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Dielectric relaxation and pinning phenomenon of (Sr,Pb)TiO₃ ceramics for dielectric tunable device application

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The behavior of ferroelectric domain under applied electric field is very sensitive to point defects, which can lead to high temperature dielectric relaxation behaviors. In this work, the phases, dielectric properties and ferroelectric switching behavior of strontium lead titanate ceramics were investigated. The structural characterization is confirmed by X-ray diffraction. The high dielectric tunability and high figure of merit of ceramics, especially Sr_{0.7}Pb_{0.3}TiO₃ (SPT), imply that SPT ceramics are promising materials for tunable capacitor applications. Oxygen vacancies induced dielectric relaxation phenomenon is observed. Pinched shape hysteresis loops appeared in low temperature, low electric field or high frequency, whereas these pinched hysteresis loops also can become normal by rising temperature, enhancing electric field or lowering frequency. The pinning and depinning effect can be ascribed to the interaction between oxygen vacancies and domain switching. A qualitative model and a quantitative model are used to explain this phenomenon. Besides, polarization and oxygen treated experiment can exert an enormous influence on pinning effect and the mechanisms are also discussed in this work.

Materials with high dielectric constant and high nonlinear dependence of the dielectric constant on applied voltage are promising candidates for high tunable dielectric devices. Ferroelectric materials are very exciting class of microwave materials because their dielectric constants depend nonlinearly on an applied electric field. Ferroelectricity is one of the most used and studied phenomena in both scientific and industrial communities. Properties of ferroelectrics make them particularly suitable for a wide range of applications, ranging from sensors and actuators to optical or memory devices^{1,2}. Those important properties are largely controlled by ferroelectric domains. Thus understanding the behavior of ferroelectric domains has been a central issue for ferroelectric research. The ferroelectric domain switching is very sensitive to point defects, which can lead to a pinched shape hysteresis loops. Many ferroelectrics show pinning effect, such as Mn-doped Pb(Zr,Ti)O₃^{3–6}, (Ba,Sr)TiO₃⁷, BaTiO₃^{8,9}, (Pb,Sr)TiO₃¹⁰, Cu-doped K_{0.5}Na_{0.5}NbO₃¹¹, K-doped Pb(Zr,Ti)O₃ ceramics¹², and BiFeO₃ thin films¹³. Various mechanisms have previously been proposed to explain pinning effect. Previous work showed that pinning effect in Pb(Mn_{1/3}Nb_{2/3})O₃-Pb(Ti,Zr)O₃ ceramics was caused by defect dipoles, and depinning effect was determined by the reorientation of dipoles in high temperature region, author believed that defect dipoles resulted in pinning effect, while the depinning effect resulted from strong p-type conductivity³. Pandey *et al.* attributed the pinning effect to internal stress or internal field which interrupted long range polar order¹⁴. Besides, according to the first-principles study, Chandrasekaran *et al.* provided several atomistic simulated diagrams to explain pinning effect¹⁵.

(Sr,Pb)TiO₃ is a promising material in the applications of dielectric tunability and pyroelectricity^{16–19}. Recently, Liu *et al.* reported that a large electro-shape-memory effect (up to 0.23% under the electric field of 5 kV/mm) in Mn-doped (Pb,Sr)TiO₃ ceramics¹⁰. SrTiO₃ is a quantum paraelectric and shows dielectric relaxation at high temperatures due to oxygen vacancies^{20–23}. While in this work, both dielectric relaxations and pinning/

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Figure 1. The simulated diagram of domain switching behavior of a single-domain crystal in equilibrium ferroelectric state during applied electric field cycling. Small ellipses represent defect dipoles, blue lines represent new domain walls. P_s refers to spontaneous polarization, P_D defect polarization aligning along P_s , P_E polarization caused by applied electric field.

depinning phenomena were observed in (Sr,Pb)TiO₃ ceramics. Results showed that the high temperature dielectric relaxation was related to oxygen vacancies. The pinning effect could be explained by a qualitative model (the symmetry-conforming property of point defects), while the depinning effect could be explained by a quantitative model (domain wall velocity during ferroelectric switching). And, both models were different from previous researches. Moreover, the effect of polarization, O₂ treatment and N₂ treatment on pinning effect were also discussed.

Two Models

It is well known that after aging, ferroelectrics could exhibit double-hysteresis-like loops^{7–11}. Aging is a process involving gradual stabilization of ferroelectric domain by defect dipoles. A various of domain stabilization theories such as the grain-boundary theory, surface-layer model, domain-wall theory, and volume theory have been proposed²⁴. Recently, based on the symmetry-conforming property of point defects (defect symmetry principle)^{8,9}, it has been shown that the domain stabilization is a volume effect. According to this view point, point defects in crystal possess a “statistical symmetry” which follows the crystal symmetry in equilibrium ferroelectric state (i.e. aged ferroelectric state) and it is the symmetry property of point defects that creates a restoring force to drive domains back to original state during polarization switching^{7–9}. Besides, in equilibrium state, the polar crystal symmetry can lead to a polar defect short range ordering distribution which creates a defect polarization P_D aligning along the spontaneous polarization P_s direction.

Normally, the process of polarization switching comprises four courses: (i) nucleation of the new domains; (ii) lengthwise growth of the domains; (iii) transverse growth of the domains; (iv) combination of the domains. However, it is highly probable that defect dipoles can prohibit the transverse growth of domains accord to defect symmetry principle. Figure 1 shows a series of domain patterns during electric field cycling in a single-domain crystal with defect polarization P_D aligning along the spontaneous polarization P_s direction, which is not parallel to the direction of applied electric field E . The sample keeps a single-domain state before applied an electric field [Fig. 1(a)]. When applied a horizontal electric field, the single-domain crystal will undergo the following several stages: (i) nucleation of the new domains [Fig. 1(b)]; (ii) lengthwise growth of the new domains [Fig. 1(c)]; (iii) transverse growth of the new domains [Fig. 1(d,e)]; (iv) back to original single-domain pattern when the electric field decreases to 0 kV/cm [Fig. 1(f)]. During transverse growth, the polar defects can hinder the domain switching and the area of original domains around P_D may be so small that it cannot be observed with a domain-level optical microscope. Thus the single-domain crystal with polar defects keeps multidomain state during electric field cycling. According to defect symmetry principle, polar defects can create a restoring force in favour of domain switching back to original single-domain pattern after removing the electric field. This process of polarization switching with point defects is different from what we have known about normal polarization switching. Besides, in order to hinder transverse growth of new domains, the point defects may deform the domain walls when they close to the point defects during polarization switching, and this is similar to the plastic deformation in metal where the second phase particles can deform dislocation lines when they pass the second phase particles²⁵. The side-wise 180° domain wall velocity ν in the low-field region can be expressed by²⁶:

$$\nu = \nu_{\infty} e^{-\delta/E} \quad (1)$$

where E is the applied electric field, and δ and ν_{∞} are essentially field independent over the measured range. Besides, δ is found to increase slightly with field and varies with temperature faster than T^{-1} .

In the case of volume effects, another relation for the wall velocity ν is proposed²⁴,

Figure 2. XRD patterns for SPT ceramics.

$$\nu = \nu_{\infty} e^{-\delta/[E_a - E_i(t)]} \quad (2)$$

where E_a is the applied electric, E_i is the internal bias field and δ and ν_{∞} are essentially field independent over the measured rang. δ increases slightly with field and varies with temperature faster than T^{-1} .

Experimental Procedure. Strontium lead titanate ceramics ($\text{Sr}_{1-x}\text{Pb}_x\text{TiO}_3$ with $x = 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55$, abbreviated as SPT100x) were prepared by a conventional solid-state reaction technique¹⁹. Reagent-grade Pb_3O_4 , SrCO_3 and TiO_2 powders were weighted according to their stoichiometric composition. Then powders in stoichiometric ratio were first mixed and calcined at 850°C for 5 h. The calcined powders were mixed with alcohol milling for 24 h and dried. After that, they were mixed thoroughly with a polyvinyl alcohol (PVA) binder solution and uniaxially pressed into discs of 12 mm in diameter and 2 mm in thickness. These discs were sintered at $1300\sim 1350^\circ\text{C}$ for 2 h in air. Silver paste was applied on both surfaces of the discs and fired at 650°C as electrode for electrical properties measurement.

The dielectric tunability was measured by using a blocking circuit, a multi-frequency LCR meter (Model SR720 of Stanford Research System), and a dc power source (Keithley 6517A). The permittivity and dielectric loss were measured by Agilent E4980A in the frequency range from 500 Hz to 1 MHz and in the temperature range from 25 to 550°C . Ferroelectric hysteresis loops were obtained by a computer-controlled virtual-ground circuit with Radiant Technologies Precision Premier II (Radiant Tech, USA). Due to the retention and relaxation, the loops are usually not closed. The temperature (T), frequency (f) and electric field (E) used here varied from 25 to 150°C , 0.05 to 50 Hz and 10 to 40 kV/cm, respectively.

Results and Discussion

Figure 2 shows the room temperature XRD patterns of SPT ceramics with different Pb content. The XRD patterns show a typical polycrystalline perovskite structure in agreement with the PDF card No. 52-1119 and with no evidence of the secondary phase formation for all the ceramics, which indicates the Pb^{2+} ions are incorporated into the SrTiO_3 matrix. The XRD patterns, dielectric and ferroelectric properties show a domination of a tetragonal structure. The precise peak splitting of the doublet near 45° to 48° of 2θ is included in Fig. 2. It is clearly seen that with the increase of Pb concentration, tetragonal phase in SPT ceramics becomes more and more obvious.

Tunability (k) is defined as the ratio of the dielectric permittivity of the material at zero electric field to its permittivity at an applied electric field. Clearly, tunability is usually used to signify the strength of dielectric nonlinearity. Generally speaking, dielectric nonlinearity contains two macroscopic manifestation: ferroelectric hysteresis loops and bias characteristics of dielectric constant (tunability). So, both tunability part and hysteresis part can be used to describe the dielectric nonlinearity. Ferroelectric materials with a high dielectric tunability and high figure of merit have potential usefulness for tunable capacitors^{27,28}. Lots of works of dielectric tunability effect have been done and have made great progress. Sun *et al.* analyzed the dielectric tunability effect in bulk LuFe_2O_4 , they achieved dielectric tunability about 80% under the electric field of 50 V/cm²⁹. In this paper, the dc field dependence of permittivity and dielectric loss for SPT samples at room temperature were measured under a dc field of 20 kV/cm and a frequency of 10 kHz. The results are shown in Fig. 3. However, the dielectric tunability of SPT55 is not shown here because of the strong ferroelectricity and high dielectric loss at room temperature.

The tunability (k) can be calculated by

$$k = [\varepsilon(0) - \varepsilon(E)]/\varepsilon(0) \quad (3)$$

where $\varepsilon(0)$ and $\varepsilon(E)$ represent the dielectric constant at zero and a non-zero electric field, respectively. The tunabilities for SPT20, SPT25, SPT30, SPT35, SPT40, SPT45 and SPT55 are 3.39%, 12.4%, 57.6%, 48.9%, 28.6%, 14.4% and 11.1%, respectively. It can be seen that the dielectric tunability of SPT30 is higher than the others. The reason

Figure 3. Permittivity and dielectric loss as a function of electric field for SPT20 (a), SPT25 (b), SPT30 (c), SPT35 (d), SPT40 (e), SPT45 (f) and SPT50 (g), which were measured at room temperature with 20 kV/cm and 10 kHz. The dielectric tunability and FOM are shown in (h).

for a higher tunability is that the investigated temperature (room temperature) is near to the Curie temperature ($T_c = 12^\circ\text{C}$) of SPT30.

The figure of merit (*FOM*) is calculated by

$$FOM = k/\tan \delta \quad (4)$$

The maximum *FOM* is 347 and the corresponding sample is SPT30. Although our results of tunability (*k*) is lower than that of bulk LuFe_2O_4 (tunability about 80%), but compared to the similar ferroelectric materials, these *k* and *FOM* of the PST, especially SPT30, are comparable to the currently studied tunable materials, such as $(\text{Ba,Sr})\text{TiO}_3$ and $\text{Ba}(\text{Zr,Ti})\text{O}_3$ ^{27,28}. The tunability effect and figure of merit of the SPT ceramics, also indicate that SPT is a promising material for tunable capacitor applications.

In perovskites, the high-temperature relaxation behavior mainly occurs in lead-based compositions^{28,30–32}. Figure 4 depicts the temperature dependence of permittivity (ϵ_r) and dielectric loss ($\tan \delta$) at different frequencies. In these results, a series of wide and prominent relaxation peaks are observed. These peaks obviously shift toward a higher temperature with increasing measuring frequency, which are typical dielectric relaxation behavior. The activation energy (*U*) of relaxation units can be calculated by the famous Arrhenius law. The relaxation time (τ) can be written as:

$$\tau = \tau_0 \exp(U/k_B T) \quad (5)$$

where *T* is the peak temperature of $\tan \delta$, τ_0 is the relaxation time at an infinite temperature, and k_B is Boltzmann constant. Using the extreme value condition:

$$\omega\tau = \sqrt{\epsilon_s/\epsilon_\infty} \quad (6)$$

where ϵ_s is the static permittivity, ϵ_∞ is the permittivity at high frequency, and angular frequency $\omega = 2\pi f$, the relationship between the measuring frequency and $\tan \delta$ peak temperature can be expressed as

$$\ln(2\pi f) = -U/k_B T + \ln(\sqrt{\epsilon_s/\epsilon_\infty}/\tau_0) \quad (7)$$

According to Eq. (5), the peak temperature of $\tan \delta$ at different frequencies for $(\text{Sr,Pb})\text{TiO}_3$ ceramics are well fitted as shown in the inset of Fig. 4. The slopes of the linear fits yield the activation energy (*U*) and the values of activation energy are between 1.059 and 1.318 eV, which are close to the typical value (1.0 eV) of activation energy for oxygen vacancies in the perovskites^{32–34}. So the relaxation peaks may be associated with the oxygen vacancies.

The variation of *P*-*E* hysteresis loops for SPT35 and SPT55 ceramics with different temperatures is shown in Fig. 5. It can be seen that the samples exhibit pinched loops and these loops are constricted at *E*=0 kV/cm. However, as the temperature increases, these loops “open” gradually and become normal loops at 45 °C for SPT35 and 150 °C for SPT55, respectively. It is also noted that the loops of SPT35 are much thinner than that of SPT55. The reason may be that the concentration of PbTiO_3 (ferroelectric phase) in SPT35 is much lower than that of SPT55. Moreover, on increasing the Pb/Sr ratio, the Curie temperature T_C increases gradually^{10,16,19}. So the ferroelectric phase of SPT35 is much smaller than that of SPT55 at the same temperature, and this case may also result in a thin loop.

Figures 6 and 7 show the electric field and frequency dependent hysteresis loops for SPT35 and SPT55 ceramics, respectively. The effect of enhancing electric field or lowering frequency on the loops has a tendency similar to that of rising temperature. The loops become “swelled” gradually with increasing electric field or lowering frequency and turn into normal loops finally.

Figure 8 shows the hysteresis loops for SPT40, SPT45 and SPT50 ceramics. As we can see, these loops are normal loops and do not show pinning effect. The reason may be that samples do not produce enough oxygen vacancies to pin the domain switching. More detail will be discussed in the following. Curie temperatures of SPT20, SPT25 and SPT30 are lower than room temperature, so their ferroelectric properties were not discuss in this work.

Just as mentioned previously, the acceptor-doped ferroelectric in aging state exhibits a double-hysteresis-like loop and the existence of defect dipoles (acceptor ions and oxygen vacancies) is the primary cause of pinning effect. Recently, the research about oxygen vacancies in materials has been done from theory and experiment^{4,5,12,15,21,35–42}. Li *et al.* and Zhang *et al.* analyzed the photoemission spectra of O 1s by X-ray photoelectron spectrum (XPS) and provided a direct evidence for the existence of oxygen vacancies in acceptor-doped ferroelectrics^{4,5}. According to defect symmetry principle, oxygen vacancies and aging is the key factor of pinning effect. In this paper, the undoped $(\text{Sr,Pb})\text{TiO}_3$ ceramics with pinched shape loops are known to contain oxygen vacancies and lead vacancies, which are created by the evaporation of lead oxide during sintering process at high temperatures. In $(\text{Pb,Zr})\text{TiO}_3$, previous researchers also observed the pinning effect which has a close relationship with oxygen vacancies^{4,6}. Before measured, ceramics were kept at high temperature environment. The time is so long that the specimens become actually aged ferroelectrics. So the defect symmetry principle can be applied to $(\text{Sr,Pb})\text{TiO}_3$ ceramics. Due to easy formation of oxygen vacancies and lead vacancies in lead-based perovskites, it is likely that the oxygen-lead divacancy could exist in an undoped material and form defect dipoles¹⁵. When an external electric field is applied to the sample, domain switching occurs abruptly (without diffusion). Based on previous research results^{12,37}, the defect polarization P_D cannot be rotated in such a diffusionless domain switching process, since the reorientation of P_D involves the oxygen vacancies migration and requires long time, thermal energy and high electric field, *i.e.*, more energy³⁸. The unchanged P_D provides a restoring force favouring the domains back to original state when the electric field is removed, so a pinched *P*-*E* loop is observed. From the experimental results, SPT40, SPT45 and SPT50 do not show pinched loops. The reason may be that the oxygen vacancies produced by lead oxide evaporation during sintering is so less that available defect dipoles are less and cannot effectively hinder domain switching. So the loops observed are normal. In addition, it is interesting to see that the activation

Figure 4. Temperature dependence of permittivity ϵ_r and dielectric loss $\tan\delta$ at various frequencies of 0.5, 1, 5, 10, 50, 100, 500, and 1000 kHz for (Sr,Pb)TiO₃ ceramics (a) SPT20, (b) SPT25, (c) SPT30, (d) SPT35, (e) SPT40, (f) SPT45, (g) SPT50 and (h) SPT55. The insets in (a–c) are the temperature dependence of permittivity between $-200 \sim 150^\circ\text{C}$. The insets in (a–h) give the plot between $\ln(2\pi f)$ and $1000/T$ according to the Arrhenius law.

energies of oxygen vacancies in SPT35 (1.204 eV) and SPT55 (1.258 eV) with pinning effect are higher than that in SPT40 (1.059 eV), SPT45 (1.179 eV) and SPT50 (1.097 eV) with no pinning effect.

Figure 5. Hysteresis loops for SPT35 (a) and SPT55 (b) measured at 10 Hz and different temperatures.

Figure 6. Hysteresis loops for SPT35 (a) and SPT55 (b) measured at 10 Hz, room temperature and different electric fields.

Concerning the depinning effect, previous researchers consider the migration of some oxygen vacancies along the direction of applied electric field at high temperature or low frequency as the main cause^{9,11}. However, in this paper, the same pinched loops can be observed immediately again at low temperature, low electric field or high frequency after the sample is measured at high temperature, high electric field or low frequency. If the pinning phenomenon can be observed again after depinning, it should involve the migration of oxygen vacancies so that the defect dipoles can pin domain switching. However, as discussed above, the oxygen vacancies migration is difficult without sufficient energy or long time. So the oxygen vacancies migration may not be the main cause for depinning effect and there should be another explanation for the observed phenomenon.

According to Eq. (1) or Eq. (2), as temperature or electric field raises, the domain wall velocity ν increases. In other words, new domain wall can move fast toward defect dipoles at high temperature or high electric field. As a result, the area of original domain around defect dipoles is small and the restoring force is insufficient to reverse the domain to original state when the external electric field decreases to zero. Thus the loops become

Figure 7. Hysteresis loops for SPT35 (a) and SPT55 (b) measured at room temperature and different frequencies.

Figure 8. Hysteresis loops for SPT40 (a), SPT45 (b) and SPT50 (c) measured at room temperature.

normal. While in the same velocity condition, the domain walls have enough time to close to defect dipoles in low-frequency measurement and the area of original domain around defect dipoles is also small. The reversal of domain to original state cannot be completed when the field decreases to zero, thus resulting in depinning effect. Besides, electrical conduction in samples at high-temperature, high-electric-field or low-frequency measurements can also contribute to the depinning effect.

To clarify the origin of pinning effect, a special treatment has been done for SPT35 sample. After measurements of hysteresis loops in different situations, the same sample was annealed in O_2 atmosphere at $600^\circ C$ for 10 h. Then a slightly constricted hysteresis loop was observed, as shown in Fig. 9. Annealing in oxygen can reduce oxygen vacancies²¹. When the concentration of oxygen vacancies is low, the restoring force from oxygen vacancies is insufficient to reverse the domain to original state, resulting in a slightly contractive loop. This result indicates that the oxygen vacancies are the main cause for pinning effect in undoped (Sr,Pb)TiO₃ ceramics and their concentration can affect the extent of pinning. It is consistent with the discussion about normal *P-E* loops in SPT40, SPT45 and SPT50. After the measurements of O_2 treated SPT35 sample, SPT35 sample was then annealed in N_2 atmosphere at $600^\circ C$ for 10 h. Then typical constricted hysteresis loop was recovered, as shown in Fig. 9c. This strongly indicates that oxygen vacancies and its concentration plays an important role in pinning effect. Additional, it could be seen that values of polarization increased slightly after N_2 treatment, which might be contributed by some defects (oxygen vacancies).

An additional work has been done for SPT55, which is selected and poled at $160^\circ C$, 15 kV/cm for 30 min. After poled, *P-E* loops of SPT55 were measured. The result is showed in Fig. 10. It was interesting to see that the sample did not exhibit pinched loop which was measured immediately after poled. While a slightly constricted loop was observed after 24 hours and a severely constricted loop was observed after annealing in air. This phenomenon can be explained as follow. Oxygen vacancies may obtain enough energy to migrate and form new

Figure 9. Hysteresis loops for SPT35 measured at 50 Hz, 10 kV/cm and room temperature, (a) as fabricated, (b) O_2 treated and (c) N_2 treated.

Figure 10. Hysteresis loops (a) and simulated diagrams of domain switching behavior (b) for SPT55 which measured before being poled (a1) and (b1), immediately after being poled (a2) and (b2), one day later after being poled (a3) and (b3) and after annealing in air (a4) and (b4). P_s , P_s' , P_D and P_D' represent spontaneous polarization, new spontaneous polarization after poled, defect polarization and new defect polarization after poled, respectively. The blue line in (b3) is domain wall.

defect polarization P_D' parallel with the direction of applied electric field during the sample being poled. The parallel defect polarization P_D' creates less force for reversible domain switching, so a loop with no pinning effect is observed. Over time, a part of single domain will change the orientation of polarization due to the influence of surrounding environment *e.g.* thermal motion, so will defect dipoles. These defect dipoles unparallel to applied electric field can hinder the transverse growth of new domain and afford restoring force for reversible domain switching, resulting in a lightly constricted loop. After annealing, the polarization state in sample can return to original state. Consequently, a severely constricted loop is observed. When sample is poled, one direction is easy to reach saturated polarization and the other is difficult to reach saturated polarization, as shown in Fig. 9(a2,a3).

Conclusions

In this work, a detailed study on the structures, dielectric properties and ferroelectric domain switching of $(Sr,Pb)TiO_3$ ceramics is investigated. The XRD pattern shows a domination of a tetragonal structure in SPT ceramics. The high dielectric tunability and high figure of merit imply the possible application in tunable capacitor. The high-temperature dielectric relaxation behavior is observed, which is caused by oxygen vacancies with activation energy between 1.059 and 1.318 eV. According to defect symmetry principle, oxygen vacancies in equilibrium ferroelectric state can create defect polarization which provides a restoring force for domain switching. So the pinched loops can be observed. The fast and sufficient motivation of new domain walls to defect dipoles and electric conduction in high-temperature, high-electric-field or low-frequency measurements are deemed to be the main cause for depinning effect. Annealing in oxygen which reduces the concentration of oxygen vacancies and polarizing by applied electric field which can transform the defect polarization to parallel to applied electric field exert enormous impact on pinning effect and result in loops with no or less constriction. Understanding the interaction between oxygen vacancies and ferroelectric domain switching is important for further application.

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Author Contributions

X.-X.H. and T.-F.Z. prepared samples, analyzed the data and wrote the paper, they contributed to this work equally and should be regarded as co-first authors. X.-G.T. supervised the project and participated in the paper correction. Y.-P.J. and Q.-X.L. contributed to the dielectric analysis. Z.-Y.F. contributed to ferroelectric analysis. Q.-F.Z. participated in the paper correction. All authors read and approved the final manuscript.

Additional Information

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