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A Ziębińska[1], D Rytz[2], K Szot[3], M Górny[1] and K Roleder[1]

[1] Institute of Physics, University of Silesia, ulica Uniwersytecka 4, 40-007 Katowice, Poland
[2] Forschungsinstitut für mineralische und metallische Werkstoffe, Edelsteine/Edelmetalle GmbH (FEE), Struthstraße 2, D-55743 Idar-Oberstein, Germany
[3] Institut für Festkörperforschung, Forschungszentrum Jülich, D-5245 Jülich, Germany

Abstract
The temperature dependence of the birefringence above T_c in high quality $BaTiO_3$ single crystals has been measured with very high accuracy. On the basis of literature data, the behaviour of the anomalous birefringence can be explained by the existence of polar clusters (microregions/nanoregions) connected with correlated jumps between the off-centre positions of Ti ions inside the oxygen octahedra. The underlying origin of the polar clusters is an intrinsic effect connected with the interdependence of the structural and polar soft modes (Bussmann-Holder *et al* 2007 *Phys. Rev. Lett.* **99** 167603). These clusters locally break the intrinsic cubic symmetry and the phase above T_c becomes birefringent. A birefringence Δn of the order of 10^{-5} has been found up to about 30° above T_c. In this temperature range $T_c < T < T_c + 30$ K, the function $\Delta n(T)$ exhibits a thermal hysteresis: the values of Δn were higher on heating than on cooling. A characteristic feature is the existence of a local $\Delta n(T)$ maximum at a temperature close to T_c on the high temperature side that appears due to a specific cluster–cluster interaction. Since the values of $\Delta n(T)$ runs were not dependent on the crystal thickness, one can conclude that in this limited temperature range above T_c the birefringence is an inherent feature of the crystal.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

After more than five decades, barium titanate $BaTiO_3$ (BT) single crystals are still considered prime examples of classical ferroelectrics and among the most interesting polar compounds from a practical point of view. BT was first obtained in ceramic form and investigated in the early 1940s by Wainer and Salomon in the USA [1], Ogawa and Waku in Japan [2] and Wul and Goldman in Russia [3]. Large single crystals of BT grown from a KF flux were produced in 1954 by Remeika [4]. Following the work of Belruss *et al* [5], high quality BT single crystals grown by top-seeded solution growth (TSSG) became available and enabled intensive investigations of the nature of the phase transitions, the domain structure, and optical, electrical and mechanical properties of this material. One of the most important experimental results on BT is the existence of local dipoles above T_c. The evidence is

based on results obtained by various experimental techniques such as diffuse x-ray scattering, Raman and hyper-Raman spectroscopy, inelastic neutron scattering, second-harmonic generation and NMR spectroscopy [6 (and references therein)]. The variety of these investigations manifests itself in a huge number of papers devoted to BT. It is now well established that the cubic to tetragonal phase transition in BT is both of displacive type and of order–disorder type [6]. While the mechanism for the appearance of polar regions above T_c is connected with the correlated jumps of Ti ion between off-centre position inside the oxygen octahedron, the answer to the question of why such jumps are realized is still elusive.

The present work is concentrated on properties above T_c that are in fact far less frequently investigated than the ferroelectric phases of BT. It should be mentioned that recently Takagi and Ishidate [7] have recorded anomalous birefringence over a broad temperature range of the cubic phase. They have

1

postulated the existence of polarization clusters above T_c that induce birefringence through anisotropy of the local lattice polarization. In this paper we report on the optical properties of BT above T_c determined with higher resolution. Similar to the report by Takagi and Ishidate [7], an anomalous behaviour of the birefringence has been found about 30 °C above T_c.

2. Crystal characterization

For birefringence investigations in the cubic phase, a special geometrical condition for the sample shape is not needed. Birefringence measurements were made on high quality samples cut from crystals grown by TSSG, polished to a thickness of 600 μm. The crystals were grown in air from a standard solution with an excess of TiO_2. One sample was post-growth annealed in a reducing 90% CO_2 + 10% CO atmosphere at 1000 °C.

3. Plano-birefringence in the phase above T_c

The birefringence has been investigated by means of an Oxford Cryosystems Metripol Birefringence Imaging System (Metripol). The sample was held by a high precision Linkam TMSG600 temperature stage combined with a birefringence imaging system. Details of this automated optical technique are described in [8–10] (www.metripol.com). In view of those papers we give here only a short description of the experimental technique. The hot stage was capable of maintaining a constant temperature to within 0.1 K. The temperature ramps were performed at rates of 0.2 K min^{-1}. The Metripol system consists of a polarizing microscope equipped with a computer controlled plane-polarizer capable of being rotated to fixed angles α from a reference position, a circularly polarizing analyser and a CCD camera. The intensity measured at any position within the captured image is given by the formula

$$I = \frac{I_0}{2}[1 + \sin(2\Phi - 2\alpha)\sin\delta]$$

where I_0 is the intensity of light passed through the sample and represents its transmittance, Φ is the angle of an axis of the optical indicatrix of the specimen projected onto the image measured from a predetermined direction (it was measured anticlockwise from the horizontal axis) and δ is the phase difference between the polarized light components and is given by

$$\delta = \frac{2\pi}{\lambda}(n_1 - n_2)d$$

where λ is the wavelength of the light, d is the thickness of the sample and $n_1 - n_2$ is the so-called plano-birefringence of the sample, i.e. the birefringence measured as seen in projection down the microscope axis. By measuring several images with varying angle α it was possible to fit for each pixel position the quantities I_0, $|\sin\delta|$ and φ separately and then to plot images in false colour representing these three values. In this way, any spatial variation in the birefringence or orientation can readily be seen with a very high sensitivity. It is an ideal technique for

checking whether an optical anisotropy occurs in a crystal. The effective retardation δ^* can be calculated according to [10]

$$\delta^* = \big([\delta_m \sin(2\varphi_m) - \delta_b \sin(2\varphi_b)]^2$$
$$+ [\delta_m \cos(2\varphi_m) - \delta_b \cos(2\varphi_b)]^2\big)^{1/2}$$

where $\delta_m = \sin^{-1}(|\sin\delta_m|)$ and φ_m are the phase shift and orientation angle measured in the sample, and $\delta_b = \sin^{-1}(|\sin\delta_b|)$ and φ_b are the phase shift and orientation angle measured as background values in the region outside the sample.

It was found that the BT crystals under investigation are birefringent over a very broad temperature range (figure 1), even 30 °C above T_c. The birefringence decreases with increasing temperature and disappears in the 160–170 °C range, i.e. near the temperature above which a deviation from linear changes of the $\varepsilon^{-1}(T)$ Curie–Weiss law, describing the dielectric permittivity, can be neglected [11]. In the same temperature range the electrostrictive and piezoelectric coefficients revealed non-typical changes [11]. It is interesting that there is a temperature hysteresis in the temperature dependence of Δn on heating and cooling, despite the fact that a very low rate of temperature change (0.2 °C min^{-1}) was used. Most importantly, a local maximum of $\Delta n(T)$ located a few degrees above T_c is observed at 2–3 °C on cooling and 6–14 °C on heating with respect to T_c. In the latter case this maximum is more pronounced and occurs further away from T_c.

Our experimental results are in agreement with the work of Tai *et al* [12] who have shown that the $|P|^2(T)$ reveals a maximum at about 5 °C above T_c. Here, $|P|$ is the mean polarization magnitude within a cluster (polar microregion/nanoregion). Tai *et al* [12] have suggested that above T_c the existence of such clusters can induce birefringence. The precise $\Delta n(T)$ results presented in the present work confirm this hypothesis. However we also show that the distribution of polar regions is not homogeneous and leads to differences in the dynamics and stability of the crystal lattice. Namely, near but above T_c the $\Delta n(T)$ dependences obtained for different volumes of the same crystal revealed different Δn values and different $\Delta n(T)$ dependences (figures 1(a)–(c)). It is interesting that in all cases the values of Δn on heating were higher than those on cooling. Another characteristic feature is the existence of a local maximum that appears at a temperature close to T_c, from the high temperature side. In our opinion this birefringence is an inherent feature of the crystal bulk and is not e.g. a surface effect, although a mechanical stress appearing after polishing may influence the birefringence measurement. By means of a scanning electron microscope ISM-5410, with an energy dispersive x-ray spectrometer (EDS), the chemical composition of the crystal was determined.

Scanning was performed for a few separate areas on the crystal surface and the ratio Ba:Ti was found to be equal to 1, within the experimental error. However the XPS spectroscopy of the surface has revealed traces of Si that most probably has been embedded into the sample during polishing. This may be one of the sources of plane stresses that could affect birefringence measurement. In fact the curves in figure 1 have been obtained after subtraction of a background. This
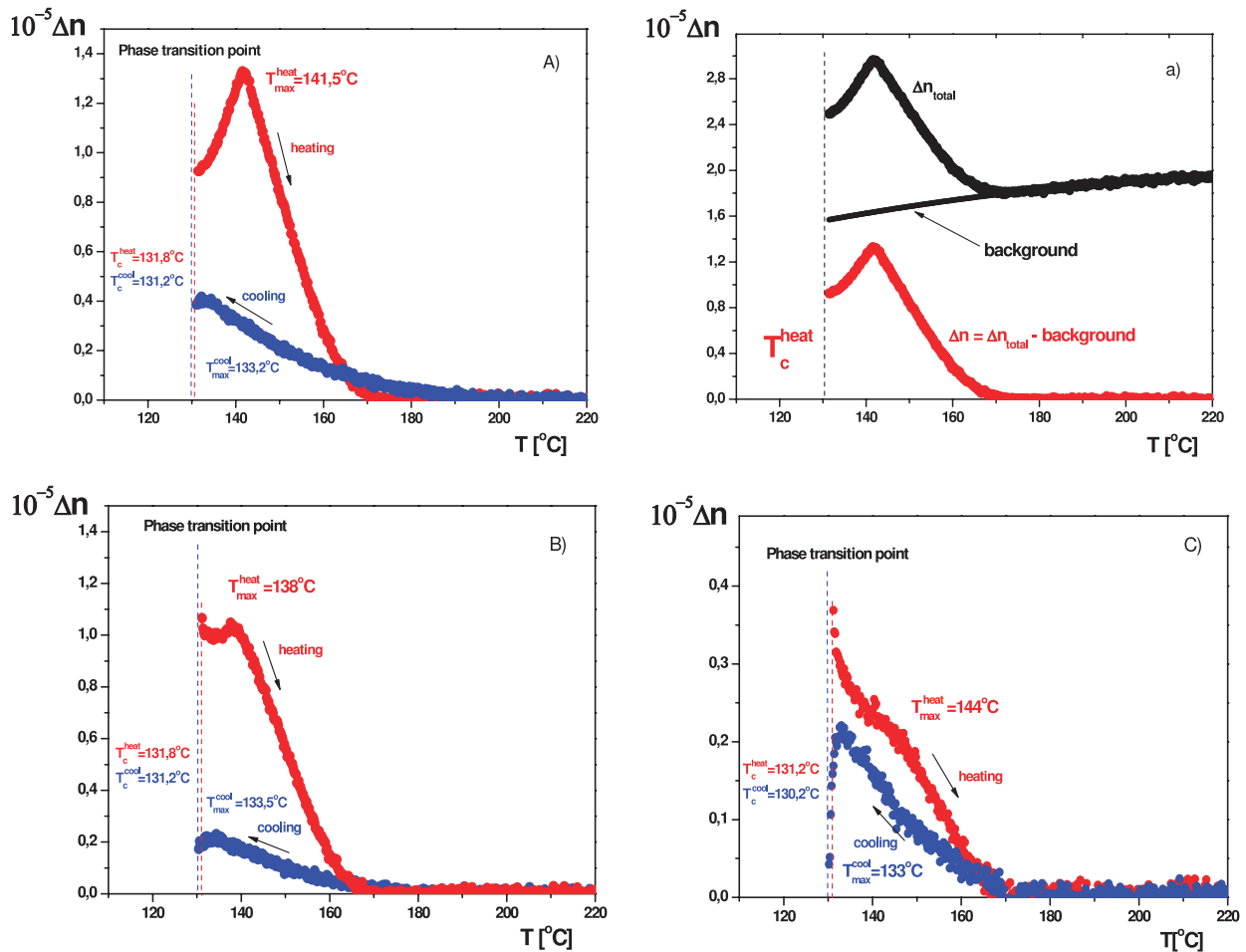
Figure 1. Temperature dependence of birefringence Δn measured on heating and cooling at three different, arbitrarily chosen, *A*, *B* and *C* locations in the crystal volume. Inset *a* explains how the background residual birefringence was subtracted to get the results for the location *A*, on heating. In the phase above T_c the birefringence $\Delta n(T)$ was obtained by subtracting a second-order polynomial ($p_1 T^2 + p_2 T + p_3$) from the $\Delta n_{total}(T)$ measured up to 260 °C. The parameters p_1, p_2 and p_3 are values fitted over the range 200 °C < T < 260 °C.

background was different for different crystal volumes for which the birefringence measurements were conducted. It is important to stress that among the numerous $\Delta n(T)$ runs obtained, each of them, after background subtraction, was similar to one of those presented in figure 1. Thus one could suppose that the birefringence above T_c is not an intrinsic phenomenon and a rejuvenation at high temperature should remove it. However for crystals heated up even to 500 °C no significant changes of the $\Delta n(T)$ runs were detected.

4. Discussion

Many years ago Lambert *et al* [13] showed that the highest symmetry phase of BT is intrinsically disordered and its microscopic structure is best described in terms of antiparallel correlation chains with a size from 40 to 100 Å, i.e. about 10–25 unit cells. Inoue [14] has measured the overdamped phonons in this phase by means of hyper-Raman scattering and the spectra obtained have been accounted for by invoking the existence of polar clusters that have already started growing at 230 °C (on cooling).

Local regions of polarization are naturally expected in BT and other ferroelectric materials that are disordered. The optical index of refraction $n(T)$ in the cubic BT has been measured by Burns and Dacol [15]. They have noticed a marked deviation from linearity at temperatures below 180 °C and assumed that this deviation is explained by the quadratic electro-optic effect due to the local polarization. Moreover they have stated that such polar regions, if they exist, are an effect of a structural disorder. It is worth noting that a long time ago Forsbergh [16] also observed local polar regions appearing near dislocations and Känzig [17] has seen a similar effect near surfaces.

The birefringence in the cubic phase of BaTiO$_3$ was also measured by Kruglyashov *et al* [18] who have observed large changes in birefringence in a temperature range limited to about 2 K above T_c. They claimed that birefringence is generated by temperature fluctuations in the crystal and as a source of birefringence, a local phase of lower symmetry was considered. According to Takagi *et al* [7] the appearance of a phase with symmetry lower than cubic is similar to the appearance of polarization clusters that already occur 200 °C above T_c and therefore cannot be interpreted in terms

3

of temperature fluctuations alone. Recently Tai *et al* [12] have observed dynamic polarization clusters in the paraelectric phase of barium titanate by a picosecond x-ray laser speckle technique. They have also found an unexpected maximum at $T_c + 5\,°C$ in the curve illustrating the temperature dependence of polarization within the clusters. It should be noted that the nature of the experiments leads to surface clusters only, not clusters in the crystal volume. Dimensions of polar clusters were of the order of a few microns (see figure 3 in paper by Tai *et al* [12]) and thus big enough to be detected by birefringence measurements at visible wavelengths. In fact polar clusters have been recognized as dots (representing different Δn values in experimental images) that disappear above 170 °C. It is worth noting that the results obtained in both experimental techniques showed a characteristic maximum on the $\Delta n(T)$ runs that occurs at a very similar temperature interval with respect to T_c.

Measurements of the plano-birefringence described in this paper provide evidence that the phase above T_c is, at least locally, non-centrosymmetric even at relatively high temperatures. According to Bussmann-Holder *et al* [19, 20] the appearance of polar clusters (precursor domains) above T_c is an intrinsic effect based on the short wavelength structural instability that is related to the long wavelength polar soft mode and driven by the temperature dependent fluctuating dipole moment. The temperature evolution of this interdependence of the structural and polar soft mode could be responsible for the $\Delta n(T)$ dependences observed. Thus this experimental fact could be accounted for the correlated Ti motion within the oxygen cage only.

However we cannot exclude the possibility of an influence of stacking faults on birefringence, the existence of which has recently been revealed by Szot *et al* in SrTiO$_3$ [21]. The nature of the stacking faults in BT single crystal would be related, like in the case for SrTiO$_3$, to oxygen vacancies arising during crystal growth. Various methods like HRTEM, XPS and AFM have provided evidence that the dominating kinds of defects in crystalline BaTiO$_3$ are extended defects, such as dislocations and shear planes. The agglomeration of point defects in the form of extended defects is not unique to barium titanate compounds and similar kinds of defects were observed in other perovskites, for example in SrTiO$_3$, KNbO$_3$ and KTaO$_3$ [22]. This is in contrast to the case for standard point defect chemistry, where the distribution of point defects is regarded as statistical in nature. It is known [21] that along such extended defects and within their surroundings the electronic structure, the lattice parameters as well as the lattice dynamics can be dramatically modified. Around these faults, which are difficult to remove by thermal rejuvenation, the local mechanical and electrical stresses are created. The dislocations themselves are sources of much higher electrical conductivity than that of the non-disturbed lattice [21]. Hence, the local lattice disturbance may influence the Ti motion inside the perfect oxygen octahedron, for example in the neighbourhood of dislocations. This may cause, depending on dislocation density, different values of $\Delta n(T)$ similar to those shown in figure 1.
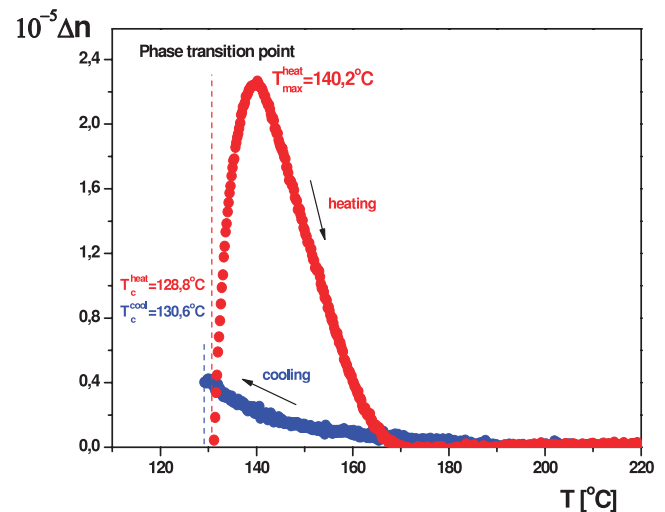
Figure 2. Temperature dependence of birefringence Δn measured on heating and cooling in a reduced (with a large density of oxygen vacancies) BT single crystal.

If we suppose that the main causes for such defects are oxygen vacancies, then we should be able to show that in a reduced single crystal, a similar and possibly even more pronounced birefringence should be present. In fact, in the reduced crystal (of pink colour) that we have used in the experiment, anomalous birefringence has been found in a similar temperature range above T_c but with a larger thermal hysteresis of the $\Delta n(T)$ runs (figure 2).

While the values of Δn and the $\Delta n(T)$ dependences in the phase above T_c vary with the locations of the scanned volumes in the bulk, it was found that Δn was not dependent on the crystal thickness. This was checked for several BT single crystals fabricated with thicknesses of 0.1, 0.2 and 1 mm by CrysTech Inc. (China). This was a demonstration that effects induced by the crystal surface can be excluded as causes for the observed birefringence behaviour.

The local maximum (or inflection point) existing on the $\Delta n(T)$ curve at a temperature close to but higher than T_c shines new light on the mechanism of the transition between the ferroelectric and non-polar phase above T_c in BT. This anomaly seems to be a signature of the existence in BT of a specific temperature range above T_c in which the coexistence of order–disorder and displacive phase transition mechanisms leads to the appearance of stable precursor clusters. Their size, evolution and interactions among themselves differ while cooling from elevated temperatures down towards T_c or heating from temperatures close to the transition to temperatures well within the macroscopically non-polar phase above T_c.

References

[1] Wainer E and Solomon A N *Report No. 8 (September 1941) and No. 9 (January 1943)* Titanium Alloy Manufacturing Co.

[2] Ogawa T and Waku S discovered 1944;
Ogawa T and Busseiron 1947 *Kenkyu* **6** 1

[3] Wul B and Goldman J M 1945 *C. R. Acad. Sci. URSS* **46** 139

[4] Remeika J P 1954 *J. Am. Ceram. Soc.* **76** 940

[5] Belruss V, Kalnajs J, Linz A and Folweiler R C 1971 *Mater. Res. Bull.* **6** 899

[6] Zalar B, Lebar A, Seliger J and Blinc R 2005 *Phys. Rev.* B **71** 064107

[7] Takagi M and Ishidate T 2000 *Solid State Commun.* **113** 423–6

[8] Glazer A M, Lewis J G and Kaminsky W 1996 *Proc. R. Soc.* A **452** 2751

[9] Geday M A, Kaminski W, Lewis J G and Glazer A M 2000 *J. Microsc.* **198** 1–9

[10] Geday M A and Glazer A M 2004 *J. Phys.: Condens. Matter* **16** 3303

[11] Wieczorek K, Ziębińska A, Ujma Z, Szot K, Górny M, Franke I, Koperski J, Soszyński A and Roleder K 2006 *Ferroelectrics* **336** 1

[12] Tai R Z, Namikawa K, Sawada A, Kishimoto M, Tanaka M, Lu P, Nagashima K, Muruyama H and Ando M 2004 *Phys. Rev. Lett.* **93** 087601

[13] Lambert M and Comès R 1969 *Solid State Commun.* **7** 305–8

[14] Inoue K 1983 *Ferroelectrics* **52** 253–62

[15] Burns G and Dacol F H 1982 *Solid State Commun.* **42** 9–11

[16] Forsbergh P W Jr 1954 *Phys. Rev.* **93** 1686

[17] Känzig W 1955 *Phys. Rev.* **98** 549

[18] Kruglyashov S B, Kovaleva L A, Petrov A A, Belous I M and Anistratov A T 1990 *Sov. Phys. Solid State* **32** 1347

[19] Bussmann-Holder A, Büttner H and Bishop A R 2007 *Phys. Rev. Lett.* **99** 167603

[20] Bussmann-Holder A and Bishop A R 2006 *Eur. Phys. J.* B **53** 279

[21] Szot K, Speier W, Bihlmayer G and Waser R 2006 *Nat. Mater.* **5** 312–20

[22] Jia C A, Thust A and Urban K 2005 *Phys. Rev. Lett.* **95** 225506