PHYSICAL REVIEW B **72**, 014104 (2005)

Diffuse ferroelectric phase transitions in Pb-substituted $PbFe_{1/2}Nb_{1/2}O_3$

V. V. Bhat,[1] A. M. Umarji,[1] V. B. Shenoy,[1,3,*] and U. V. Waghmare[2]
[1]*Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India*
[2]*Theoretical Sciences Unit, J Nehru Centre for Advanced Scientific Research, Bangalore, 560 064, India*
[3]*Centre for Condensed Matter Theory, Indian Institute of Science, Bangalore, 560 016, India*

(Received 28 October 2004; revised manuscript received 7 March 2005; published 1 July 2005)

We investigate effects of cation (K, Ca, Sr, Ba, La, Bi, Tl, Ag) substitution at Pb-site in $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) on its diffuse ferroelectric phase transition (DPT) through measurements and modeling of the temperature dependence of its dielectric constant. We find that the chemical trends in experimentally determined rates of change of transition temperature and diffuseness with substituent concentration are governed by two parameters, nominal and Born effective charges calculated within first-principles density functional theory. We introduce "ferroactivity" of an atom using these charges and use it in a generalized Weiss molecular field theory that accounts for the disorder to explain chemical trends in the DPT found experimentally, suggesting guidelines to tune properties of ferroelectrics.

DOI: 10.1103/PhysRevB.72.014104 PACS number(s): 77.80.Bh, 61.43.−j, 77.84.Dy

I. INTRODUCTION

ABO_3 ferroelectric perovskites[1] form an important class of materials, rich in their physical properties, of technological importance. While the pure compounds typically show sharp ferroelectric transitions, their solid solutions ($A_yA'_{1-y}B_xB'_{1-x}O_3$) often have diffuse transitions[2] characterized by a broad peak in dielectric constant as a function of temperature. Relaxors[3] form a subclass of such ferroelectrics with diffuse ferroelectric phase transitions (DPTs) which exhibit interesting dynamical response similar to that of glassy systems and have very large electromechanical response. Random local fields and couplings[4–6] arising from compositional disorder and their interaction[7] with polar soft modes are considered to be necessary to cause diffuse ferroelectric transitions. While it is fundamentally interesting to uncover the mechanisms of DPTs, it is also of technological relevance to understand the chemical trends in DPTs in the context of perovskite ABO_3 ferroelectrics, as these solutions can be used in tailoring the properties complex pervoskites used, for example, in multilayer capacitors.

In the context of $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN), two models for DPT were used: (a) Smolenskii's composition inhomogeneity model,[8,9] and (b) Bokov's octahedral distortion model.[10,11] Both the models assume that the fluctuations in the local Curie temperatures cause the DPT. Smolenskii's model[8,12] hypothesizes that the disordered distribution of *B*-site cations results in the chemically inhomogeneous microregions with different transition temperatures. In substituted compounds, this model also predicts a correlation between the rate of change of temperature T_M of dielectric maximum and that of diffuseness. The model (b) proposes[10,11] that when the *B* site is occupied by the cations having large radius difference Δr $(=r_{B'}-r_{B''})$, the octahedra are distorted. Due to the random distribution of *B*-site ions, the distortions of the octahedra are also randomly ordered. This leads to the distribution of local T_C resulting in DPT. Bokov *et al.*[11] suggested that this model explains observations on DPT in substituted $PbFe_{1/2}Nb_{1/2}O_3$, namely, (*i*) the diffuseness of DPT is uninfluenced by the Pb site substitution with elements in group II and (*ii*) the rate of change of T_M with substitution is uncorrelated with the diffuseness of DPT.

The aim of this paper is twofold: (*i*) to determine how the chemical nature of the substituent ions influences the T_M (temperature of the dielectric maximum) and the diffuseness (width of the dielectric peak) of the DPT in PFN and (*ii*) to investigate how the diffuseness of transition and T_M are correlated. These objectives are achieved via detailed experiments in cojunction with theoretical work. In course, we identify that the chemical factor controlling the transition temperature and diffuseness can be characterized by a quantity called "ferroactivity" (related to the Born effective charge of the cation). The experimental part of this work consists of systematic investigations of the T_M and diffuseness as a function of the substituent concentration. The theoretical work consists of two components, viz., the determination of "ferroactivity" from first-principles electronic structure calculations and the use of this quantity in a generalized mean field theory to uncover how the chemical factors and lattice level disorder affect the transition temperature and diffuseness of the DPT.

The paper is organized as follows. In Sec. II, we describe first-principles calculations of the Born effective charges (Z^*). In Sec. III, we present details of systematic experiments on PFN with different cation substituted at the Pb site, and discuss how the chemical trends can be understood with only two parameters, namely the nominal (Z) and Born effective charges Z^*. In Sec. IV, we present quantitative analysis of the DPT using these parameters in a generalized mean field theory, and finally conclude in Sec. V.

II. FIRST-PRINCIPLES CALCULATIONS OF Z^* AND FERROACTIVITY

Polar soft modes responsible for the ferroelectric ground state have been shown to be correlated with giant LO-TO splitting[13,14] that arise from anomalously large Born effective charges Z^*:

TABLE I. The properties [nominal ionic charge (Z), ionic radius (r) (Ref. 26), and ferroactivity ζ] of the substituted cations and their effect on $(1/x)\Delta T_M/T_M^0$ and $\Delta\sigma/x$. T_M^0 is the transition temperature of unsubstituted PFN.

Atom	r^a (Å)	Z^*	$\zeta = \frac{Z^*-Z}{Z}$	$\frac{\Delta F}{x}^b$	$\frac{1}{x}\frac{\Delta T_M}{T_M^0}$	$\frac{\Delta\sigma}{x}$
K^{1+}	1.64(XII)	1.07	0.07	−0.455	−0.017 43	0.0156
Ca^{2+}	1.34(XII)	2.54	0.27	−0.68	−0.026 81	0.0292
Sr^{2+}	1.44(XII)	2.55	0.275	−0.675	−0.026 81	0.0267
Ba^{2+}	1.61(XII)	2.74	0.37	−0.58	−0.029 49	0.0278
La^{3+}	1.36(XII)	4.42	0.48	−0.895	−0.04 83	0.0412
Bi^{3+}	1.17(VIII)	6.63	1.21	−0.165	−0.00 94	0.0108
Tl^{3+}	1.12(VIII)	⋯	⋯	⋯	⋯	⋯
Ag^{1+}	1.42(VIII)	1.63	0.63	0.105	−0.00 27	0.0068
Tl^{1+}	1.84(XII)	1.84	1.05	0.525	0.0054	−0.0056
Pb^{2+}	1.49(XII)	3.9	0.95	⋯	⋯	⋯
Fe^{3+}	0.55(VI)	3.5	0.167	⋯	⋯	⋯
Nb^{5+}	0.64(VI)	9.24	0.85	⋯	⋯	⋯

[a] Radius of substituents in the corresponding coordination site mentioned in the bracket.

[b] $\Delta F/x=(\zeta_A-\zeta_{Pb})+\zeta_{Nb}(2-Z/2)$ (ΔF is the change of ferroactivity with A site substitution)

$$Z^*_{i,\alpha,\beta}=\Omega\frac{\partial P_\alpha}{\partial u_{i\beta}},$$

where P is polarization, Ω is the unit cell volume, and u is the atomic displacement. Z^*'s determine the strength of dipolar interactions[15] and were found to capture the structural origin of ferroelectricity in nonperovskite ferroelectric $BaTi_2O_5$.[16] Since Z^*'s *are* the couplings of soft mode with electric field E,

$$H_{coup}=-Z^*_{i,\alpha,\beta}E_\alpha u_{i\beta},$$

influence of random local fields[5] on the polar modes is felt primarily through Z^*'s. Z^*'s are thus expected to be relevant to chemical trends in DPT behavior.

We use a standard density functional theory (DFT) method as implemented in the ABINIT code[17] for first-principles total energy and linear response calculations. We used Teter pseudopotentials with and an energy cutoff of 80 Ry on the plane-wave basis. Integrations over the Brillouin zone (BZ) were performed by sampling the BZ with a uniform mesh of 6×6×6 k points. Various parameters and pseudopotentials have been tested to reproduce earlier results. Z^*'s (Table I) have been obtained using DFT linear response. As these calculations are quite demanding for large supercells of PFN, we used simpler perovskite compounds containing each substituted cation. For each case, we used at least two compounds, making sure that the values of Z^* do not change by more than 10%.[18]

We define "ferroactivity" (FA) as the tendency of a cation to be off-centered giving an electric dipole, quantified with $\zeta=(Z^*-Z)/Z$, which is a measure of the anomalous part of the Born effective charge Z^*. This choice is motivated by the findings of previous works.[13,14]

III. EXPERIMENTS ON PFN

A. Experimental methods

PFN is a ferroelectric material that undergoes a DPT between 383 K and 393 K.[19] The dielectric loss of this material is very high (~50%).[20] To reduce the dielectric loss, generally 0.15 wt % of Mn is added,[21] which brings down the T_M to 373 K.[22] In this study, we substitute cation A (A =K,Ca,Sr,Ba,La,Bi,Tl,Ag) at the Pb site of PFN according to the formula $Pb^{2+}_{(1-x)}A^{Z+}_xFe^{3+}_{(1-(2-Z)x/2)}Nb^{5+}_{(1+(2-Z)x/2)}O_3$, Z being the nominal charge and x the concentration of A ($0\leqslant x\leqslant 0.1$). The substitutions are carried out using modified solid state method.[23] The starting materials are taken according to the stoichiometric ratio, ground in acetone medium, and calcined at 973 K for 4 h followed by Mn addition. After the Mn addition the samples are ground and sintered in the PbO rich atmosphere. The phase purity of the sintered samples are studied by powder x-ray diffraction. Except for Ag^{1+} and Tl^{1+} substituted compounds, the rest exhibit pure perovskite compound formation. In Ag^{1+} and Tl^{1+} substituted compounds, a major concentration of perovskite phase is observed along with a small percentage (≤10%) of pyrochlore.

The dielectric properties of the substituted compounds are measured at 10 KHz as a function temperature at a heating rate 1 K min^{-1} and data collection in an interval of 2 K. The instrumental error in measuring the T_M is determined by three independent runs on a pure PFN sample and found to be ±2 K. In order to eliminate any discrepancy in measuring the dielectric constant due to the contribution from the imaginary part, the dielectric loss of PFN is measured and observed to be well below the 5% acceptable limit for all the samples. The width of DPT used to quantify "diffuseness" (σ) is defined[24] as the full width at half maximum of normalized peak of dielectric constant vs. $(T-T_M)/T_M^0$. Our efforts to fit a phenomenological theory[25] to dielectric behavior confirmed that PFN is *not* a relaxor.

B. Experimental results and discussion

The observed effects of substituents on the T_M and diffuseness of the substituted compounds are shown in Fig. 1. T_M is found to decrease linearly with x, except in the case of Tl^{1+} and Tl^{3+} substituted samples, for which it marginally increases with x. The diffuseness of all the samples is observed to increase with x except in the Tl^{1+} substituted samples. It is clear that the substitution for Pb in PFN does strongly influence the diffuseness, irrespective of change or no change in the chemical composition in the B site, in contrast with Ref. 11. In Table I, we present $(1/x)\Delta T_M/T_M^0$ and $\Delta\sigma/x$ for various substitutions along with chemical parameters characterizing each substitution.

In order to uncover the factors that influence the T_M and diffuseness, we have categorized the substituent ions into four different groups: (a) $Z=2$, the same nominal charge of Pb, but *different sizes* and relatively lower ferroactivity

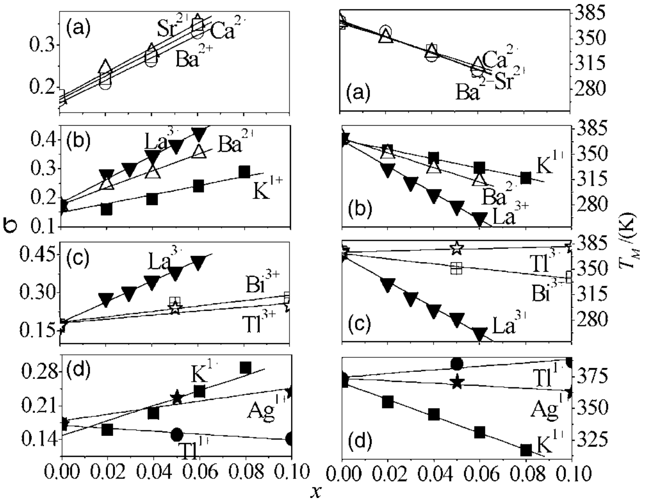

FIG. 1. The variation of diffuseness and T_M as a function of substituent concentration showing the effect of (a) size (ionic radius), (b) valence, (c) trivalent cations, and (d) monovalent cations of substituent ion.

(Ba^{2+}, Sr^{2+}, and Ca^{2+}); (b) *different nominal charges* and comparable sizes (La^{3+}, Ba^{2+}, and K^{1+}), with low ferroactivity; (c) *varied ferroactivity*, trivalent ions of comparable sizes (La^{3+}, Bi^{3+}, and Tl^{3+}); and (d) *varied ferroactivity*, monovalent ions of different sizes (K^{1+}, Ag^{1+}, and Tl^{1+}).

Figure 1(a) shows the effect of ferroinactive ions with the same nominal charge as that of Pb^{2+} but different sizes. The substituents Ba^{2+}, Sr^{2+}, and Ca^{2+}, despite having different sizes, decrease the T_M and increase the diffuseness by the same magnitude at any given x. This is clearly seen from Table I. It is, therefore, evident that the size of the Pb-site substituent does not influence the T_M or the diffuseness of PFN-based materials. Henceforth, any influence on T_M and diffuseness due to the variation in the ionic size of group (b), (c), and (d) substituents are ignored.

The effect of ferroinactive ions with different nominal charge Z (La^{3+}, Ba^{2+}, and K^{1+}) is shown in Fig. 1(b). This figure and data in Table I demonstrate that the nominal charge Z has a strong influence on $(1/x)\Delta T_M/T_M^0$ and the $\Delta\sigma/x$ of DPT. The $(1/x)\Delta T_M/T_M^0$ decreases and the $\Delta\sigma/x$ increases with increasing Z. The effect of ferroactive tri- and monovalent ion substitutions are compared with ferroinactive ions in Fig. 1(c) and Fig. 1(d), respectively. The figures (also see Table I) show that the ferroactive ion substitution [Tl^{3+} and Bi^{3+} in Fig. 1(c) and Tl^{1+} and Ag^{1+} in Fig. 1(d)] vary the T_M and diffuseness of PFN by lower magnitude compared to ferroinactive ions [La^{3+} in Fig. 1(c) and K^{1+} in Fig. 1(d)]. In other words, for trivalent ions $[(1/x)\Delta T_M/T_M^0]_{La^{3+}} \ll [(1/x)\Delta T_M/T_M^0]_{Bi^{3+}}$ and $[(1/x)\Delta T_M/T_M^0]_{Tl^{3+}}$, and $(\Delta\sigma/x)_{La^{3+}} \gg (\Delta\sigma/x)_{Bi^{3+}}$ and $(\Delta\sigma/x)_{Tl^{3+}}$. Similarly for monovalent ions, $[(1/x)\Delta T_M/T_M^0]_{K^{1+}} \ll [(1/x)\Delta T_M/T_M^0]_{Ag^{1+}}$ and $[(1/x)\Delta T_M/T_M^0]_{Tl^{1+}}$, and $(\Delta\sigma/x)_{K^{1+}} \gg (\Delta\sigma/x)_{Ag^{1+}}$ and $(\Delta\sigma/x)_{Tl^{1+}}$.

IV. MEAN FIELD THEORY ANALYSIS

We now present a simple model based on the Weiss molecular field theory (WMFT) (Ref. 27) that develops the ideas of Smolenskii[8,9] and Bokov[10] and is similar to the Landau theory for inhomogeneous systems worked out by Li *et al.*[28] (see also Ref. 29). The parameters input to this analysis are based on the "ferroactivity" defined earlier and the nominal charge of the substituted ion. This allows us to connect the microscopic parameters determined from first-principles calculations to chemical trends in the DPTs.

Within WMFT of systems with no chemical disorder, the average polarization p at a temperature T is obtained self-consistently as arising from an effective field of dipoles with dipole moment p_0 in a lattice (in the limit of zero externally applied field):

$$p = p_0 \tanh\left(\frac{J_e p_0 p}{k_B T}\right) = p_0 \tanh\left(\frac{T_c}{T}\frac{p}{p_0}\right), \tag{1}$$

where J_e is an effective coupling (which depends both on the short range and dipole-dipole coupling, and the number of neighbors) and k_B is the Boltzmann constant. The theory predicts a sharp phase transition at $k_B T_c = J_e p_0^2$; the main point to be noted is that the transition temperature is governed by the effective coupling constant.

We develop a generalization of WMFT to the case of a diffuse transition (DWMFT). Developing from the Smolenskii-Bokov argument, we begin with a premise that the lattice has microdomains that have different local transition[28] temperatures due to different effective coupling J_e. The effective coupling depends on the details of the microregion such as arrangement of ferroactive ions, etc., and varies randomly from one microdomain to another. In this sense, coupling constant J in a microdomain may be thought of as being sampled from a probability distribution $P(J)$. The main idea of the model is that spatial averaging (over microdomains) of the polarization is equivalent to averaging over the probability distribution $P(J)$. This is physically plausible, since, on averaging over a large number $N \rightarrow \infty$ of microdomains, the entire distribution of the coupling constants J will be sampled. The main assumption of the model is that we neglect correlations between microregions with different coupling constants. This is expected to be quite accurate when the substituent atom concentration is small ($<10\%$), especially since our aim is to understand the chemical trends. The average polarization can now be written as

$$\langle p \rangle(T) = \frac{1}{N}\sum_i p_i \approx \int dJ\, P(J) p(T,J,E), \tag{2}$$

where $p(T,J,E)$ is the polarization in a microdomain with coupling constant J at temperature T and external field E obtained through self-consistency condition (1). This approach is similar in spirit to the generalized mean field theory of spin glasses proposed by Thouless, Anderson, and Palmer, Binder Young[30] who suggested a relation similar to Eq. (1), but with a crucial additional term in the argument of the tanh function in Eq. (1) called the "reaction field term." However, as shown by,[31] this term is negligible in the ferromagnetic case with long-range interactions (see Ref. 31, Sec. IV C, p. 876) and, thus, equivalently, in the present ferroelectric case especially since the dipole-dipole interactions are long ranged. Thus, Eq. (2) is expected to describe the diffuse

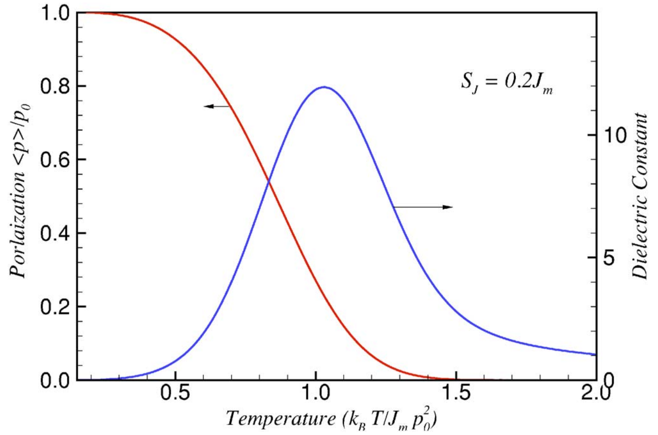

FIG. 2. (Color online) The polarization and dielectric constant as a function of temperature obtained from the diffuse Weiss molecular field theory. The coupling constant is distributed as $P(J) = \exp[-(J-J_m)^2/(2S_J^2)]/(\sqrt{2\pi}S_J)$. The result shown is for $S_J = 0.2J_m$.

ferroelectric transition quite accurately even without the reaction field term.

We assume that the coupling constants are Gaussian distributed with a mean J_m and variance S_J^2. Mean field results of such a model are illustrated in Fig. 2; it is evident that the model captures the essence of diffuse phase transitions. Our calculations indicate that the T_M of the dielectric peak is the same as mean-field T_c determined by the mean (and most probable) coupling constant J_m. Further, the diffuseness σ is linearly related to S_J.

Due to substitution at the Pb site in PFN, chemical disorder arises at both A and B sites. To quantify effects of this disorder on the DWMFT parameters J_m and S_J, we note three points: (1) Long range dipolar coupling depends quadratically on the Born-effective charges and changes in the intersite coupling are reflected in the on-site quadratic interaction.[32] This, correlates with ferro-activity of an atom ζ. (2) Coupling between the local random field and dipole depends linearly on the effective charge. (3) Change in Nb concentration depends linearly on the nominal charge of the substituted A cation. The effective coupling constant of the substituted compound can be taken, in a first approximation, as a linear sum of Pb-site coupling constant and the B-site coupling constant. On Pb substitution with A the change in J_m and S_J can be calculated as

$$\Delta J_m \sim \underbrace{\alpha(\zeta_A - \zeta_{Pb})x}_{\text{Pb-site}} + \underbrace{\beta\zeta_{Nb}\left(\frac{2-Z}{2}\right)x}_{\text{B-site}} \qquad (3)$$

$$\Delta S_J \sim \alpha(|\zeta_A - \zeta_{Pb}|)\sqrt{x} + \beta\left(\frac{\zeta_{Nb}}{8}\right)(Z-2)x \qquad (4)$$

where α and β are positive constants (not determined here). The above two relations are determined by assuming that Pb and A are distributed uniformly (without short-range order) in the sample, with a similar assumption for Nb and Fe. Taking α and β to be of equal order of magnitude, we see that $\Delta J_m \sim \Delta F$, where ΔF is the effective change in ferroactivity (see Table I). The DWMFT developed above suggests that $\Delta T_M \sim \Delta J_m$ and predicts $(1/x)\Delta T_M/T_M^0 \sim \Delta F/x$. Similarly, $\Delta\sigma/x$ is predicted to fall (although not linearly) with increasing $\Delta F/x$. Relations (3) and (4) provide a causal connection between a microscopic property (ζ) and the parameters of the diffuse phase transition.

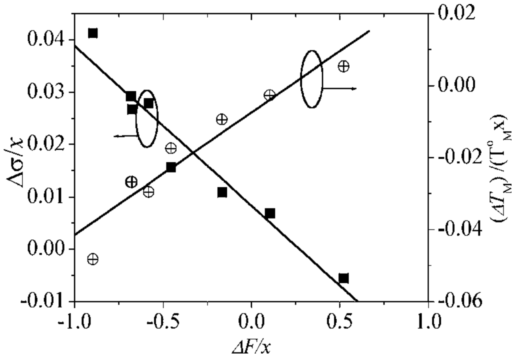

FIG. 3. The variation of $(1/x)\Delta T_M/T_M^0$ and $\Delta\sigma/x$ as a function of $\Delta F/x$. For the data points, $(1/x)\Delta T_M/T_M^0$ and $\Delta\sigma/x$ are determined from experimental data, while $\Delta F/x$ is from Table. I. Solid lines are linear fits suggested by Eqs. (3) and (4).

Figure 3 shows the correlation of $(1/x)\Delta T_M/T_M^0$ and $\Delta\sigma/x$ with $\Delta F/x$. It is seen that the trends are in close agreement with predictions of DWMFT with input from density functional calculations. The theory also provides additional insights that explain several experimental observations. It argues that there is a DPT in pure PFN because of the chemical disorder among ferroactive Nb and ferroinactive Fe. At the same time, it also predicts that $PbZr_{1-x}Ti_xO_3$ (PZT) would not have a DPT as both Ti and Zr ferroactive ions (with a small relative difference) as is seen experimentally.[33] In the main, it suggests that *it is hetero-ferroactive substitution (rather than heterovalent substitution) that controls the DPT in ferroelectric perovskites.*

V. SUMMARY AND CONCLUSION

In the case of divalent ferroinactive ions [group (a)], it is evident that the coupling constant J_m falls and the standard deviation S_J increases with x. This is well in agreement with the experimental results [Fig. 1(a) and Table I]. In the case where the substituent is ferroinactive [group (b)], the fall in the coupling constant is largest in the case where $Z=3$ and so is the increase in S_J, as is evident from Eqs. (3) and (4). This is also in agreement with experiment [Fig. 1(b)]. In the case of ferroactive ions ($\zeta_{Pb} - \zeta_A \approx 0$), when $Z=1$, the Nb concentration increases, increasing J_m and decreasing S_J, leading to DPT with higher T_m and lower σ. On the other hand, for cases with $Z=3$, J_m decreases and S_J increases due to reduction in Nb concentration, resulting in a broader transition at a lower T_M. These inferences from Eqs. (3) and (4) are consistent with the experimental observations.

We have investigated phase transitions in substituted PFN with the aim of understanding the factors that affect DPT. The experimental component of this work consists of controlled Pb-site substitutions to PFN with different size, nominal charge, and ferroactivity. We explain the results of the experiments based on a diffuse Weiss molecular field theory (DWMFT). Our main conclusion is that the distribution of coupling constants brought about by substitution is the primary governing factor in determining the nature of DPT. In particular, Pb substitution with trivalent ferroinactive substituent produces the highest reduction in T_M accompanied by the broadest transition. In contrast, a sharper transition at a higher T_M can be achieved using monovalent ferroactive substituents. Our results can also explain the reason for a sharp transition in PZT $[\mathrm{Pb}(\mathrm{Zr}_{1-x}\mathrm{Ti}_x)\mathrm{O}_3]$ where both Zr and Ti are ferroactive. This work provides evidence that a few parameters can describe the chemical trends in DPT behavior, and gives clues to the design of ferroelectric materials with desired dielectric properties.

---

*Electronic address: shenoy@mrc.iisc.ernet.in

[1] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1979).

[2] G. A. Smolenskii and A. I. Agranovaskaya, Sov. Phys. Solid State **1**, 1429 (1960).

[3] L. E. Cross, Ferroelectrics **76**, 241 (1987).

[4] V. V. Laguta, M. D. Glinchuk, S. N. Nokhrin, I. P. Bykov, R. Blinc, A. Gregorovic, and B. Zalar, Phys. Rev. B **67**, 104106 (2003).

[5] M. D. Glinchuk and R. Farhi, J. Phys.: Condens. Matter **8**, 6985 (1996).

[6] N. Setter and L. E. Cross, J. Appl. Phys. **51**, 4356 (1980).

[7] P. M. Gehring, S. Wakimoto, Z. G. Ye, and G. Shirane, Phys. Rev. Lett. **87**, 277601 (2001).

[8] G. A. Smolenskii and V. A. Isupov, Sov. Phys. Tech. Phys. **24**, 1375 (1954).

[9] V. A. Isupov, Sov. Phys. Solid State **5**, 136 (1963).

[10] A. A. Bokov, Ferroelectrics **131**, 49 (1992).

[11] V. A. Bokov, L. A. Shpak, and I. P. Rayevsky, J. Phys. Chem. Solids **54**, 495 (1993).

[12] V. A. Isupov, Ferroelectrics **90**, 113 (1989).

[13] W. Zhong, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).

[14] U. V. Waghmare, N. Spaldin, H. C. Kandpal, and R. Seshadri, Phys. Rev. B **67**, 125111 (2003).

[15] P. Ghosez, J. P. Michenaud, and X. Gonze, Phys. Rev. B **58**, 6224 (1998).

[16] U. V. Waghmare, M. C. F. Sluiter, T. Kimura, T. Goto, and Y. Kawazoe, Appl. Phys. Lett. **84**, 4917 (2004).

[17] The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, the Université de Liège, the Commissariat à l'Energie Atomique, Mitsubishi Chemical Corp and other contributors (URL http://www.abinit.org).

[18] V. V. Bhat, Ph.D. thesis, IISc, Bangalore, India, 2003.

[19] A. A. Bokov, I. E. Myl'nikova, and G. A. Smolenskii, Sov. Phys. JETP **15**, 447 (1962).

[20] M. Yokosuka, Jpn. J. Appl. Phys., Part 1 **32**, 1142 (1993).

[21] B. H. Lee, K. K. Min, and N. K. Kim, J. Mater. Sci. **35**, 197 (2000).

[22] D. Mohan, S. Prasad, and R. Banargee, J. Mater. Sci. Lett. **15**, 2149 (1996).

[23] V. V. Bhat, B. Angadi, and A. M. Umarji, Mater. Sci. Eng., B **116**, 131 (2005).

[24] W. Z. Zhu, M. Yan, A. L. Kholkin, P. Q. Mantas, and J. L. Baptista, J. Mater. Res. **17**, 1779 (2002).

[25] S. A. Prosandeev, I. P. Raevsky, and U. V. Waghmare, AIP Conf. Proc. **677**, 41 (2003).

[26] R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

[27] P. M. Chaikin and T. C. Lubensky, *Principles of Consensed Matter Physics* (Cambridge University Press, Cambridge, UK, 1995).

[28] S. Li, J. A. Eastman, R. E. Newnham, and L. E. Cross, Phys. Rev. B **55**, 12067 (1997).

[29] R. Pirc and R. Blinc, Phys. Rev. B **60**, 13470 (1999).

[30] D. J. Thouless, P. W. Anderson, and R. G. Palmer, Philos. Mag. **35**, 593 (1977).

[31] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[32] P. Ghosez, E. J. Cockayne, U. V. Waghmare, and K. M. Rabe, Phys. Rep. **60**, 836 (1999).

[33] M. Adachi *et al.*, *Numerical Data and Functional Relationships in Science and Technology*, Vol. III/16A, edited by K. H. Hellwege and A. M. Hellwege (Springer Verlag, New York, 1981).