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Extraordinary enhancement of Néel transition temperature in nanoparticles of multiferroic tetragonal compositions of $(1 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3$ solid solutions

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The Néel temperature (T_N) in conventional antiferromagnets (AFM) decreases with decreasing particle size. In contrast, we present here evidence for an exotic facet of multiferroicity, whereby one can raise the T_N by more than 200 K by decreasing the particle size. We illustrate this by taking the example of a tetragonal composition with $x = 0.5$ in the solid solutions of $(1 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3$ (BF- x PT). We attribute it to the increase in the strength of the superexchange interaction via a decrease in the ferroelectric distortion in nanocrystalline powder of BF-0.5PT. The BF-0.5PT nanoparticles also exhibit exchange bias effect due to AFM core-FM shell type magnetic nanostructure.

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The properties of nanostructured magnetic materials differ significantly from their bulk counterparts and have been exploited for several technological applications. The nanostructured ferromagnetic (FM) and ferrimagnetic (FerM) materials are commonly used in permanent magnets, magnetic data storage, logic devices, ferrofluids, biomedical devices, etc.^{1–4} In recent years, nanostructured antiferromagnetic (AFM) materials have also received considerable attention for applications like spin valves, magnetic random access memory, and AFM and FM composite based hard magnets.⁵ Finite size effects in AFMs nanoparticles, nanorods, and thin films have been investigated extensively,^{6–10} and it has been shown that T_N decreases with decreasing particle size or the thin film thickness as per the predictions of Néel. The decrease in T_N is found to be consistent with Binder's scaling theory of critical phenomena in reduced dimension systems, which gives the following universal power law dependence of transition temperature:¹¹

$$\frac{T_N^b - T_N^{\text{grain}}}{T_N^b} = \left(\frac{d}{\xi_0}\right)^{-\left(\frac{1}{\nu}\right)},$$

where T_N^b and T_N^{grain} are the bulk and finite size AFM transition temperatures, d is the grain diameter, ξ_0 is the magnetic correlation length at 0 K, and ν the critical exponent related to ξ .

In marked contrast to conventional AFMs materials, we show here that it is possible to raise the Néel temperature (T_N) substantially (up to ~ 200 K) through particle size reduction in multiferroic AFM (MFAFM) materials. We also show that this extraordinary enhancement of T_N in MFAFMs is linked with the tunability of the strength of the

superexchange interaction through a decrease in the ferroelectric (FE) distortion in low dimensional systems due to finite size effects. We illustrate our finding using a tetragonal composition $x = 0.50$ of solid solutions of BiFeO_3 with PbTiO_3 , i.e., $(1 - x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3$ (BF-0.5PT), where T_N is shown to increase from ~ 120 K in bulk powders to ~ 350 K in 18 nm size ferroelectric powders. While multiferroics are well known for magnetoelectric coupling involving controllability of electrical polarisation (P) through magnetic field (H) and magnetisation (M) through electric field (E) with potential for applications in new generation multifunctional sensor, actuator, and data storage devices,^{12–14} the present work brings out yet another exotic facet of multiferroicity, whereby one can raise T_N systematically and design room temperature single phase multiferroics (which are extremely rare), useful for multifunctional devices operating at room temperature.

Amongst the magnetoelectric multiferroic compounds, BiFeO_3 (BF) is the only room temperature multiferroic with very high FE and AFM transition temperatures of $T_c = 1103$ K and $T_N = 643$ K, respectively.^{12,15} This material therefore holds considerable promise for multifunctional devices operating at room temperature.^{12,13,15} Solid solutions of BF with other perovskite oxides have received considerable attention from the point of view of release of latent magnetization from melting of the spin cycloid of BF.¹⁶ We have considered the solid solution BF- x PT system for our study as it shows an interesting phase diagram having a critical point¹⁷ and a rich variety of structural and magnetic phase transitions like FE, antiferrodistortive (AFD),¹⁸ ferroelectric to ferroelectric isostructural,¹⁷ morphotropic,^{18,19} AFM,²⁰ spin reorientation,²¹ and spin glass (SG) transitions.²² PbTiO_3 substitution modifies the rhombohedral $R3c$ symmetry of BF to monoclinic Cc symmetry,¹⁸ similar to that in thin films of BF under epitaxial constraints.^{23,24} The

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monoclinic Cc phase is stable for $x \leq 0.27$ and transforms to a tetragonal (space group P4mm) phase for $x = 0.31$ via a thin phase coexistence region for $0.27 < x < 0.31$ across a first order morphotropic phase boundary (MPB).^{18,19} The tetragonal phase of BF-xPT, stable for $0.31 \leq x \leq 1.0$, has got several unusual characteristics such as (1) anomalously high tetragonality ($\eta = (c/a - 1)$) that is more than three times that of the commercial MPB ceramics like PZT,¹⁹ (2) increasing tetragonality with increasing BF content on approaching the MPB and becoming as high as $\sim 18.73\%$ for $x = 0.31$ ^{18,19} (η decreases on approaching the MPB in PZT and other PbTiO₃ based commercial MPB piezoceramics), (3) not resulting from the paraelectric (PE) cubic phase directly but through an isostructural phase transition from a low tetragonality (η) phase, which gets formed first from the cubic paraelectric phase below the Curie temperature,¹⁷ and (4) possessing rather low T_N (~ 209 K for $x = 0.31$) as compared to neighbouring monoclinic compositions with $T_N \sim 473$ K for $x = 0.27$.²⁰ We now proceed to show extraordinary enhancement of T_N as a result of particle size reduction in tetragonal compositions of BF-xPT powders taking $x = 0.50$ (i.e., BF-0.5PT) as a representative composition.

BF-0.50PT powders of approximate average sizes of 120 nm, 45 nm, 31 nm, and 18 nm were synthesized by sol-gel route, the details of which are given in the supplementary material (Sec. A).²⁵ Figure 1(a) shows the Synchrotron x-ray powder diffraction (SXRPD) profiles of the 100, 110, and 111 pseudocubic reflections of BF-0.5PT with average particle sizes of ~ 18 , 31, 45, and 120 nm. The SXRPD profiles of 120 nm size particles show that the 100 and 110 peaks are doublet, while 111 is a singlet as expected for the tetragonal phase with P4mm space group. With decreasing particle size, the splitting of 100 and 110 peaks decreases and the peak broadening increases. There is an asymmetric broadening of the 001 peak and other peaks with decreasing size. The 120 nm powder possesses a single tetragonal phase (space group P4mm), whereas the smaller size powders show coexistence of two tetragonal phases, a dominant tetragonal phase with higher tetragonality, and a minority phase with relatively lower tetragonality, both in the P4mm space group, as confirmed by Rietveld refinement using SXRPD data. The details of Rietveld refinements are presented in the supplementary material (Sec. B).²⁵ The 18 nm size particles do not show any obvious splitting of 200 and 220 and may appear to be cubic in the first appearance. However, Rietveld analysis of the SXRPD data (as explained in Sec. B of supplementary material)²⁵ shows that the sample is still tetragonal with a tetragonality of 5.75% that is comparable to the tetragonality of PbTiO₃. The variation of *a* and *c* parameters of BF-0.5PT, as obtained from Rietveld refinements, with particle size is shown in Fig. 1(b). The spontaneous polarisation of the dominant tetragonal phase of BF-0.5PT as calculated using Born effective charges of various cations and anions in BF²⁶ and PT²⁷ and the refined positional coordinates of BF-0.5PT are 32.1, 28.2, 24, and 23.1 $\mu\text{C}/\text{cm}^2$ for 120, 45, 31, and 18 nm size particles, respectively, confirming that significant ferroelectric polarization is present at room temperature even in the 18 nm particles. The reduction in tetragonality and spontaneous polarization with size is due to the well known “size effect” in ferroelectrics caused by

FIG. 1. (a) SXRPD profiles of 100, 110, and 111 pseudocubic reflections of BF-0.5PT samples with average particle sizes of ~ 18 , 31, 45, and 120 nm. (b) Variation of *c* and *a* lattice parameters and its ratio with particle size of BF-0.5PT.

the competition between depolarization and domain wall energies.²⁸

Figs. 2(a)–2(d) depict the results of magnetization (*M*) measurements as a function of temperature (*T*) at an applied field of 5000 Oe for 120 nm, 45 nm, 31 nm, and 18 nm size powders in zero-field cooled (ZFC) and field cooled (FC) modes. The ZFC *M*-*T* plot of the 120 nm size particles shows a Néel transition temperature $T_N \sim 120$ K (see the inset also) similar to that reported in bulk powders of BF-0.5PT.¹¹ Intriguingly, on reducing the particle size to 45, 31, and 18 nm, the Néel temperature increases drastically to 230, 250, and 350 K, respectively, as can be seen from various insets to Fig. 2. The anomaly at $T_f \sim 17$ K in the ZFC *M*-*T* plot of the bulk is known to be due to spin glass freezing.²²

The enhancement of T_N revealed by *M*(*T*) measurements was confirmed by neutron powder diffraction studies as well. The temperature evolution of the magnetic peak corresponding to propagation vector $\mathbf{k} = \frac{1}{2} \frac{1}{2} \frac{1}{2}$ in the neutron powder diffraction patterns is shown in Figs. 3(a) and 3(b) for bulk and 18 nm size powders, respectively. In the bulk samples, the AFM peak (marked with asterisk in the figure) appears below $T_N \sim 120$ K, whereas it is present even at room temperature in 18 nm size powder. This clearly shows a drastic enhancement of T_N in 18 nm size powder. The variation of the integrated intensity of the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ magnetic peak with temperature shown in Fig. 3(c) reveals $T_N \sim 120$ K in agreement with the T_N determined from ZFC *M*-*T* measurements (Fig. 2(a)). The magnetic neutron peaks of 18 nm particles

FIG. 2. The temperature dependence of the FC and ZFC magnetizations of BF-0.5PT: (a–d) 120, 45, 31 and 18 nm size powders under magnetic field of 5000 Oe, The insets of (a to d) depict magnified plot near T_N .

have sharp and diffuse (broad) components (see Fig. 3(d) which depicts two deconvoluted Lorentzians) linked with the coexisting high and low tetragonality phases, respectively, as confirmed by Rietveld refinements using SXRPD data (see Sec. B of supplementary material).²⁵ The diffuse component of the magnetic scattering is dominant above 250 K. The variation of the integrated intensity of the sharp component with temperature for 18 nm size powder shows a linear behaviour up to ~ 250 K and its extrapolation to zero intensity gives a T_N of ~ 350 K in agreement with the $M(T)$ results. Thus, there is a drastic enhancement of T_N with respect to $T_N = 120$ K of the bulk powder. The diffuse component shows a temperature dependence different from that of the sharp component and the corresponding T_N is still higher, as small residual intensity can be seen at the AFM peak position even in 360 and 400 K profile in Fig. 3(b).

We propose that the diffuse component of the magnetic peak with shorter correlation length is due to spin disorder in a thin shell region of the surface layers of the nanoparticles. Both the shell and the core contain the BF-0.50PT solid solution only. In this scenario, one expects weak ferromagnetism due to spin canting in the shell region of the 18 nm size nanoparticles of BF-0.5PT as observed in similar core-shell type systems in non multiferroic AFM oxides.²⁹ This weak ferromagnetism should be present even at room temperature as the corresponding T_N is well above the room temperature for 18 nm size particles. This was confirmed by the M-H measurements, the results of which are shown in

FIG. 3. The evolution of the magnetic peak corresponding to pseudocubic $k = \frac{1}{2} \frac{1}{2} \frac{1}{2}$ with temperature for (a) 120 and (b) 18 nm size powders of BF-0.5PT. (c) Variation in the integrated intensity of the magnetic peak with temperature for 120 and 18 nm size powders. Dots represent measured data points, while the continuous line corresponds to the least-squares fitted Lorentzian(s). (d) Deconvolution of the magnetic peak of 18 nm size powder showing two different magnetic correlation lengths (ξ).

Fig. 4. It is evident from Fig. 4(a) that the M-H plots for 120 nm, 45 nm, and 31 nm size powders are straight lines confirming their paramagnetic nature at room temperature, whereas the 18 nm size particles exhibit nonlinear M-H curve, with a little loop opening. With decreasing temperature, the M-H loop of 18 nm size particles opens up further as can be seen from the two insets of Fig. 4(b), which compare the M-H plots for 18 nm size particles at 300 K and 5 K. Further, the M-H loop in inset of Fig. 4(b) reveals an exchange bias (E_B) of ~ 337 Oe at 5 K, which decreases with increasing temperature for the same particle size. The E_B decreases with increasing particle size also for the same temperature. For example, the E_B at 5 K is ~ 17 Oe and ~ 8 Oe for 31 nm and 45 nm size powders, respectively, while it is absent for the bulk powder (see inset of Fig. 4(c)). The more pronounced E_B , as shown in the inset of Fig. 4(b), in the smallest size particles (~ 18 nm), is due to higher surface to volume ratio of 18 nm particles leading to more number of spins in the surface layers constituting the shell region. The interface between the FM component of

FIG. 4. M-H plots for (a) 18, 31, 45, and 120 nm size powders at 300 K, (b) 18 nm particles at 300 and 5 K and (c) 18, 31, 45, and 120 nm size powders at 5 K. Insets of (b) and (c) compare exchange bias at 5 K and 300 K for 18 nm and at 5 K for 120 and 31 nm powders.

the canted spins in the shell region and the collinear AFM spins in the core (of BF-0.50PT) is responsible for the exchange bias effect as observed in other systems also.^{29–31} Thus, our M-H plot showing E_B effect not only confirms the coexistence of AFM and weak FM ordering but also reveals that they arise from a core-shell type of nanostructure of individual nanoparticles.

The enhancement of T_N with size reduction is unique to MFAFMs with large uniaxial ferroelectric distortion like tetragonal BF-0.5PT. It is a consequence of the subtle interplay between the ferroelectric distortion and the strength of the superexchange interaction in the multiferroic BF-0.5PT. Table I lists the lengths of $\text{Fe}^{3+}\text{-O}^{2-}$ bond lengths in the [001] direction for the bulk and the 18 nm size powder, as calculated using the positional coordinates obtained by Rietveld analysis of SXRPD patterns. The longer $\text{Fe}^{3+}\text{-O}^{2-}$ bond length (labelled as Fe-O_{1b} in Table I) in the bulk powder is too big (2.571 Å) as compared to the sum of the ionic radii of Fe^{3+} and O^{2-} (~ 2.045 Å) to have any orbital overlap required for superexchange interactions in [001] direction in

TABLE I. Fe-O bond lengths (Å) and tetragonality of the dominant phase constituting the core of BF-0.5PT samples as a function of particle size.

Size (nm)	Tetragonality (η) %	Bond length (Å)		
		Fe-O _{1a}	Fe-O _{1b}	Fe-O ₂
18	5.75	1.787	2.348	2.013
31	6.64	1.790	2.369	1.970
45	9.60	1.792	2.460	1.973
120	14.16	1.822	2.571	1.968

the bulk powders. As a result, the AFM superexchange interaction pathways are confined to [100] and [010] directions only. As the longer $\text{Fe}^{3+}\text{-O}^{2-}$ bond in the [001] direction decreases systematically with particle size reduction (see Table I for bond length of the 18 nm size powder), there is a gradual enhancement of superexchange interaction in the [001] direction also. This leads to a crossover from essentially 2d AFM interactions in the bulk powders to 3d AFM interactions in nanoparticles of BF-0.50PT and it is this crossover that is responsible for the drastic rise in the T_N as a result of size reduction. It is interesting to note that such an enhancement of T_N with decreasing particle size does not happen in BiFeO_3 where T_N instead decreases with particle size as per the predictions of the scaling theories.³² This is because there is no crossover from 2d AFM to 3d AFM interactions in BiFeO_3 due to particle size reduction, as BF shows 3d AFM interactions in the bulk itself. Ti^{4+} substitution decreases the T_N as result of dilution of the magnetic sublattice of BF monotonically up to $x \sim 0.27$ but drops abruptly in the tetragonal phase region of BF-xPT for compositions with $x \geq 0.31$ because of the crossover from $\sim 3d$ AFM interactions for $x \leq 0.27$ to $\sim 2d$ interactions for $x \geq 0.31$ as a result of large anisotropic ferroelectric distortion in the tetragonal structure.²⁰ For example, the experimentally observed $T_N \approx 120$ K for bulk BF-0.5PT powders is far less than the expected value of $T_N \approx 365$ K for 3d AFM interactions obtained by extrapolation of T_N versus x plot for BF-xPT with $x \leq 0.27$ with monoclinic structure to $x = 0.50$ in the tetragonal phase region. On the other hand, $T_N \sim 350$ K of ~ 18 nm size BF-0.50PT particles is comparable to the estimated value of $T_N \sim 365$ K for 3d AFM interactions in BF-0.5PT. For ~ 18 nm size particles, T_N of BF decreases substantially due to purely size effect,³³ whereas that of BF-0.5PT increases substantially due to crystal distortion effect, but interestingly both become comparable in spite of magnetic lattice being diluted by 50% with Ti^{4+} in the latter. In this respect, BF-0.5PT nanoparticles are superior to BF nanoparticles but the ferroelectric polarization and magnetization appear to be larger for BF nanoparticles.

To summarize, our results reveal that the effect of decrease in AFM correlation length with particle size leading to reduction in T_N as per scaling theories is overwhelmed by the enhancement in the superexchange interactions due to crystal distortion effects leading to reduced bond length in nanoparticles of BF-0.50PT in the [001] direction. Thus, the physics of size effect in multiferroic AFM systems with large uniaxial ferroelectric distortion is entirely different from that in conventional AFM systems with 3d AFM interactions. We believe that our results will stimulate more work as it has

tremendous potential for designing room temperature multi-ferroics useful for multifunctional devices by tuning the T_N to room temperature through a manipulation of the ferroelectric distortion via size reduction.

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