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Directional light scattering by domain walls in $\text{Sn}_2\text{P}_2\text{S}_6$ uniaxial ferroelectrics

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Abstract. It was revealed that specific directional light scattering takes place in $\text{Sn}_2\text{P}_2\text{S}_6$ ferroelectric semiconductors in polydomain states. This scattering is observed at 90° to the light beam direction. The behaviour of this effect suggests that it is caused by light reflection by layers formed by charge carriers which screen charged domain walls between opposing 180° domains. The orientation of the reflecting layers was determined. This effect allows one to check easily the degree of unipolarity throughout the sample and refine optically the complete crystallographic orientation.

1. Introduction

Elastic light scattering has found application in studying the inhomogeneities of crystal structure, including ferroelectric domains [1–3]. Measurements of the angular dependence of the scattering intensity can provide information on their size, shape and orientation. The peaks of these dependencies can be connected with oriented planar defects (dislocations [1], growth bands [2]) or domain walls [3]. The latter is possible when the domains are optically inequivalent or the domain walls are thick enough in comparison with the light wavelength to reflect the light. In this case the light scattering technique can be applied for domain study.

The brightness of the track of a light beam propagating through a sample is a simple indicator of the homogeneity and optical quality of the material being studied. Diffuse light scattering observed in such a way is typically quite weak in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals. However, in studies of laser radiation transmission through these samples it was found that the intensity of the light scattering increases substantially at certain mutual orientations of the beam direction and point of observation. Under these conditions the light track looks like shining string inside the sample and can be easily observed by the naked eye. More careful studies show that this effect is not caused by impurities, because it is observed in all samples including optically perfect ones, and a necessary condition for directional scattering is a polydomain state of a sample.

Investigation of the directional light scattering and its connection with the domain structure of $\text{Sn}_2\text{P}_2\text{S}_6$ was the purpose of this work.

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2. Experimental procedure

$\text{Sn}_2\text{P}_2\text{S}_6$ single crystals constituted the object of our investigations. These materials are ferroelectric semiconductors. They belong to the monoclinic system, and undergo a second-order phase transition with a symmetry change from the $P2_1/n$ space group in the paraelectric phase to Pn in the ferroelectric one at a temperature $T_c = 337$ K [4, 5]. The crystals were grown by the vapour transport method [4] using iodine as a transporter. The $\text{Sn}_2\text{P}_2\text{S}_6$ crystals are transparent in the $0.53\text{--}8\ \mu\text{m}$ spectral range. At ambient temperature and for $0.6328\ \mu\text{m}$ light wavelength (from a He–Ne laser), the main values of the refractive index are $n_1 = 2.930$, $n_2 = 3.024$ and $n_3 = 3.093$ [6], and the absorption coefficient does not exceed $1\ \text{cm}^{-1}$ [5, 6]. The samples being studied were cut out along the main X -, Y - and Z -axes and polished. A conventional orientation of the crystals was used, in which the X -axis is directed along the $[100]$ crystallographic direction, which is close to the direction of the spontaneous polarization vector \mathbf{P}_s , and the Y -axis is normal to the (010) symmetry plane [8]. Note that in $\text{Sn}_2\text{P}_2\text{S}_6$ the \mathbf{P}_s -direction does not coincide precisely with the X -axis: as was shown by Vysochanskii *et al* [9], the polar direction deviates by $(13 \pm 2)^\circ$ from $[100]$ in the (010) plane. Also, a variation of the \mathbf{P}_s -vector direction in the (010) mirror plane with temperature is not forbidden, because of the monoclinic symmetry of the crystal.

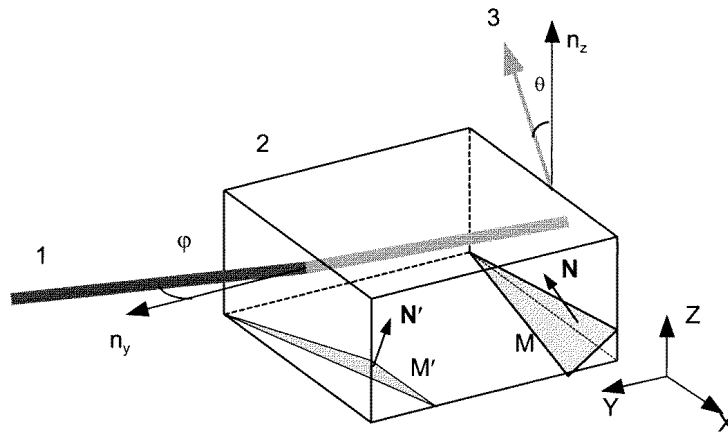


Figure 1. A schematic diagram of the set-up used for the observation of the directional light scattering. Key: 1: input laser beam; 2: sample; 3: an arrow indicating the direction of the maximum scattering; n_y , n_z : normals to the (010) and (001) crystallographical faces; φ : the angle of incidence, varied by the sample rotation; θ : the angle of observation; \mathbf{N} , \mathbf{N}' : normals to the reflecting planes M , M' .

Our experiments consist in the observation of the light scattering at 90° with respect to the direction of the laser beam propagating through the $\text{Sn}_2\text{P}_2\text{S}_6$ sample. By varying the direction of the light beam and the angle of observation, we find their mutual positions such that the intensity of the directional light scattering reaches its maximum. The set-up used for the experiment is shown schematically in figure 1. As a light source, a single-mode He–Ne laser ($0.6328\ \mu\text{m}$) with 40 mW power was used. The radiation of the laser was focused by a spherical lens (focal length $f = 500$ mm), a cylindrical lens ($f = 100$ mm) or an unfocused beam. The experiments were carried out on several samples. One of them, measuring $5 \times 6.5 \times 4\ \text{mm}^3$ along the X -, Y - and Z -directions respectively, is depicted in figure 2.

Two aspects of the observed phenomena were studied: the scattering pattern and its orientation relative to the crystallographic axes. The scattering pictures, as well as their transformation with electric field and temperature variation, were observed using an ordinary microscope or camera lens. In other studies, the crystal was mounted on a Fedorov stage, permitting us to vary the incidence angle φ by rotation of the sample around the vertical axis and to change the observation direction (the angle θ in figure 1). The direction of maximum scattering was determined visually, and the correspondence between the sample orientation φ and the azimuth for maximum directional scattering θ was established.

3. Pictures of the scattering

The photographs of the $\text{Sn}_2\text{P}_2\text{S}_6$ samples and the patterns of maximum light scattering obtained as described above are shown in figures 2(a)–2(d). In the photographs the input beam passes through the (010) surface, and the scattering pictures are observed through the (001) face. On examining several crystals while varying the external conditions, various pictures of scattering were observed. Summarizing these observations, we can conclude that the most important features of the phenomenon are the following.

- (i) The scattering takes place only for a polydomain state. For single-domain samples the effect vanishes but is recovered after depolarization of the sample by thermal annealing.
- (ii) The effect is observed only for well defined mutual orientations of the light beam and the direction of observation. These directions always make a significant angle with the polar X -axis. The effect is unobservable if the incident beam or the direction of observation is close to the X -direction.

The scattering aperture is rather small (several degrees) in the plane perpendicular to the incident beam but is of tens of degrees in its plane of propagation. This effect looks similar to light reflection by mirror-like planes: the direction of maximum scattering changes on turning the crystal, and the tracks are also seen when we interchange the directions of the incident light beam and the observation point. The scattering intensity depends on the light polarization analogously to the Brewster law: it is predominantly only s-polarized light (i.e. light polarized along the X -direction in the situation depicted in figure 1) that is scattered, whereas the light scattering track is almost unobservable for a p-polarized beam.

If the sample is poled in such a manner that only a part of its volume is in a single-domain state, the shining tracks are observed only in the non-poled area (figures 2(c) and 2(d)). The tracks are typically non-uniform, and the scattering pictures are formed of bright and dark stripes. Under illumination by a laser beam focused by a cylindrical lens (figure 2(b)), V-like structures with stripes, positioned at a fairly large angle to the X -direction, are observed distinctly.

The scattering intensity decreases gradually with sample heating. At temperatures 5–10 K below the phase transition point, the scattering almost disappears and it is absent in the paraelectric phase. The scattering is restored after the sample has been returned to the ferroelectric phase.

Under repolarization of the sample by the external dc electrical field (up to 500 V cm^{-1}), the switching ‘on’ and ‘off’ of some sites of the track was observed. Full reversal of the polarization at ambient temperature was not achieved, because this requires the application of a field above the sparkover value.

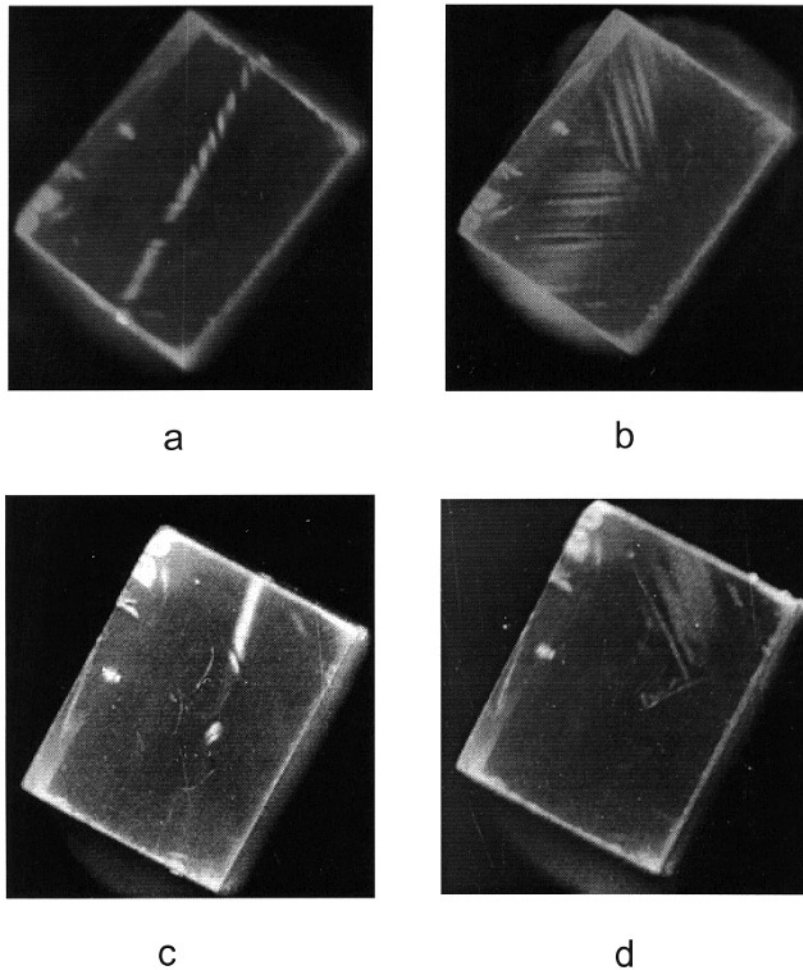


Figure 2. Photographs of the directional light scattering inside the $\text{Sn}_2\text{P}_2\text{S}_6$ sample: (a), (b) for the polydomain sample; (c), (d) for the partially poled sample. The pictures shown as (a) and (c) were obtained with beam focusing by a spherical lens; while those shown as (b) and (d) were obtained with beam focusing by a cylindrical lens. The sample is oriented as is shown in figure 1: the input beam passes through the face parallel to the (010) plane; the scattering is observed along the [001] direction.

4. The orientation of the reflecting layers

Information about the orientation of the reflecting layers can be obtained from the relations between the angle of incidence of the beam φ and the maximum angle of scattering of the light θ (see figure 1). These data were obtained by means of a Fedorov stage as described above and shown in figure 3. Here the dependence of the angle of incidence φ' between the laser beam and the [010] direction inside the crystal on the 'internal' scattering angle θ' is plotted. These values were both calculated from their 'external' values (φ and θ) taking into account the light refraction at the input and output faces, using $n = 3.0$ as an average refractive index value. This dependence is described well by a straight line. This means that the character of the directional scattering on rotating the sample is analogous to the

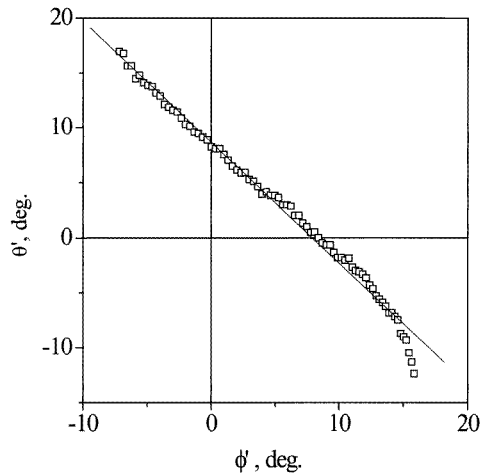


Figure 3. The dependence of the ‘internal’ values of the maximum scattering angle θ' on the angle of incidence ϕ' , taking into account the refraction of light by the sample surfaces.

reflection by the mirror-like planes fixed inside the crystal. Choosing the coordinate system X , Y and Z as shown in figure 1, one can describe the directions of both the incident and the reflected light inside the crystal in terms of the unit vectors with the components $\mathbf{a} = \{\sin \phi'; \cos \phi'; 0\}$ and $\mathbf{b} = \{\sin \theta'; 0; \cos \theta'\}$, respectively. It is easy to see that the unit vector \mathbf{N} normal to reflecting plane \mathbf{M} is $\mathbf{N} = (\mathbf{a} + \mathbf{b})/|\mathbf{a} + \mathbf{b}|$. The components of \mathbf{N} were calculated on the basis of the data presented in figure 3. For the sample position shown in figure 1, they are $\{-0.107; 0.703; 0.703\}$. This means that the orientation of \mathbf{M} is close to the (197) crystallographic plane.

The measurements described above were repeated at all variants of the initial positions of the sample when the crystal was turned sequentially around the X -, Y - and Z -axes through 180° . The input beam was thereby directed onto the (010) and (001) faces in the two opposite directions. As a result, it was established that there are only two reflecting planes: \mathbf{M} and \mathbf{M}' , corresponding to the $\{-0.107; 0.703; 0.703\}$ and $\{-0.107; -0.703; 0.703\}$ normal unit vectors, which are symmetrical relative to (010) mirror plane. In each case only one of them reflects the light toward the observer, whereas the other reflects it in the opposite direction. The two reflecting planes (\mathbf{M} , \mathbf{M}') and their normals (\mathbf{N} , \mathbf{N}') are shown schematically in figure 1.

We believe that the reflecting planes coincide with some of the domain boundaries. It is evident that the spontaneous polarization vector is not parallel to these planes. This result contradicts the conclusion reached earlier in [10] concerning the shape of domains in $\text{Sn}_2\text{P}_2\text{S}_6$, where the domains were described as cylinders extended along \mathbf{P}_s . The above-mentioned conclusion was based on domain observations for surfaces of the sample made using the liquid-crystal method, whereas the domain picture in a volume can be more complicated. On the other hand, the data on the distribution of \mathbf{P}_s in the volume of $\text{Sn}_2\text{P}_2\text{S}_6$ obtained using the beam-coupling topography technique [11] correlate well with the assumption of the presence of domain walls that are not parallel to \mathbf{P}_s . Further study of the light scattering in samples with various crystallographic orientations could provide additional information about the configuration of the domain walls relative to \mathbf{P}_s and the crystallographic axes.

The problem of the domain wall orientation is connected with the task of complete

orientation of monoclinic crystals. As was mentioned above, the P_s -direction deviates slightly from [100]. To obtain the polar direction precisely on the basis of the results of x-ray orientation studies, it is necessary to know not only the three main crystallographic axes, but also their positive directions. In this case we are able to determine whether 'right' or 'left' rotation around [010] by 12° gives the polar direction. This is important also for correct experimental determination of the signs of the different tensor values (electro-optical and piezo-optical, piezoelectric etc).

The peculiarities of the above-described effect of the directional light scattering provide a complementary way for the crystal orientation to be determined. In fact, for normal light incidence on the face parallel to the (010) plane ($\varphi = 0$), the maximum scattering is observed at the angle $\theta = 28^\circ$ or $\theta = -28^\circ$, depending on the crystal position. The sign of the angle changes to the opposite one when the sample is turned through 180° (Y to $-Y$). So, with the sample cut along the main crystallographic axes, knowing the (010) mirror plane and the [100] direction (for instance, as a result of their x-ray orientation being established using the conventional Laue method) and measuring the sign of the scattering angle θ , as is shown in figure 1, we are able to distinguish the 'positive' and 'negative' directions of the Y -axis. Carrying out this procedure for the reference sample in accordance with complete x-ray diffraction analysis and (or) other measurements, it is possible to offer a very simple and useful method for the complete crystal orientation.

5. Discussion

It is believed that the origin of the directional scattering described above is probably the existence of a reflecting layer in the vicinity of charged 180° domain walls.

It is known [12, 13] that the existence of domain walls that are not parallel to the vector of spontaneous polarization becomes possible in crystals with high enough conductivity, owing to screening by the mobile charge carriers. The surface charge density can be expressed as $\sigma = 2|P_s| \cos \alpha$, where α is the angle between the P_s -vector and the normal to the domain wall. The screening charge is located within some layer with thickness comparable with Debye screening length. Non-uniform charge distribution in this area results in the occurrence of electrical fields, which causes local changes of the refractive index due to electro-optic effects. For light reflection to be observable, the layer must have a thickness of the order of the light wavelength and a relatively large variation of the refractive index. In crystals with high enough values of the spontaneous polarization, $\cos \alpha$, the electric conductivity and the electro-optic coefficients, the magnitudes of both the layer thickness and the variation of the refractive index seem to be sufficient for light reflection, scattering or diffraction, according to the configuration of the domain walls.

The characteristics of the inter-domain screening layers depend on a variety of parameters, and the calculation of these parameters is a difficult task. The analysis of the electrical field distribution in a near-surface screening layer is given in [13]. Here it is shown that in semiconducting ferroelectrics (such as SbSI and BaTiO₃), the estimated local voltage drop is of the order of 1 V, and the layer thickness is of the order of the Debye screening length. This means that the local electric field in these layers can reach 10^4 – 10^6 V cm⁻¹. Close parameters characterize the Sn₂P₂S₆ crystals at ambient temperature: $P_s = 15$ mC cm⁻², the relative dielectric susceptibility $\varepsilon_{11} = 200$ – 250 and the electric conductivity $\sim 10^{-10}$ Ω⁻¹ cm⁻¹ [4, 5, 9].

As an example, let us assume that the maximum value of the electric field in the screening layer is $E = 10^4$ V cm⁻¹. Accepting the effective value of the electro-optic coefficient $r_{eff} = 7 \times 10^{-11}$ cm V⁻¹ and the average refractive index $n = 3.0$ [6, 7], the

field-induced variation of n could be as high as $\Delta n = n^3 r_{eff} E/2 \approx 10^{-3}$, which corresponds to the reflection factor $R = (\Delta n/2n)^2 = 3 \times 10^{-8}$ in the case of normal light incidence. Assuming $\sim 50 \mu\text{m}$ as the average equilibrium width of domains [10], the total reflection factor at 1 cm beam path could reach a magnitude of about 10^{-6} – 10^{-5} .

It should be noted that there have been a number of observations of near-domain layers with $\sim 1 \mu\text{m}$ thickness reported in the literature. It was noticed [12] that in BaTiO_3 the coloured inter-domain walls ($\sim 1 \mu\text{m}$) were visible under a polarizing microscope when opposite neighbouring domains had the same contrast. In [13] it was reported that the domain boundary between two counterdomains in SbSI is seen as a narrow dark band in red (near-edge) transmitted light. According to [14], areas of variation of the refractive index with thicknesses of about $1 \mu\text{m}$ are formed in highly resistive LiNbO_3 in the process of fast cooling. These areas are induced by pyroelectric non-screened charge and were observed under a polarizing microscope. So, the presence of the near-domain layers, which are able to interact with the light waves, is observable in other compounds, not solely $\text{Sn}_2\text{P}_2\text{S}_6$, and can be caused by different phenomena. It would be interesting to search for similar light scattering effects in other ferroelectric materials.

6. Conclusion

The effect of the directional light scattering described above is apparently connected with the reflection of light by the layers arising near the charged domain walls due to electric screening. This is possible only in the presence of domain walls that are not parallel to the axis of the spontaneous polarization. This phenomenon provides the basis of a new method for observation of the domain states in $\text{Sn}_2\text{P}_2\text{S}_6$ uniaxial ferroelectrics, which enables the degree of unipolarity throughout the sample to be checked simply. Using the peculiarity of the directional scattering, it is possible to refine the sample orientation and establish which directions of the crystallographic axis are positive. The presence of the above-described scattering must be taken into account in future optical investigations of polydomain ferroelectric crystals.

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