

This is the accepted version of the article:

Narvaez J., Saremi S., Hong J., Stengel M., Catalan G.. Large Flexoelectric Anisotropy in Paraelectric Barium Titanate. *Physical Review Letters*, (2015). 115. 037601: - .
10.1103/PhysRevLett.115.037601.

Available at:

<https://dx.doi.org/10.1103/PhysRevLett.115.037601>

Large Flexoelectric Anisotropy in **Paraelectric** Barium Titanate

Authors

Jackeline Narvaez^{1,2,+}, Sahar Saremi¹, Jiawang Hong³, Massimiliano Stengel^{4,5} and Gustau Catalan^{1,5,*}

¹ICN2- Institut Catala de Nanociencia i Nanotecnologia, Campus UAB, 08193 Bellaterra (Barcelona), Spain.

²CSIC- Consejo Superior de Investigaciones Cientificas, ICN2 Building, Campus UAB, 08193 Bellaterra (Barcelona), Spain.

³Materials Science and Technology Division, Oak Ridge National Laboratory, Tennessee, 37831, USA

⁴Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra (Barcelona), Spain.

⁵ICREA- Institutio Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain.

⁺jackeline.narvaez@cin2.es

^{*}gustau.catalan@cin2.es

Abstract.

The bending-induced polarization of barium titanate single crystals has been measured with an aim to elucidate the origin of the large difference between theoretically predicted and experimentally measured flexoelectricity in this material. The results indicate that part of the difference is due to polar regions (short range order) that exist above T_C and up to $T^* \approx 200$ - 225°C . Above T^* , however, the flexovoltage coefficient still shows an unexpectedly large anisotropy for a cubic material, with (001)-oriented crystals displaying 10 times more flexoelectricity than (111)-oriented crystals. Theoretical analysis shows that this anisotropy cannot be a bulk property, and we therefore interpret it as indirect evidence for the theoretically predicted but experimentally elusive contribution of surface piezoelectricity to macroscopic bending-induced polarization.

The flexoelectric effect is by definition the linear response of dielectric polarization to strain gradient. This effect has two particularly useful features. First, in contrast to the piezoelectric effect, flexoelectricity is universal and not only limited to non-centrosymmetric crystal structures, because strain gradients break by themselves inversion symmetry. Second, since maximum achievable strain gradients grow in inverse proportion to sample size, flexoelectricity can be very large at the nanoscale [1]. The magnitude of flexoelectric coefficient (the constant of proportionality between polarization and strain gradient) was predicted for the first time by Kogan. He estimated the coefficients to be of the order of e/a , where e is the electronic charge and a is the lattice parameter; it is a very small value of around 10^{-10} C/m for almost all insulators [2]. Bursian and Trunov [3], and then Tagantsev [4], later predicted an enhancement of flexoelectric effect in materials with high dielectric permittivity, a prediction backed up by first principle calculations [5,6,7] and validated by multiple experimental work on relaxor ferroelectrics and ferroelectric materials, such as lead magnesium niobate ceramic (PMN) [8], barium strontium titanate ceramic (BST) [9], lead zirconate titanate ceramic (PZT) [10], Strontium titanate single crystal (STO) [11] and barium titanate ceramic (BTO) [12]. Measurements on BST and BTO also revealed a remarkable magnitude of the flexoelectric coefficient in the order 10^{-5} C/m, which is 10^3 - 10^5 times larger than the flexoelectric coefficient estimated by Kogan and is too large even when the dielectric constant is factored in. The origin of this enormous flexoelectric coefficient is not known.

The high dielectric constant of BaTiO_3 (BTO) makes it a good candidate to obtain high flexoelectric performance. On cooling below the Curie temperature ($T_C \approx 125^\circ\text{C}$), the material undergoes a phase transition from paraelectric cubic to ferroelectric tetragonal [13, 14], and the dielectric constant shows a peak; since flexoelectricity is proportional to permittivity, one may indeed expect large flexoelectricity. However, even factoring in the large permittivity, the experimentally measured flexoelectric coefficient of BTO [12] is still between one and two orders of magnitude too high compared to theoretical predictions [15,16]. Recently, two different explanations have been put forward. Biancholi et al. [17] have observed net polarization in nominally paraelectric SrTiO_3 and $(\text{Ba,Sr})\text{TiO}_3$. Such built-in macroscopic polarizations are inherent to fabrication processes and common to all materials and may therefore explain the large bending-induced polarization of BTO. In contrast, Bersuker's theoretical analysis concludes instead that the large flexoelectric response is due to a flexoelectrically-induced alignment of precursor polarization that exists in the paraelectric

phase of BTO [18]. In this scenario, BTO would behave similarly to relaxor ferroelectrics [19]. In this article we report a thorough experimental investigation on the magnitude and origin of the enhanced flexoelectricity in BTO single crystals. We conclude that the enhancement is consistent with the existence of precursor polarization in the paraelectric phase but we additionally find a strong anisotropy that cannot be a bulk effect. We attribute this anisotropy to the predicted [20, 21,22] but experimentally unconfirmed contribution of surface piezoelectricity to the total flexoelectricity of even bulk crystals.

In order to identify different contributions to the total bending-induced polarization, we have studied the flexoelectricity of BTO single crystals of different orientation in the temperature range between 25 °C and 300 °C. The samples were commercially acquired from SurfaceNet and MTI crystal, and their dimensions were 10 mm long, 1mm wide and 0.5 mm thick. In order to characterize anisotropy, we examine crystals with surfaces parallel to the (111), (110) and (001) crystallographic planes respectively. Platinum electrodes were deposited on the top and bottom surfaces using pulsed Laser Deposition, and platinum wires were attached to the electrodes using small drops of silver paint in order to connect to the measuring instruments. The bending-induced polarization (P_3) was measured using the method first described by Zubko et al [11] and previously used in our lab to study the flexoelectricity of relaxor single crystals [19]: a customized dynamic mechanical analyser (Perkin Elmer DMA 8000) generates a time-periodic three point bending deformation in the temperature range between 0 °C and 300 °C (ramp-rate of 3 °C/min). The DMA force signal (drive frequency $\nu=13\text{Hz}$) is used as reference for a lock-in amplifier (Stanford Research Instruments model 830), while the sample electrodes are connected to the measurement channel of the lock-in, which thus measures the displacement current generated by the bending. This current is converted to polarization using $P_3 = I/(2\pi\nu A)$, (A is the area of the electrodes between the two sample supports), and the effective flexoelectric coefficient is calculated as μ_{13}^{eff} using $P_3 = \mu_{13}^{\text{eff}} \frac{\partial \epsilon_{11}}{\partial x_3}$, where $\frac{\partial \epsilon_{11}}{\partial x_3}$ is the average strain gradient across the electrode area. The dielectric constant was also measured in the same range of temperature and with the same ramp rate using an Agilent Precision LCR Meter (Model E-4980A).

Figure 1 plots the dielectric constant and dielectric loss as a function of temperature for BTO-(001), BTO-(011) and BTO-(111). A sharp peak in dielectric constant, corresponding to the first order transition between the paraelectric and ferroelectric phase, is observed around

$T_C \sim 120\text{-}125^\circ\text{C}$ for all samples. The cubic phase is orthotropic and the dielectric constant above T_C is the same for these three orientations, while in the ferroelectric phase (below T_C) it is sensitive to both crystal orientation and domain configuration [13]. The dielectric loss is increased by domain wall motion below T_C and falls sharply on entering the cubic phase before increasing again at high temperatures due to rising conductivity.

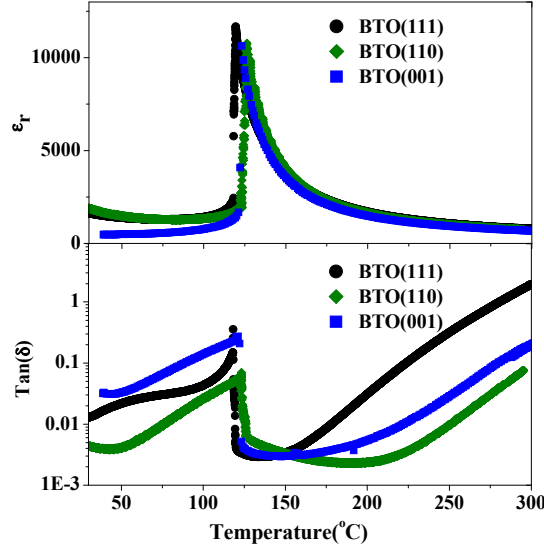


Figure 1. Dielectric constant and dielectric loss at 1 kHz as a function of temperature for (111), (110) and (001)-oriented BTO.

The effective flexoelectric coefficients are plotted in Figure 2. The peaks at T_C mirror those observed in the permittivity. The maxima for the flexoelectric coefficient are in the 10-100 $\mu\text{C/m}$ range, but these values fall sharply to 1-10 $\mu\text{C/m}$ immediately above T_C , coinciding with the disappearance of ferroelectricity. Once in the paraelectric phase, the flexoelectric coefficients continue to gradually decrease from 1-10 $\mu\text{C/m}$ to $\sim 0.1 \mu\text{C/m}$. Reported values for BTO ceramics in this temperature range are much larger, between 50-5 $\mu\text{C/m}$ [10], suggesting an important role of grain boundaries in enhancing the effective flexoelectric coefficient of the paraelectric phase – the grain boundaries of a closely related compound, SrTiO_3 , are known to be piezoelectric [23, 24], and in fact surfaces in general are known to be polar even in non-polar materials [25, 26]. This, as we will show, is important to understand the total flexoelectric polarization even in thick single crystals such as ours.

Even above T_C , there is still thermal hysteresis: flexoelectricity is higher on heating than on cooling up to a temperature labelled as T^* . This hysteresis is identical to that observed in relaxor ferroelectric PMN-PT [19], where it was attributed to the presence of polar regions

that contribute to the flexoelectric response; there are more residual polar domains when heating from the low-T polar phase than when cooling from the high-T paraelectric phase, and the difference explains the hysteresis. Though polar domains are expected in relaxors, it may seem surprising to find them in “normal” ferroelectrics such as BTO. Yet, the existence of short range order in the paraphase of BaTiO₃ has been proposed before in order to explain the birefringence, acoustic emission and anelastic softening [27, 28, 29, 30]. For all samples T^* falls in the 200-225 °C range, which coincides with the range of T^* measured by acoustic emission [30] and resonant ultrasound spectroscopy [31]. The evidence does not allow discriminating whether such polar regions are located inside the bulk of the crystal, or confined within polar surface layers [32, 33], and piezoelectric surface layers are in fact expected to respond in a manner that is functionally identical to flexoelectricity [20, 21, 22].

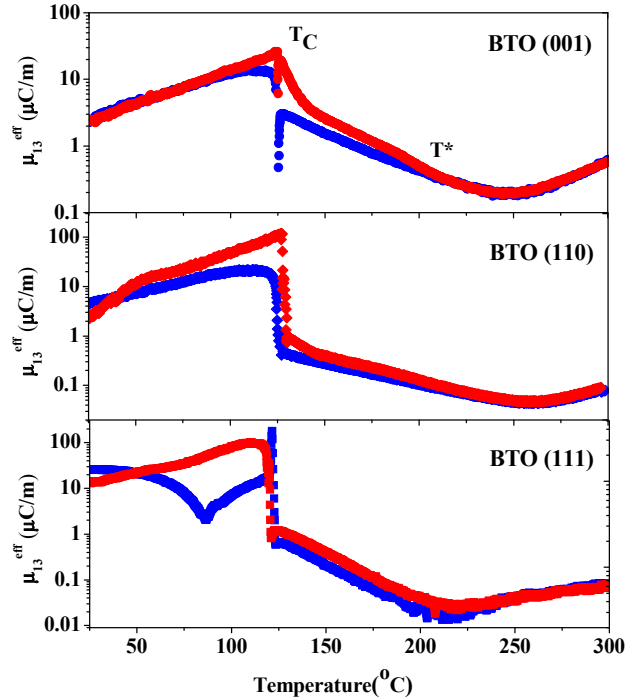


Figure 2. Effective flexoelectric coefficient as a function of temperature for BTO crystals with different orientations. The red curves are measured on heating and the blue ones on cooling. There is a difference between flexoelectricity measured on heating and on cooling for temperatures up to $T^* \sim 200-225$ °C.

The flexoelectric coefficient normalized by the dielectric constant is known as flexocoupling (or flexovoltage) coefficient, f (Figure 3). Theoretically, for an intrinsic flexoelectric effect, f should be of the order of $1 < f < 20$ V and temperature-independent [5, 6, 7, 1]. Experimentally, we found f to be close to 10000 V immediately below T_C , but this is clearly due to the

piezoelectric response of the ferroelectric phase and not a real flexoelectric effect; verification of this piezoelectric origin can be found in the 180 degree phase inversion of the low temperature signal upon turning the crystal upside down, shown in figure 4. At T_C , the flexovoltage f decreases sharply (first order phase transition), and then more gradually up to T^* , consistent with a picture of gradual extinction of the precursor polar regions. Meanwhile, at temperatures around 250 °C or higher, leakage currents artificially increase the apparent flexocoupling again.

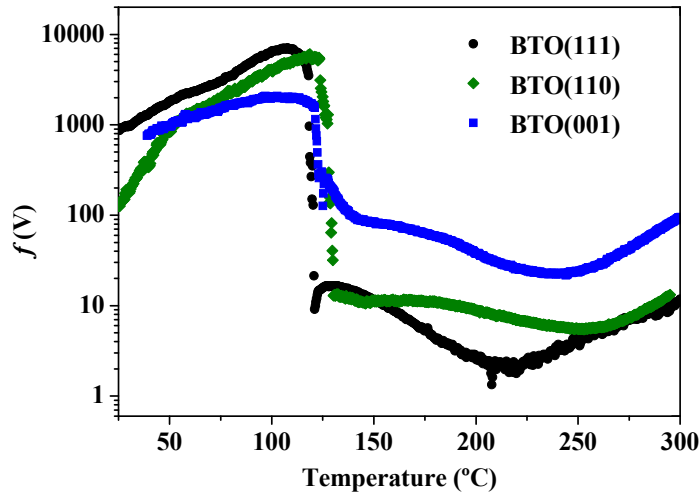


Figure 3. The flexocoupling coefficient as a function of temperature for (111), (110) and (001)-oriented BTO.

There has been a suggestion that some or all of the anomalous flexoelectric enhancement of BaTiO₃ and related compounds may be due to built-in piezoelectricity caused by gradients in defect concentration that appear during sample fabrication [17]. We have examined this hypothesis by looking at the phase angle of the bending-induced current: if the polarization is piezoelectric in nature, it should be inverted (i.e., the phase delay of the current with respect to the strain gradient should change by 180 degrees) when the crystal is turned upside-down. The measurement of the phase angle also allows us to determine the sign of the flexocoupling coefficient, as shown in table 1. A typical phase measurement is shown in figure 4. At room temperature, there is indeed a difference of 180 degrees, fully consistent with the existence of a preferential macroscopic orientation of the ferroelectric polarization. However, above T_C there is no difference between the phase angles. Any macroscopic polarization, if it exists, is switching in response to the strain gradient and is therefore not fixed.

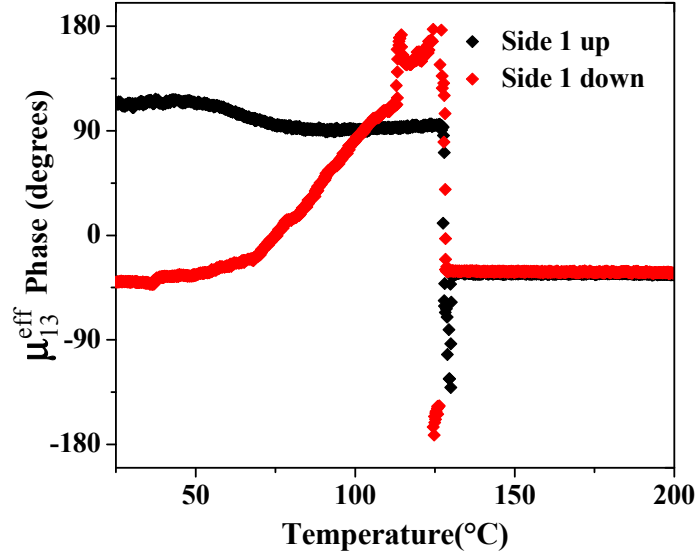


Figure 4: Phase angle between applied force and bending-induced current for a crystal measured twice consecutively, with its orientation flipped upside down between the two measurements. The room-temperature polarization changes phase by 180 degrees, indicating a net macroscopic polarity. In contrast, above T_C the phase angle between force and current is identical for the two measurements, indicating that the flexoelectric enhancement in the paraelectric phase is not due to macroscopically fixed polarization.

The experimental results place an upper limit for the intrinsic flexocoupling coefficient that is 22V for (001)-oriented BTO, -6 V for (110), and -2 V for (111). These values are all consistent with intrinsic flexoelectricity and support the idea that, for perovskite dielectrics, the flexoelectric coefficient is a number of the order of ~ 10 V multiplied by the permittivity. Nevertheless, there is a very large and unexpected anisotropy: the flexovoltage is $10\times$ bigger for (001) than for (111) crystals. The tenfold anisotropy is also bigger than observed in homomorphic SrTiO_3 [11], for which it is a factor smaller than three. **Anisotropy may of course have been expected in the ferroelectric phase of BTO, but it is surprising in the cubic phase.** We turn our attention to the origin of this large anisotropy.

x_1	x_2	x_3	$\mu_{13}(\mu C/m)$	$f(V)$
[100]	[010]	[001]	0.20	22
$[\bar{1}\bar{1}0]$	[001]	[110]	-0.05	-6
$[10\bar{1}]$	$[\bar{1}2\bar{1}]$	[111]	-0.01	-2

Table 1 shows the orientation of the sample edges with respect to the crystallographic axes, determined using X-ray diffraction. As was previously reported [11], the effective coefficient for any given crystal orientation is always a linear combination of the coefficients for the other two, meaning that there are no three independent equations required to obtain the three independent tensor components in cubic symmetry. On the other hand, the linear dependence provides a “sanity check”: if the measured coefficients are only dependent on the bulk properties of the sample (i.e., if there is no surface piezoelectricity), then the effective flexoelectric coefficient of, say, the (001)-oriented sample can in principle be calculated from the effective flexoelectric coefficients measured for (111) and (011) orientations. Conversely, if the calculated and measured values do not coincide, it is a strong indication that non-bulk contributions must be present. For the specific case of our samples, it can be shown (**see supplementary materials**) that the effective flexoelectric coefficients measured for the (100), (110) and (111) crystals must fulfil the relationship:

$$-\frac{(C_{11}-C_{12})(C_{11}+2C_{12})+2C_{11}C_{44}}{2C_{44}(C_{11}-C_{12})}f_{110}^{beam} + \frac{(C_{11}+2C_{12}+4C_{44})(C_{11}-C_{12})}{C_{44}(C_{11}+C_{12})}f_{111}^{beam} = f_{100}^{beam} \quad (1)$$

Using the elastic constants of BTO single crystals in the paraelectric phase [34], $C_{11} = 173GPa$, $C_{12} = 82GPa$, $C_{44} = 108GPa$, we arrive at the final relationship:

$$1.47f_{111}^{beam} - 1.24f_{110}^{beam} = f_{100}^{beam} \quad (2)$$

Because the permittivity (figure 1) is the same for the three orientations, this identity must be fulfilled both for flexoelectric and flexocoupling coefficients. The minimal measured values of the flexocoupling coefficients are $f(110)=-6V$ and $f(111)=-2V$, so, according to eq. 2, we should have $f(100)=4.5V$, instead of which the experimental value is 22V: about five times as much. This large anisotropy is experimentally robust (the variation between different

measurements was less than 10%) and indicates an additional effect that (i) is not part of the bulk response and (ii) is above T^* , so it is not due to precursor polar regions. We therefore interpret this result as a first (indirect) indication of the contribution of surface piezoelectricity to the total effective flexoelectricity.

Summarizing, then, the results indicate that there are at least two additional contributors to the enhancement of effective flexoelectricity in the paraelectric phase of BaTiO_3 : precursor polar regions and surface piezoelectricity. Though barium titanate is regarded as an archetypal ferroelectric, it displays precursor polar behaviour (short range order) in its paraphase up to T^* [27, 28, 29, 30, 31]. The polar precursor contribution to flexoelectricity has been predicted by Bersuker [18], who proposes a gradient-induced collapse of the dynamic $\langle 111 \rangle$ polar fluctuations of the paraelectric phase (8-site model of the order-disorder phase transition [35]). In this scenario, the precursor polarization would be from dynamic rather than static polar nanoregions [36]. On a sidenote, it is interesting that the effect of precursor polarization is evident in the electromechanical response but not in electrostatic measurements: the dielectric constant does not significantly deviate from Curie-Weiss behaviour, nor change when we apply up to 40 V DC bias during measurement (see figures S1 and S2 in supplementary materials).

Even above T^* , however, there remains a large anisotropy that is incompatible with bulk flexoelectricity, and which we therefore interpret as indirect evidence for surface piezoelectricity. This is a theoretically inevitable effect [20, 21, 22] that has been calculated to be as big as or even bigger than bulk flexoelectricity [37], but whose experimental detection is elusive because it behaves functionally identically to bulk flexoelectricity. Because the effect is independent of the relative thicknesses of bulk and surface layers, the best way to identify the effect of surfaces is by changing the surface type, which was accomplished here by using different crystal orientations. The experimental results suggest that indeed the effect of surfaces can be even bigger than that of the bulk itself, and this has an important practical consequence: maximizing flexoelectric performance requires not just optimizing material properties, but also careful surface engineering.

Note Added: after the submission of this manuscript, a new work has been published that provides further evidence for the contribution of polar nanoregions to the flexoelectric enhancement of $(\text{Ba,Sr})\text{TiO}_3$ ceramics [38].

ACKNOWLEDGEMENTS

This research has been funded by an ERC Starting grant from the EU (ERC 308023) and by National Plan grants FIS2013-48668-C2-1-P and FIS2013-48668-C2-2-P from the Spanish MINECO. ICN2 acknowledges support by the Severo Ochoa Excellence Programme SEV-2013-0295. J.H thanks the support from “Next Big Ideas” project at Oak Ridge National Laboratory.

References.

1. P. Zubko, G. Catalan and A. K. Tagantsev, *Annu. Rev. Mater. Res.* 43 (2013).
2. S. M. Kogan *Sov. Phys.—Solid. State* 5, 2069 (1964).
3. E. V. Bursian, N.N. Trunov, *Sov. Phys. Sol. State* 16, 760 (1974).
4. A. K. Tagantsev, *Phys. Rev. B* 34, 5883 (1986).
5. I. Ponomareva, A. K. Tagantsev, and L. Bellaiche, *Phys. Rev. B* 85, 104101 (2012).
6. J. Hong and D. Vanderbilt, *Phys. Rev. B* 88, 174107 (2013).
7. M. Stengel, *Phys. Rev. B* 88, 174106 (2013).
8. W. Ma and L. E. Cross, *Appl. Phys. Lett.* 78, 2920 (2001).
9. W. Ma and L. E. Cross, *Appl. Phys. Lett.* 81, 3440 (2002).
10. W. Ma and L. E. Cross, *Appl. Phys. Lett.* 82, 3293 (2003).
11. P. Zubko, G. Catalan, A. Buckley, P. R. L. Welche, and J. F. Scott., *Phys. Rev. Lett.* 99, 167601 (2007).
12. W. Ma and L. E. Cross, *Appl. Phys. Lett.* 88, 232902 (2006).
13. A. F. Devonshire, *Philos. Mag.* 40, 1040, (1949).
14. A. Von. Hippel, *Rev. Mod. Phys.* 22, 221 (1950).
15. R. Marangati and P. Sharma, *Phys. Rev. B* 80, 054109 (2009).
16. J. Hong, G.Catalan, J.F.Scott and E. Artacho, *J. Phys.: Condens. Matter* 22, 112201 (2010).
17. A. Biancoli, C. M. Fancher, J. L. Jones and D. Damjanovic. *Nature Materials* 14, 224–229 (2015).
18. I. B. Bersuker, *Applied Physics Letters* 106, 022903 (2015).
19. J. Narvaez and G. Catalan, *Appl. Phys. Lett.*, 104 162903 (2014).
20. A. K. Tagantsev and A. S. Yurkov, *J. Appl. Phys.* 112, 044103 (2012).
21. M. Stengel, *Nat. Commun.* 4, 2693 (2013); M.Stengel, *Phys. Rev. B* 90, 201112 (2014).

22. J. Hong and D. Vanderbilt, Phys. Rev. B 84, 180101 (2011).
23. J. Petzelt, T. Ostapchuk, I. Gregora, I. Rychetský, S. Hoffmann-Eifert, A. V. Pronin, Y. Yuzyuk, B. P. Gorshunov, S. Kamba, V. Bovtun et al., Phys. Rev. B 64, 184111 (2001).
24. A. Kholkin, I. Bdikin, T. Ostapchuk and J. Petzelt, Appl. Phys. Lett. 93, 222905 (2008).
25. J. F. Scott, J. Chem. Phys. 48, 874–876 (1968).
26. R. Munprom, P. A. Salvador, and G. S. Rohrer, Chem. Mater 26, 2774–2776 (2014).
27. M. Zenkner, U. Straube & G. Schmidt, Ferroelectrics 460,1–10 (2014).
28. A. Ziebinska, D. Ryts, K. Szot, M. Gorny and K. Roleder, J. Phys.: Condens. Matter 20, 142202 (2008).
29. G. Burns and F. H. Dacol, Solid. State. Commun.42, 9 (1982).
30. E. Dul'kin, J. Petzelt, S. Kamba, E. Mojaev and M. Roth, Appl. Phys. Lett. 97, 032903 (2010).
31. E. K. H. Salje, M. A. Carpenter, G. F. Nataf, G. Picht, K. Webber, J. Weerasinghe, S. Lisenkov, and L. Bellaiche., Phys. Rev. B 87, 014106 (2013).
32. W. Känzing, Phys. Rev. 98, 549 (1955).
33. G. Schmidt and F. Prokert, Ann. der Physik 7, 120 (1966).
34. D. Berlincourt, H. Jaffe, Phys. Rev. 111, 143 (1958).
35. R. Comes, M. Lambert, and A. Guinner, Solid State Commun. 6, 715 (1968).
36. J. Hlinka, J. Adv. Dielectrics 2, 1241006 (2012).
37. M. Stengel Phys. Rev. B 90, 201112 (2014).
38. L. M. Garten and S. Trolier-McKinstry, J. Appl. Phys 117, 094102 (2015).