*Journal of*
**Ceramic Science**
and Technology

# Enhancement of Piezoelectric Properties in Lanthanum-Modified Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ Ceramics via Spontaneous Relaxor-to-Ferroelectric Transition

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## Abstract

In relaxor ferroelectrics, spontaneous relaxor-to-ferroelectric transition has attracted much attention due to its unique performance. However, despite extensive studies over several decades, the effect of spontaneous relaxor-to-ferroelectric transition on the piezoelectric, dielectric and ferroelectric properties of relaxor ferroelectrics remains obscure. In this work, the piezoelectric, dielectric and ferroelectric properties of 12 % La-modified Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ ceramics, which exhibit spontaneous relaxor-to-ferroelectric transition with a wide composition range (0.44 ≤ x ≤ 0.51), were systematically investigated. It has been found that the spontaneous transition composition with x = 0.48 shows enhanced piezoelectric, dielectric and ferroelectric properties compared to the adjacent compositions. The x = 0.48 composition has a piezoelectric coefficient $d_{33}$ of 235 pC/N, accompanied by a high relative permittivity (up to 12230) and a high maximum polarization (up to 20.4 µC/cm$^2$). This enhancement effect originates from the easy polarization rotation induced by its instability state and the coexistence of micro-sized domain and polar nanodomain configuration. Our work may provide new insights into the exploration of the mechanism that enhances the piezoelectric, dielectric, and ferroelectric properties of relaxor ferroelectric materials.

*Keywords: Relaxor ferroelectric, spontaneous transition, piezoelectric property, dielectric property, ferroelectric property*

## I. Introduction

Ferroelectric materials with a long-range ordered structure have been widely used in industry due to their dielectric, piezoelectric, pyroelectric, and ferroelectric properties [1-5]. These properties can be modified by introducing point defects, which is known as doping. When doping exceeds a critical concentration, ferroelectrics transform into relaxor ferroelectrics, which are characterized by a short-range ordered structure [6-10]. Relaxors possess many extraordinary properties, such as frequency-dependent diffusion permittivity, slim polarization hysteresis loops and strain loops, and are therefore of considerable technological importance in applications such as capacitors, transducers and sensors [6, 9-12].

In relaxor ferroelectrics, short-range ordered relaxor ferroelectrics can transform into long-range ordered ferroelectrics around the crossover regime under large electric fields [13-17]. Unexpectedly, the relaxor ferroelectrics undergo a spontaneous relaxor-to-ferroelectric transition during cooling in the absence of an external field, which was first observed by Chu *et al.* in Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ in 1993 [18-22]. This special phenomenon has been reported in several ferroelectric systems with narrow composition range, such as lead-based Pb(Sc$_{1/2}$Nb$_{1/2}$)O$_3$, (Pb,La)TiO$_3$, (Pb,La)(Zr,Ti)O$_3$ and lead-free (Bi$_{1/2}$K$_{1/2}$)TiO$_3$, and has attracted much attention due to its unique behavior [18-20, 22-25]. However, despite extensive studies over several decades, the effect of spontaneous relaxor-to-ferroelectric transition on the piezoelectric, dielectric and ferroelectric properties of relaxor ferroelectrics remains obscure.

In this work, the effects of spontaneous relaxor-to-ferroelectric transitions on the piezoelectric, dielectric and ferroelectric properties of relaxor ceramics are systematically investigated. In the lanthanum-doped (1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (0.35 ≤ x ≤ 0.51) system (PLMN-PT), the spontaneous transition is obtained over a wide range of compositions, and the composition of x = 0.48 is in the spontaneous transition state at room temperature. Further studies reveal that the x = 0.48 composition exhibits enhanced piezoelectric, dielectric, and ferroelectric properties at room temperature compared to the adjacent compositions. The temperature-dependent piezoelectric coefficient $d_{33}$ curve also shows that the performance of the sample is significantly enhanced at the spontaneous transition temperature. The enhanced piezoelectric, dielectric, and ferroelectric properties of ferroelectric materials induced by spontaneous transition may originate from the unstable state of spontaneous transition in which the ferroelectric phase and the relaxor ferroelectric phase coexist. This work is expected to provide

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new avenues for enhancing piezoelectric, dielectric, and ferroelectric properties of relaxor ferroelectric materials.

## II. Materials and Methods

12 % lanthanum-doped $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ $(0.35 \leq x \leq 0.51)$ ceramics were fabricated with the columbite precursor method, and the pre-dried starting chemicals were PbO (99.9 %), $Nb_2O_5$ (99.9 %), MgO (99.9 %), $TiO_2$ (99.9 %) and $La_2O_3$ (99.9 %). The columbite precursor $MgNb_2O_6$ was prepared by calcining a mixture of MgO and $Nb_2O_5$ at 1 200 °C for 12 h. The obtained $MgNb_2O_6$ precursor powder was mixed with PbO, $TiO_2$, and $La_2O_3$ powders and ball-milled in ethanol for 24 h. The calcining and sintering were carried out in sealed crucibles at 900 °C for 4 h and 1 250 °C for 3 h under a PbO atmosphere.

The crystal structures of all samples were analyzed by means of an X-ray diffractometer (XRD Shimadzu 700) using Cu K α radiation ($\lambda$ = 1.5406 Å) at room temperature and low temperature. The dielectric permittivity was evaluated at different frequencies ($10^2$ Hz – $10^5$ Hz) and at different temperatures (from - 160 °C to 150 °C) using a HIOKI3532 LCR meter. The polarization electric field hysteresis loops were measured with a Radiant Ferroelectric Workstation, and the strain electric field hysteresis loops were measured with a MTI-2100 photonic sensor at 10 Hz frequency. The samples were poled with an electric field of 2 kV/mm for 30 minutes at room temperature, and then piezoelectric measurements were performed, and the piezoelectric coefficient $d_{33}$ was tested with a commercial Berlincourt-type $d_{33}$ meter (ZJ-3B, Chinese Academy of Sciences).

## III. Results

The room-temperature XRD patterns of different compositions of 12 %La-doped $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ $(0.35 \leq x \leq 0.51)$ system are shown in Fig. 1.
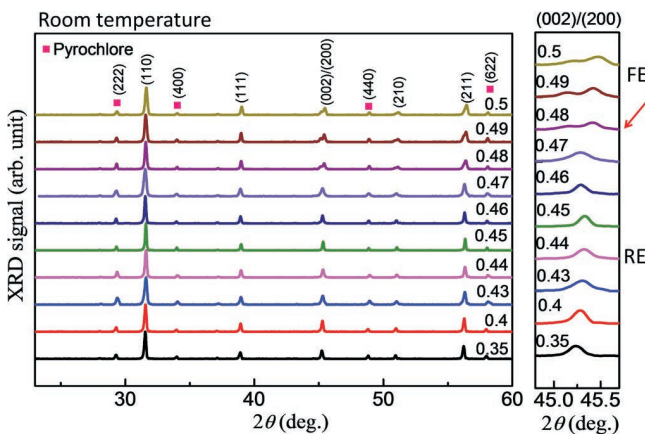


**Fig. 1:** XRD patterns of PLMN-xPT ceramics with x = 0.35 – 0.5 measured at room temperature in the range of $2\theta$ = 23 – 60° and corresponding XRD profiles of the 200 peak. FE represents the ferroelectric state, and RE represents the relaxor state.

The results indicate that a second pyrochlore phase is present in all samples. This phenomenon is common in the doped $Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMN-PT) sys-

tem [20, 25, 26]. From the typical splitting of the two characteristic 200 peaks, the compositions with x = 0.35 – 0.47 display the feature of cubic (pseudo-cubic), and the compositions with x = 0.48 – 0.5 shows typical ferroelectric feature with tetragonal (P4mm) phase. These results are consistent with previous reported results [11, 15].

Fig. 2 exhibits the temperature-dependent permittivity curves at different frequencies ($10^2$ Hz – $10^5$ Hz) for different compositions with x = 0.43, 0.44, 0.47 during cooling, and the corresponding *in situ* XRD patterns of the 200 and 220 peaks at room temperature and low temperature. It can be seen that all samples around the temperature of the dielectric maximum ($T_m$) show a pronounced frequency dispersion behavior, which is typical of relaxor ferroelectrics [6, 27, 28]. As the temperature decreases, a spontaneous transition from relaxor to ferroelectric occurs, and samples below the spontaneous transition temperature ($T_S$) are in the normal ferroelectric state. Here, $T_S$ is the spontaneous transition temperature, indicating the transition temperature from the relaxor state to the ferroelectric state during cooling. As the PT content increases, the frequency dispersion behavior at $T_m$ becomes less pronounced and the spontaneous transition temperature $T_S$ becomes higher. *In situ* X-ray diffraction patterns revealed that the samples display cubic or pseudo-cubic phase above $T_S$, indicating their relaxor states, and show typical tetragonal (P4mm) ferroelectric phase feature below $T_S$. These results are consistent with the temperature-dependent dielectric permittivity results and previously published works [11, 15].

According to the temperature-dependent dielectric permittivity curves and the *in-situ* X-ray diffraction (XRD) patterns, we can draw the composition-temperature phase diagram of the PLMN-xPT $(0.35 \leq x \leq 0.51)$ system, as shown in Fig. 3. This phase diagram is characterized by the presence of a relaxor-to-ferroelectric spontaneous transition over a wide composition range, which separates the relaxor ferroelectric state and normal ferroelectric state. In the phase diagram, $T_B$ is the Burns temperature of relaxor ferroelectric material, $T_m$ is the temperature of the dielectric maximum at 100 Hz, and $T_S$ is the spontaneous transition temperature. The Burns temperature ($T_B$) is determined based on the deviation of dielectric permittivity from Curie-Weiss Law, at which paraelectric phase transforms into the ergodic glass state and the polar nanoregions (PNRs) appear [29, 30]. And the spontaneous transition temperature ($T_S$) is evaluated based on the sudden decrease in the dielectric constant on cooling (or the peak of the temperature derivative of permittivity ($d\varepsilon_r/dT$) in the cooling run) revealed a rapid switching between ferrothe electric and relaxor states [31, 32]. The spontaneous transition temperature of the composition with x = 0.48 is around room temperature. In the following, we will show the enhancement effect of spontaneous transition on the piezoelectric, dielectric and ferroelectric properties of relaxor ferroelectrics.
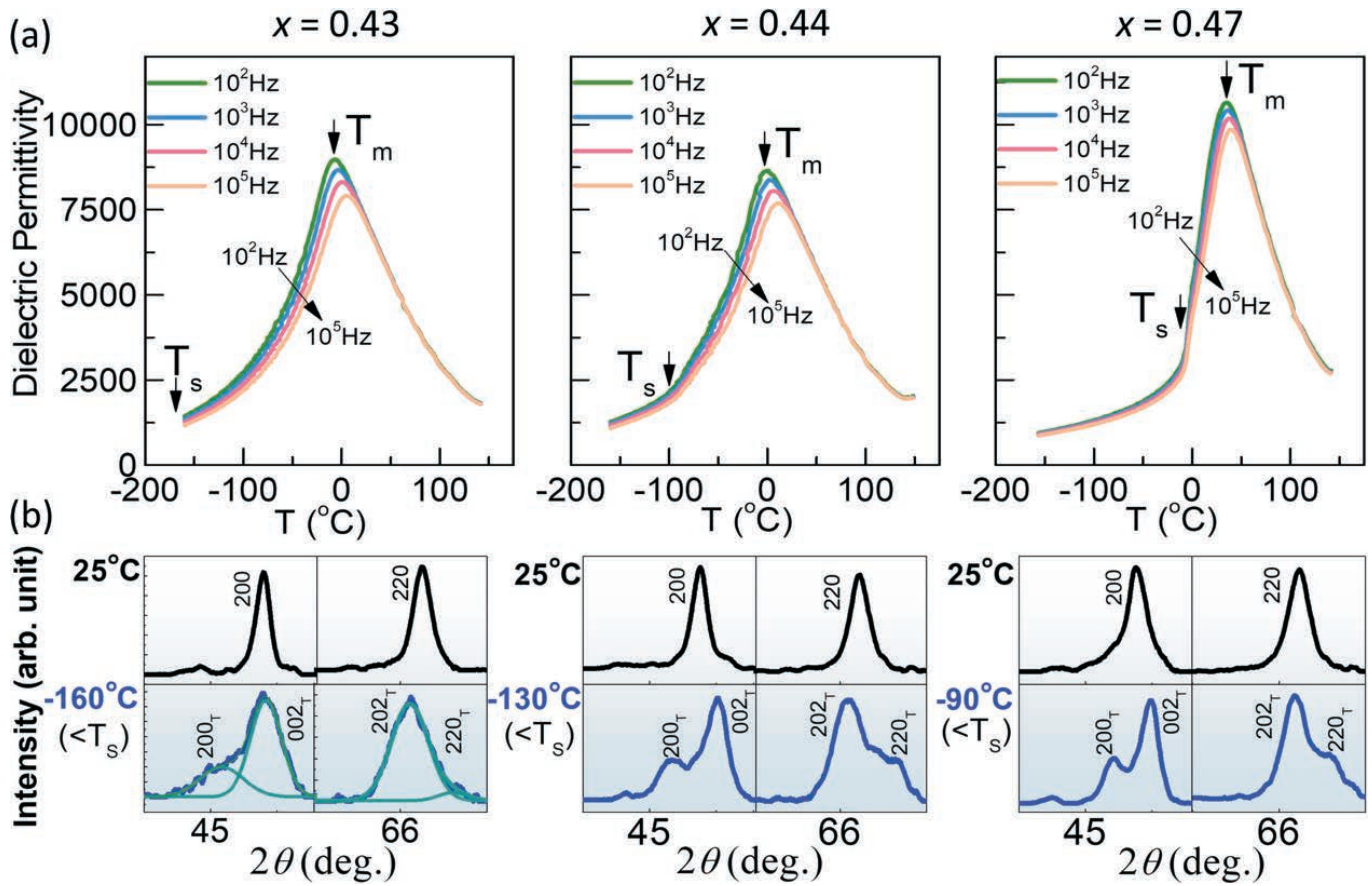
**Fig. 2:** (a) Temperature-dependent permittivity curves measured at different frequencies (10$^2$Hz, 10$^3$Hz, 10$^4$Hz, 10$^5$Hz) for PLMN-xPT compositions with x = 0.43, 0.44, and 0.47 upon cooling. T$_m$ is the temperature of the dielectric maximum at 100 Hz; T$_S$ is the spontaneous transition temperature, indicating the transition temperature from the relaxor state to the ferroelectric state during cooling. (b) Corresponding *in situ* XRD profiles of the {200} and {220} peaks of PLMN-xPT ceramics measured at room temperature and low temperature.
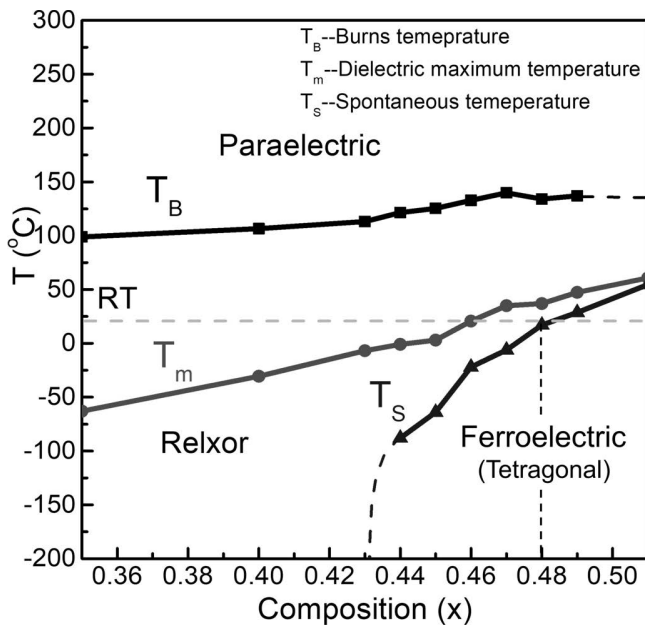


**Fig. 3:** Phase diagram of the PLMN-xPT ceramics. T$_B$ is the Burns temperature of ferroelectric materials; T$_m$ is the temperature of the dielectric maximum at 100 Hz and T$_S$ is the spontaneous transition temperature; RT represents room temperature.

Fig. 4 presents the polarization-electric field loops and strain-electric field loops for different PLMN-xPT compositions with x = 0.45, 0.46, 0.48, 0.49 and 0.51 measured at room temperature with an electric field of 30 kV/cm.

With the increase of the content of PT, both the polarization-electric field loops and strain-electric field loops exhibit a clear transformation from a slim hysteresis loop to a hypertrophic ferroelectric hysteresis loop, accompanied by an increase in the material hysteresis. But with the increase of PT content, the maximum polarization (P$_m$) and the maximum electrostrain (S) gradually increase and then decrease. The composition of x = 0.48, which has a spontaneous transition temperature at room temperature, presents the largest P$_m$ and electrostrain values.

Fig. 5 exhibits the composition-dependent permittivity ($\varepsilon_r$), maximum polarization (P$_m$), remanent polarization (P$_r$), coercive field (E$_C$), electrostrain (S), and piezoelectric coefficient ($d_{33}$) curves. With the increase of PT content, the dielectric constant ($\varepsilon_r$), maximum polarization (P$_m$), electrostrain (S) and piezoelectric coefficient ($d_{33}$) increase and then decrease, while the remanent polarization (P$_r$), coercive field (E$_C$) of the samples increase first and then remain almost unchanged. The spontaneous transition composition with x = 0.48 exhibits significantly enhanced dielectric permittivity ($\varepsilon_r$), maximum polarization (P$_m$), electrostrain (S) and piezoelectric coefficient ($d_{33}$), as well as moderate remanent polarization (P$_r$) and coercive field (E$_C$) values. This result indicates that the spontaneous relaxor-to-ferroelectric transition can obviously enhance the dielectric, ferroelectric and piezoelectric properties of relaxor ferroelectric ceramics. It should be noted that the piezoelectric coefficient ($d_{33}$) as a function
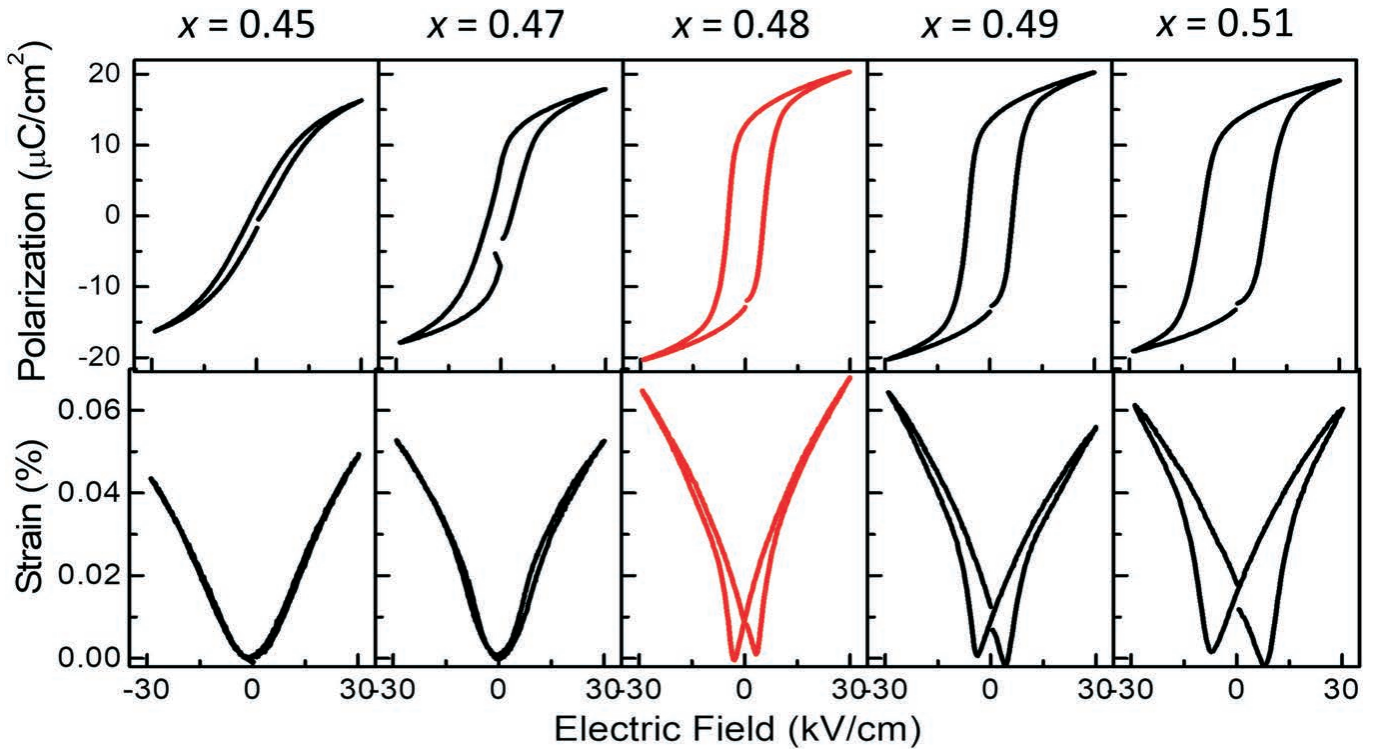
**Fig. 4:** Polarization-electric field and strain-electric field loops of different PLMN-xPT compositions with x = 0.45, 0.46, 0.48, 0.49 and 0.51 measured at an electric field of 30 kV/cm.

of the temperature profile of the x = 0.48 sample (shown in Fig. 6) presents a significant enhancement of the piezo-electric coefficient ($d_{33}$) at the spontaneous transition temperature. This temperature dependence of the piezo-electric coefficient ($d_{33}$) result also suggests that sponta-neous relaxor-to-ferroelectric transition can enhance the piezoelectric property of relaxor ferroelectrics.
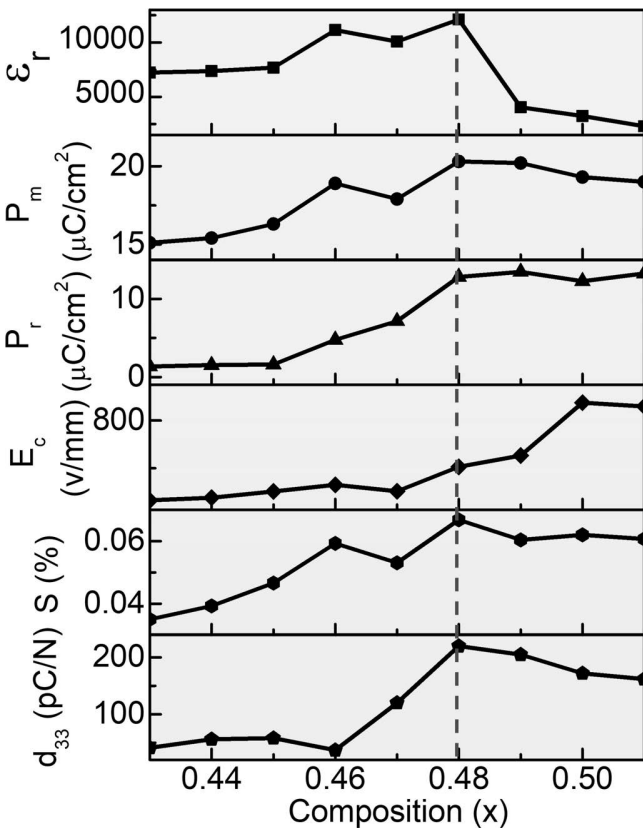


**Fig. 5:** Composition-dependent dielectric permittivity ($\varepsilon_r$), maxi-mum polarization ($P_m$), remanent polarization ($P_r$), coercive field ($E_C$), electrostrain (S) and piezoelectric coefficient ($d_{33}$) curves.
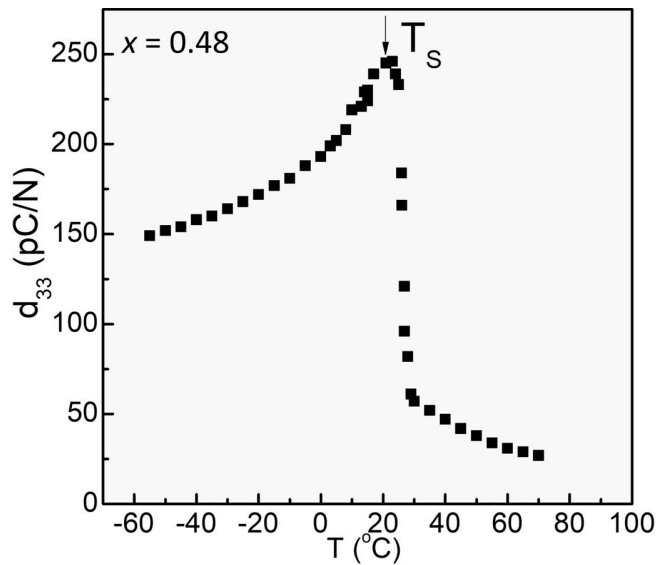


**Fig. 6:** Temperature-dependent piezoelectric coefficient ($d_{33}$) curve for the x = 0.48 sample.

## IV. Discussion

The origin of the enhancement effect of spontaneous relaxor-to-ferroelectric transition on the piezoelectric, dielectric and ferroelectric properties is considered to be caused by the unstable state of spontaneous transitions, in which relaxor and ferroelectric phases coexist. It is well

known that relaxor ferroelectrics possess a nanodomain configuration, while ferroelectrics have normal ferroelectric domains (macrodomains) [6]. Therefore, a spontaneous transition state in which relaxor ferroelectric and normal ferroelectric phases coexist, exhibiting the coexistence of macrodomain and polar nanodomain configurations [15,33,34]. When the temperature decreases or an electric field is applied, the relaxor state transforms into a ferroelectric state, which is accompanied by a rapid transition of nanodomains to microdomains. It is because the existing ferroelectric microdomains can serve as seeds for nanodomain growth. When the temperature is increased or the electric field is removed, the ferroelectric state transforms into a relaxor state, while the microdomains transform into nanodomains [15,33]. As a result, the spontaneous transition between relaxor and ferroelectric states generates a lower energy barrier for polarization rotation, and thus compositions with spontaneous transitions and the coexistence of macrodomain and polar nanodomain configurations present enhanced piezoelectric, dielectric and ferroelectric properties. It should be noted that the spontaneous relaxor-to-ferroelectric transition composition does not show the lowest coercive field, which is different from the morphotropic phase boundary (MPB) case. This is because the MPB separates two ferroelectric states with different symmetries, while the spontaneous relaxor-to-ferroelectric transition separates ferroelectric and relaxor states with the same symmetry. And the relaxor state exhibits a much lower coercive field than the ferroelectric state due to the nanodomain structure of relaxors. Therefore, although the spontaneous relaxor-to-ferroelectric transition composition shows an unstable state with the coexistence of the ferroelectric and relaxor phases, the coercive field of such a composition is still higher than the relaxor phase but lower than ferroelectric phase.

## V. Conclusions

In conclusion, the effect of the spontaneous relaxor-to-ferroelectric transition on the piezoelectric, dielectric and ferroelectric properties of La-modified Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ system was systematically investigated. The sample with spontaneous transition state shows an enhanced piezoelectric coefficient ($d_{33}$), electrostrain, permittivity ($\varepsilon_r$) and maximum polarization ($P_m$). The enhancement effect of spontaneous transitions on piezoelectric, dielectric and ferroelectric properties may originate from the low energy barrier of polarization rotation induced by unstable state and the coexistence of macrodomain and polar nanodomain configurations. Our work demonstrates that spontaneous relaxor-to-ferroelectric transitions may be a new approach to enhance the piezoelectric, dielectric and ferroelectric properties of relaxor ferroelectric materials.

## Conflict of Interest

There are no conflicts to declare.

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