New Journal of Physics
The open-access journal for physics

The ferroelectric phase transition of calcium barium niobate: experimental evidence of Smolenskii's model for diffuse phase transitions?

Urs Heine[1], Uwe Voelker[2], Klaus Betzler[1,4], Manfred Burianek[3] and Manfred Muehlberg[3]

[1] Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany
[2] Institut für Technische Physik, Deutsches Zentrum für Luft- und Raumfahrt, D-70569 Stuttgart, Germany
[3] Institut für Kristallographie, Universität zu Köln, D-50674 Köln, Germany
E-mail: Klaus.Betzler@uos.de

New Journal of Physics **11** (2009) 083021 (9pp)
Received 12 May 2009
Published 19 August 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/8/083021

Abstract. We present investigations on temperature-dependent changes in the size distribution of ferroelectric domains in single crystals of the novel tungsten bronze type calcium barium niobate (CBN). Since its congruently melting composition has a relatively high ferroelectric phase transition temperature of about 265 °C, CBN can be considered as an interesting material for various future applications. Using *k*-space spectroscopy, both unpoled polydomain crystals and crystals poled at room temperature have been investigated in the vicinity of the ferroelectric phase transition. In unpoled CBN, an intermixture of domain-size dependent phase transitions has been observed, which can be described with the model for diffuse phase transitions established by Smolenskii.

[4] Author to whom any correspondence should be addressed.

Contents

1. Introduction

Ferroelectric materials have been investigated for several decades due to their interesting dielectric and electrooptic properties. Relaxor ferroelectrics, in particular, exhibit a high-dielectric constant over a wide temperature range around the ferroelectric phase transition. Therefore, knowledge of the phase transition behaviour is of essential importance for possible applications. Particularly, microscopic switching processes of the domain structure are of great interest. The uniaxial tungsten bronze type strontium barium niobate (SBN) is one of the most investigated examples. For SBN, many publications give detailed insight into its material characteristics [1]–[6], despite the fact that the nature of its phase transition is currently controversially discussed [7, 8].

Up to now, the behaviour of the novel tungsten bronze type calcium barium niobate (CBN) has not been investigated in detail, since single crystals have been available for just a few years. Considering that the congruently melting composition ($x = 0.28$) undergoes its phase transition at about 265 °C [9], CBN—due to its high dielectric constant [10]—might be of great interest for technical applications, especially those which require excellent optical quality for its ferroelectric components, such as frequency converters for laser systems or holographic data storage. The possibility of tuning the phase transition temperature further widens the future field of applications [11].

Using *k*-space spectroscopy [5], we present investigations on the ferroelectric phase transition behaviour of poled and unpoled CBN single crystals, grown from the congruently melting composition. This technique has emerged as a powerful tool to observe domain structures in ferroelectric bulk materials [6, 12]. Microscopic changes in the domain structure of poled and unpoled samples are studied.

2. Experimental details

The measuring technique *k*-space spectroscopy uses noncollinear quasi-phase matched optical second harmonic generation (SHG). Momentum conservation can be described by

$$\mathbf{k}_2 = 2\mathbf{k}_1 + \mathbf{k}_g, \tag{1}$$

with $\mathbf{k}_1$ and $\mathbf{k}_2$ representing the wave vectors of the fundamental and second harmonic (SH) wave, respectively, with $|\mathbf{k}_1| = 12.97\,\mu\mathrm{m}^{-1}$ and $|\mathbf{k}_2| = 27.89\,\mu\mathrm{m}^{-1}$. $\mathbf{k}_g$ stands for the additional vector, which is needed to fulfil the momentum conservation condition. Due to the low

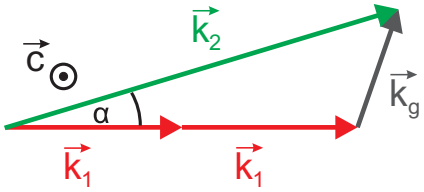

Figure 1. Momentum conservation scheme for noncollinear quasi-phase matching. All vectors are orientated in a plane perpendicular to the crystallographic *c*-axis.

birefringence of CBN [9], conventional phase matching cannot be achieved. As is known for quasi-phase matching scenarios in ferroelectrics, an additional momentum contribution is provided by the Fourier representation of the domain structure [13]–[15].

With $\mathbf{k}_1$ propagating in an arbitrary direction perpendicular to the crystallographic *c*-axis, a plane of SH intensity is emitted from the CBN crystal, similar to the situation reported for SBN [14]. This anisotropic distribution can be attributed to ferroelectric domains in CBN, which are needlelike along the *c*-axis [16]. They form random polar structures of alternating polarization directions. The Fourier transformation of these random domain structures leads to a broad planar distribution of $\mathbf{k}_g$-vectors with different lengths perpendicular to the *c*-axis, contributing to noncollinear SH generation as shown in figure 1.

Thus, measuring the angular distribution of the SH intensity and using

$$|\mathbf{k}_g| = \left(4\,|\mathbf{k}_1|^2 + |\mathbf{k}_2|^2 - 4\,|\mathbf{k}_1|\,|\mathbf{k}_2|\cos\alpha\right)^{1/2} \tag{2}$$

to calculate the corresponding $|\mathbf{k}_g|$ as a function of the measuring angle α, we gain an insight into the density distribution of $\mathbf{k}_g$-vectors. The density distribution is directly connected to the size distribution of domains inside the crystal [5, 17]. The density of large domains is represented by intensity for small $|\mathbf{k}_g|$, an increase in the density of small domains causes an intensity gain for large $|\mathbf{k}_g|$.

Changes of the domain size distribution at the ferroelectric phase transition were measured with the crystals mounted on a temperature-controlled holder with an accuracy of $\pm 0.2\,^{\circ}\mathrm{C}$ and maximum temperature $T_{\max} = 350\,^{\circ}\mathrm{C}$. Phase transition measurements were performed with unpoled samples and samples poled at room temperature with an electric field up to $E_{\mathrm{pol}} = 1.2\,\mathrm{kV\,mm^{-1}}$. The heating and cooling rate was $10\,\mathrm{K\,h^{-1}}$. To obtain unpoled, polydomain samples, the crystals were annealed at 500 °C for approximately 6 h prior to the measurements.

In all measurements, the fundamental wave at 1064 nm was provided by a pulsed Nd:YAG laser (repetition rate: 1 kHz, pulse length: 7 ns, pulse energy: 80 μJ, beam diameter: 1 mm, polarization: extraordinary). The generated SH intensity was detected via a photomultiplying system mounted on a motorized rotation stage. Appropriate filters have been used in order to suppress the fundamental intensity.

3. Results and discussion

To show some main characteristics of the measurement data, a comparison of the SH intensity distribution of unpoled and poled CBN crystals at room temperature is exemplarily plotted in figure 2 as a function of $|\mathbf{k}_g|$.

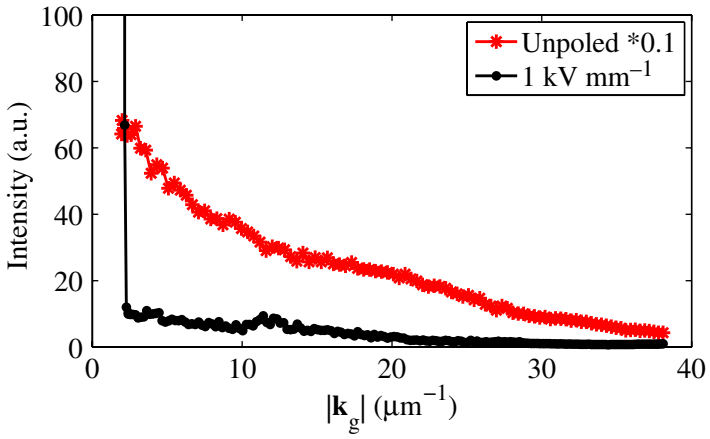

Figure 2. Comparison of the SH-intensity distribution of unpoled CBN (red) and CBN poled with 1 kV mm^{-1} at room temperature (black). $|\mathbf{k}_g|$ was calculated using equation (2). For a better comparison of the two dependences, the intensity of unpoled CBN was divided by 10.

Table 1. Comparison of the average site occupancies for the A1 and A2 sites in CBN and SBN from the congruently melting compositions.

Compound	A1(Sr,Ca)	A2(Sr,Ca)	A1(Ba)	A2(Ba)
CBN	63%	0%	0%	95.25%
SBN	71.84%	40.38%	0%	48.76%

The SH emission of both unpoled and poled CBN exhibits a pronounced dependence on $|\mathbf{k}_g|$. In poled CBN, significant SH intensities are only measured at small $|\mathbf{k}_g|$, whereas the SH intensities at larger $|\mathbf{k}_g|$-values are rather low. This reflects the structure of the poled state of the crystal [5], a dominance of large polar structures in the poling direction with a small amount of narrower structures remaining in the opposite direction. The small intensity peaks at $|\mathbf{k}_g| = 3$ and 11 μm^{-1} might indicate persistent structures of corresponding size.

The overweight of larger polar structures in unpoled CBN, which has not been observed in unpoled SBN, might be explained by differences in the structural disorder between the two materials. To compare the two compounds, the average site occupancies for the A1 and A2 sites are listed in table 1, both for the congruently melting compositions of CBN [9] and SBN [19].

The comparison shows that in CBN calcium is restricted to the two foursquare A1 sites, whereas the four pentagonal A2 sites are nearly fully occupied by barium exclusively. In contrast, in SBN strontium is equally distributed between A1 and A2, additionally A2 is less than 50% occupied by barium. Thus in CBN, composition fluctuations are expected to be much smaller than in SBN. This should result in lower internal random fields and should abet the formation of larger domains due to increased electrical long range order. Hence, the phase transition should be less relaxor-like, which has indeed been observed in dielectric constant measurements on CBN [20].

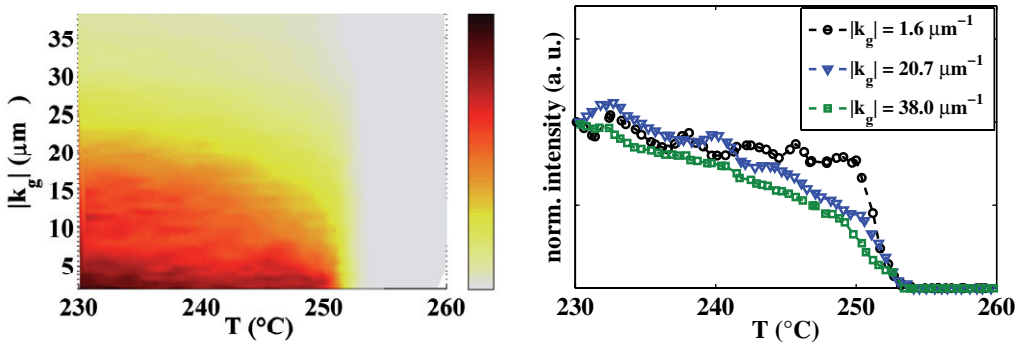

Figure 3. (3 MB MPEG-video available from stacks.iop.org/NJP/11/083021/mmedia). (a) Dependence $I_{SHG}(T, |\mathbf{k}_g|)$ of unpoled CBN, including the phase transition point region. The SH intensity is colour coded as a function of the temperature and $|\mathbf{k}_g|$, dark regions indicating high values and bright regions indicating low values. The phase transition appears at approximately 251 °C. (b) Normalized SH intensity of unpoled CBN in the vicinity of the phase transition for different $|\mathbf{k}_g|$.

3.1. Unpoled samples

Figure 3(a) shows the $|\mathbf{k}_g|$-spectrum for unpoled CBN while heating through the ferroelectric phase transition. The intensity is colour coded as a function of the temperature and $|\mathbf{k}_g|$, dark regions indicating high values and bright regions indicating low values. Additionally, a 3 MB MPEG-video is available from stacks.iop.org/NJP/11/083021/mmedia, in which the development of the SH intensity is shown in a three-dimensional graph.

In good agreement with figure 2, the SH intensity exhibits a $|\mathbf{k}_g|$-dependence in the ferroelectric phase. Additionally, a slight decrease in the SH intensity for all $|\mathbf{k}_g|$ values with increasing temperature can be seen. For $T \geqslant 251$ °C, a dramatic breakdown of the SH intensity for all $|\mathbf{k}_g|$ occurs, and above 255 °C the intensity vanishes completely due to the centric symmetry of the paraelectric phase.

In figure 3(b), the development of SH intensity for the smallest, a medial, and the biggest investigated value of $|\mathbf{k}_g|$, extracted from figure 3(a), is shown. For better comparability, the intensities are normalized to their values at $T = 230$ °C.

It can be seen in figures 3(a) and (b), that the SH intensity for large $|\mathbf{k}_g|$ decays at lower temperatures than for small $|\mathbf{k}_g|$. For the latter, the intensity decreases with a very steep edge, whereas larger $|\mathbf{k}_g|$ perform a more smooth transition. This leads to the conclusion that the crystal does not perform a unique phase transition, but undergoes a spectrum of different phase transitions, whose properties depend on the size of the polar structures involved. The temperature range of approximately 4 °C, in which the SH intensity for small $|\mathbf{k}_g|$ decays, is much smaller than for SBN (≈12 °C, [18]), pointing to a less relaxor-like behaviour for CBN. This can be referred to the increased electrical long-range order as stated above.

3.2. Poled samples

In unpoled CBN, the measurements reveal a nonuniform behaviour of the broad domain size distribution. In the following, the behaviour of poled CBN, in which the crystal volume is mainly occupied by large domains, is investigated.

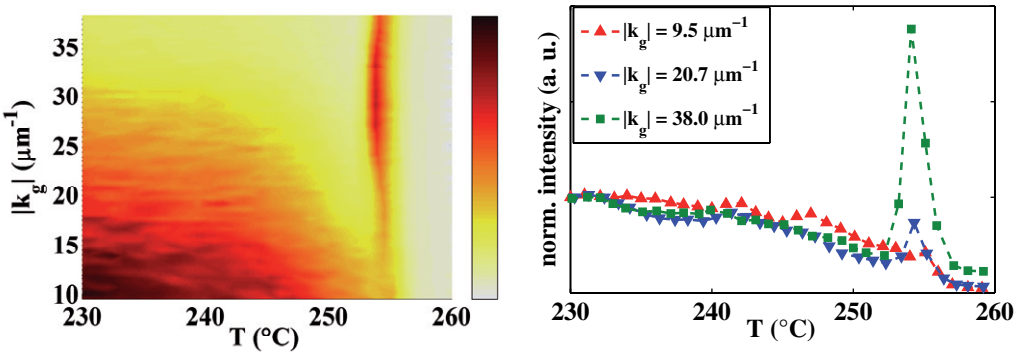

Figure 4. (3 MB MPEG-video available from stacks.iop.org/NJP/11/083021/mmedia) (a) Dependence $I_{SHG}(T, |\mathbf{k}_g|)$ of CBN poled at room temperature with $E_{pol} = 1.2\,kV\,mm^{-1}$, including the phase transition point region. The SH intensity is colour coded as a function of the temperature and $|\mathbf{k}_g|$, dark colours indicating high values and bright colours indicating low values. In the phase transition point region, a pronounced maximum for nearly all $|\mathbf{k}_g|$-values occurs. (b) Normalized SH intensity of poled CBN in the vicinity of the phase transition for different $|\mathbf{k}_g|$.

In figure 4(a), the SH intensity emitted from poled CBN while being heated through the ferroelectric phase transition is shown. The sample has been poled previous to the measurement with $E_{pol} = 1.2\,kV\,mm^{-1}$ at room temperature. Again, the SH intensity is plotted as a function of the crystal temperature and $|\mathbf{k}_g|$, and a 3 MB MPEG-video is available from stacks.iop.org/NJP/11/083021/mmedia, in which the development of the SH intensity is shown in a three-dimensional graph.

In the ferroelectric phase ($T \leqslant 251\,°C$), the poled state is reflected by a strong $|\mathbf{k}_g|$-dependence of the SH intensity, with high values for small $|\mathbf{k}_g|$. In the vicinity of the phase transition, the temperature dependent intensity for large $|\mathbf{k}_g|$ undergoes a pronounced maximum. Coming from a state consisting mainly of large domains and very small ones (poled), a decay of the large structures into smaller ones has to be assumed. The significant broadening of the intensity spectrum during the phase transition resembles the $|\mathbf{k}_g|$-spectrum of an unpoled crystal, which thus can be seen at the peak temperature at about 255 °C in figure 4(a), several degrees above the vanishing point of the SH intensity for unpoled CBN (cf figure 3(a)).

This difference in temperature can be explained considering the observation for unpoled CBN, with larger structures decaying at higher temperatures. Poled CBN has a high density of large domains, with sizes even outside the measurable range. Thus, the decay of such structures, which leads to the formation of smaller ones, occurs at temperatures above those for which the SH emission vanishes for unpoled CBN.

For better visualization, the SH intensity for three different $|\mathbf{k}_g|$, taken from figure 4(a), is exemplarily plotted in figure 4(b). Again, the data is normalized to the values at $T = 230\,°C$. From figure 4(b), the temperature range covering the increase of the SH intensity for large $|\mathbf{k}_g|$ and the decrease to zero, i.e. the width of the peak, can be derived to approximately $258\,°C - 251\,°C = 7\,°C$. This is just about half of the value for field-cooled SBN of approximately 15 °C, using data from figure 5 in [5]. This behaviour can again be explained considering the lower internal random fields due to lower composition fluctuations. They reduce

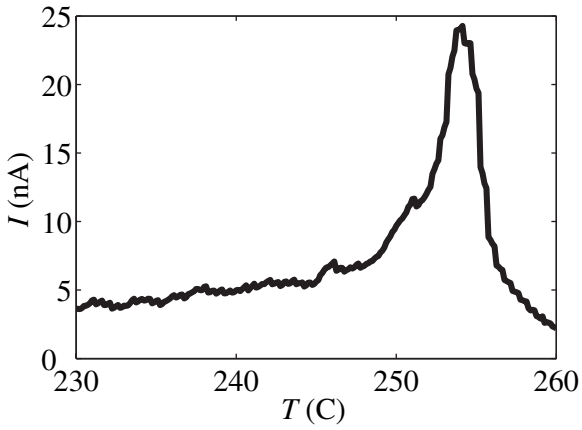

Figure 5. Current flow from poled CBN while heating through the ferroelectric phase transition.

the relaxor behaviour at the phase transition compared to SBN, resulting in a narrower phase transition region.

Along with the SH intensity maximum, the poled sample's current flow due to the pyroelectric effect undergoes a maximum too, indicating a macroscopic change of the polarization, as shown in figure 5. Here, the current flow is plotted as a function of the crystal temperature. The jumps in the data may be attributed to a Barkhausen-like behaviour of the domain structure with polar regions spontaneously changing their orientation or vanishing completely. This hints at defect dominated domain wall motion. The current peak indicates the phase transition region, further heating in the paraelectric phase results in an ebbing of the current flow.

When cooling down from the paraelectric phase, no current flow occurs, and the poled state is not restored in the crystal. Instead, a domain state is established, which generates a broad SH intensity distribution. As argued in [12], this corroborates the fact that the poled crystal is far from thermal equilibrium.

4. Conclusion

Concluding our work, we have found that CBN from the congruently melting composition exhibits interesting phase transition characteristics, both in the unpoled and in the poled state. In unpoled CBN, an inhomogeneous $|\mathbf{k}_g|$-spectrum in the ferroelectric phase, indicating a majority of large polar structures, could be measured (cf figure 2). This is in clear contrast to the data published for unpoled SBN from the congruently melting composition, where a homogeneous spectrum was found [5]. The overweight of larger structures may be attributed to lower composition fluctuations in CBN, resulting in higher electrical long-range order. Regarding this finding, $\mathrm{CBN}_{(x=0.28)}$ may be compared to SBN with small strontium content (i.e. small x). For the latter, the relaxor behaviour was found to be reduced with respect to the congruently melting composition $\mathrm{SBN}_{(x=0.61)}$ [21].

Phase transition measurements have shown that unpoled CBN exhibits a $|\mathbf{k}_g|$-dependent decay of the SH intensity in the phase transition region. This indicates a nonuniformity of the ferroelectric phase transition for differently sized polar structures, resembling the phase

transition model established by Smolenskii. He describes the diffuse phase transition of ferroelectric materials as a coexistence of different phases over a wide temperature interval [22]. In the case of CBN, the occurance of the phase transitions obviously depends on the size of the ferroelectric domains involved.

Additionally, we could observe different temperature dependences for different domain sizes. Thus, CBN exhibits not only microscopic phase transitions at various temperatures, but also an agglomeration of different transitions with heterogeneous behaviour. This finding clearly extends Smolenskii's model, since the relaxor transition of CBN obviously features both different phase transition temperatures and different phase transition behaviour, depending on the particular domain size.

Poled CBN develops into a polydomain state during the phase transition. In accordance with a similar finding for SBN, this is interpreted as a disintegration of the majority of large domains. The phase transition point region of CBN, however, is much smaller than for SBN. This should also be a consequence of the lower composition fluctuations of CBN, with the implications mentioned above. Nevertheless, there might be additional effects contributing to the observed differences of CBN to SBN.

The conclusion that the phase transition of poled CBN is comparable to that of poled SBN indicates that it might be a challenging task to classify CBN's phase transition, since the phase transition in SBN is currently under controversial discussion [7, 8, 12].

Recapitulating, the phase transition in CBN, regarding poled samples, is qualitatively similar to SBN. Additionally, even unpoled, thermally annealed CBN exhibits a domain-size dependent phase transition behaviour, which can be explained using the model for diffuse phase transitions by Smolenskii.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft and the federal state of Niedersachsen within the graduate college GRK 695 'nonlinearitites of optical materials' is gratefully acknowledged.

References

[1] Gladkii V V, Kirikov V A, Nekhlyudov S V, Volk T R and Ivleva L I 2000 Polarization and depolarization of relaxor ferroelectric strontium barium niobate *Phys. Solid State* **42** 1334–40

[2] Gladkii V V, Kirikov V A, Proninia E V, Volk T R, Pankrath R and Wöhlecke M 2001 Anomalies in the slow polarization kinetics of a ferroelectric relaxor in the temperature region of a diffuse phase transition *Phys. Solid State* **43** 2140–5

[3] Granzow T, Woike Th, Wöhlecke M, Imlau M and Kleemann W 2002 Polarization-based adjustable memory behavior in relaxor ferroelectrics *Phys. Rev. Lett.* **89** 127601

[4] Wesner M, Wischmeier L, Krätzig E, Rosenfeldt A, Flörsheimer M and Kip D 2003 Spatially-resolved investigations of domain switching in the ferroelectric relaxor SBN by photorefractive self-focusing *Trends Opt. Photonics* **87** 22

[5] Voelker U and Betzler K 2006 Domain morphology from k-space spectroscopy of ferroelectric crystals *Phys. Rev.* B **74** 132104

[6] Isakov D V, Belsley M S, Volk T R and Ivleva L I 2008 Diffuse second harmonic generation under the ferroelectric switching in $Sr_{0.75}Ba_{0.25}Nb_2O_6$ crystals *Appl. Phys. Lett.* **92** 032904

[7] Scott J F 2006 Absence of true critical exponents in relaxor ferroelectrics: the case for defect dynamics *J. Phys.: Condens. Matter* **18** 7123–34
[8] Kleemann W 2006 Absence of true critical exponents in relaxor ferroelectrics: the case for nanodomain freezing *J. Phys.: Condens. Matter* **18** L523–6
[9] Eßer M, Burianek M, Held P, Stade J, Bulut S, Wickleder C and Muehlberg M 2003 Optical characterization and crystal structure of the novel bronze type $Ca_xBa_{1-x}Nb_2O_6$ ($x = 0.28$; CBN-28) *Cryst. Res. Technol.* **38** 457–64
[10] Song H, Zhang H, Jiang Q, Xu X, Lu C, Hu X, Wang J and Jiang M 2006 Growth, dielectric, ferroelectric and optical properties of $Ca_{0.28}Ba_{0.72}Nb_2O_6$ single crystals *J. Cryst. Growth* **290** 431–5
[11] Muehlberg M, Burianek M, Joschko B, Klimm D, Danilewski A, Gelissen M, Bayarjargal L, Görler G P and Hildmann B O 2008 Phase equilibria, crystal growth and characterization of the novel ferroelectric tungsten bronzes $Ca_xBa_{1-x}Nb_2O_6$ (CBN) and $Ca_xSr_yBa_{1-x-y}Nb_2O_6$ (CSBN) *J. Cryst. Growth* **310** 2288–94
[12] Voelker U, Heine U, Goedecker C and Betzler K 2007 Domain size effects in a uniaxial ferroelectric relaxor system: the case of $Sr_xBa_{(1-x)}Nb_2O_6$ *J. Appl. Phys.* **102** 114112
[13] Armstrong J A, Bloembergen N, Ducuing J and Pershan P S 1962 Interactions between light waves in a nonlinear dielectric *Phys. Rev.* **127** 1918
[14] Kawai S, Ogawa T, Lee H S, DeMattei R C and Feigelson R S 1998 Second-harmonic generation from needlelike ferroelectric domains in $Sr_{0.6}Ba_{0.4}Nd_2O_6$ single crystals *Appl. Phys. Lett.* **73** 768–70
[15] Hum D S and Fejer M M 2007 Quasi-phasematching *C. R. Phys.* **8** 180–98
[16] Lu C J, Nie C J, Duan X F, Li J Q, Zhang H J and Wang J Y 2006 180° domain structure and its evolution in $Ca_{0.28}Ba_{0.72}Nb_2O_6$ ferroelectric single crystals of tungsten bronzes structure *Appl. Phys. Lett.* **88** 201906
[17] Vidal X and Martorell J 2006 Generation of light in media with a random distribution of nonlinear domains *Phys. Rev. Lett.* **97** 013902
[18] Voelker U 2008 *k*-Raum spektroskopie zur charakterisierung optisch nichtlinearer ferroelektrika am beispiel strontiumbariumniobat *PhD Thesis* Universität Osnabrück
[19] Podlozhenov S, Graetsch H A, Schneider J, Ulex M, Wöhlecke M and Betzler K 2006 Structure of strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN) in the composition range $0.32 \leqslant x \leqslant 0.82$ *Acta Crystallogr.* B **62** 960–5
[20] Niemer A 2009 private communication, to be published
[21] Shvartsman V V, Kleemann W, Lukasiewicz T and Dec J 2008 Nanopolar structure in $Sr_xBa_{(1-x)}Nb_2O_6$ single crystals tuned by Sr–Ba ratio and investigated by piezoelectric force microscopy *Phys. Rev.* B **77** 054105
[22] Smolensky G 1984 Ferroelectrics with diffuse phase transition *Ferroelectrics* **53** 129–35