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Size effects of ferroelectric and magnetoelectric properties of semi-ellipsoidal bismuth ferrite nanoparticles

Victoria V. Khist [a], Eugene A. Eliseev [b], Maya D. Glinchuk [b], Maxim V. Silibin [c], Dmitry V. Karpinsky [d], *, Anna N. Morozovska [e], **

[a] Institute of Magnetism, National Academy of Sciences of Ukraine and Ministry of Education and Science of Ukraine, 36-b, pr. Akademika Vernadskoho, 03142, Kyiv, Ukraine
[b] Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Krjijanovskogo str. 3, 03142, Kyiv, Ukraine
[c] National Research University of Electronic Technology "MIET", 124498, sq. Shokina bld.1, Zelenograd, Moscow, Russia
[d] Scientific-Practical Materials Research Centre of NAS of Belarus, P. Brovka str. 19, 220072, Minsk, Belarus
[e] Institute of Physics, National Academy of Sciences of Ukraine, 46, pr. Nauky, 03028, Kyiv, Ukraine

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A B S T R A C T

Bismuth ferrite ($BiFeO_3$) is one of the most promising multiferroics with a sufficiently high ferroelectric (FE) and antiferromagnetic (AFM) transition temperatures, and magnetoelectric (ME) coupling coefficient at room temperature. So $BiFeO_3$ is highly sensitive to the impact of cross-influence of applied electric and magnetic fields. According to the urgent demands of nanotechnology to miniaturize the working elements for ultra-high density data storage in advanced nonvolatile memory cells, it is very important to reduce the sizes of multiferroic nanoparticles in the self-assembled arrays without serious deterioration of their properties. This work studies size effects of the phase diagrams, FE and ME properties of semi-ellipsoidal $BiFeO_3$ nanoparticles clamped to a rigid conductive substrate. The spatial distribution of the spontaneous polarization vector inside the nanoparticles, phase diagrams and paramagnetoelectric (PME) coefficient were calculated in the framework of the modified Landau-Ginzburg-Devonshire (LGD) approach. Analytical expressions were derived for the dependences of the FE transition temperature, average polarization, linear dielectric susceptibility and PME coefficient on the particle sizes for a general case of a semi-ellipsoidal nanoparticles with different semi-axes *a*, *b* and height *c*. The analyses of the obtained results leads to the conclusion that the size effect of the phase diagrams, spontaneous polarization and PME coefficient is rather sensitive to the aspect ratio of particle sizes in the polarization direction, and less sensitive to the absolute values of the sizes.

1. Introduction

1.1. *Multiferroic $BiFeO_3$ for fundamental studies and advanced applications*

Multiferroics, which are ferroics with two or more interacting long-range order parameters, are ideal systems for fundamental studies of the couplings among the ferroelectric (**FE**) polarization, structural antiferrodistortive (**AFD**), and antiferromagnetic (**AFM**) order parameters [1–5]. These couplings are in response of unique physical properties of multiferroics [6]. For instance, biquadratic and linear magnetoelectric (**ME**) couplings lead to intriguing effects, such as a giant ME tunability of multiferroics [7]. Biquadratic coupling of the structural, polar and dielectric order parameters introduced in Refs. [8,9], are responsible for the unusual behavior of the dielectric, polar and other physical properties in ferroelastics-quantum paraelectrics. The linear-quadratic paramagnetoelectric (**PME**) effect should exist in the paramagnetic phase of all ferroics, below the temperature of the paraelectric to ferroelectric phase transition, where the electric polarization is nonzero. This effect was observed in $NiSO_4{\cdot}6H_2O$ [10], Mn-doped $SrTiO_3$ [11], $Pb(Fe_{1/2}Nb_{1/2})O_3$ [12], and $Pb(Fe_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ solid solution [13]. Note that PME effect can be expected in many nanosized ferroics, which becomes paramagnetic due to the size-induced transition from the ferromagnetic or antiferromagnetic phase.

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* Corresponding author.
** Corresponding author.

E-mail addresses: dmitry.karpinsky@gmail.com (D.V. Karpinsky), anna.n.morozovska@gmail.com (A.N. Morozovska).

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$BiFeO_3$ is the one of the most interesting multiferroics with a strong ferroelectric polarization, antiferromagnetism at room temperature [4,5], local ferromagnetism [14], spin-lattice coupling phase transition and phonon anomalies [15] as well as enhanced electrotransport properties at domain walls [16–21]. Bulk $BiFeO_3$ exhibits AFD order at temperatures below 1200 K; it is FE order with a large spontaneous polarization below 1100 K and AFM with a cycloid spin order below Neel temperature $T_N \approx 650$ K [22,23]. The pronounced multiferroic properties maintain in $BiFeO_3$ thin films [24–27] and heterostructures [28]. Despite extensive experimental and theoretical studies of the physical properties of bulk $BiFeO_3$ and its thin films [20–22,29–35] many important issues concerning the emergence and theoretical background of multiferroic, polar, magnetic and various electrophysical properties of $BiFeO_3$ nanoparticles remain almost unexplored [36,37].

1.2. Multiferroelectric nanoparticles. State-of-art

According to the urgent demands of nanotechnology to miniaturize the working elements for ultra-high density of data storage in advanced nonvolatile memory cells, it is very important to reduce the sizes of multiferroic nanoparticles in the self-assembled arrays without serious deterioration of their FE, AFM and ME properties. There are many intriguing and encouraging examples of the FE and ME properties conservation, enhancement and modification in ferroelectric nanoparticles. In particular Yadlovker and Berger [38] presented the unexpected experimental results, which reveal the enhancement of FE properties of cylindrical nanoparticles of Rochelle salt. Zhao et al. [39] and Erdem et al. [40] demonstrated the possibility to control the temperature of the ferroelectric phase transition, the magnitude and position of the dielectric constant maximum for $BaTiO_3$ and $PbTiO_3$ nanopowders and nanoceramics. The studies of $KTa_{1-x}Nb_xO_3$ nanopowders and nanograin ceramics [41] discover the appearance of novel FE phases, the shift of FE transition temperature in comparison with bulk crystals. Strong size effects in $SrBi_2Ta_2O_9$ nanoparticles have been revealed by *in situ* Raman scattering by Yu et al. [42] as well as by thermal analysis and Raman spectroscopy by Ke et al. [43].

Size-dependent ferroelectric phase transition, magnetic properties [44], infrared phonon modes [45], optical and photocatalytic properties [46] have been observed in $BiFeO_3$ nanoparticles. $BiFeO_3$ nano-island can be promising candidates for resistive switching memory [47]. The physical properties of nanosized $BiFeO_3$ can be controlled and tuned by doping with different rare-earth metals. For instance, the co-substitution of Gd and Mn in $BiFeO_3$ nanoparticles leads to the magnetization saturation and band gap tuning [48]. Nd and Nb co-doping of $BiFeO_3$ nanoparticles strongly affects on their structural, magnetic and optical properties [49]. Fe doped $BaZrO_3$ nanoceramic is a room temperature ferromagnetic [50]. The list of experimental studies should be continued making any new experimental and theoretical study of ferroelectric nanoparticles important for both fundamental science and applications.

In particular, the surface and finite size effects impact on the phase diagrams, polar and electrophysical properties of $BiFeO_3$ nanoparticles are very poorly studied [36,37]. Such study may be very useful for science and applications, because the theory of finite size effects in nanoparticles allows one to establish the physical origin of the properties anomalies, transition temperature and phase diagrams changes appeared with the sizes decrease. In particular, using the continual phenomenological approach Niepce [51], Huang et al. [52,53], Ma [54], Eliseev et al. [55] and Morozovska et al. [56–60] have shown, that the changes of the transition temperatures, the enhancement or weakening of FE properties in spherical and cylindrical nanoparticles are conditioned by the various physical mechanisms, such as correlation effect, depolarization field, flexoelectricity, electrostriction, surface tension and Vegard-type chemical pressure.

1.3. Research motivation

Nanoparticles of semi-ellipsoidal shape can be considered as the model objects to study the size effects of physical properties in ferroic nano-islands. $BiFeO_3$ nano-islands and their self-assembled arrays can be formed on anisotropic substrates by different low-damage fabrication methods [61–63]. The particles typically have different in-plane axes due to the anisotropic thermal conductivity of substrate. Recent advances in the production technology of ferroelectrics have resulted in a cost-effective synthesis of these nanoparticles, which are beginning to be used in fabrication of microactuators, microwave phase shifters, infrared sensors, transistor applications, energy harvesting devices, etc. A correlation mechanism between the scaling factor, geometry of the nanoparticles and their physical parameters, and related phenomena viz. spontaneous FE polarization, AFM and AFD order, width of the domain walls and the domains stability is needed to be further investigated using both experimental methods and theoretical modeling. Most intriguing fundamental issues to be addressed include the estimation of the intrinsic limit for FE polarization stability, mechanism of domain wall motion, and polarization reversal in nanoscale regions [1–6].

The analyses of the above state-of-art motivated us to study theoretically the size effects influence on FE, AFM and ME properties of semi-ellipsoidal $BiFeO_3$ nanoparticles in the framework of the Landau-Ginzburg-Devonshire (**LGD**) approach, classical electrostatics and elasticity theory.

2. Theory

2.1. Problem statement

It is known that ferroelectricity is a cooperative phenomenon associated with the dipole moments aligned on both short-range and long-range scale level. This alignment is characterized by a certain transition temperature justified by the temperature-dependent forces, which are related with the size effects, dimension of the material, its structural homogeneity etc. It is accepted that the size effects are associated either with intrinsic (mainly related to the atomic polarization) or extrinsic (stresses, microstructure, polarization screening etc.) factors [56–59].

Let us consider ferroelectric nanoparticles in the form of semi-elliptical islands precipitated on the rigid conducting substrate electrode. The ellipsoid has different values of semi-axis length, a, b and height c along X-, Y- and Z-axis, respectively. We denote ε_b and ε_e as the dielectric permittivity of ferroelectric background and external media, respectively. The one-component ferroelectric polarization $\mathbf{P}(\mathbf{r})$, directed along the crystallographic axis 3 inside the particle, that is parallel to the interface $z = 0$ (Fig. 1).

The considered crystal system is pseudo-cubic with the crystallographic axes {1, 2, 3}. Since we are working in the LGD approach, in which framework the equations of state are derived from the variation of free energy functional, the functional is a continuous function of polarization in the pseudo-cubic parent phase without long-range FE and AFM orders as well as in the long-range ordered rhombohedral ferroelectric phase. Therefore true symmetry of the free energy functional corresponds to the irreducible representation of the pseudo-cubic parent phase symmetry. The symmetry is broken spontaneously with the appearance of the order parameter with the temperature decrease.

Hence we can assume that in the pseudo-cubic crystallographic frame {1, 2, 3} the dependence of the in-plane components of