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Supporting Information

Simultaneous Enhancement of Piezoelectricity and Temperature Stability in (K,Na)NbO_3-Based Lead-Free Piezoceramics by Incorporating Perovskite Zirconates

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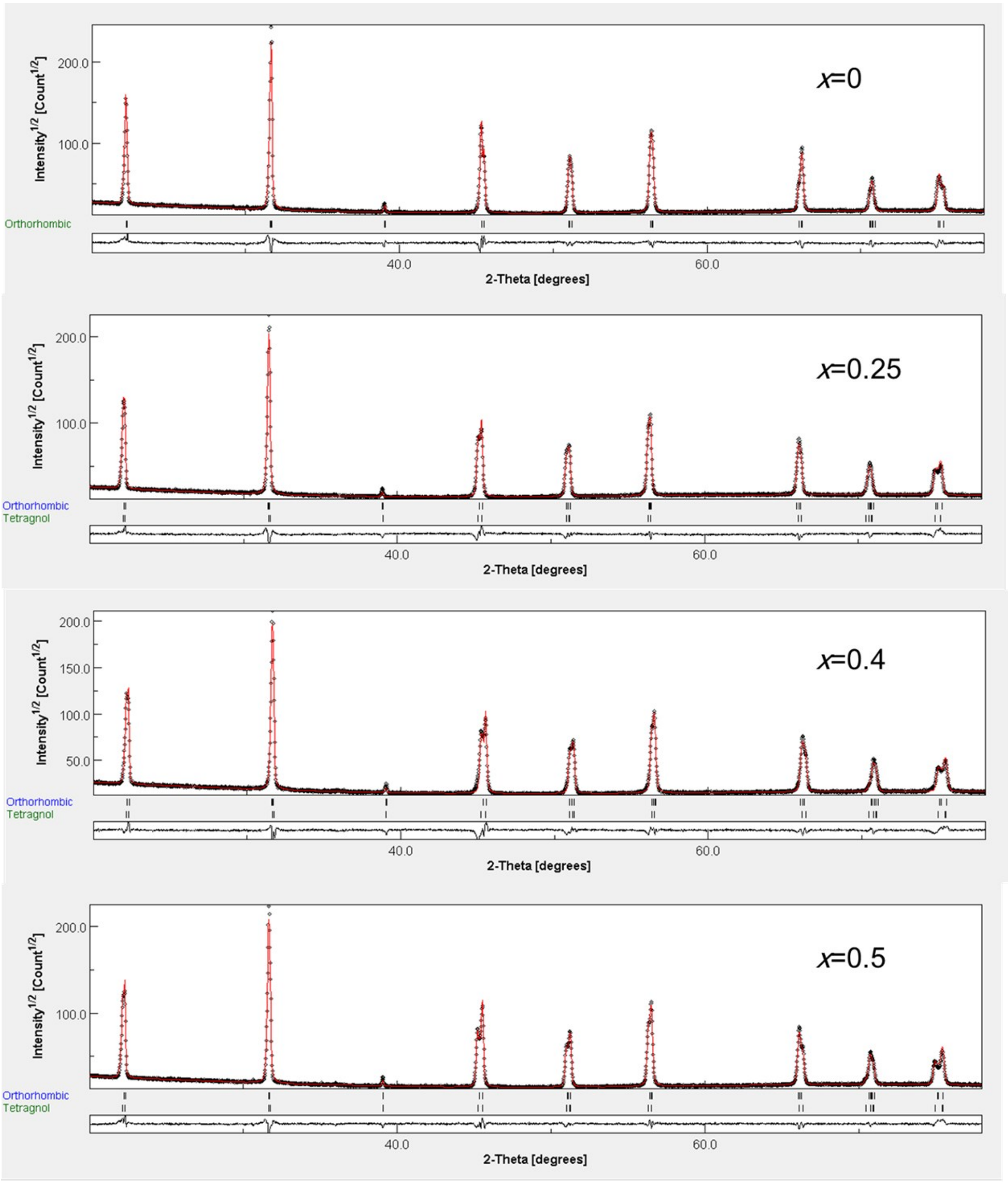

	O(Amm2)							T(P4mm)			R_b
	Original unit cell				Pseudocubic unit cell						
	Fraction	**a** (Å)	**b** (Å)	**c** (Å)	**a′(≈c′)** (Å)	**b′** (Å)	**β′** (°)	Fraction	**a (=b)** (Å)	**c** (Å)	
x=0	100.0%	5.6476	3.9832	5.6574	3.9969	3.9832	90.099	0.0%	-	-	8.75%
x=0.25	35.3%	5.6439	3.9819	5.6520	3.9937	3.9819	90.082	65.7%	3.9793	4.0048	9.08%
x=0.4	29.6%	5.6448	3.9827	5.6517	3.9939	3.9827	90.070	70.4%	3.9814	4.0061	8.96%
x=0.5	21.9%	5.6467	3.9803	5.6534	3.9951	3.9803	90.068	78.1%	3.9794	4.0055	8.56%

Fig. S1 Rietveld refinement for the XRD patterns of the ceramics.

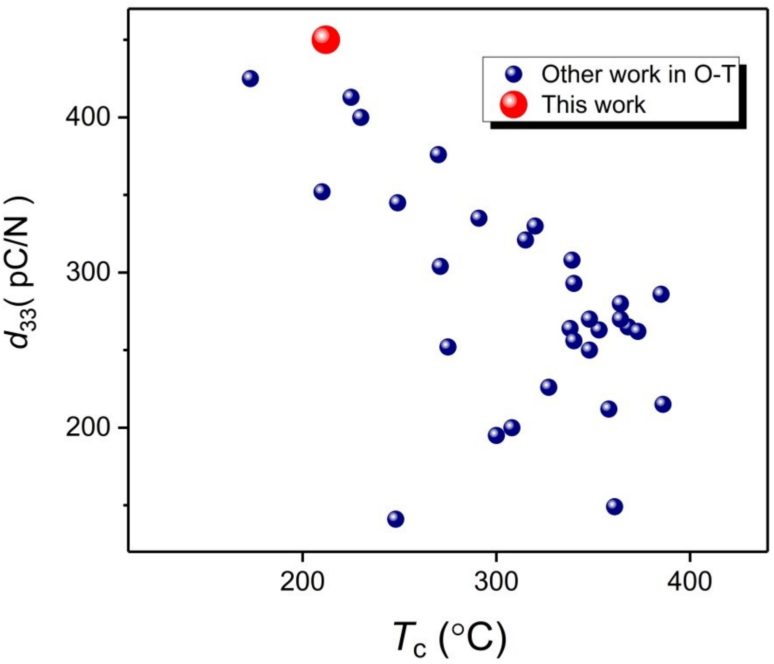

Fig. S2 d_{33} as a function of T_c for KNN-based piezoceramics featured with O-T phase transition.[1-4]

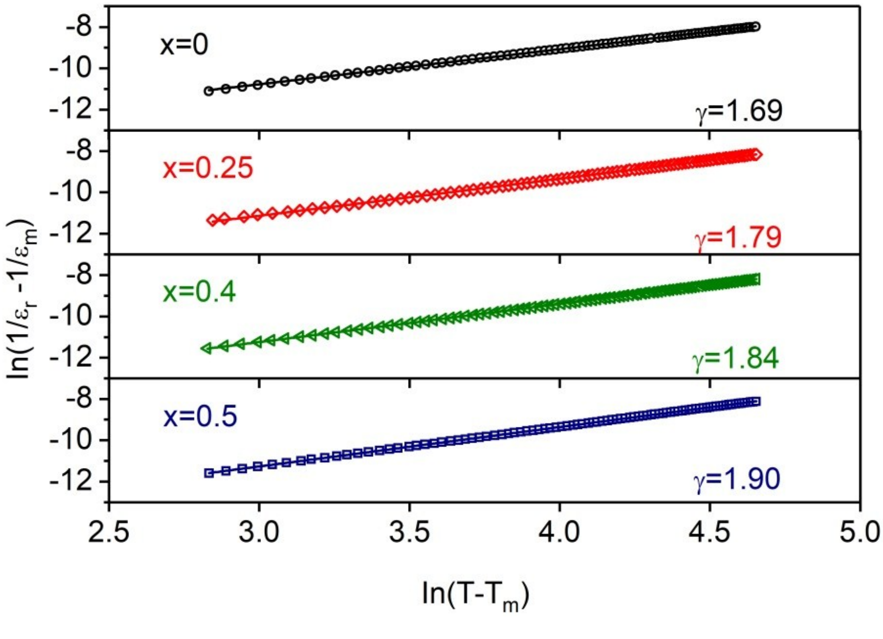

Fig.S3 Relationship of In($1/\varepsilon_r-1/\varepsilon_m$) versus In($T-T_m$) for the LKNNS-6.5(xBNZ- (1-x)BZ)-1wt%MnO_2 ceramics, γ values inserted suggests their diffuseness according to the modified *Curie Weiss* law.

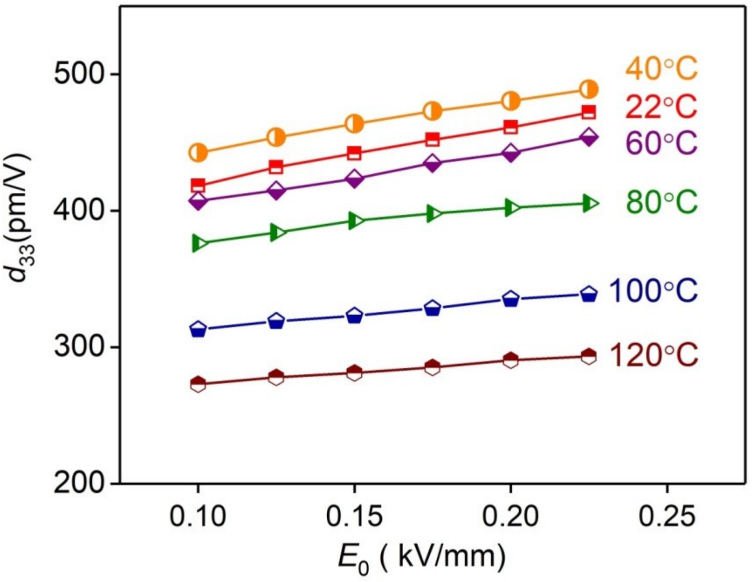

Fig.S4 The electric field dependence of d_{33} for the x=0.25 sample at various temperatures.

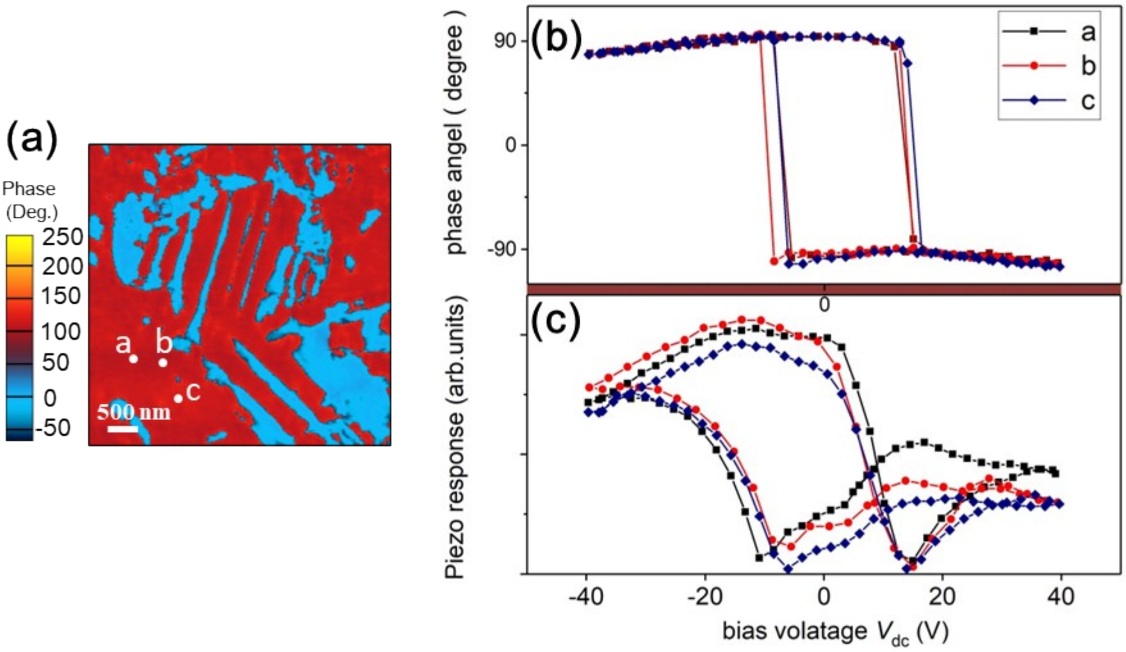

Fig. S5 (a) The in-plane PFM phase image of the x=0.25 specimen. Local representative phase (b) and amplitude (c) hysteresis loops measured at different locations a, b and c of the x=0.25 specimen as shown in the PFM phase image.

To further explore the local response to the external excitations at different local regions, the study of the local switching spectroscopy piezoresponse force microscopy (SS-PFM) was performed. Local phase and amplitude hysteresis loops for the areas marked with a,b and c in PFM phase image of **Figure S5** were obtained by applying a triangular signal voltage ranging from −40 to 40 V superimposed with an AC signal of 1 V. To make the results trustworthy, the measurements are conducted multiple times. The representative and reliable curves for the various areas are presented in **Figure S5(b) and Figure S5(c)**, respectively**.** Sufficient polarization switching behavior could be perceived as 180° contrast is observed in all the phase curves. All the piezoresponse curves reveal a butterfly shaped feature but different areas exhibit the different amplitudes of the piezoresponse under zero and the maximum electrical field. These results indicate that the formation of multi-scale structural heterogeneities results in different local microscopic responses to the external excitations in the KNN-based ceramics.

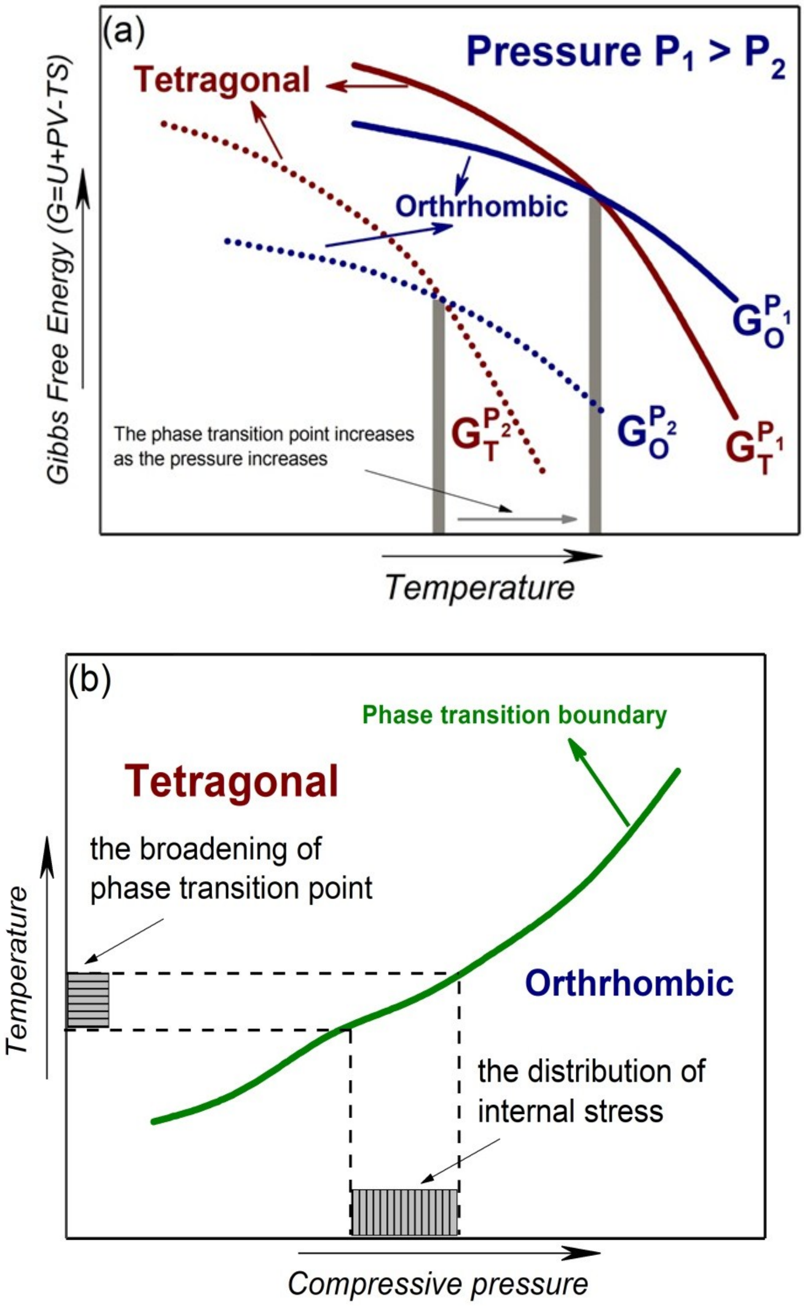

Fig.S6 (a) Sketch diagram of thermodynamic analysis of the local phase transition point shifts due to the local internal stress, the dash lines and solid lines denote the Gibbs free energy of the local region with low and high internal stress, respectively. **(b)** The schematic for the sharply defined temperature point into a broadened temperature range.

As the temperature increases, the tetragonal phase becomes more thermodynamically stable than orthorhombic one since the Gibbs free energy of the tetragonal phase becomes lower than that of orthorhombic one. The Gibbs free energy (*G*) is defined as the following thermodynamics equation: $G = U + PV - TS$. where U, P, V, T and S denotes internal energy, pressure, volume, temperature and entropy, respectively. It is obvious that the increase of the pressure or the decrease of temperature can cause the increase of Gibbs free energy (*G*). The Gibbs free energy for a local region varies with the local internal stress. As shown in **Fig. S6(a)**, the phase transition temperature would increases with the pressure. The local region with a different internal stress would exhibit a different phase transition point. As shown in **Fig. S6(b)**, the sharply defined phase transition temperature point changes into a broadened phase transition temperature range.

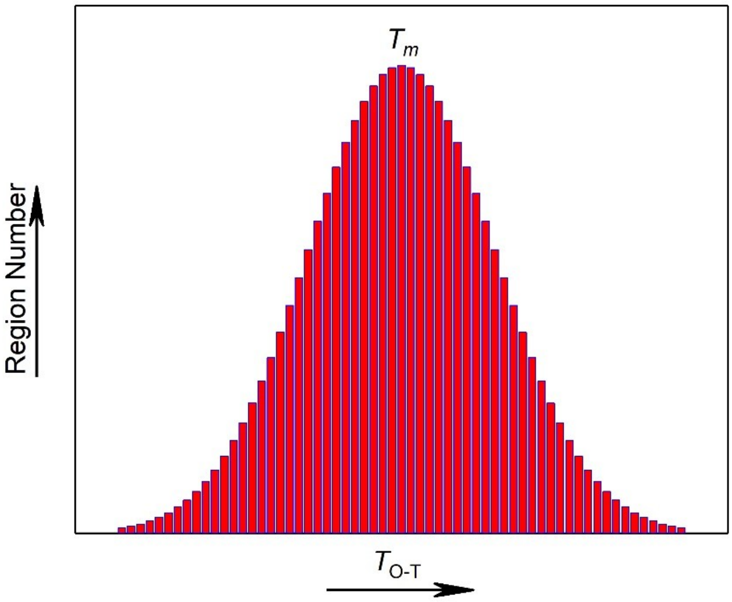

Fig. S7 The supposed distribution for the number of the regions with the $T_{O\text{-}T}$

The localized phase transition points in complex ferroelectric ceramics should fluctuate in a certain range and the number of the regions with the $T_{\mathrm{O\text{-}T}}$ decreases when the $T_{\mathrm{O\text{-}T}}$ deviates from the average O-T phase transition point. In this case, as shown in **Figure S7**, the distribution for the number of the regions with the $T_{\mathrm{O\text{-}T}}$ is assumed to be governed by a normal distribution around a mean value of the O-T phase transition point, T_{m}, with a width of the distribution δ and the $T_{\mathrm{O\text{-}T}}$ is considered to range from T_{m} minus three times the width of the normal distribution to T_{m} plus three times the width of the normal distribution. Thus, the distribution is then given by

$$Number(T_{O-T}) = N\frac{1}{\delta\sqrt{2\pi}}\exp\left(-\frac{(T_{O-T}-T_m)^2}{2\delta^2}\right), \qquad T_m - 3\delta \le T_{O-T} \le \; T_m + 3\delta$$

where N is a matched constant. Thus, the fraction of the regions with a $T_{\mathrm{O\text{-}T}}$ decrease when the $T_{\mathrm{O\text{-}T}}$ deviates from the mean O-T phase transition point T_{m}, the distribution of which can be roughly described by approximately normal distribution:

$$f(T_{O-T}) = \frac{1}{\delta\sqrt{2\pi}}\exp\left(-\frac{(T_{O-T}-T_m)^2}{2\delta^2}\right) \Big/ \int_{-3\delta+T_m}^{3\delta+T_m} \frac{1}{\delta\sqrt{2\pi}}\exp\left(-\frac{(T_{O-T}-T_m)^2}{2\delta^2}\right) dT_{O-T}$$

Where T_{m} represents the mean value of $T_{\mathrm{O\text{-}T}}$ and δ is the coefficient signifying the diffused level of phase transition.

For simplicity, we first consider an extreme case in a local region, where the local response *r* at a particular temperature *T* is described as follows.

$$r(T,\ T_{O-T}) = \begin{cases} constant\ A\ ,\ \ if\ T = T_{O-T} \\ constant\ B,\ \ if\ T \neq T_{O-T} \end{cases}$$

Where constant A denotes the response level at the temperature $T_{\text{O-T}}$, and constant B is the response level at any other temperatures. The macro piezoelectric performance can be determined by statistically averaging of the micro piezoelectric performance. Thus, the macro piezoelectric performance R at a particular temperature T can be calculated as follows.

$$R(T,T_m,\delta) = \frac{\int_{-3\delta+T_m}^{3\delta+T_m} r(T,\ T_{O-T})\, f(T_{O-T},T_m,\delta)\ dT_{O-T}}{\int_{-3\delta+T_m}^{3\delta+T_m} f(T_{O-T},T_m,\delta)\ dT_{O-T}}$$

Since $f(\mathrm{T}_{\text{O-T}},T_{\text{m}},\delta)$ is an approximately normal distribution with

$$\int_{-3\delta+T_m}^{3\delta+T_m} f(T_{O-T},T_a,\delta)\ dT_{O-T} = 1$$

Thus,

$$R(T,T_a,\delta) = (\int_{3\delta+T_m}^{-3\delta+T_m} Bf(T_{O-T},T_{O-T} \neq T)\ dT_{O-T} + \int_{3\delta+T_m}^{-3\delta+T_m} Af(T_{O-T},T_{O-T} \neq T)\ dT_{O-T}$$

$$= \begin{cases} constant\ B\ ,\ \ if\ T > 3\delta + T_m\ or\ T < -3\delta + T_m \\ B + \dfrac{C(A-B)\dfrac{dT_{O-T}}{\delta\sqrt{2\pi}}\exp\left(-\dfrac{(T-T_m)^2}{2\delta^2}\right)}{\int_{-3\delta+T_m}^{3\delta+T_m} \dfrac{1}{\delta\sqrt{2\pi}}\exp\left(-\dfrac{(T_{O-T}-T_m)^2}{2\delta^2}\right) dT_{O-T}},\ \ if\ \ 3\delta + T_m \leq\ T \leq 3\delta + T_m \end{cases}$$

According to the derived R(T)-T expression of the correlation function, we can deduce that the less intensive change of the performance around the average phase transition point T_m is anticipated in the ceramics with a higher δ.

To demonstrate general evolution of the macro piezoelectric performance and the acompanyed thermal stability around the phase transition point, the common temperature-dependent local response arround the phase transition point $T_{O\text{-}T}$ is assumed to have the following charateristic. With the temperature T approaching $T_{O\text{-}T}$, the local response and the rate of the local response change becomes larger and larger since the change of the phase structure is most intense at $T_{O\text{-}T}$. Thus, the local response at a certain temperature T in a local region with the phase transition point $T_{O\text{-}T}$, $r(\mathrm{T},\mathrm{T}_{O\text{-}T})$, can be described as follows.

$$r(T,\ T_{O-T}) = \begin{cases} \frac{dr}{dT}|_T \geq 0,\ \ \frac{d^2r}{dT^2} \geq 0,\ \ if\ T < T_{O-T} \\ \frac{dr}{dT}|_T \leq 0,\ \ \frac{d^2r}{dT^2} \geq 0,\ \ if\ T > T_{O-T} \\ r|_{T \neq T_{O-T}} < r|_{T = T_{O-T}} \end{cases}$$

Here, it is reasonable to assume that the local region with different $T_{O\text{-}T}$ can exhibit the similar temperature dependence of the local response except the different $T_{O\text{-}T}$ if the $T_{O\text{-}T}$ doesn't changes hugely , which can be described by the relationship:

$\mathrm{r}(T,\ \ T_{O\text{-}T}) = \mathrm{r}(T+\Delta T,\ \ T_{O\text{-}T}+\Delta T\,)$, $\Delta T < \Delta T_m$

The function R(T) describing the relationship between macro performance and temperature could be written as

$$R(T) = \frac{\int_{T_{m-3\delta}}^{T_{m+3\delta}} r\left(T_m,T_{O-T}\right) f\left(T_m,T_{O-T}\right) dT_{O-T}}{\int_{T_{m-3\delta}}^{T_{m+3\delta}} r\left(T_m,T_{O-T}\right)\ dT_{O-T}}$$

To evaluate the fluctuation of the macro performance around the phase transition point, we can consider how the variation of the macro performance, *ΔR* , in a temperature range deviating from T_m ,*ΔT,* changes. *ΔR* can be written as

$$\Delta R = R\left(T_m\right) - R\left(T_m + \Delta T\right)$$

$$= \frac{\left(\int_{T_m-3\delta}^{T_m+3\delta} r(T_m,T_{O-T})\, f(T_{O-T},T_m)\, dT_{O-T} - \int_{T_m-3\delta}^{T_m+3\delta} r(T_m+\Delta T,T_{O-T})\, f(T_{O-T},T_m)\, dT_{O-T}\right)}{\int_{-3\delta}^{+3\delta} f(T_{O-T},T_m)\, dT_{O-T}}$$

It is reasonable to consider that δ is not too large in well fabricated ceramics to help maintain a good performance. For simplicity, we consider the condition that *ΔT* is larger than three times the width of the normal distribution δ.

It's easy to prove that R(T_m) decreases while R(T_m+*ΔT*) increases as δ increases as follows.

$$\int_{T_m-3\delta}^{T_m+3\delta} f\left(T_{O-T},T_m\right) dT_{O-T} = constant\ \ A \approx 0.9974\ \ > 0$$

With the condition ξ= （T_m -T_{O-T}） / δ and r(T, T_{O-T}) = r(T+$\mathit{\Delta} T$, T_{O-T}+$\mathit{\Delta} T$)

$$= \frac{\int_{3}^{-3} r\left(T_m,T_m-\delta\xi\right) f\left(T_m,T_m-\delta\xi\right) d\left(T_m-\delta\xi\right)}{A}$$

$$= \frac{1}{A}\int_{-3}^{3} r(\delta\xi\ ,0)\ f\left(T_m,T_m-\delta\xi\right)\delta\ d\xi = \frac{1}{A\sqrt{2\pi}}\int_{-3}^{3} r(\delta\xi\ ,0)\ exp^{-\xi^2} d\xi$$

$$\frac{dR}{d\delta}|_{T_m} = \frac{1}{A\sqrt{2\pi}}\int_{-3}^{3} \xi\frac{dr(\delta\xi\ ,0)}{dT}\ exp^{-\xi^2} d\xi$$

$$= \frac{1}{A\sqrt{2\pi}}\int_{-3}^{0^-} \delta\frac{dr(\delta\xi\ ,0)}{dT}\ exp^{-\xi^2} d\xi + \frac{1}{A\sqrt{2\pi}}\int_{0^+}^{3} \delta\frac{dr(\delta\xi\ ,0)}{d(\delta\xi\ )}\ exp^{-\xi^2} d\xi$$

With the condition $\delta\xi < 0$, $\frac{dr(\delta\xi\ ,0)}{dT} \geq 0$ while $\delta\xi > 0$, $\frac{dr(\delta\xi\ ,0)}{dT} \leq 0$

Thus $\frac{dR}{d\delta}|_{T_m} < 0\ ,\delta > 0$

Similarly,

$$\frac{dR}{d\delta}|_{\Delta T} = \frac{1}{A\sqrt{2\pi}}\int_{-3}^{0^-} \delta\frac{dr(\delta\xi + \Delta T\ ,0)}{dT}\ exp^{-\xi^2} d\xi + \frac{1}{A\sqrt{2\pi}}\int_{0^+}^{3} \delta\frac{dr(\delta\xi + \Delta T\ ,0)}{dT}\ exp^{-\xi^2} d\xi$$

$$= \frac{1}{A\sqrt{2\pi}}\int_{0^+}^{3} \delta\left(\frac{dr(\delta\xi + \Delta T\ ,0)}{dT} - \frac{dr(-\delta\xi + \Delta T\ ,0)}{dT}\right) exp^{-\xi^2} d\xi$$

With the condition $\Delta T>0$, $-3\delta\xi+\Delta T>0$, $\frac{d^2r}{dT^2}|_T \geq 0$

$$\frac{dr(\delta\xi+\Delta T,0)}{dT} \geq \frac{dr(-\delta\xi+\Delta T,0)}{dT}$$

Thus, $\frac{dR}{d\delta}|_{T_m+\Delta T} > 0, \delta > 0$

$$\frac{d\Delta R}{d\delta}|_{\Delta T} = \frac{dR}{d\delta}|_{T_m} - \frac{dR}{d\delta}|_{T_m+\Delta T} < 0, \delta > 0$$

Thus, ΔR decreases as δ increases. δ can be affected by various factors such as chemical inhomogeneity, non-uniform internal stress and lattice disorder due to small free energy changes.[5, 6] This analysis presented here might demonstrate the general feature in diffused phase transition, where the fluctuation of the piezoelectric performance around the phase transition increases as the diffused degree increases, thereby deepening our understanding of the thermal stability of the piezoelectric performance around the diffused transition in KNN-based ceramics. In most other cases, this relationship would appear to be intuitively right. It is reasonable to say that a higher lattice disorder degree can help to depress the fluctuation around the phase transition as δ increases with the higher lattice disorder degree.

Based on the free-energy expressions from Landau-Ginzburg-Devonshire (LGD) model, the free energy of each region $R_{\mathrm{TO\text{-}T}}$ can be written as a power series of the order parameter θ:

$$F_{R_{T_{O-T}}} = F_{0_{R_{T_{O-T}}}} + \sum_{n} \frac{1}{n} \alpha_{nR_{T_{O-T}}} \theta_{R_{T_{O-T}}}^{\;n}$$

Where $\theta_{R_{T_{O-T}}}^{\;n}$ is the order parameter while $\alpha_{nR_{T_{O-T}}}$ is a function of temperature and varies with region $R_{T_{O-T}}$.The spatial distribution of these regions can be very complicated, resulting in inenarrable coherent coupling behavior at the interfaces between various regions. For simplicity, the system is assumed to be a finite model where each region independent thermodynamic behavior since the coupling behavior between these regions is neglected. [7, 8] Besides, the same order parameter θ can be chosen as the order parameter for each region since these regions undergo the same change of the crystal symmetry. The free energy of a heterogeneous system could be described as follows:

$$F = \int (F_{0_{R_{T_{O-T}}}} + \sum_{n} \frac{1}{n} \alpha_{nR_{T_{O-T}}} \theta^{n})\, f(T_{O-T}) dT_{O-T}$$

It is reasonable to assume that the local regions with different $T_{\mathrm{O\text{-}T}}$ can exhibit a similar temperature dependence of potential well except for the different $T_{\mathrm{O\text{-}T}}$ if the $T_{\mathrm{O\text{-}T}}$ does not change colossally. The flatness of θ-F curves can be evaluated by the second derivative of order parameter versus the free energy, $\frac{d^2F}{d\theta^2}$. $\frac{d^2F}{d\theta^2}|_{\theta} = 0$ $=\alpha_2$ (T), which and the change rate of which becomes larger and larger as T approaches $T_{\mathrm{O\text{-}T}}$ since the change of the phase structure is most intense at $T_{\mathrm{O\text{-}T}}$.

$$\alpha_2(T,\ T_{O-T}) = \begin{cases} \frac{d\alpha_2}{dT}|_T \geq 0,\ \ \frac{d^2\alpha_2}{dT^2} \geq 0,\ \ if\ T < T_{O-T} \\ \frac{d\alpha_2}{dT}|_T \leq 0,\ \ \frac{d^2\alpha_2}{dT^2} \geq 0,\ \ if\ T > T_{O-T} \\ \alpha_2|_{T \neq T_{O-T}} < \alpha_2|_{T = T_{O-T}} \end{cases}$$

The foregoing consideration can be applied to analyze the free energy curve. Similar conclusion can be acquired under the similar assumption that the local region with different $T_{\text{O-T}}$ can exhibit the similar temperature dependence of α_2 except the different $T_{\text{O-T}}$ if the $T_{\text{O-T}}$ doesn't changes hugely.

Reference

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