin films. Ho<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> 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, Fukumura *et al* [2] have shown, using Raman scattering, that Ho<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> may exhibit ferroelectricity because of lattice strains induced by

the substrate. Another example is STO thin films. STO is an incipient ferroelectric, remaining paraelectric down to 0 K. However, chemical substitution, such as Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>, or stress due to substrate effects can disturb this state, resulting in ferroelectricity [3].

There are many studies of BFO thin films using different substrates [4–9] in order to enhance the polarization. Jang *et al* [10] have grown epitaxial (001) BFO films on (001) STO substrates which are subjected to a compressive strain due to the lattice mismatch of –1.4%. In contrast, epitaxial (001) BFO films grown on (001) Si substrates [10] are under biaxial tensile strain due to the difference in thermal expansion between the film and the substrate. Strain-induced effects on phase transitions in BFO thin films deposited on (001) STO and (001) yttria-stabilized zirconia oxide ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) (YSZ) substrates are studied by Kartavtseva *et al* [11]. A saturation magnetization much higher than that reported for the bulk is obtained by Thery *et al* [12] in BFO thin films on STO.

Thermodynamically YMnO<sub>3</sub> (YMO) can only exist with a hexagonal structure at ambient conditions. Hsieh *et al* [13] have demonstrated that the strain between the film and the substrate, for example LaAlO<sub>3</sub> (LAO), can play an important role in forming orthorhombic YMO films. Dho *et al* [14] have studied the crystal growth behavior of MF YMO films synthesized by pulsed laser deposition on several different substrates. The (0001) oriented hexagonal YMO phase was a stable one under tensile stress by the (0001) Al<sub>2</sub>O<sub>3</sub> (ALO) substrate, while it competed with the (011)-oriented orthorhombic YMO phase under compressive stress by the

(111) STO substrate. Son *et al* observed that the remanent magnetic moment of epitaxial BiMnO<sub>3</sub> thin films on the STO substrate [15] (or on the LAO substrate [16]) is larger than a BiMnO<sub>3</sub> thin film on the Pt/Ti/SiO<sub>2</sub>/Si substrate. Lee *et al* [17] have fabricated epitaxial thin films of hexagonal DyMnO<sub>3</sub> via deposition on Pt(111)/ALO(0001) and YSZ(111) substrates and have observed a polarization enhancement by a factor of 10 compared to that of the bulk material. The magnetic and ferroelectric properties of hexagonally grown HoMnO<sub>3</sub> thin films on Pt(111)/Al<sub>2</sub>O<sub>3</sub> (0001) and YSZ(111) substrates were investigated by Murugavel *et al* [18]. The HoMnO<sub>3</sub> films differ from the bulk material in a significantly lower Neel temperature. Magnetization measurements of HoMnO<sub>3</sub> films on YSZ(111) also reveal some differences in comparison with a single crystal [19]. These differences are possibly related to the larger *a* and *c* lattice parameters of the film, which are likely to alter the bond lengths, and, thus, the magnetic super-exchange interactions.

It must be mentioned that the substrate can provide magnetic field controlled strain to the film [30]. It is desirable to construct multiferroic structures using a carefully selected substrate that is magnetically and elastically functional by itself. Then a ferroelectric film can be epitaxially grown on the substrate, which results in a heterostructure with an efficient in-plane elastic coupling. Such a substrate must satisfy several conditions: (1) a giant anisotropic magnetostriction; (2) a good in-plane lattice match to the ferroelectric film; (3) a reasonably good conductivity that eliminates the need for a separate electrode at the interface. A very attractive material family that may meet these criteria are the naturally layered manganites. Mixed-valent (Mn<sup>3+</sup>–Mn<sup>4+</sup>) manganites have captured much attention in condensed matter science recently due to their exotic electronic and magnetic properties, including complex insulator–metal transitions and colossal magnetoresistance. In some mixed-valent manganites, the strong coupling between the magnetic field and the lattice results in giant anisotropic magnetostriction, especially if the structural transition temperature (*T<sub>S</sub>*) is close to the ferromagnetic ordering temperature (*T<sub>C</sub>*) [31]. It is important to note that unlike in conventional ferromagnets, the giant magnetostriction in layered manganites is a result of a field-induced change in the orbital-state occupancy [32].

The influence of the substrates on the properties of MF thin films has not been so intensively studied theoretically. Ederer and Spaldin [20] have used first principles calculations to calculate the effect of epitaxial strain on the spontaneous polarization of the ferroelectrics BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and LiNbO<sub>3</sub>, and the MF material BFO. They have shown that the epitaxial strain dependence varies considerably for the different systems, but in the case of BFO it is very small. The strain effects and thickness dependence of ferroelectric and magnetic properties in epitaxial BFO thin films using the Landau–Devonshire theory are investigated by Liu *et al* [21], Jiang and Qiu [22] and Ma *et al* [23]. Lu *et al* [24], based on the thermodynamic model, have studied the critical phase transition temperatures of the ferroelectric and ferromagnetic phase in MF composite thin films. A single-domain thermodynamic theory is employed by Zhang *et al* [25]

to predict the spontaneous polarizations of epitaxial BFO thin films grown on dissimilar substrates.

Most of the theoretical studies are performed using the phenomenological Landau theory. The aim of the present paper is to study the influence of substrates on the properties of MF thin films based on the Heisenberg and the transverse Ising models using Green's function technique beyond the random phase approximation (RPA), taking into account the transverse correlation functions.

## 2. The model

We consider a thin MF film deposited on different substrates and composed of *N* atomic layers in the *z*-direction. The layers are numbered by *n* = 1, . . . , *N*, where the layers *n* = 1 and *n* = *N* represent the free surface and the surface on the substrate, respectively. The thickness of each layer is nearly 10 Å or 1 nm. The proposed Hamiltonian (1) can be applied to MF hexagonal RMnO<sub>3</sub> and perovskite BFO with *T<sub>C</sub>* ≫ *T<sub>N</sub>*. Moreover, it can be used for description of other composite nanostructures, such as BaTiO<sub>3</sub>–CoFe<sub>2</sub>O<sub>4</sub> composite films [33–35], and for the study of their magnetic and dielectric properties as a function of a continuously varied composition. The Hamiltonian is presented as:

$$H = H^e + H^m + H^{me}. \quad (1)$$

$H^e$  is the Hamiltonian of the transverse Ising model (TIM) for the electrical subsystem:

$$H^e = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z, \quad (2)$$

where  $S_i^x$ ,  $S_i^z$  are the spin-1/2 operators of the pseudo-spins,  $J_{ij}$  denotes the nearest-neighbor pseudo-spin interaction, and  $\Omega$  is the tunneling frequency. In this system the mean electric polarization is proportional to the *z* component of the pseudo-spins introduced in the TIM. In the ordered phase we have the mean values  $\langle S^x \rangle \neq 0$  and  $\langle S^z \rangle \neq 0$ , and it is appropriate to choose a new coordinate system by rotating the original one used in (2) by the angle  $\theta$  in the *xz* plane. The rotation angle  $\theta$  is determined by the requirement  $\langle S^{x'} \rangle = 0$  in the new coordinate system.

$H^m$  is the Hamiltonian for the magnetic subsystem, which is given by the Heisenberg Hamiltonian:

$$H^m = -\frac{1}{2} \sum_{\langle ij \rangle} A_1(i, j) \mathbf{B}_i \cdot \mathbf{B}_j - \frac{1}{2} \sum_{[ij]} A_2(i, j) \mathbf{B}_i \cdot \mathbf{B}_j, \quad (3)$$

where  $\mathbf{B}_i$  is the Heisenberg spin at the site *i*, and the exchange integrals  $A_1$  and  $A_2$  represent the coupling between the nearest and next-nearest neighbors, respectively.  $\langle ij \rangle$  and  $[ij]$  denote the once summation over the nearest neighbors and the next-nearest neighbors, respectively.

The most important term is  $H^{me}$  which describes the coupling between the magnetic and the electric subsystems in the MF compound:

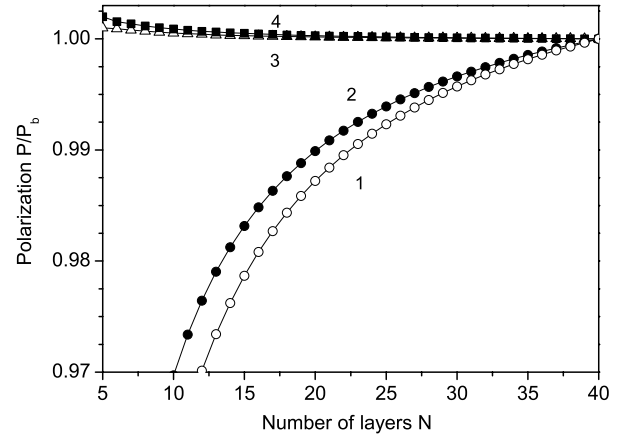
$$H^{me} = -g \sum_{\langle ij \rangle} \sum_{kl} S_k^z S_l^z \mathbf{B}_i \cdot \mathbf{B}_j. \quad (4)$$

Here  $g$  is the coupling constant between the magnetic and the electric order parameters.

Because our numerical calculations are done with the model parameters of BFO we will discuss the above proposed model for this substance. BFO is one of the most studied multiferroics due both to its strong ferroelectric polarization below  $T_C = 1100$  K and its antiferromagnetic order at room temperature, below  $T_N = 640$  K. In BFO, the magnetic and polarization orders are driven by different causes. The magnetization is due to a small canting of the mainly antiferromagnetically coupled magnetic moments of the Fe cations. Hill [36] has shown that a Bi A-site cation is favorable for ferroelectricity in perovskite oxides, regardless of whether the mechanism for ferroelectricity is electronic or soft-mode. For the calculation of the magnetic and ferroelectric order parameters we have used the Heisenberg (2) and transverse Ising model (3), respectively, and a linear coupling between them (4). The last magnetoelectric coupling influences and renormalizes all the properties of the multiferroic substances—magnetic, ferroelectric, elastic, lattice etc. There are investigations of the interplay between lattice vibrations and magnetic excitations which appear very useful because lattice distortions strongly affect the ferroelectric polarization and therefore their coupling to magnetic order [37]. This problem will be considered in our next paper.

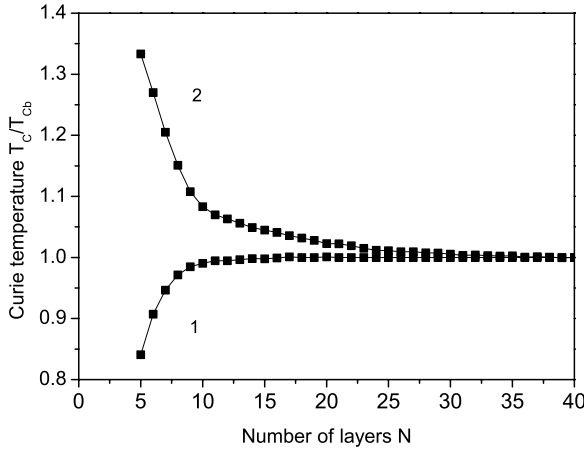
### 3. Numerical results and discussion

The properties of MF thin films are strongly affected by lattice parameter changes induced by the stress, but the mechanism of this effect has not been completely clarified. In our previous paper [26], using Green's function method, we have calculated the polarization, the magnetization, the critical temperatures, the spin-wave energies, and the damping, and have studied the influence of surface and size effects on these properties. Now we will discuss the influence of different substrates in order to explain the experimentally observed electric and magnetic properties of a MF thin film. We are taking the following model parameters which are appropriate for BFO with  $T_N = 640$  K and  $T_C = 1100$  K:  $A_{1b} = 158$  K,  $A_{2b} = -60$  K,  $\Omega_b = 2$  K,  $J_b = 910$  K,  $g = 50$  K,  $S = 2$  for the magnetic spins and  $S = 0.5$  for the pseudo-spins. The numerical calculations are done for a cubic lattice and wavevector  $\mathbf{k} = 0$ . Due to the changed number of next neighbors on the surface and to the reduced symmetry, the exchange interaction constants  $J$  and  $A_1$  can take different values on the free surface ( $n = 1$ )  $J_s$  and  $A_{1s}$  compared to the bulk values  $J_b$  and  $A_{1b}$ . Moreover, due to the different lattice parameters of the thin film and the substrate the exchange interaction constants in the surface layer deposited on the substrate ( $n = N$ ) are changed and denoted as  $J_{ss}$  and  $A_{1ss}$ . It is important to mention that  $J_{ij} \equiv J(r_i - r_j)$  and  $A_{1ij} \equiv A_1(r_i - r_j)$  depend on the distance between the spins, i.e. on the lattice parameter, on the lattice symmetry and on the number of next neighbors. Therefore, for a greater lattice constant and a respectively greater distance between the spins, the exchange interaction is weaker, whereas for a smaller lattice constant it is greater. So we can discuss the properties on a microscopic level.



**Figure 1.** Thickness dependence of the polarization  $P$  of a BFO thin film for  $T = 500$  K,  $J_b = 910$  K,  $A_{1b} = 158$  K and different exchange interaction constants on the substrates: (1)  $J_{ss} = 0.16J_b$ ,  $J_s = 0.5J_b$ ,  $A_{1ss} = 0.16A_{1b}$ ,  $A_{1s} = 0.5A_{1b}$ ; (2)  $J_{ss} = 0.5J_b$ ,  $J_s = 0.5J_b$ ,  $A_{1ss} = 0.5A_{1b}$ ,  $A_{1s} = 0.5A_{1b}$ ; (3)  $J_{ss} = 3J_b$ ,  $J_s = 2J_b$ ,  $A_{1ss} = 3A_{1b}$ ,  $A_{1s} = 2A_{1b}$ ; (4)  $J_{ss} = 6J_b$ ,  $J_s = 2J_b$ ,  $A_{1ss} = 6A_{1b}$ ,  $A_{1s} = 2A_{1b}$ .

The results for the film thickness dependence of the polarization of a MF BFO thin film for  $T = 500$  K and different exchange interaction parameters in the surface layer deposited on the substrate  $J_{ss}$  and  $A_{1ss}$  are presented in figure 1. For the case where  $J_{ss}$  and  $A_{1ss}$  are smaller than the bulk values  $J_b$  and  $A_{1b}$ , and smaller than the surface interaction constants  $J_s$  and  $A_{1s}$ , the polarization (figure 1, curves 1 and 2) is reduced compared to the bulk case without strain. The polarization  $P$  decreases with decreasing film thickness. For  $J_{ss} > J_s > J_b$  and  $A_{1ss} > A_{1s} > A_{1b}$  the polarization is enhanced (figure 1, curves 3 and 4) compared to the strain free bulk sample. The differences between the polarization curves are smaller for the second case because for  $T = 500$  K the polarization is nearly saturated and can not be further enhanced. For higher temperatures we obtain a stronger increase of  $P$  with decreasing film thickness. The increase or decrease of the polarization with decreasing film thickness is due to the lattice matching between the thin film and substrate. The bulk pseudo-cubic lattice constants of BFO, STO, LAO and MgO are 3.95, 3.905, 3.79 and 4.22 Å, and lattice mismatch with BFO is 1.1, 4.1, -6.4%, respectively [27]. The bulk lattice parameter of BFO is lower than that of MgO, i.e.  $a_{sub} > a_b$  or  $J_{ss} < J_b$  and  $A_{1ss} < A_{1b}$ , and hence we would expect the film to be under a tensile in-plane strain where  $P$  decreases with decreasing film thickness (figure 1, curves 1 and 2). This case could explain the experimentally obtained decrease of the polarization for tensile substrates MgO and Si [4, 10]. The effect of the tensile stress is generated by the large mismatch of the in-plane lattice constants between the film and the substrate. In the other case, the bulk lattice parameter of BFO is larger than that of STO and LAO, i.e.  $a_{sub} < a_b$  or  $J_{ss} > J_b$  and  $A_{1ss} > A_{1b}$ , and hence we would expect the film to be under a compressive in-plane strain where  $P$  increases with decreasing film thickness (figure 1, curves 3 and 4). This case could explain the experimentally obtained increase of the polarization for compressive substrates STO



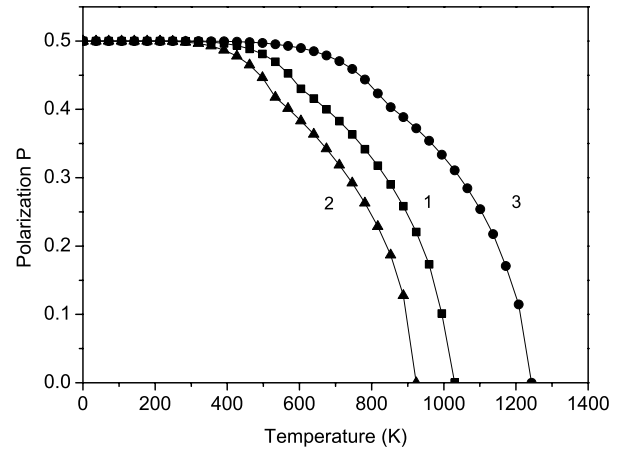
**Figure 2.** Thickness dependence of the Curie temperature  $T_C$  of a BFO thin film for  $J_b = 910$  K,  $A_{1b} = 158$  K and different exchange interaction constants on the substrates: (1)  $J_{ss} = 0.16J_b$ ,  $J_s = 0.5J_b$ ,  $A_{1ss} = 0.16A_{1b}$ ,  $A_{1s} = 0.5A_{1b}$ ; (2)  $J_{ss} = 6J_b$ ,  $J_s = 2J_b$ ,  $A_{1ss} = 6A_{1b}$ ,  $A_{1s} = 2A_{1b}$ .

and LAO [1, 4, 10]. Earlier we have obtained an enhancement of polarization even in the absence of substrate effects, due to surface and size effects [26]. But in the present paper we have shown that the compressive substrate effects lead to additive enhancement of  $P$ , contrary to the theoretical results reported by Ederer and Spaldin [20].

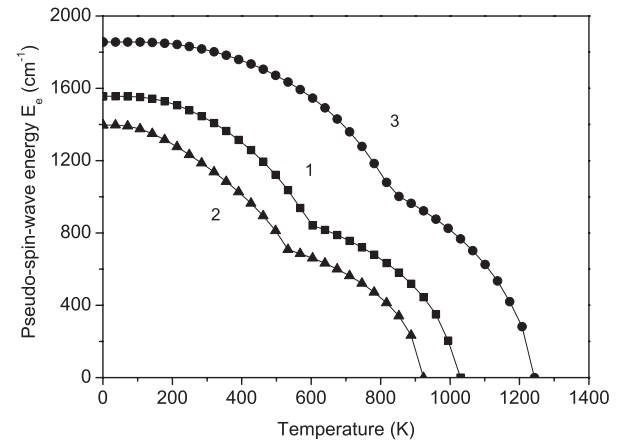
In the case of a BFO film on STO and LAO substrates the relatively smaller substrate lattice parameter compressively strains the film and causes enhanced polarization, whereas for Si and MgO substrates the strain is tensile and the polarization is reduced. This indicates that the substrate-induced strain has an influence on the crystal structures and on the properties of the thin films. But due to the lattice matching, different substrates have different strain effects on different thin films. For example the bulk in-plane hexagonal lattice parameters of YMO, ALO, Si and STO are 3.533, 4.758, 3.840 and 2.758 Å, respectively [14]. The surface morphology of the YMO films are clearly dependent on the lattice matching between the substrate and the YMO. As seen, the in-plane lattice constant of YMO is smaller that of ALO and Si, so the YMO layer on the ALO and Si substrates is under in-plane tensile stress. This would correspond in our model to the case  $J_{ss} < J_b$  and  $A_{1ss} < A_{1b}$ . The STO substrate gives a strong compressive strain to the YMO layer ( $a_{sub} < a_b$ , i.e.  $J_{ss} > J_b$  and  $A_{1ss} > A_{1b}$ ). This indicates that the compressive strain of the YMO layer should be fully relaxed to produce a good ferroelectric property.

Figure 2 shows the dependence of the ferroelectric phase transition temperature  $T_C$  on the film thickness and different  $J_{ss}$ - and  $A_{1ss}$ -values. It can be seen that for  $J_{ss} < J_b$  and  $A_{1ss} < A_{1b}$ , with increasing film thickness  $T_C$  increases and for  $N = 40$  layers it reaches the critical temperature of the bulk without strain, whereas for  $J_{ss} > J_b$  and  $A_{1ss} > A_{1b}$  we obtain the opposite behavior,  $T_C$  decreases with increasing film thickness  $N$ . The first case describes a tensile stress whereas the second case describes a compressive stress.

We have shown that stress affects the polarization  $P$  of MF films. Strain shifts also the ferroelectric phase transition

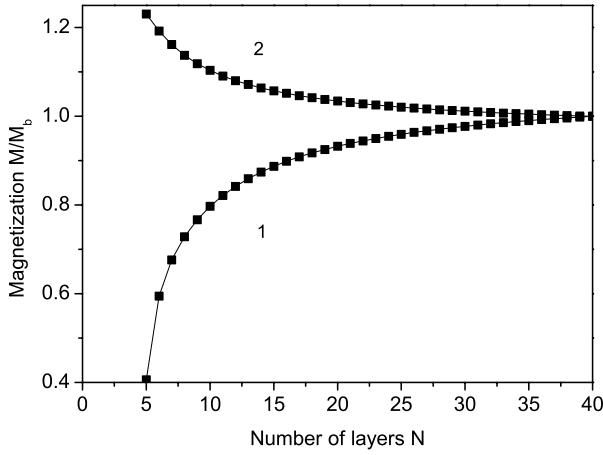


**Figure 3.** Temperature dependence of the polarization  $P$  of a BFO thin film for  $J_b = 910$  K,  $A_{1b} = 158$  K,  $N = 5$  and different exchange interaction constants on the substrates: (1)  $J_{ss} = J_b = J_s$ ,  $A_{1ss} = A_{1b} = A_{1s}$ ; (2)  $J_{ss} = 0.3J_b$ ,  $J_s = 0.5J_b$ ,  $A_{1ss} = 0.3A_{1b}$ ,  $A_{1s} = 0.5A_{1b}$ ; (3)  $J_{ss} = 2.2J_b$ ,  $J_s = 2J_b$ ,  $A_{1ss} = 2.2A_{1b}$ ,  $A_{1s} = 2A_{1b}$ .

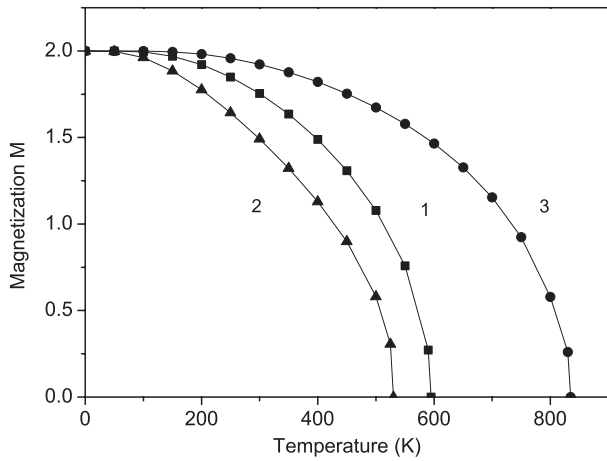


**Figure 4.** Temperature dependence of the pseudo-spin-wave energy  $E_e$  of a BFO thin film for  $J_b = 910$  K,  $A_{1b} = 158$  K,  $N = 5$  and different exchange interaction constants on the substrates: (1)  $J_{ss} = J_b = J_s$ ,  $A_{1ss} = A_{1b} = A_{1s}$ ; (2)  $J_{ss} = 0.3J_b$ ,  $J_s = 0.5J_b$ ,  $A_{1ss} = 0.3A_{1b}$ ,  $A_{1s} = 0.5A_{1b}$ ; (3)  $J_{ss} = 2.2J_b$ ,  $J_s = 2J_b$ ,  $A_{1ss} = 2.2A_{1b}$ ,  $A_{1s} = 2A_{1b}$ .

temperature  $T_C$ . The polarization decreases with increasing temperature to vanish at the critical temperature  $T_C$  of the thin film (figure 3). In the dependence of the exchange interactions on the substrate  $J_{ss}$  and  $A_{1ss}$  the ferroelectric properties, polarization  $P$  and the pseudo-spin-wave energy  $E_e$  can be smaller (for  $J_{ss} < J_b$  and  $A_{1ss} < A_{1b}$ ) or larger (for  $J_{ss} > J_b$  and  $A_{1ss} > A_{1b}$ ) in comparison to the strain free thin film (figures 3 and 4). The obtained temperature dependence clearly illustrates the coupling between the two order parameters below  $T_N$ . This coupling is observed as a kink at the magnetic phase transition temperature in the  $P(T)$  and  $E_e(T)$  plots. This anomaly can be explained as an influence of vanishing magnetic ordering on electric ordering in the system. The dielectric response study with temperature in BFO thin films on a Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrate of Palkar *et al* [28]



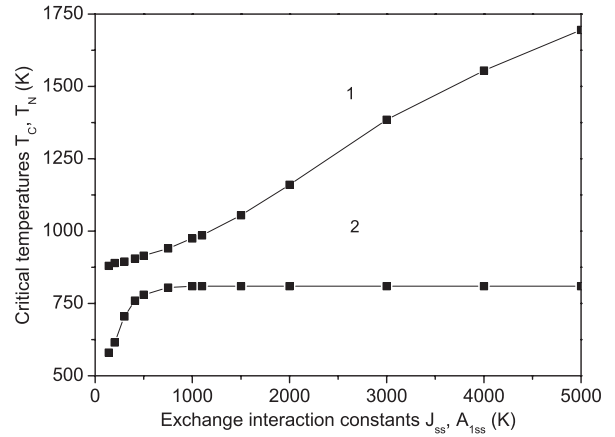
**Figure 5.** Thickness dependence of the magnetization  $M$  of a BFO thin film for  $T = 500$  K,  $J_b = 910$  K,  $A_{1b} = 158$  K and different exchange interaction constants on the substrates: (1)  $A_{1ss} = 0.16A_{1b}$ ,  $A_{1s} = 0.5A_{1b}$ ,  $J_{ss} = 0.16J_b$ ,  $J_s = 0.5J_b$ ; (2)  $A_{1ss} = 6A_{1b}$ ,  $A_{1s} = 2A_{1b}$ ,  $J_{ss} = 6J_b$ ,  $J_s = 2J_b$ .



**Figure 6.** Temperature dependence of the magnetization  $M$  of a BFO thin film for  $J_b = 910$  K,  $A_{1b} = 158$  K,  $N = 5$  and different exchange interaction constants on the substrates: (1)  $J_{ss} = J_b = J_s$ ,  $A_{1ss} = A_{1b} = A_{1s}$ ; (2)  $J_{ss} = 0.3J_b$ ,  $J_s = 0.5J_b$ ,  $A_{1ss} = 0.3A_{1b}$ ,  $A_{1s} = 0.5A_{1b}$ ; (3)  $J_{ss} = 2.2J_b$ ,  $J_s = 2J_b$ ,  $A_{1ss} = 2.2A_{1b}$ ,  $A_{1s} = 2A_{1b}$ .

indicates an anomaly in the dielectric constant  $\epsilon(T)$  in the vicinity of the Neel temperature  $T_N$ .

The substrate effects on the magnetization  $M$  of a MF BFO thin film are demonstrated in figures 5 and 6. It can be seen that  $M$  increases with decreasing film thickness for  $A_{1ss} > A_{1b}$ , i.e. for compressive substrates (STO or LAO), whereas for the opposite case  $A_{1ss} < A_{1b}$ , i.e. for tensile substrates (MgO or Si) it decreases with decreasing  $N$  (figure 5). This is in qualitative agreement with the experimental data of BFO [12] and BiMnO<sub>3</sub> thin films [15, 16]. We have obtained a similar behavior for the Neel temperature in the dependence of the film thickness. In figure 6 are shown the substrate effects on the temperature dependence of  $M$  with  $N = 5$  layers. The magnetization decreases with increasing temperature to vanish at the magnetic critical temperature  $T_N$  of the thin film. This



**Figure 7.** Dependence of the critical temperatures on the exchange interaction constants on the substrate of a BFO thin film for  $N = 5$ ,  $J_b = 910$  K =  $J_s$ ,  $A_{1b} = 158$  K: (1)  $T_C$  for different  $J_{ss}$ -values; (2)  $T_N$  for different  $A_{1ss}$ -values.

vanishing of the magnetic order causes the kink in the electric properties at  $T_N$  (see figures 3 and 4). In the dependence of the exchange interactions on the substrate's  $J_{ss}$  and  $A_{1ss}$  the magnetization  $M$  and the phase transition temperature  $T_N$  can be smaller (curve 2, for  $J_{ss} < J_b$  and  $A_{1ss} < A_{1b}$ ) or larger (curve 3, for  $J_{ss} > J_b$  and  $A_{1ss} > A_{1b}$ ) in comparison to the strain free thin film (curve 1).

In figure 7 we have compared the influence of the substrate exchange interaction constants on the critical temperatures  $T_C$  and  $T_N$ . Above the bulk values ( $J_b = 910$  K and  $A_{1b} = 158$  K) the critical temperatures  $T_C$  and  $T_N$  increase with an increase of the interaction constants  $J_{ss}$  or  $A_{1ss}$ , respectively, i.e. with increasing compressive strain. With decreasing  $J_{ss}$  or  $A_{1ss}$  below the bulk values, i.e. with an increase of tensile strain, the critical temperatures decrease. The Curie temperature for  $J_{ss} = 9100$  K reaches saturation with  $T_C = 1885$  K, whereas  $T_N$  is already saturated at  $A_{1ss} = 1200$  K with  $T_N = 815$  K. It can be seen that the Neel temperature  $T_N$  is not so sensitive to the strain in comparison with the Curie temperature  $T_C$ . Similar results are observed experimentally [18, 29]. We obtain that the Curie temperatures for the substrates STO and LAO are very close, that of STO is a little bit larger than  $T_C$  of LAO. The reason is the nearly identical changes of the lattice parameters of the BFO thin film. The critical temperatures due to the compressive substrates STO and LAO are significantly larger compared to the Curie temperature  $T_C$  due to the tensile substrate MgO. This is in agreement with the experimental data of Kartavtseva *et al* [11]. The possibility of a significant decrease in the ferroelectric ordering temperature in BFO films by epitaxial stresses is of interest for practical use. The direct measurement of the optical properties at high temperatures is not possible [9], since it was found that the effect of a laser on a sample in combination with heating up to 800 °C leads to the bismuth loss from the film surface.

#### 4. Conclusions

In conclusion, the physical properties of MF thin films can be adjusted by using different substrates due to lattice mismatch.

However, there are some controversial arguments about the origin of the enhanced magnetization and polarization observed in epitaxial constrained MF thin films. To clarify this fact we have investigated the surface, size and substrate effects on the properties of MF BFO thin films. We have shown that  $P$  and  $M$  could be increased or decreased, first due to surface and doping effects [26], and further due to compressive or tensile substrate effects, respectively. This strongly depends on the lattice mismatch between the film and the substrate. For example for BFO thin films STO and LAO are compressive substrates ( $a_{\text{sub}} < a_{\text{b}}$ ,  $J_{\text{ss}} > J_{\text{b}}$ ) whereas MgO is a tensile substrate ( $a_{\text{sub}} > a_{\text{b}}$ ,  $J_{\text{ss}} < J_{\text{b}}$ ). For YMO thin films the STO substrate causes compressive strain, whereas ALO causes tensile strain. Our results show that the critical temperatures are also significantly affected by the substrate-induced stresses. The obtained results are in qualitative accordance with the experimental data. It must be mentioned that our method and approximation can be also applied in order to obtain quantitative comparison with the experimental data [38], because by the analytical calculations we go beyond the random phase approximation (RPA) and take into account the correlation functions [26]. But for quantitative comparison the structure of the thin film and the substrate must be considered in more detail. This will be done in the next paper.

## Acknowledgment

Financial support from the Bulgarian National Science Fund, Grant No. DO02-264/2008, is greatly acknowledged.

## References

- [1] Wang J *et al* 2003 *Science* **299** 1719
- [2] Fukumura H, Tonari N, Hasuie N, Harima H, Kisoda K, Koide T, Seki M and Tabata H 2009 *J. Phys.: Condens. Matter* **21** 064221
- [3] Haeni J H *et al* 2004 *Nature* **430** 758
- [4] Nechache R, Gupta P, Harnagea C and Pignolet A 2007 *Appl. Phys. Lett.* **91** 222908
- [5] Rana D S, Takahashi K, Mavani K R, Kawayama I, Murakami H, Tonouchi M, Yanagida T, Tanaka H and Kawai T 2007 *Phys. Rev. B* **75** 060405(R)
- [6] Wang J, Zheng H, Ma Z, Prasertchoung S, Wuttig M, Droopad R, Yu J, Eisenbeiser K and Ramesh R 2004 *Appl. Phys. Lett.* **85** 2574
- [7] Wang D H, Yan L, Ong C K and Du Y W 2006 *Appl. Phys. Lett.* **89** 182905
- [8] Kim H H, Dho J H, Qi X, Kang S K, MacManus-Driscoll J L, Kang D J, Kim K N and Blamire M G 2006 *Ferroelectrics* **333** 157
- [9] Liu Z, Liu H, Du G, Zhang J and Yao K 2006 *J. Appl. Phys.* **100** 044110
- [10] Jang H W *et al* 2008 *Phys. Rev. Lett.* **101** 107602
- [11] Kartavtseva M S, Gorbenko O Yu, Kaul A R, Murzina T V, Savinov S A and Barthelemy A 2007 *Thin Solid Films* **515** 6416
- [12] Thery J, Dubourdieu C, Baron T, TERNON C, Roussel H and Pierre F 2007 *Chem. Vapor Depos.* **13** 232
- [13] Hsieh C C, Lin T H, Shih H C, Lin J-Y, Hsu C-H, Luo C W, Wu K H, Uen T M and Juang J Y 2009 *J. Phys.: Conf. Ser.* **150** 042062
- [14] Dho J, Leung C W, MacManus-Driscoll J L and Blamire M G 2004 *J. Cryst. Growth* **267** 548
- [15] Son J Y and Shin Y H 2008 *Appl. Phys. Lett.* **93** 062902
- [16] Son J Y, Kim B G, Kim C H and Cho J H 2004 *Appl. Phys. Lett.* **84** 4971
- [17] Lee J H, Murugavel P, Lee D, Noh T W, Jo Y, Jung M H, Jang K H and Park J G 2007 *Appl. Phys. Lett.* **90** 012903
- [18] Murugavel P, Lee J H, Lee D, Noh T W, Jo Y, Jung M H, Oh Y S and Kim K H 2007 *Appl. Phys. Lett.* **90** 142902
- [19] Kim J W, Nenkov K, Schultz L and Dorr K 2009 *J. Magn. Mater.* **321** 1727
- [20] Ederer C and Spaldin N A 2005 *Phys. Rev. Lett.* **95** 257601
- [21] Liu G, Nan C-W, Xu Z K and Chen H 2005 *J. Phys. D: Appl. Phys.* **38** 2321
- [22] Jiang Q and Qiu J H 2006 *J. Appl. Phys.* **99** 103901
- [23] Ma H, Chen L, Wang J, Ma J and Boey F 2008 *Appl. Phys. Lett.* **92** 182902
- [24] Lu X Y, Wang B, Zheng Y and Ryba E 2007 *J. Phys. D: Appl. Phys.* **40** 1614
- Lu X Y, Wang B, Zheng Y and Ryba E 2009 *J. Phys. D: Appl. Phys.* **42** 015309
- [25] Zhang J X, Li Y L, Wang Y, Liu Z K, Chen L Q, Chu Y H, Zavaliche F and Ramesh R 2007 *J. Appl. Phys.* **101** 114105
- [26] Kovachev St and Wesselinowa J M 2009 *J. Phys.: Condens. Matter* **21** 225007
- [27] Lofland S E, McDonald K F, Metting C J, Knoesel E, Murakami M, Aronova M A, Fujino S, Wuttig M and Takeuchi I 2006 *Phys. Rev. B* **73** 092408
- [28] Palkar V R, John J and Pinto R 2002 *Appl. Phys. Lett.* **80** 1628
- [29] Kim B G, Son J Y, Kim C H and Cho J H 2005 *J. Korean Phys. Soc.* **46** 33
- [30] Wu T, Zurbuchen M A, Saha S, Wang R-V, Streiffer S K and Mitchell J F 2006 *Phys. Rev. B* **73** 134416
- [31] Asamitsu A, Moritomo Y, Tomioka Y, Arima T and Tokura Y 1995 *Nature* **373** 407
- [32] Kimura T, Tomioka Y, Asamitsu A and Tokura Y 1998 *Phys. Rev. Lett.* **81** 5920
- [33] Zheng H *et al* 2004 *Science* **303** 661
- [34] Liu G, Nan C-W, Xu Z K and Chen H 2005 *J. Phys. D: Appl. Phys.* **38** 2321
- [35] Barbosa J, Almeida B, Pereira A M, Arajo J P, Gomes I and Mendes J 2008 *J. Non-Cryst. Solids* **354** 5250
- [36] Hill N A 2000 *J. Phys. Chem.* **104** 6694
- [37] Cazayous M, Sacuto A, Lebeugle D and Colson D 2009 *Eur. Phys. J. B* **67** 209
- [38] Wesselinowa J M and Apostolov A 1997 *Phys. Status Solidi b* **203** 53