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Supporting Information

Interactive Human - Machine Learning Framework for Modelling of Ferroelectric-Dielectric Composites

Ning Liu, Achintha Ihalage, Hangfeng Zhang, Henry Giddens, Haixue Yan, Yang Hao

Brief Description of Original Vendik Model

Model derivation

The vendik model was initially developed based on the conventional Landau theory, which gives Helmholtz free energy F with respect to the vector macroscopic polarization P (order parameter in Landau theory):

$$F = F_0 + aP^2 + \frac{b}{2}P^4$$
 (A.1)

According to the Landau theory, the coefficient *a* is assumed to be a linear function of temperature and equals to zero at the Curie-Weiss temperature T_c , i.e. $a = a_T(T - T_c)$ and *b* are constants as well.

As verified in Ref.⁷ in terms of ferroelectric polarization, a cubic equation corresponding to parameter y was found as:

$$y^{3} + 3\eta(T)y - 2\xi(E) = 0$$
 (A.2)

Where in equation A.2, *y* is normalized polarization induced by DC bias and can also be represented by $y = \frac{Q_{DC}}{D_N S} \sqrt{3\epsilon_{00}}$. η and ξ are two variables corresponding to temperature and electric fields, which can expanded as:

$$\xi(E) = \sqrt{\left(\frac{E}{E_N}\right)^2 + \xi_s^2}$$
(A.3)

$$\eta(E) = \sqrt{\left(\frac{\theta_F}{4T_c}\right)^2 + \left(\frac{T}{T_c}\right)^2} - 1$$
 (A.4)

In equations A.3 and A.4, the following model parameters are used. T_c is the curie temperature of the materials; θ_F is the effective Debye temperature; ξ_s is the statistical dispersion of the biasing field; E_N is the normalizing field. And the parameter can be written as $E_N = 2D_N/\varepsilon_0(3\varepsilon_{00})^{3/2}$, where D_N is constant in original cubic equation, ⁷ and ε_{00} is analog of Curie-Weiss constant *C* and can be represented as $\varepsilon_{00} = C/T_c$. If we pay attention to the mathematical analysis of the cubic equation A.2, the solution to the equation depends on the value of the coefficients η and ξ . If the following inequality is fulfilled:

$$\xi(E)^2 + \eta(T)^3 \ge 0 \tag{A.5}$$

Equation A.2 has one real root. From the physical point

of view, the single root to equation (2) indicate the absence of the spontaneous polarization and the presence of the polarization induced by the biasing field. In other words, when the inequality in A.5 satifies, it indicate the ferroelectrics stay at the paraelectric state.

On the other hand, under the condition:

$$\xi(E)^2 + \eta(T)^3 < 0$$
 (A.6)

Equation A.2 will have three real roots. One of the roots is connected with an unstable state and therefore has no physical sense. For $\xi = 0$, we can have $y_{1,2} = \pm \sqrt{-3\eta}$, and $y_3 = 0$.

It can be found that the other two roots $y_{1,2}$ correspond to the spontaneous polarization. Existence of the spontaneous polarization indicates the ferroelectric state of the sample.

Furthermore, in order to calculate the complex permittivity of ferroelectrics, another model is discussed in⁸ by considering the factors from energy dissipation. There are four mechanisms of energy dissipation $\Gamma_{1,2,3,4}$ elaborated in⁸:

1. Multiphonon scattering of the soft ferroelectric mode:

$$\Gamma_1 = -i\frac{\pi}{2}\frac{\omega_{00}}{\omega_m} \left(\frac{T}{T_c}\right)^2 G^{0.5}\omega \tag{A.7}$$

2. Quasi-debye mechanism of the energy dissipation:

$$\Gamma_2 = \frac{A_2}{1 + i\omega/\omega_2} \left(\frac{y^2}{1 + E/E_N}\right) \tag{A.8}$$

3. Transformation of microwave electric field oscillations into acoustic oscillations due to the field generated by charged defects:

$$\Gamma_3 = \frac{A_3}{1 + i\omega/\omega_3} \xi_s^2 \tag{A.9}$$

4. Low frequency relaxation:

$$\Gamma_4 = A_4 / (1 - i\omega/\omega_4) \tag{A.10}$$

where $A_{2,3,4}$ and $\omega_{2,3,4}$ are model constants and resonant angular frequency values of which were found by empirical relations and literature data⁸ respectively responsible for loss mechanism 2, 3 and 4. Angular frequency is $\omega = 2\pi f$ and f is operating frequency of biasing field E. In addition, T_c is Curie temperature of pure ferroelectrics, y is normalized polarization induced by DC bias E_N is the normalizing field and ξ_s is the statistical dispersion of the biasing field. The parameter ξ_s (also known as defect factor) reflects the 'quality' of the material and corresponds to defects (including oxygen vacancies and inhomogeneity) in ferroelectrics, which will be well explained in the next section.

Analysis on parameter ξ_s in the model

As analyzed, for the model we used in the present paper, three external factors (temperature, electric field, frequency) will impact the dielectric response of ferroelectric material. In terms of material itself, the proportion of barium in BST and defects in the ferroelectrics, which was found related to ξ_s^{27} , can both affect the dielectric response as well. Especially for fixed proportion, it is quite worthy to investigate the dielectric response under different scales of ξ_s .

The defects in the ferroelectric materials will induce local fields and lead to a statistical dispersion under the external DC bias field²⁷. In oxides, the oxygen vacancies are the most common positively charge defects, which induce local mechanical strain and electric field around them. Not only charged, but also neutral defects may also cause local polar phases and associated local fields in single crystal paraelectrics. The parameter ξ_s takes these effects into account via statistical averaging of the applied DC and local electric fields^{27,28}.

In original model, the measure of defects in ferroelectrics ξ_s was emphasized as a measure of mechanical and electrical strains responsible for diffuseness of the phase transition. It is found that ξ_s is tightly correlated with the calculation of ferroelectric phase transition temperature (T_c') and also temperature of the maximum dielectric permittivity (T_m) . In the model, the 'defect parameter' ξ_s figures out the important correlations among curie temperature of pure ferroelectric (T_c) , T_c' and T_m , which can be simply interpreted as²⁷:

$$T_c'(\xi_s) < T_c < T_m(\xi_s) \tag{A.11}$$

This agrees to the work in⁵¹, which indicate the curie temperature of ferroelectrics can be affected by impurities and defects in material.

Model constants

For the original Vendik model, the relevant values/formulas of each model constants can be found in the Table A.1.

Simulation results using improved theoretical model

In the current section, we will briefly present the simulation results by employing the modified model for both pure BST and BST-MgO composites. More specifically, in section B.2, we will elaborate the how we consider the impact from MgO doping onto modelling works.

Pure BST

In the present work, it could be found that the dielectric constant and loss tangent can be related to external ap-

plied factors: electric fields (E), temperature (T) and frequency (f). In the following section, we will show some simulation results for the permittivity of BST materials versus corresponding with these three parameters. In the following section, we will employ Vendik's model on pure BST 64 (proportion of barium=0.6) and also MgO-doped BST64 as example materials to investigate the relationship between dielectric constant (or dielectric loss) and three different factors (electric fields, temperature and frequency). Furthermore, defect parameter ξ_s , i.e. statistical dispersion of the biasing field will be considered as well in the simulation.

For pure BST material, Fig. B.1 an B.2 give a how dielectric constants and loss tangent of different BST64 materials change with temperature at three different frequencies. In Fig. B.1, at three frequencies, when the temperature rises, it can be easily found that the permittivity value initially goes up to a maximum value at T_m and falls thereafter. With higher values of ξ_s , we can find lower value of permittivity and lower T_m as well. It should be noted that due to the presence of built-in electric field and mechanical strains, represented by a statistical dispersion of the biasing field ξ_s , T_m can be displaced to higher value with respect to Curie temperature T_c (theoretical value). However, with higher value of ξ_s , we will have lower value in phase transition temperature, as discussed in section A.2. This explains at 100kHz, the peak of the dielectric constant vs. temperature moves to the left in the Fig. B.1.

In Fig. B.2, it shows how dielectric loss tangent changes with temperature under different frequencies and statistical dispersions of the biasing fields. It can be found that at the lower frequency ranges (100kHz and 100MHz), the loss tangent decreases with higher ξ_s . However, when the frequency goes up to 10 GHz, the trend goes the other way around, higher level of defects will lead to more dielectric loss in the material.

As shown in Figures B.3 and B.4, which both permittivity and loss tangent are plotted against the frequency at different temperatures (250K 290K and 320K). For both sets of simulations (dielectric constants and loss tangent), the external bias field was set to be E=0. In Fig. B.3, at all selected temperatures , it can be easily found that the permittivity keep decreasing with the frequency. Generally, the dielectric constant drops with the increase of ξ_s .

Furthermore, if we carefully observe the trend of loss tangent versus frequency at different values of ξ_s , it becomes tricky. Taking example of simulation data at 320K (easier to be follow in Fig. B.4), it can be found that when the frequency is below certain value around 100 MHz, with lower ξ_s , we have higher dielectric losses. However, if the

Parameter	Value	Parameter	Value
$A_2(x)$	$0.8(1+20x)^{-1}$	<i>f</i> ₂ (Hz)	30 GHz
A_3	0.05	<i>f</i> ₃ (Hz)	10 GHz
A_4	0.005	<i>f</i> ₄ (Hz)	10 MHz
θ_F (K)	175	$E_N(x)$ (kV/cm)	$19 + 340x - 50x^2 - 65x^3$
$\omega_{00}(x)$ (s ⁻¹)	$0.67(1+6x) \times 10^{13}$	$T_c(x)$ (K)	$42 + 439x - 96x^2$
ω_M (s ⁻¹)	$2.6 imes 10^{13}$	C(x) (K)	$(0.78 + 0.76x^2) \times 10^5$

Table A.1 Model constants in original Vendik model



Fig. B.1 Dielectric constant vs Temperature of various pure BST64, at different levels of defects and frequencies at external biasing field E=0.



Fig. B.2 Dielectric Loss vs Temperature of various pure BST64, at different levels of defects and frequencies at external biasing field E=0.

frequency goes over than certain value around 200MHz, with a higher the dielectric loss will also increase. This can be explained by the fact that defects can play a more important and contributing role in dielectric loss at higher frequencies.

In Figures B.5 and B.6, by employing the improved theoretical modelling, we reveal how loss tangent and tunability change with different types of the BST material, i.e. different proportion of barium (x) and different values of ξ_s . During the simulation, the frequency was set to be 100 kHz and temperature is set be 290 K (room temperature).

From Fig. B.5 and B.6, we can observe that, if the proportion of barium is fixed, the overall tunability n_r and loss tangent both decrease with higher level of defects in the



Fig. B.3 Dielectric Constant vs Frequency of various pure BST64, at different levels of defects and temperatures at external biasing field E=0.



Fig. B.4 Dielectric Loss vs Frequency of various pure BST64, at different levels of defects and temperatures at external biasing field E=0.

material. And if ξ_s remains the same, it can be summarized that when proportion barium (x) increases from 0.2 to 0.6, the tunability gets enhanced whereas the loss tangent becomes larger as well. Moreover, when the barium ratio continues to increase till 0.8, both tunability and loss tangent drop dramatically. This trend can be concluded with a higher overall tunability, there will always be a higher loss associated in the material.

MgO-Doped BST

In this part, we will initially discuss the new mechanisms in details brought by MgO doping on BST material and elaborate the modified equations considering that accordingly. And the simulated dielectric properties of BST-MgO composites using the improved model will be presented at the



Fig. B.5 Tunability versus Electric Fields for different pure BST (x varying from 0.2 to 0.8, ξ_s varying from 0.2 to 0.8).



Fig. B.6 Loss tangent versus Electric Fields for different pure BST (x varying from 0.2 to 0.8, ξ_s varying from 0.2 to 0.8).

end.

After MgO doping, Ti⁴⁺ ions can be replaced by Mg²⁺, a negatively charged defect $Mg_{Ti}^{"}$ will accompany the corresponding number of positively charged oxygen vacancies, which satisfy the site balance and charge neutrality conditions as follows^{32,52,53}:

$$BaO + MgO \rightarrow Ba_{Ba} + Mg_{Ti}'' + 2O_O + V_O^{\bullet\bullet}$$
(B.1)

With the generation of $V_O^{\bullet\bullet}$ in the material, oxygen vacancy concentration can effectively increase. Oxygen vacancies are formed to compensate the defect centres (Mg"Ti) in MgO-doped BST. More mobile vacancies would be attracted to the vicinity of the oppositely charged impurity center. The formation of defect complexes from the individual defects can be written as follows^{32,52,53}:

$$Mg_{Ti}'' + V_O^{\bullet\bullet} \leftrightarrow (Mg_{Ti}'' - V_O^{\bullet\bullet})$$
(B.2)

As is described elsewhere, dipoles may produce local electric fields and reduce the irreversible domain wall motion. Furthermore, the electric dipoles could be ordered under external electric field. It will, in turn, form a lower net internal field and reduce the polarization of polar clusters and then decrease the permittivity and dielectric loss. So, these defect dipoles $Mg''_{Ti} - V_O^{\bullet\bullet}$ are thought of as defects pinning domain wall motion.

For multi-phase ceramics, at low frequency, the interfaces between BST and MgO will further create more charged defects in the material. As a consequence, the value of ξ_s related to the defects in the material needs to be elevated. Therefore, another term ξ_{Mg} , which is positively correlated with MgO doping content is added to the previous parameter ξ_s , where the new defect parameter ξ'_s could be presented as:

$$\xi_s' = \xi_s + \xi_{Mg} \tag{B.3}$$

Moreover, dielectric loss will also be affected by MgO doping. Both the losses Γ_1 and Γ_2 originate from the interaction between a.c. field with the phonons of the material⁸, i.e. lattice oscillations and soft mode phonons contribute to the total loss, and they exhibit very high importance at microwave-frequencies. MgO doping causes a considerable distortion of the average lattice parameter, i.e. expansion of Ti-Ti lattice distance and stiffening of softmode in BST material. Therefore, we can postulate that Γ_1 and Γ_2 will both reduce after MgO doping by a factor of K_{Mg} . Moreover, we let this K_{Mg} dependent on the degree of doping. With no doping ($\xi_{Mg} = 0$), K_{Mg} should be equal to 1. Here, we assume the form of K_{Mg} conforms to an exponential function, as indicated in equation B.4.



Fig. B.7 Curve fitting with BST64 experimental permittivity data to find the constants k_a, k_b, k_c, k_d .

$$K_{Mg} = \exp(-c\xi_{Mg}) \tag{B.4}$$

The value of *c* is positive and determines the dependence of K_{Mg} on doping content factor ξ_{Mg} . For the sake of convenience, we assume c = 1 for the present model.

Therefore, both shrunk losses (Γ'_1 and Γ'_2) by the factor of K_{Mg} can be expressed in following two equations:

$$\Gamma_1' = -iK_{Mg}\frac{\pi}{2}\frac{\omega_{00}}{\omega_m}\left(\frac{T}{T_c}\right)^2 G^{0.5}\omega \tag{B.5}$$

$$\Gamma_2' = \frac{K_{Mg}A_2}{1 + i\omega/\omega_2} \left(\frac{y^2}{1 + E/E_N}\right) \tag{B.6}$$

And for Γ_3 considering the contribution of charged defects in the material, with more oxygen vacancies emerging, we replace the parameter ξ_s by referring to equation B.3.

$$\Gamma'_{3} = \frac{A_{3}}{1 + i\omega/\omega_{3}} (\xi_{s} + \xi_{Mg})^{2}$$
 (B.7)

In regard to Γ_4 , which the is universal low-frequency loss³², there is a clear clue showing that the overall loss is reduced, but the resonant frequencies are elevated due to the increment of impurities in the dipolar complexes introduced by MgO doping. Γ_4 is supposed to be decreasing with the rise of MgO content, but resonant angular frequency ω_4 needs to be elevated, i.e. $\omega'_4 = \omega_4/K_{Mg}$, and therefore the modified equation of Γ_4 could be expressed as:

$$\Gamma_4' = K_{Mg} A_4 / (1 - i\omega/\omega_4') \tag{B.8}$$

In order to address the frequency dependence of permittivity, a new factor K(f) is introduced as:

$$K(f) = k_a \tanh[k_b \ln(f) + k_c] + k_d \tag{B.9}$$

Hence, the dielectric constant of ferroelectric can be written as:

$$\varepsilon(E,T,f) = \frac{\varepsilon_{00}}{[G(E,T)K_f(f)]^{-1} + \sum_{q=1}^4 \Gamma_q(E,T,f)}$$
(B.10)

In equation B.9, k_a, k_b, k_c, k_d are constants remained to be found for the modified model. This can be done through curve fitting process between our measurement data on BST64 and the updated equation for $\varepsilon(E, T, f)$, as shown in Fig. B.7. And model constants k_a, k_b, k_c, k_d were found as -0.442, 0.490, -3.2 and 0.453 respectively.

By considering the MgO doping on the original Vendik modelling, we further utilize it to run a couple of simulations on dielectric response at different temperature, frequency and biasing electric field. Here, we took BST64 as an example and set the range of ξ_{Mg} from 0 to 0.6. For sake of convenience, ξ_s is set to be constant at 0.5.

Therefore, from Fig. B.8 to B.10, we can observe that:

(1) At all frequencies, dielectric constant and tunability will decrease with the increase of MgO doping content.

(2) For loss tangent at 10MHz, the reducing effect on loss tangent caused by MgO doping is most obvious at 100kHz and 100MHz. But at high frequencies at 10 GHz, the loss tangent can be slightly enhanced by MgO doping when E > 5 kV/cm.



Fig. B.8 Dielectric Constant versus Electric Field at different frequencies and MgO doping content



Fig. B.9 Tunability versus Electric Field at different frequencies and MgO doping content



Fig. B.10 Loss Tangent versus Electric Field at different frequencies and MgO doping content

Experimental Section

BST64 powders were prepared by solid state synthesis. Stoichiometric amounts of Barium carbonate (Aldrich, 99.99%), strontium carbonate (Aldrich, 99.9%) and titanium dioxide (Aldrich, 99.8%) were weighted and mixed within a nylon ball mill jar with ethanol and zirconium oxide balls. The ball milling process was carried out in the ball mill machine at 360 rpm for 4 hours followed by drying. The powder was sieved through 250 mm sieve and calcinated at 1100°C for 4 hours. Following this, the powder was subjected to a repeated ball milling process, dried and sieved. For conventional sintering process, the resulting powder was mixed with a PVA binder and uniaxially pressed into 15 mm to 40 mm diameter pellets with ap-

proximate 200MPa. The pellets were sintered at temperatures ranging from 1200 to 1500 °C for 3 hours with 3 °C/m ramping rate and slow cooling.

It is also important to discuss the discrepancy between the simulation and the experimental data below the Curie point as can be observed in Fig. 9 of the manuscript. Experimentally, at lower temperature, the ferroelectric material will experience several phase transitions below the order-disorder transition temperature. For an example, BST70/30 ferroelectric materials exhibit three dielectric peaks at around 176 K, 225 K, 298 K corresponding to rhombohedral-orthorhombic-tetragonal-cubic phase transitions respectively under the Curie point of the material. However, Vendik model provides a relationship between the dielectric constant, temperature, frequency and biasing field based on the calculation of polarization by solving cubic equations. This model only defines the boundary between order-disorder transition (ferroelectric to paraelectric at Curie temperature) and assumes the other phase transitions occurring under the Curie point are smooth. To sum up, the discrepancy of the fitting at lower temperature till around the Curie point is due to the simplified calculation of Landau-Ginzburg equations used to derive the Vendik model.

Deep learning model

Deep learning architecture selection

Based on the experiments conducted in *Neural Network Design* book by Hagan et al.,⁴¹ several discussions have been made to come up with an upper bound for the number of neurons in hidden layer(s) that prevents the network from overfitting the data. This upper bound depends on the amount of training data available and the number of input and output neurons. As a rule of thumb, the maximum number of hidden neurons (N_h) is defined by;

$$N_h = N_s / (\alpha * (N_i + N_o)) \tag{D.1}$$

where,

 N_i = number of input neurons

 N_o = number of output neurons

 N_s = number of samples in training set

 α = an arbitrary scaling factor (usually 2-10)

Considering the fact that we have 35000 data points in the initial training stage, the number of hidden neurons should approximately be less than 1250 (α =2). It is also understood that having more hidden layers enable learning as much information as possible from the training data as long as the network does not overfit. Therefore, we developed a NN with four hidden layers. Each branch was given three layers to have the capability to learn the different charac-

Table D.1 Tunability and loss t	angent validation M	SE comparison
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Network architecture	Tunability val- idation MSE	Loss tangent validation MSE
Separate networks	$5x10^{-6}$	$8x10^{-5}$
Proposed architecture	$2.8x10^{-6}$	$1.18x10^{-5}$

teristics of tunability and loss tangent separately. There is no specific rule for number of hidden layers or number of neurons in each layer; this is usually done by intuition or trial-and-error. We experimented with hidden layers up to 6 with different neurons in each layer and observed the initial variation of the training and validation losses. Having 1-2 hidden layers trained the network very fast, however, had a relatively high settled validation loss. Higher number of hidden layers resulted in slow training. The proposed network architecture yielded the lowest validation loss. However, it should be noted that selecting slightly different number of neurons in each layer instead of the proposed numbers would not make a considerable change to the final training/validation losses as long as they fall well below the upper limit (i.e. some [30, 70, 150, 80] neurons instead of [50, 100, 100, 50] neurons).

Cross-validation and training performance

Another important point to note is that we used one single neural network that branches off to predict tunability and loss tangent separately instead of have two separate networks for tunability and loss tangent. by inspecting the simulated and experimental data, we found that the materials that have higher tunability tend to have a higher loss tangent as well. Therefore, we observed a rough proportional relation between the two quantities, which is generally true, but not always. We realized that a neural network could learn this relationship and it would help to make better predictions. In order to learn this information, tunability and loss tangent should be integrated in the same neural network and should have at least one common layer. Thus, we developed a single NN with one common hidden layer and then branches off. Once the errors of tunability and loss tangent are backpropagated till this common layer, it adjusts its weights to reduce the total training loss (tunability + loss tangent) instead of individual losses. Hence, we believe that this layer could learn the stated proportionality. The validation loss of the proposed architecture is lower than that of two separate networks, which confirms that the relationship between the two quantities is indeed helpful when learning. Table D.1 summarizes the settled validation losses.

Unlike in classical machine learning algorithms, it is practically difficult to perform K-fold cross validation with

K=5 or 10 as there is usually no terminating condition to stop the training (i.e. validation loss should be constantly monitored and likewise the best model should be selected). However, K-fold cross validation with K=2 is certainly possible.

We performed K-fold cross validation with K=2 by having 3 separate databases for training, validation and testing. After training with the small experimental database in the second phase, the model with the lowest validation loss was selected (early stopping method was employed to avoid overfitting) and tested on the test set. Fig. 7 in the manuscript shows the prediction results for the test set. It can be observed that the predictions are quite accurate (as quantified and compared using equations 8 and 9 respectively) for the test set and the model has avoided overfitting.



Fig. D.1 Variation of training and validation losses during training

Deep learning parameters

Table D.2 One-hot vectors of discrete frequencies

Frequency	One-hot Encoding	
1kHz	1000000	
10kHz	01000000	
100kHz	00100000	
1MHz	00010000	
10MHz	00001000	
100MHz	00000100	
1GHz	0000010	
10GHz	00000001	

Table D.2 shows the one-hot vectors derived for discrete frequencies present in the simulated database. One-hot encoding significantly improves the machine learning model performance rather than using bare categorical values.