Abstract

We report the anisotropic focusing characteristics of a spherically configured region of micro-domains that have been induced within a cubic shaped crystal of Ce-doped Sr$_{0.61}$Ba$_{0.39}$Nb$_2$O$_6$. The internal spherical structure focuses extraordinary polarised light, but not ordinary polarised. The spherical region, which is easily observed via scattering, is formed as the crystal cools down, after a repoling cycle through the Curie temperature, with an applied field. Analytic modelling of the thermal gradients that exist within the crystal during cooling reveals a small (<1) temperature difference between the central and outside regions. The similarity in shape between these temperature profiles and the observed scattering region suggests a possible mechanism for the growth of this spherical micro-domained structure.

Introduction

Strontium barium niobate (SBN:x, Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$) is a crystalline material which is a solid solution of strontium and barium niobates [1]. For values of x in the range 0.5-0.75, crystals are readily available with good optical quality for applications in photorefraction, optical memories, electro-optic devices and phase conjugation. SBN is one of several glassy ferroelectric crystals that have unusual structural (and micro-structural) properties [2]. The phase transition from ferroelectric to paraelectric states is diffuse, and as such, the values reported for Curie temperature, $T_c$, range quite widely in the literature. Single domain crystals are obtained by heating through $T_c$ with an applied field present larger than the coercive field, and subsequently letting the crystal cool down below $T_c$. Experimentally, however, the exact procedure adopted for this, namely duration of applied field, rate of crystal cooling, whether the nominal value for $T_c$ is reached, and very importantly, the previous crystal repoling history, all affect both the net dipole moment obtained, and the extent of formation of any regions of micro-domains.

Recent studies using the technique of X-ray diffraction imaging have revealed the extent to which domains, and micro-domains, may be present in nominally well poled samples of SBN. For a range of different crystals, 180° anti-parallel domains were observed, predominantly near the crystal edges, with an average size of the order of 10 µm or less [3]. For SBN:50, rapid cooling through $T_c$ can produce domains with average widths of 100Å, while subsequent annealing for a few days at lower temperatures can change this value to the order of microns [4]. Other materials such as lead magnesium niobate, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, also reveal this variation in domain size: field cooling (FC) and zero field cooling (ZFC) produce distinctly different domain size distributions [5]. SBN will always tend to show this variability of domain sizes, the precise length and width of which is a strong function of the poling procedure adopted, and earlier poling/repoling cycles.

Scattering experiments have been performed for SBN which allow domain size distributions to be inferred [6]. The experiments reported used two nominally identical crystals of SBN:61 which were subjected to differing poling treatments. Crystal number one remained unpoled throughout the measurements. Crystal number two however was given an initial FC thermal poling, followed by several ZFC thermal cycles. The Rayleigh scattering, viewed at 90°, differed
markedly between the two crystals, both in intensity and polarisation dependence. The hundredfold difference reported for the scattered light intensity between the two crystals is indicative of their respective domain size, as Rayleigh scattering depends strongly on dimensions of the scatterer.

The crystal we discuss in this paper however, contains a spherical micro-domain structure that represents both of the above cases reported in [6], but within a single crystal. The central region is an efficient scatterer, and the visual appearance is striking: the crystal contains a scattering ‘ball’ which is completely enclosed within the crystal cube. Also, unlike the results reported in [6], the scattering is easily observable with the naked eye. While the polarisation properties of the scattered light are similar, the intensity of the scattering is many orders of magnitude larger, measurable with standard optical power meters, rather than using photon counting. The anisotropic focusing we observe is generated by the presence of this spherical region within the uniaxial SBN crystal structure.

**Anisotropic properties of the crystal ball**

Figure 1 shows the scattered light generated from the central region of the crystal. Fig 1(a) was obtained by viewing at 90° to the incident beam direction, which was provided from either an Ar+ ion laser operating at 514.5nm or a He-Ne laser at 633nm. Figure 1(b) shows the scattering viewed along a crystal edge direction, the two images clearly showing the volume nature of the scattering region. An analyser placed in the path of the scattered light revealed a polarisation dependence as indicated in figure 2. O-polarised light was scattered uniquely as e-polarised, whereas e-polarised light yielded almost equal intensity contributions of both e-polarised, and o-polarised light. The scattering ball appeared following a normal FC poling cycle. The field applied was 2 kV across the crystal c axis, and the cooling cycle took the crystal from a temperature of typically 120° C to room temperature (~25° C), over a time period of ~2 hours. The crystal was situated within a thermal enclosure, so the cooling curve showed exponential behaviour. The scattering ball was observed each time the crystal was FC poled in this way. Subsequent room temperature electrical repoling
could be used to make the scattering ball disappear, but a FC cycle was required to produce the structure. The exact location of the centre of the ball could be shifted laterally along the crystal c-axis by \( \leq 1 \text{mm} \), depending on the poling field polarity, but the overall size remained constant however.

The origin of the scattering and anisotropic focusing lies in the orientation and size of the microdomains present within this uniaxial medium. We have performed two-beam coupling experiments using the ‘Swiss cheese’ arrangement [7] in which the signal beam propagates down the c-axis, and a pump beam is incident at an arbitrary angle (45° in our case) to the crystal entrance face. This beam coupling arrangement allows visualisation of the domain orientation, as coupling will either augment or deplete the signal beam intensity, depending on the domain polarity. For SBN, the largest electro-optic coefficient normally accessed is \( r_{33} \), but for the Swiss cheese coupling experimental set-up, this is not possible. Additionally, when viewing normal to the c-axis direction, circular interference patterns were observed, generated by the ball, which masked the outline of the central region, viewed through conventional beam coupling in the symmetric orientation utilising \( r_{33} \). A unity beam intensity ratio was used, and the transiently diffracted light was captured with a frame grabber and CCD camera. Figure 3 shows the optimum results obtainable, using the smaller \( r_{13} \) coefficient. The image shows a central approximately circular region which is noticeably darker than the outer regions, indicating less overall coupling has taken place here. This is indicative of the simultaneous presence of 0° and 180° domains within this region. Note that while the shape of the microdomain region is very similar to that shown in figure 1, due to the difference in physical processes involved in scattering and beam coupling, there is no reason for an exact match.

Measurement of the angular dependence of He-Ne laser light diffracted from within the ball also lead to the conclusion that the central region consists of a spherically configured array of parallel and anti-parallel domains, with transverse widths at the sub-micron to few microns scale length. Light was diffracted as a wide angular fan, rather than as discrete points, indicating the presence of a distribution of domain widths. The peak intensity within this diffracted fan indicated a modal width of \( \sim 2 \mu \text{m} \). No significant scattering was observed along the c-axis direction however, indicating that the length of domains greatly exceeds their width. Additionally, no such diffraction was observed when He-Ne light was directed at regions of the crystal outside the central spherical region.
Figure 3. Image of ball, viewed by transient two-beam coupling, showing the central region of disordered microdomains. Coupling occurred down the crystal c-axis, hence coupling efficiency was not optimal.

Birefringent focusing

When the crystal is illuminated with collimated light from a He-Ne laser, the internal microdomain region acts as a converging lens for e-polarised light, but not for o-polarised. The focal length achieved at the He-Ne wavelength of 633 nm was measured to be ~140cm, producing a spot size, \( \omega \), of 290µm, measured using a beam profiler. Experimentally however, the incident Gaussian beam overfilled the crystal input aperture, so that the normal conditions applicable to diffraction limited Gaussian beam focusing (lens not acting as a limiting aperture) do not apply. For comparison however, using an average value of ball diameter of 3mm, obtained from scattering and beam coupling observations respectively, we deduce a diffraction limited value of spot size of ~ 190µm, for the measured focal length of 140cm.

There was no focusing action at all for o-polarised incident light. To our knowledge, no other such birefringent focusing structures have been reported, in this passive compact form. It is, of course, possible to assemble such a birefringent device, using specially constructed doublets, made from differently orientated anisotropic elements. However, the crystal here achieves this in a single element. One additional advantage is that this lens is field erasable. A room temperature repoling field makes the ball disappear. By further optimised field cooling procedures, lens structures may be achievable with larger dimensions, and smaller values of focal length.

Discussion

The scattering observed reflects the underlying lack of single domain ordering within the central region. The presence of 0° and 180° domains, with associated domain boundaries, internal stresses, and charge compensation than can occur at the ends of domains, all affect the bulk properties of a ferroelectric. When a region of microdomained material exists within a bulk single domain crystal, then the microscopic structure can have a pronounced affect on the macroscopic optical properties, such as refractive index and birefringence. In our case,
while the exact cause for formation of this ball is uncertain, we suggest that the thermal cycling required to FC pole the crystal also influences the domain growth habit, through the finite temperature differences that exist between the central and outside regions. The spherical shape suggests that some diffusion process may be involved. Material in- or out-diffusion is unlikely, as the ball could be formed and erased many times, and the temperatures involved in poling were only of order 100 °C. Furthermore, the lateral poling field polarity dependent shift that was observed, suggests a more general explanation. It is known in SBN that domain size is a function of external pressure [8]. There is also a small, but systematic temperature difference between the central and outer regions of the crystal following a FC poling. In figure 4 we show the results of an analytic solution to the 3-dimensional heat flow equation within the SBN, following a heating cycle to beyond its Curie temperature, and slow cooling to room temperature. The calculation assumed that heat diffusion was isotropic, and used the known value for thermal diffusivity in SBN \( D = 6.77 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} [9] \). A more complete discussion of the analytic solution to this problem is given in an appendix. Two equal temperature contours are shown within the crystal. It can be seen that there is a good similarity between the inner contour plot and the region showing pronounced optical scattering, shown in figure 1. This can be qualitatively understood by considering heat loss from the outside faces of the crystal cube. There will be a systematic thermal smoothing of the temperature contours, resulting in a quasi-spherical shape as the centre of the cube is reached. The maximum calculated temperature difference between the centre and outside edges of the crystal does not exceed ~ 0.2 °K at any time during the cooling period. As stated earlier, it is known however that the dielectric properties and value of Curie temperature for SBN are sensitive to external factors, and we suggest here that this temperature difference, while small, may have a pronounced affect on the growth habit experienced by the central region, which will be under constant stress during the cooling phase.

We observe a progressive increase in the scattered light intensity from the central region rather than a sudden onset at a specific temperature, as the crystal cools. We conclude therefore that the microdomains in the central region grow through continuous response to forces such as pressure, or stress. As the material cools through the Curie temperature, the transition from the paraelectric to the ferroelectric anisotropic phase will occur first at the cooler outer crystal regions. Progressive cooling may exert further pressure on the central region, which in turn affects the internal structure, and the whole process continues. In this way, there can be a large internal stress...
accumulated within the crystal, which as stated earlier, is a known method for microdomain formation. Although it may seem surprising that this can occur from such a small value of temperature difference, such glassy ferroelectrics are known to be very sensitive to small temperature differences at, for example, their domain freezing temperature [10].

Conclusions

In conclusion, the scattering central ball we have grown within the cube shaped SBN crystal displays interesting optical properties. E-polarised light is selectively focused by the central region, while o-polarised light is unaffected. The underlying mechanism for the formation of this region is not certain, but may well be due to temperature gradients experienced during cooling, following a poling cycle. If the domain size could be controlled dynamically, then variable focal length optical elements could be constructed by this route. Further work is in progress concerning this aspect.

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Appendix

Figure 4 shows the results of analytically modelling the heat flow. As a starting point, a solution of the diffusion equation in a cube of edge $2L$ is

$$T(x,y,z,t) = \frac{64}{\pi^3} \sum_{\text{odd } p, q, r} \sum_{p, q, r} (-1)^{p+q+r} \frac{p\pi x}{2L} \cos \frac{q\pi y}{2L} \cos \frac{r\pi z}{2L} \times \exp\left\{-\frac{D\pi^2 t}{4L^2} [p^2 + q^2 + r^2]\right\}.$$

At $t=0$ the temperature $T$ is uniform except on the surface $x=\pm L, y=\pm L, z=\pm L$ where $T$ is always zero. This solution therefore corresponds to the physical situation where the initial temperature of the cube is unity and the surface temperature makes a step function change to $T=0$ at $t=0$.

If the temperature of the oven containing the crystal changes from $T_i$ to $T_f$ according to

$$T(t)=\begin{cases} (T_i-T_f) e^{-\alpha t} + T_f & t>0 \\ T_i & t\leq0 \end{cases}$$

the response of the crystal can be obtained by replacing each factor of the form $\exp(-\beta t)$ by

In the experiment $\alpha$ was $5.834 \times 10^4 \text{ s}^{-1}$, $D$ was taken as $6.77 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ [9], and assumed to be isotropic, and $L=2.5 \text{ mm}$ These values give the minimum value of $\beta$, corresponding to $p=q=r=1$ as 0.801; it follows that for times greater than a few seconds after the start of cooling $\exp(-\beta t)$ is negligible; also $\alpha L^2/D\pi^2 << 1$. With these approximations the temperature difference between the crystal surface and the point $x,y,z$, at time $t$, is

$$T_f + (T_i-T_f)\frac{\beta e^{-\alpha t} - \alpha e^{-\beta t}}{(\beta - \alpha)}.$$

The value of the triple sum at the centre of the cube is 1.27 and with the constants above, the temperature difference between the crystal faces and the centre of the cube never exceeds 0.19K.

Figure 4 has been generated by plotting equal temperature contour shells from the 3 dimensional matrix of points derived from the analytic solution above, and two such shells are illustrated, to show the increasingly spherical shape obtained.
References


