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ARTICLE

Relaxation ferroelectric in thin films of Diisopropylammonium Perchlorate

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Molecular ferroelectric thin films are highly desirable for their easy and environmentally friendly processing, light weight, and mechanical flexibility. A thin film of Diisopropylammonium Perchlorate (DIPAP) processed by spin-coating method shows a good roughness and texture structure with (101) orientation in ferroelectric phase with space group of P1. Simultaneously, the thin film shows above room temperature ferroelectricity and ferroelectric relaxivity, which is completely different from crystals. These properties make DIPAP a candidate in sensing, data storage, electro-optics, and molecular/flexible electronics.

Introduction

Ferroelectrics are electroactive materials which have been widely used in thermal imaging, data storage, mechanical actuation, energy harvesting and so on,[1, 2] since their spontaneous polarizations can be controlled by temperature, electric field and mechanical stress, as well as magnetic field.[3-7] Presently, applications of ferroelectrics have been dominated by inorganic perovskite-type materials, such as lead zirconate titanate (PZT) and barium titanate (BTO).[8-11] It should be noted that the ferroelectricity was first discovered in an organic crystal, Rochelle salt [12] and later some other molecular crystals were found to be ferroelectric, such as triglycine sulfate, thiourea. The mechanism of most molecular ferroelectrics comes from order-disorder transition, while that of inorganic perovskite ferroelectrics comes from displacive of cations and/or anions. The drawbacks in spontaneous polarization, transition temperature, and thermal stability limit the applications of molecular ferroelectrics. However, molecular ferroelectrics have some advantages including light weight, mechanical flexibility, easily designing, and environmentally friendly synthesizing compared with inorganic ferroelectrics, especially those containing toxic heavy metals like Lead. In recent years, many molecular ferroelectrics have been discovered, which have large spontaneous polarizations and high transition temperatures. For example, the spontaneous polarization of croconic acid is as high as $23 \, \mu C/cm^2$.[13] Most recently Diisopropylammonium bromide (DIPAB)[14] and Diisopropylamine chlorine (DIPAC)[15] were found to have a large spontaneous polarization of $20 \, \mu C/cm^2$ and $8 \, \mu C/cm^2$ with a high ferroelectric-paraelectric transition temperature of 426 K and 440 K, respectively. Therefore, these molecular ferroelectrics have broad application prospect in the future. To widely apply molecular ferroelectrics, the most important is to grow smooth thin films. However, it is difficult to fabricate thin films for most organic ferroelectric materials, which has limited the development and application of these materials. Only a few polymer ferroelectric materials, such as poly (vinylidene fluoride) (PVDF) and its copolymer poly (vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)), have been fabricated relatively mature thin films. Ferroelectric thin films may exhibit different properties from that of crystals, for example, thin film of Imidazolium Perchlorate shows superior electromechanical coupling.[16] The dimensional effect and surface/interface effect may play an important role on polarization in ferroelectric thin films.[17, 18] There are a series of ferroelectrics, called relaxor ferroelectric, which displays attractive and extraordinary dielectric properties.[19-21] For instance, they are characterized by more gradual change in temperature dependence of the dielectric constant than normal ferroelectric, and show a frequency dependent behavior. Diisopropylammonium Perchlorate (DIPAP) [22] is a newly discovered molecular ferroelectric, which displays an above-room-temperature ferroelectric to paraelectric transition temperature (Tc =338 K). Here, we report a high performance thin film of DIPAP on silicon (001) substrate by a spin-coating method, which show some exotic relaxor ferroelectric properties compared with the crystal.

Experimental section

Diisopropylamine and perchloricacid, based on molar concentration 1:1, were mixed into methylalcohol solution. The thin films were fabricated on Si (001) substrates by spin-coating method using a SpinMaster-100 spin coater. Finally, the films were baked in a 50℃ atmosphere for 4 hours before becoming an ideal DIPAP thin film. X-ray diffraction (XRD) was measured on a Rigaku Dmax-rB X-ray diffractometer, with a step-scan mode. The thickness was measured on S-3400N II Scanning electron microscope (SEM). The complex dielectric constant was measured by a Tonghui TH2828A LCR meter using a sinusoidal wave with V_{pp} of 2V. The Au electrodes were used as Au-DIPAP-Au construction as illustrated in Fig.S1, which is similar for pyroelectric and ferroelectric measurements. The temperature dependence of spontaneous polarization was carried out by integration of the pyroelectric current, which was measured by a Keithley 6517B electrometer with a constant heating rate. The dynamic pyroelectric current was obtained using the Chynoweth technique at room temperature. A pulsed laser

with wavelength of 1470 nm was used to control temperature of samples periodically. AFM and PFM were measured by an Asylum Research Cypher scanning probe microscope with Olympus AC240TM. Phase and amplitude hysteresis loops were collected in the DART (dual a.c. resonance tracking) mode with a triangular pulse of amplitude of 5.0V applied to the tip. Ferroelectric hysteresis loops were measured in a Radiant RT6000 Premier II tester which was in touch with the top and bottom electrodes of a parallel plate capacitor Au/DIPAP/Au.

Results and discussion

Single crystals of DIPAP have a ferroelectric (with space group P1) to paraelectric (with space group of $P2_1/c$) phase transition at about 343 K as reported in Ref.22. More experiments are necessary to do in determining that thin films of DIPAP also have ferroelectricity and finding out the difference between films and crystals. Fig.1a. shows Atomic Force Microscope (AFM) image of a DIPAP film deposited on the (001) silicon substrate, and the roughness is less than 4 nm within area of $10 \mu m \times 10 \mu m$. The thickness of the film is about 2.5 μm as measured by SEM (Fig. S2). X-ray diffraction (XRD) measurements were taken on these films to determine the orientation of the film. Typical XRD pattern is shown in Fig.1b. Reflections are located at $2\theta = 12.775°, 25.570°, 38.240°$, which are indexed to be reflections from (101), (202), (303) planes of the ferroelectric phase P1, respectively. No other reflections are detected in our experiments. Therefore, DIPAP films can be considered as textured structure.[23]
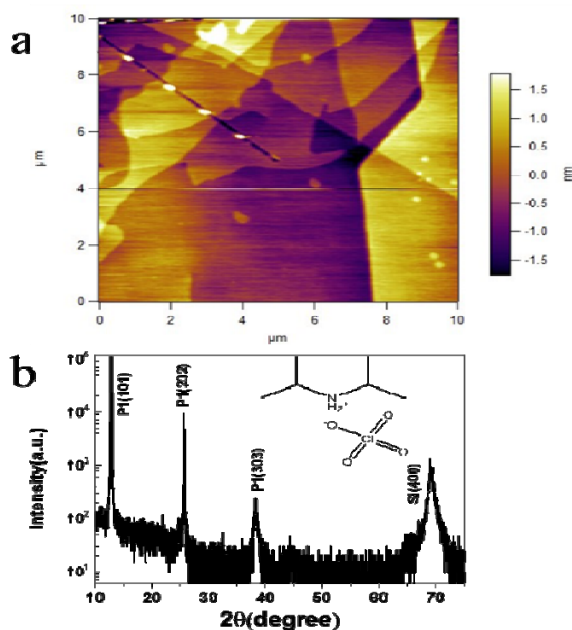
Figure 1. (a) AFM image and (b) X-ray diffraction pattern of DIPAP film. The inset shows DIPAP structural formula.

Improper ferroelectric[24] is different from the proper ferroelectric in dielectric behavior, namely, stepwise behavior in the temperature dependence of dielectric constants corresponds to improper ferroelectric, while a sharp peak behavior corresponds to a proper one. Switchable dielectric property is promising materials in data communication, signal processing, and sensing,[25] because it could undergo transition between high and low dielectric states. It is reported that DIPAP belongs to improper ferroelectric below 343 K. The temperature dependence of real part (ε') of the complex

dielectric constant ($\varepsilon = \varepsilon' - i\varepsilon''$, where ε'' is the imaginary part) at frequency range from 1 KHz to 1 MHz is shown in Fig.2a and Fig. S3. The dielectric behavior of the DIPAP films shows a distinguished characterization of improper ferroelectric. It has been reported that switchable molecular dielectric (SMD) materials of metal-organic frameworks (MOF) and molecular-ionic compounds experience dielectric mutation below room temperature.[26-28] It indicates that thin film of DIPAP with switchable dielectric property between low and high states above room temperature will have exciting prospect in the future. However, the film exhibits a broad dielectric mutation below the F-P transition temperature (T_c =338K, as observed in crystals). This will be also verified by pyroelectric measurements. The Fig.2a shows that dielectric transition temperature T_m shifts progressively toward higher temperature with frequency increasing, which is a characteristic feature of relaxor ferroelectrics. However, the dielectric constant of DIPAP crystals changes sharply at same transition temperature for all frequencies.[22] The imaginary part of dielectric constant, ε'', is also utilized to characterize the relaxation of DIPAP thin film as manifested in Fig.2b, which does change with temperature and frequency, and generates a peak in vicinity of T_m. It is noted that the electric filed (of about 4 kV/cm) exceeds the coercive filed as mentioned below, which will cause polarization switch and domain wall movements. Specifically, the relationship between frequency and transition temperature T_m is in according with Arrhenius' equation: $f = f_0 e^{-\frac{E_a}{kT}}$, that is $\ln(f) = \ln(f_0) - \frac{E_a}{kT}$, where E_a is activation energy, k is the Boltzmann constant. The activation energy E_a can be fitted with the value of E_a=3.30 eV from the linear relation between $\ln(f)$ and $\frac{1}{T}$ as shown in the inset of Fig.2b. We compared the activation energy with that of some other inorganic and organic relaxor ferroelectric, for example, $[Im]_5Bi_2Cl_{11}$ has an activation energy of 0.47 eV , and that of $[Me_2NH_2]_3Sb_2Br_9$ is 0.24 eV.[29] The activation energy of the thin film of DIPAP reaches 3.30 eV, much larger than others, which means it is more difficult to change the balance with respect to the other relaxor ferroelectric. In addition, the Debye-type relaxation in ferroelectrics is also following the Arrhenius' equation[30] , which may also cause dielectric dispersion. In short, DIPAP thin film has dielectric relaxation, which is not present in the crystal.
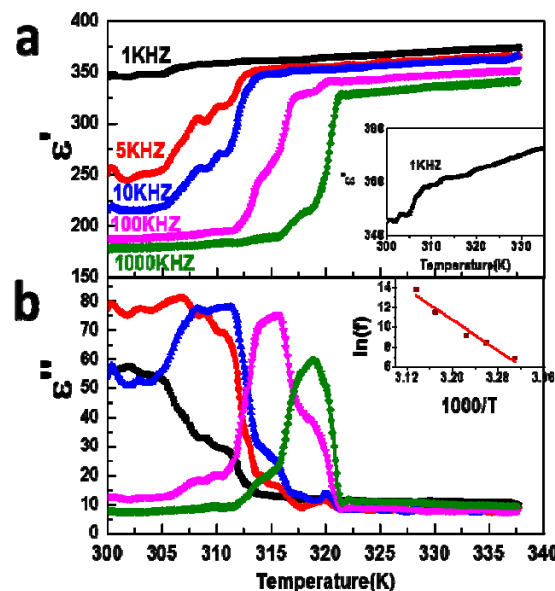
Figure 2. Temperature dependence of (a) real part (ε') and (b) imaginary part (ε'') of the complex dielectric constants at different frequencies. The inset of (a) is zoom of ε' at frequency of 1 KHz to see the transition more clarity. The inset of (b) shows transition frequency vs. the inverse of temperature.

The appearance of spontaneous polarization P_s was confirmed by pyroelectric measurements. We measured the pyroelectric current in the absence of an electric field in heating processes without a poling procedure. The secondary or constant-stress pyroelectric effect was measured. The spontaneous polarization can be integrated: $P = \int \frac{i}{A \times R} \, dT$, where i is the current, A is the area of sample, and R is heating rate. A peak of pyroelectric current was obtained at about 318 K as shown in Fig.3a, which is accordant with the high frequency dielectric transition temperature. The spontaneous polarization (P_s) value is about 0.1 $\mu C/cm^2$ at T=310K, which is very close to the value of DIPAP single crystals. The transition temperature of 318 K in the films is below that of the crystal (338 K), which can be also observed in some relaxor thin films, whose polarization changes very gradually with the temperature.[31] Furthermore, we also measured the pyroelectric current using the Chynoweth technique[32] by turning a infrared laser on and off, which changes the temperature of sample periodically in vicinity of room temperature as shown in Fig.3b. A negative current peak of about -0.01 nA is observed when the laser is turned on, due to the sudden increase of temperature. The current declines to zero as temperature is stabilized. When the laser is turned off, a positive current peak of about 0.01 nA is observed due to the suddenly decrease of temperature. The current between each ON/OFF and OFF/ON switching appears in the opposite direction, consistent with polarization change induced by increase and decrease of the temperature. Notice that during ON and OFF processes, the current are approximately symmetrical to each other, indicating that thermal-stimulate current can be ignored.[33] These phenomena exclude interference of other processes like trapped charge or electrets, and proved that the observed current is the unambiguous pyroelectric current.
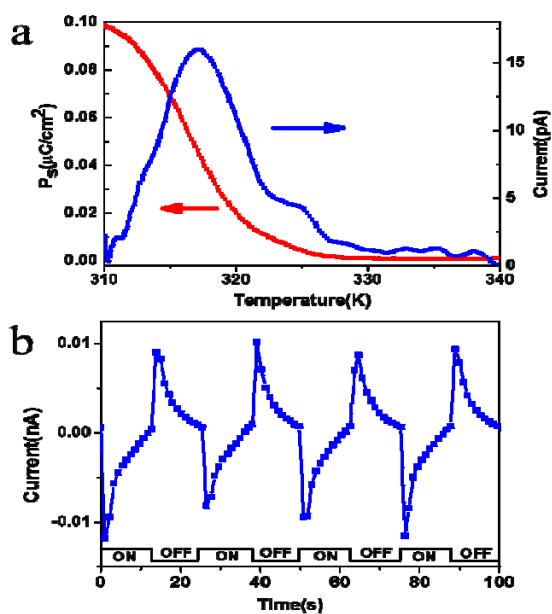
Figure 3. (a) The temperature dependence of spontaneous polarization (Ps) (left), calculated by integrating the pyroelectric current (right). (b) Pyroelectric current measured at room temperature when the Infrared laser changes between ON and OFF state.

Piezoresponse force microscopy (PFM) is always treated as a powerful technique to prove the characteristic feature of ferroelectric materials[34], particularly in some fields, like some biological tissues,[35] where ferroelectric hysteresis loops are very difficult to be obtained. DIPAP films show a single domain structure with the measurement range (Fig. S4). The remnant phase and piezoelectric switching hysteresis loops were observed. The phase signal (Fig.4a) exhibits a square-shaped hysteresis loop, which further reveals the ability of electric field to switch the spontaneous polarization. When the poling voltage is negative, the direction of polarization is downward. With the voltage decreases and changes into positive value, some antiparallel polarization domains are forming while the overall direction is unchanged. When the voltage exceeds the coercive field, the overall direction of polarization becomes upward. Therefore, the phase signal has a nearly 180° sharp transition. The amplitude signal shows a butterfly-like curve (Fig. 4b) which has two nearly symmetrical minimum points at the coercive field, revealing the switching of the ferroelectric domains. This indicates that it may be superior to ceramic perovskite ferroelectric like BTO and PTZ. The PFM results reveal that the ferroelectric domain of DIPAP thin films can be switched by electric field.
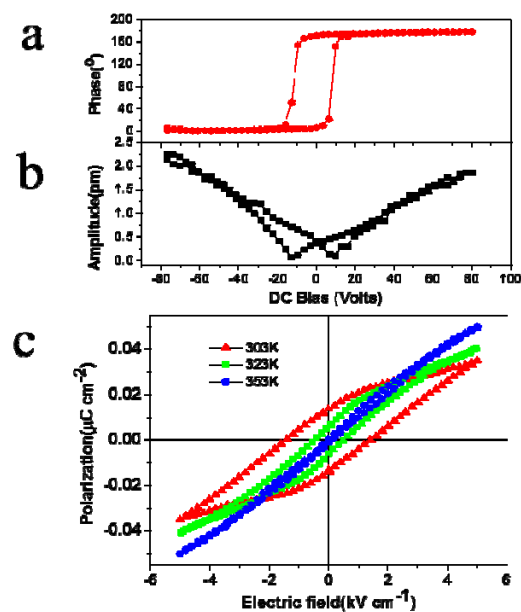
Figure 4. (a) The phase and (b) amplitude signals of local PFM hysteresis loops measured on the film surface. (c) The ferroelectric hysteresis loops of thin film at different temperatures.

To further verify the ferroelectric effect, ferroelectric hysteresis loops were measured by polarization response to different voltages between the top and bottom Au electrodes. As shown in Fig.4c, the loop shows a typical ferroelectric shape curve at room temperature, as a basic feature of ferroelectric properties, which means that we only need a quite small voltage like 2-3 V to alter the direction of polarization. The coercive field is about 5 kV/cm, larger than that of the crystals[22] which is

presented as 2 kV/cm, but it is much smaller than some typical ferroelectric like $BaTiO_3$ (10 $kVcm^{-1}$) and PVDF (500 kV/cm).[36] The remanent polarization is 0.02 $\mu C/cm^2$, which is only one fifth of the polarization of the crystals. The ferroelectric hysteresis loops is observed below the Curie temperature (338 K), and almost becomes linear dependence at 353 K, which is above the F-P transition temperature (Fig. 4c). With the temperature increasing, the remanent polarization and coercive field reduced, while they show nearly temperature independence in the crystals. This also explains that the thin film is a typical relaxor ferroelectrics.[37]

These results demonstrate that the thin film of DIPAP has many features in common with the relaxor ferroelectric systems in inorganic and organic materials, such as the polarization P_s that changes gradually comparing with crystals, a slimmer polarization loop with the temperature increasing and the temperature and frequency dependent dielectric mutation, which follows the Arrhenius' equation.

Conclusions

In summary, DIPAP, as a newly discovered ferroelectric material, has a Curie temperature higher than room temperature. We use the convenient and inexpensive spin-coating method to make a smooth thin film with single orientation at (101) plane on Si (001) substrates. The roughness of DIPAP thin film is less than 4 nm in a range of $10\,\mu m$, which fully meets the requirements of practical applications. The dielectric properties show that the thin film of DIPAP is a typical ferroelectric relaxor, which is completely different from the crystal. The ferrolelectricity of DIPAP thin films are confirmed by PFM, pyroelectricity, and hysteresis loop, which show a very small coercive electric filed. It is very important for the applications of ferroelectric thin films.

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Notes

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References

1. S. B. Lang, S. A. Tofail, A. L. Kholkin, M. Wojtas, M. Gregor, A. A. Gandhi, Y. Wang, S. Bauer, M. Krause and A. Plecenik, *Scientific reports*, 2013, **3**, 2215.
2. S. H. Baek, J. Park, D. M. Kim, V. A. Aksyuk, R. R. Das, S. D. Bu, D. A. Felker, J. Lettieri, V. Vaithyanathan, S. S. Bharadwaja, N. Bassiri-Gharb, Y. B. Chen, H. P. Sun, C. M. Folkman, H. W. Jang, D. J. Kreft, S. K. Streiffer, R. Ramesh, X. Q. Pan, S. Trolier-McKinstry, D. G. Schlom, M. S. Rzchowski, R. H. Blick and C. B. Eom, *Science*, 2011, **334**, 958-961.
3. H. Lu, C. W. Bark, D. Esque de los Ojos, J. Alcala, C. B. Eom, G. Catalan and A. Gruverman, *Science*, 2012, **336**, 59-61.
4. P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf and S. V. Kalinin, *Science*, 2009, **324**, 1421-1425.
5. B. Neese, B. Chu, S. G. Lu, Y. Wang, E. Furman and Q. M. Zhang, *Science*, 2008, **321**, 821-823.
6. J. F. Scott, *Science*, 2007, **315**, 954-959.
7. K. F. Wang, J. M. Liu and Z. F. Ren, *Advances in Physics*, 2009, **58**, 321-448.
8. H. Megaw, *Nature*, 1945, **155**, 484-485.
9. B. Jaffe, *Journal of Applied Physics*, 1954, **25**, 809.
10. C. Chao, Z. Ren, Y. Zhu, Z. Xiao, Z. Liu, G. Xu, J. Mai, X. Li, G. Shen and G. Han, *Angewandte Chemie*, 2012, **51**, 9283-9287.
11. E. Kan, H. Xiang, C. Lee, F. Wu, J. Yang and M.-H. Whangbo, *Angewandte Chemie*, 2010, **122**, 1647-1650.
12. V. J, *Phys Rev*, 1921, **17**, 475-481.
13. S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, *Nature*, 2010, **463**, 789-792.
14. D. W. Fu, H. L. Cai, Y. Liu, Q. Ye, W. Zhang, Y. Zhang, X. Y. Chen, G. Giovannetti, M. Capone, J. Li and R. G. Xiong, *Science*, 2013, **339**, 425-428.
15. D. W. Fu, W. Zhang, H. L. Cai, J. Z. Ge, Y. Zhang and R. G. Xiong, *Advanced materials*, 2011, **23**, 5658-5662.
16. Y. Zhang, Y. Liu, H. Y. Ye, D. W. Fu, W. Gao, H. Ma, Z. Liu, Y. Liu, W. Zhang, J. Li, G. L. Yuan and R. G. Xiong, *Angewandte Chemie*, 2014, **53**, 5064-5068.
17. J. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. Li, S. Choudhury, W. Tian, M. Hawley and B. Craigo, *Nature*, 2004, **430**, 758-761.
18. K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L. Q. Chen, D. G. Schlom and C. B. Eom, *Science*, 2004, **306**, 1005-1009.
19. J.-H. Ko, D. H. Kim and S. Kojima, *Applied Physics Letters*, 2007, **90**, 112904.
20. V. V. Shvartsman, D. C. Lupascu and D. J. Green, *Journal of the American Ceramic Society*, 2012, **95**, 1-26.
21. A. Peláiz-Barranco, I. González-Carmenate and F. Calderón-Piñar, *Solid state communications*, 2005, **134**, 519-522.
22. K. Gao, M. Gu, X. Qiu, X. Ying, H.-Y. Ye, Y. Zhang, J. Sun, X. Meng, F. Zhang and D. Wu, *Journal of Materials Chemistry C*, 2014, **2**, 9957-9963.
23. E. V. Balashova and B. B. Krichevtsov, *Ferroelectrics*, 2014, **469**, 26-42.
24. M. E. Lines and A. M. Glass, *Principles and applications of ferroelectrics and related materials*, Clarendon press Oxford, 2001.
25. Z. Czapla, S. Dacko and A. Waśkowska, *Journal of Physics: Condensed Matter*, 2003, **15**, 3793.
26. W. Zhang, Y. Cai, R. G. Xiong, H. Yoshikawa and K. Awaga, *Angewandte Chemie*, 2010, **49**, 6608-6610.
27. H.-B. Cui, K. Takahashi, Y. Okano, H. Kobayashi, Z. Wang and A. Kobayashi, *Angewandte Chemie International Edition*, 2005, **44**, 6508-6512.
28. Z. Paja k, P. Czarnecki, J. Wa sicki and W. Nawrocik, *The Journal of Chemical Physics*, 1998, **109**, 6420.
29. T. Hang, W. Zhang, H.-Y. Ye and R.-G. Xiong, *Chemical Society Reviews*, 2011, **40**, 3577-3598.
30. A. A. Bokov and Z. G. Ye, *J Mater Sci*, 2006, **41**, 31-52.
31. Q. M. Zhang, *Science*, 1998, **280**, 2101-2104.
32. A. G. Chynoweth, *Journal of Applied Physics*, 1956, **27**, 78.
33. I. Lubomirsky and O. Stafsudd, *The Review of scientific instruments*, 2012, **83**, 051101.
34. Y. Kutes, L. Ye, Y. Zhou, S. Pang, B. D. Huey and N. P. Padture, *The Journal of Physical Chemistry Letters*, 2014, **5**, 3335-3339.
35. Y. Liu, Y. Zhang, M.-J. Chow, Q. N. Chen and J. Li, *Physical Review Letters*, 2012, **108**.
36. S. Horiuchi and Y. Tokura, *Nature materials*, 2008, **7**, 357-366.
37. L. E. Cross, *Ferroelectrics*, 1987, **76**, 241-267.