

Birefringence of lead titanate (PbTiO₃)

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Since lead titanate was first grown in single-crystal form in the 1930s, several independent reports of its linear birefringence have been published. Whilst there is overall qualitative agreement on its behaviour with temperature, the absolute values show some degree of variation. At 298 K they range from -0.009 to -0.013 , a relative spread of 40%, whilst at 673 K the discrepancy is even greater. This paper reports unexpected results obtained from independent measurements of a selection of crystals that have been grown recently, in which the birefringence is some four times greater than hitherto believed. This has important consequences for the use of birefringence measurement as a means of studying phase transitions in crystals. Intrinsic values of birefringence for lead titanate are measured for the first time.

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1. Introduction

As early as the 1930s, lead titanate (PbTiO₃) was recognized to possess the perovskite structure (Cole & Espenschied, 1937), though it was not until 1943 that its symmetry at room temperature was correctly determined to be tetragonal (Náray-Szabó, 1943). The lattice parameters were measured to be $a = 3.89$ Å and $c = 4.13$ Å, values which were later corroborated by other authors (*e.g.* Megaw, 1946; Shirane & Hoshino, 1951). On heating to approximately 760 K, the crystal undergoes a first-order phase transition to a cubic phase. Shirane & Hoshino (1951), and later Mabud & Glazer (1979), carried out temperature-dependent measurements of the lattice parameters, revealing that the volume of the unit cell showed a slight decrease up to the transition temperature, beyond which it rose. The separation of the c and a axes became smaller with temperature in the tetragonal phase, with a sudden decrease to zero at the phase transition point.

Forsburgh (1952) conducted one of the first studies on the temperature dependence of the birefringence of lead titanate. PbTiO₃ is always optically negative: henceforth we shall quote the absolute value of the birefringence without ambiguity. The birefringence was found to be anomalous in that, as the temperature increases, it rises to peak at around 670 K, then decreases again and eventually rapidly falls to zero at the ferroelectric paraelectric first-order phase transition. Values of the birefringence at 298 K were also published by Rogers (1952) for various wavelengths of light: 0.011 at 580 nm, 0.013 at 550 nm, 0.014 at 515 nm, and 0.024 at 430 nm. It is unclear which method was used to synthesize the crystals used for these measurements, as several growth techniques were reported. It would seem, however, that the measurements were carried out on as-grown crystals by measuring the distance between interference fringes produced in wedge-shaped domains by illumination with monochromatic light.

Shirane *et al.* (1956) also carried out a temperature-dependent investigation with sodium light ($\lambda = 589$ nm) on unpolished flux-grown single crystals. The results from measuring fringes of wedge-type domains, as well as by compensation using a calibrated quartz wedge, were of a similar magnitude to those of Rogers. Specifically, the birefringence rose from about 0.01 at 273 K, to a maximum value of 0.017 at around 670 K.

Further measurements were made soon after by Fesenko & Kolesova (1959) and by Kobayashi & Yamada (1959). The former were carried out on crystals produced from a slow-cooled melt of lead metaborate, and results similar to those of Shirane *et al.* were achieved. Kobayashi and Yamada, on the other hand, employed crystals grown from a flux of potassium fluoride (KF), with PbTiO₃ as a starting material, which in turn was synthesized by a PbCl₂ method (Kobayashi, 1958). Birefringence was measured with a Berek compensator on multi-domain crystals. In common with the measurements of Shirane *et al.* and Fesenko and Kolesova, the birefringence displayed the broad peak in the vicinity of 670 K. However, whilst of a similar absolute magnitude, the overall curve *versus* temperature was much flatter than those obtained by the aforementioned authors.

The birefringence was also studied by Mabud & Glazer (1979), measurements again being taken with a Berek compensator, on crystals grown from TiO₂ in a PbO flux. Results very similar to those of Kobayashi and Yamada were obtained. In addition, the behaviour of the birefringence with temperature was correlated with the lattice parameter and spontaneous polarization measurements, and it was suggested that the peak in birefringence arises through a competition between photoelastic and electro-optic effects.

More recently, the birefringence of lead titanate was determined by Kleeman *et al.* (1986). Single crystals of PbTiO₃ were prepared by top-seeded solution growth using PbO as a

solvent. The crystals were cut and polished, the sample used for the measurements having a final thickness of 0.34 mm. The data, collected using a computer-controlled modulation

method (Schäfer & Kleemann, 1985), represented the highest values thus far, at about 0.013 at room temperature.

The data gathered from the papers published hitherto are summarized in Fig. 1. Even taking into account the range of wavelengths of light used, the agreement between the various curves is qualitative at best. As a result, we have re-examined the birefringence of lead titanate, making measurements on a selection of recently grown single crystals. To our surprise, we found the actual values to be some four times the magnitude of all those previously reported.

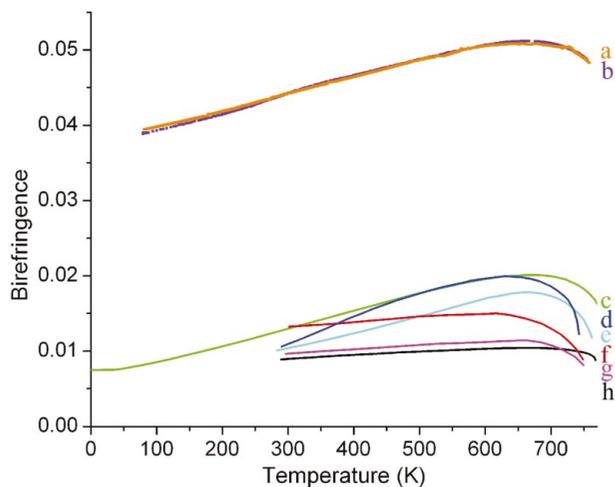


Figure 1 Literature birefringence data: (a) measurements made in Oxford (600 nm); (b) measurements made in Katowice (546 nm); (c) Kleemann *et al.* (1986); (d) Fesenko & Kolesova (1959); (e) Shirane *et al.* (1956) (589 nm); (f) Kobayashi & Yamada (1959) (550 nm); (g) Kobayashi & Yamada (1959) (600 nm); (h) Mabud & Glazer (1979).

2. Experimental

Single crystals of lead titanate were obtained from the Institute of Physics, Rostov State University, Russia. These crystals were grown from a convection-mixed melt of PbO, TiO₂ and B₂O₃ as a flux, under a simultaneous temperature gradient and cooling of the mixture. This technique resulted in natural plate-like crystals with well formed faces (Fesenko *et al.*, 1972) and a relatively simple domain structure. Fig. 2(a) is a photograph of a typical *a*-domain crystal showing little or no evidence of any twin domains.

Birefringence measurements were carried out on these crystals using a birefringence imaging system (Metripol; www.metripol.com) on a microscope equipped with a plane-

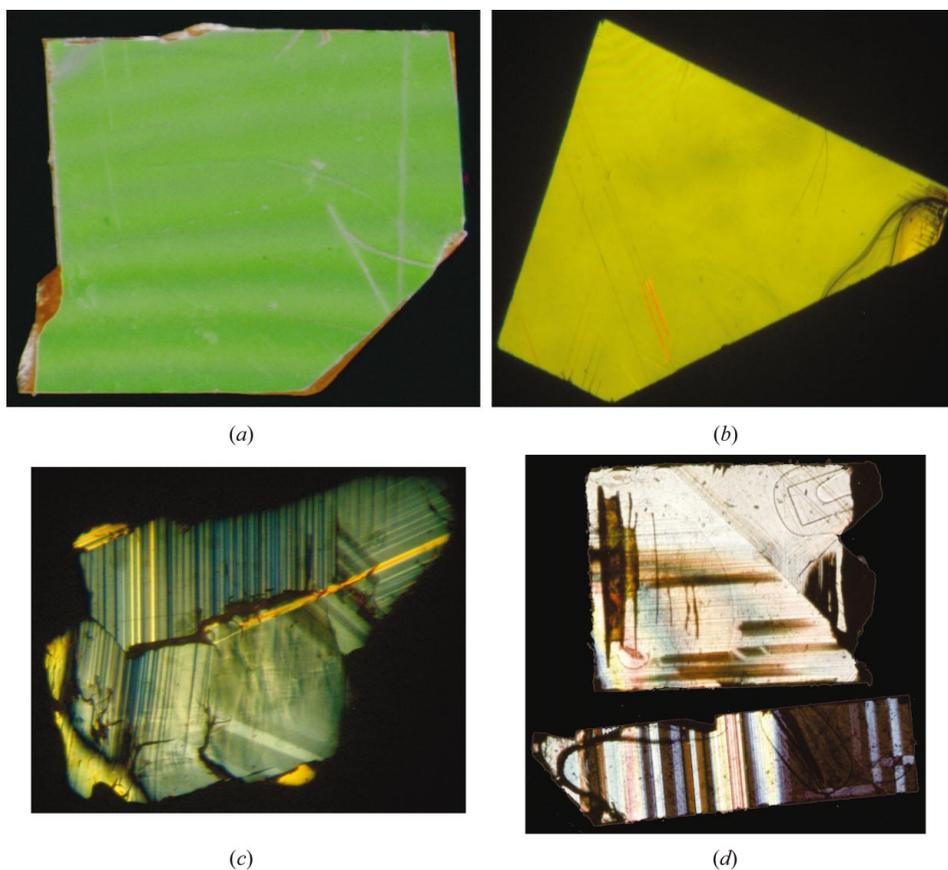


Figure 2 (a) Lead titanate single crystal, grown at the Institute of Physics, Rostov State University, shown between crossed polars. (b) Lead titanate crystal grown at the University of Silesia, Poland. (c) Lead titanate crystal grown by Oka. As can be seen, many lateral domains appear when viewed between crossed polars. (d) Lead titanate crystals measured for birefringence by Mabud and Glazer.

polarizer capable of being rotated to fixed angles α from a reference position, a circular-polarizing analyser, and a CCD camera (Glazer *et al.*, 1996). The intensity measured at any position within the image captured by the camera is given by the formula

$$I = (I_0/2)[1 + \sin(2\varphi - 2\alpha) \sin \delta],$$

where I_0 is the intensity of light passing through the sample and represents its transmittance, φ is the angle of the optical axis of the crystal measured from a predetermined origin, and δ is the phase shift introduced by the sample between the two orthogonal components of the polarized light, given by

$$\delta = (2\pi/\lambda)\Delta n\tau.$$

Here, λ is the wavelength of the light, τ is the thickness, and Δn the birefringence of the sample. By measuring several images with varying angle α , it is possible to refine at each pixel in the image the quantity $|\sin \delta|$. Such measurements were collected automatically as the crystal was heated from 83 to 773 K, just into the cubic phase. Because an imaging technique was used, we were able to track the average value of $|\sin \delta|$ over a small uniform area of the sample, and so the temperature dependence of the birefringence could be obtained.

The relative birefringence can be derived from $|\sin \delta|$ knowing the wavelength of the light and sample thickness, in our case 600 nm and 69 μm , respectively. As the ferroelectric paraelectric phase transition is of first order, the discontinuous jump in the birefringence at this point is indeterminable by the method outlined above. In order to ascertain the absolute value of the birefringence, an Ehringhaus compensator was used to measure the birefringence at room temperature, which then served as a reference on which the temperature-dependent measurements were based. The results are plotted in Fig. 1(a), where it can be seen that the measured birefringence curve is remarkably higher than for all of the earlier measurements.

As a result of this obvious discrepancy, we measured the birefringence of a different crystal of lead titanate (Fig. 2b) at the University of Silesia, Poland, grown from $\text{PbO}:\text{B}_2\text{O}_3:\text{TiO}_2$ (Fesenko *et al.*, 1972) in the molar ratio of 0.60:0.255:0.145. This was measured by means of a Sénarmont compensator at a wavelength of 546 nm on a crystal of 69 (1) μm thickness. The transmitted intensity was sampled over a very small region of the crystal by a CCD camera and the minimum in the intensity was found during rotation of the analyser. The angle β corresponding to the minimum was used to calculate the birefringence from the formula

$$\Delta n = \beta\lambda/\pi\tau.$$

To determine the absolute value of the birefringence, an interference-polarized microscope operating in stripe mode (Pluta, 1982) was used to measure the shift of interference pattern, from which it was possible to determine the starting position of the Sénarmont compensator. The observed very regular interference pattern showed the crystal to be optically homogeneous. The results of this investigation are also plotted

in Fig. 1(b). Further verification of the measurements was also made in Oxford on the same sample using the rotating-polarizer technique at 600 nm, described above, and this gave similar results.

Finally, we received some lead titanate crystals from Dr K. Oka of the National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan, grown by the top-seeded solution-growth technique (Oka *et al.*, 1996). Fig. 2(c) shows a photograph of one of these crystals, in which it can be seen that there are many domains. Examination of the birefringence within any domain gives values similar to the older work. This crystal is similar in appearance to the crystals grown by Mabud, shown in his thesis and reproduced in Fig. 2(d) (Mabud, 1978), and used in the work of Mabud & Glazer (1979).

3. Discussion

As is evident, our recent values of the birefringence are approximately four times greater than those of all previous reports. We believe, however, that our present results represent the true value for lead titanate, as the measured data on two independently grown single crystals, and using independent methods, are in excellent agreement.

It is worth noting that Fushimi & Ikeda (1965) performed an optical study on the solid-solution lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, where $0 \leq x \leq 1$), measuring the temperature-dependent birefringence of samples with compositions $x = 0.2$, 0.3 and 0.4. They discovered the value of the birefringence in each case to be greater than that previously reported for lead titanate, and the birefringence increased as the composition tended to the titanium-rich end of the phase diagram. Unfortunately, these authors overlooked this trend and did not carry out independent measurements on pure lead titanate, instead taking the previous values for granted.

Further support is provided by our own work (to be published) on the solid-solution series lead magnesium niobate titanate [$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$, where $0 \leq x \leq 1$], which in a similar way to Fushimi and Ikeda's work on PZT, shows a steadily growing birefringence as the material tends towards pure lead titanate. Similarly, Ye & Dong (2000) measured a room-temperature value of birefringence of about 0.35 for $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.5}\text{Ti}_{0.5}\text{O}_3$.

We believe the discrepancy between our latest results and those of previous publications originates in the domain structure of the crystals under observation. Fig. 2 shows both our crystal (from Rostov, Fig. 2a) and that from Poland (Fig. 2b) to be very uniform. On the other hand, Mabud and Glazer's crystal (Fig. 2d) and that of Oka (Fig. 2c), which we also examined, contain numerous domains. Whilst lateral domains (striped domains cutting through the crystal) are conspicuous owing to their contrasting brightness between crossed polars, 'stacked' planar domains (with domain walls parallel to the viewing surfaces of the crystal) may remain unnoticed. A stacked domain structure will tend to reduce the measured level of the birefringence from its optimal single-domain value, as domains with their *c*-axis orthogonal to the

plane of the crystal will be optically isotropic. Similarly, stacked *a*- and *b*-axis domains will compensate each other internally and also reduce the measured birefringence. It is believed, therefore, that the crystals measured previously must have contained stacked planar domains which the authors were unaware of, resulting in an erroneously low value of the birefringence being attributed to the material. It is easy to understand how this mistake could have been made, as it was observed that after our crystals had been heated into the cubic phase, and subsequently cooled, the net birefringence of the crystal reduced to a fraction of its original value, without changing the appearance of the crystal. This is attributable to the formation of stacked planar domains, even though they are difficult to detect by optical observation: provided that the new domain structure extends evenly over the crystal, the crystal will continue to appear optically uniform when viewed transversely.

Evidence for stacked planar domains in the single-crystal supplied by Oka was obtained using the interference-polarized microscope operating in the stripe mode. In addition to initial estimation of absolute values of birefringence, this allows one to judge immediately the quality of the crystal. In this case it revealed a very irregular interference pattern. Even in the large area (bottom-right part in Fig. 2c), which at a first glance looks like a single domain, it was seen that the interference stripes were bent in addition to exhibiting some shift. The bending effect just reflects the presence of a distribution of birefringence along the crystal. Surprisingly, a small but significant shift of the stripes was also observed when the crystal was in a position where its optical axis was set at 45° to the direction of the stripes. In this case, no shift of the interference pattern should normally be observed. Even more unusually, after rotating the microscope stage by 180° to an equivalent position, the interference stripes were shifted in the opposite direction. In addition, the absolute values of these shifts were different. The single crystal presented in Fig. 2(b), on the other hand, behaved normally in this respect.

Certainly the crystals used by Mabud and Glazer resemble in appearance that of Oka (Fig. 2c), in which many narrow domains are observed laterally, and we think that such twinning was probably common in the earlier crystal growths. The evidence from our comparison of our recent crystals with that of Oka suggests to us that when extensive lateral twinning is seen in this material, it also occurs throughout the depth of the crystal to form the stacked domains. Because such a large variation can occur within one type of crystal, this must raise questions about the use of birefringence as a means of studying structural phase transitions in crystals. Recent work (Geday & Glazer, 2004) on the study of birefringence at the cubic to tetragonal phase transition in SrTiO₃ has produced a temperature variation that is slightly different from that published many years earlier, thus affecting the interpretation

of critical behaviour at this transition. Although the effect in SrTiO₃ is much smaller than in PbTiO₃, it is possible that here too, the presence of stacked domains may account for the difference. Moreover, Jankowska-Sumara *et al.* (2003) reported new measurements on birefringence for lead zirconate which perfectly follow the formula derived on the basis of mean-field theory for an antiferroelectric phase transition. In an older paper by Whatmore & Glazer (1979), only moderate agreement between theory and experiment was reported.

Such variations just reinforce the view that the use of birefringence measurements to determine precise behaviour, particularly at phase transitions, must be made with particular care, taking into account the possibility of domain effects that can be significantly larger than hitherto considered.

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