Generation of difference frequencies in nonhelicoidal smectic liquid crystals

A.L. Andreev, T.B. Andreeva, I.N. Kompanets

Abstract. **Generation of six difference frequencies in cells with nonhelicoidal smectic liquid crystals for six argon laser lines has been experimentally obtained for the first time. The maximum energy conversion efficiency is about 3% at a total input radiation power of 125 mW.**

1. Introduction

The specific features of nonlinear-optical phenomena in liquid crystals (LCs) are related to their high optical anisotropy ($\Delta n = 0.1 - 0.3$) and high sensitivity to external effects. In particular, the position of the major axis of the ellipsoid of refractive indices, the direction of which coincides with the orientation of the long axes of LC molecules (i.e., director orientation), may change, depending on the magnitude and direction of electric fields, including light fields [1].

In the least ordered nematic liquid crystals (NLCs), a preferred orientation of long molecular axes arises under certain conditions; in this case, the centres of mass of molecules are located absolutely randomly (point symmetry D_∞). In the absence of external effects an NLC has a central symmetry, and even-order nonlinearities are forbidden in it. However, due to the director reorientation caused by the electric field of the light wave, the central symmetry is violated. If the change in the director distribution is accompanied by the formation of a macroscopic dipole moment in the NLC volume, the second harmonic and the sum and difference frequencies can be generated [2–4].

Initially, cholesteric and smectic LCs, which are composed of chiral (optically active) molecules, do not possess a central symmetry, as a result of which their quadratic nonlinear susceptibility $\chi^{(2)}$ is nonzero. The nonlinear processes in these LCs (with the point symmetry D_∞) are weakly pronounced. A necessary condition for the effective generation of the second harmonic and the sum and difference frequencies is the reduction of the LC symmetry to the C_2 group [5, 6]. In smectic LCs (SLCs) this symmetry is reduced at a transition from the paraelectric phase, which is accompanied by the

A.L. Andreev, T.B. Andreeva, I.N. Kompanets P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia; e-mail: ala-2012@yandex.ru

spontaneous inclination of molecules in smectic layers and, as a consequence, the formation of spontaneous polarisation and ferroelectric properties.

We consider below the generation of difference frequencies in SLCs with ferroelectric properties. The objects of study were nonhelicoidal SLCs whose structure is most similar to that of nonlinear optical crystals.

2. Specific features of the SLC structure and director reorientation by the electric field

A distinctive feature of all SLCs is the periodic order of the centres of mass of molecules in the direction of their long axes, with a period of the same order of magnitude as the molecule length (the so-called smectic layers). Boundary conditions make it possible to orient the SLC director planarly [in this case the smectic layers are orthogonal to the substrates (Fig. 1a)] or homeotropically (smectic layers are parallel to the substrates).

If the molecules are not specularly symmetric (chiral) and make some angle θ_0 with the normal to the smectic layers, there is only one element of symmetry in each layer: twofold polar axis. Spontaneous layer polarisation P_s may arise along this axis if the molecules have a dipole moment oriented perpendicularly to their long axes (Fig. 1b).

In the absence of external effects, the polar axes of different smectic layers are rotated with respect to each other, as a result of which the SLC director becomes helicoidally twisted (Fig. 1a). In each layer the position of the director is determined by the polar angle θ_0 and the azimuthal angle φ, which changes from 0 to 2π at a distance equal to the helicoidal pitch p_0. Each smectic layer has a point symmetry: C_2.

Application of the electric field oriented parallel to smectic layers (along the x coordinate axis) orients the vector P_s in all layers along the field. As a consequence, the director becomes similarly oriented throughout the entire SLC volume, i.e., the helicoid becomes untwisted. With a change in the field sign, the vector P_s is reoriented by 180°, so that the long axes of molecules form a cone with an opening angle $2\theta_0$. Thus, the azimuthal director orientation angle φ changes by 180°.

Nonhelicoidal SLCs were used in the cells under study. The helicoidal twist of the director in the SLC volume was suppressed due to the interaction of chiral additives with the optical activity of opposite signs. The coincidence of the spontaneous polarisation signs for chiral additives makes it possible to obtain spontaneous SLC polarisation at a level of 100 nC cm^{-2} or higher [7].

The nonlinear optical properties of nonhelicoidal SLCs should be similar in many respects to the characteristics of
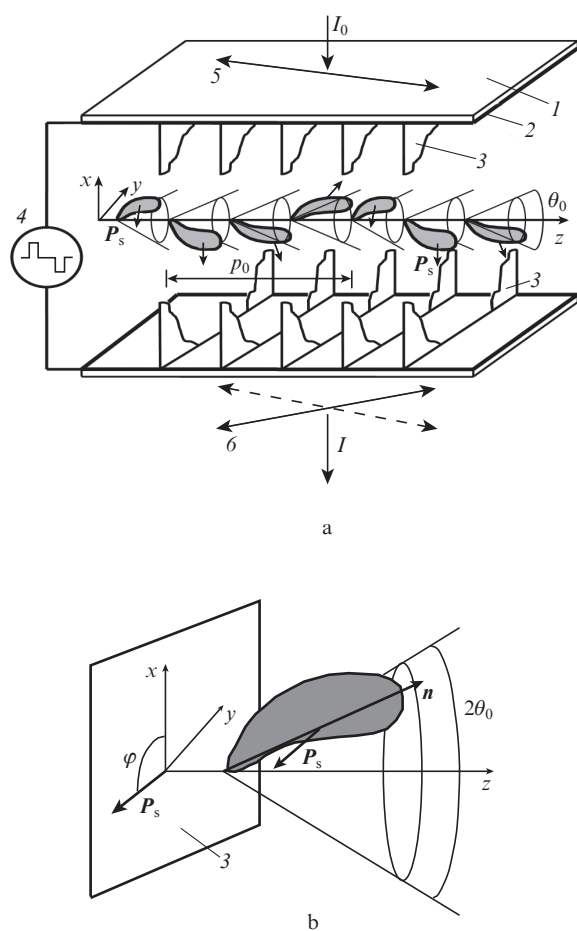
Figure 1. (a) Helicoidal SLC with a planar director orientation in an electro-optical cell and (b) mutual arrangement of the spontaneous-polarisation vector of the smectic layer and SLC director: (*1*) glass substrates; (*2*) transparent conducting coatings; (*3*) smectic layers; (*4*) control voltage generator; (*5*) polariser; and (*6*) analyser; n is the SLC director; P_s is spontaneous-polarisation vector; p_0 is the helicoidal pitch; θ_0 is the inclination angle of molecules in smectic layers; φ is the azimuthal angle of director orientation; and I_0 and I are, respectively, the intensities of light incident on the SLC cell and transmitted through it.

solid crystals with the point symmetry C_2, because, provided that the helicoid is suppressed, the polar axes in all smectic layers are oriented virtually in the same direction. The quadratic nonlinear susceptibility $\chi^{(2)}$ in solid ferroelectrics is known to be proportional to the spontaneous polarisation P_s. For SLCs this relation is satisfied at $P_s > 50$ nC cm^{-2} [5].

3. Dynamics of SLC director reorientation in the electric field of the light wave

The rate of the increase in the optical response during SLC director reorientation in the electric field of a light wave depends on the light intensity, the dielectric anisotropy, and the rotational viscosity of the SLC.

The time of light-induced director reorientation for both planar and homeotropic orientation is inversely proportional to the light intensity. For a SLC with a rotational viscosity of 0.7 P and $\Delta n = 0.17$, irradiated by argon laser radiation with a modulation frequency of 7 Hz and output power of 75 mW, the light-induced director reorientation time does not exceed 5 ms (Fig. 2). A change in the position of the principal optical axis leads to a change in the light transmission of the SLC cell
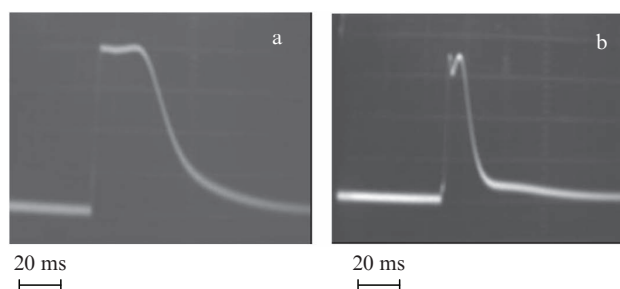

Figure 2. Change in the SLC cell transmission in the electric field of light wave for (a) planar and (b) homeotropic director orientations; the SLC cell thickness is 75 μm, the modulation frequency of argon laser radiation is 7 Hz, and the output power is 75 mW.

in crossed polarisers. The maximum change in light transmission is obtained at an output laser power of 75 mW.

After blocking the light beam, the director returns (relaxes) to the unperturbed state. The relaxation time is mainly determined by the modulus of SLC elasticity. For a homeotropically oriented director the relaxation time has two components (Fig. 2b); however, the total SLC relaxation times to the unperturbed state coincide for the planar and homeotropic orientations.

4. Experimental

A schematic of the experimental setup for generating difference frequencies in a SLC cell is shown in Fig.3. The light source is a cw argon laser, generating at six spectral lines: 0.4579 μm (12.5 mW), 0.4765 μm (35 mW), 0.4880 μm (210 mW), 0.4965 μm (14 mW), 0.5018 μm (7 mW), and 0.5145 μm (71 mW). The laser radiation is linearly polarised, with a degree of polarisation of 300 : 1, and is modulated at a specified frequency using an electro-optical modulator. A special filter is applied to cut off the IR background in the laser tube.
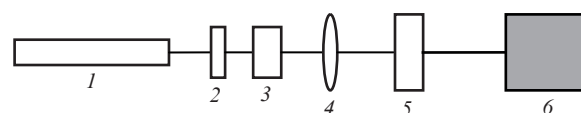

Figure 3. Schematic of the experimental setup: (*1*) argon laser; (*2*) IR filter; (*3*) electro-optical modulator (gate); (*4*) focusing lens ($f = 120$ mm); (*5*) SLC cell on a tilt-and-swivel table; and (*6*) spectrum analyser.

The spectral characteristics of the radiation generated were determined using an SR780 spectrum analyser (Stanford Research System), modified for operation in the IR range. The optical system of this instrument included, in particular, dispersion filters, a Fabry–Perot interferometer (or two successively positioned interferometers), and photodetectors. The spectrum analyser made it possible to measure the power of radiation with wavelengths from 1.5 μm to the near THz range. In the range from 1.5 to 7 μm the resolution of the spectrum analyser was ~10 cm^{-1}. For wavelengths of 7 μm or more the resolution was 5–7 cm^{-1}.

The vibrational absorption bands of the SLC were investigated using an FTC-6000 spectrometer (Bio-Rad Laboratories) with an open aperture (resolution 2 cm^{-1}).

The thickness of the SLC layer in the cell was set by quartz balls (spacers) with a characteristic size of 75 μm, which were placed beyond the cell working region. The initial director orientation (planar or homeotropic) was set by polymer coatings (70–100 nm thick), deposited on the quartz substrate of the SLC cell. The laser radiation fell on the SLC layer through the quartz substrate. The second (zinc selenide substrate), with a thickness of 5 mm, transmitted 75%–78% of radiation with wavelengths from 3 to 12 μm; in this range the light transmission barely depended on the wavelength.

5. Results and discussion

5.1. Phase-matching condition

The phase-matching condition for nonhelicoidal SLCs is reduced to the choice of the proper angle between the polarisation plane of incident light and the principal optical axis (director) and the angle α between the light propagation direction and the plane of substrates. This means that light propagates at angles of α and $\pi/2 - \alpha$ with respect to the normal to the plane of smectic layers for the homeotropic and planar director orientations, respectively. In both cases the phase-matching condition is met when the polarisation plane of the incident light is parallel to the principal optical axis of the SLC, and the angle α is approximately equal to the angle of inclination of molecules in the smectic layers (θ_0) (Fig. 4). The above-considered method of phase matching is also used when the helicoid is suppressed by the surface (Quasi-Bookshelf Geometry) or is untwisted by electric field, as well as for the SLCs stabilised by a polymer network [8].
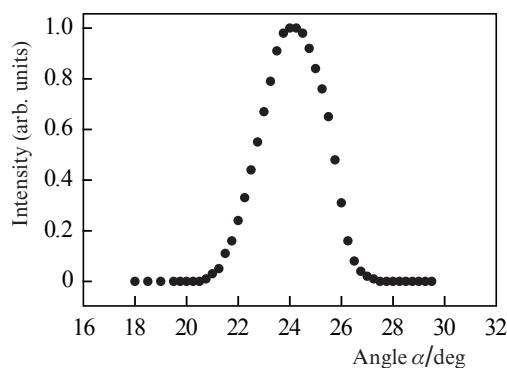
Figure 4. Dependence of the normalised intensity of generated radiation on the angle between the light propagation direction and the plane of smectic layers in the case of homeotropic director orientation. The plane of polarisation of incident light is parallel to the principal optical axis of SLC, the inclination angle of molecules in smectic layers is $\theta_0 = 23.5°$, the SLC cell thickness is 75 μm, the modulation frequency of argon laser radiation is 5 Hz, and the output power is 200 mW.

5.2. Spectrum of generated radiation

The spectrum of the radiation generated at difference frequencies, recorded in the range of 4–10 μm, is shown in Fig. 5.

The peak of the radiation generated at the wavelength $\lambda = 9.475$ μm corresponds to the differences in the frequencies of argon laser lines at 0.5145 and 0.4880 μm (the generated radiation wavelength $\lambda = 9.4746$ μm) and at 0.4765 and 0.5017 μm
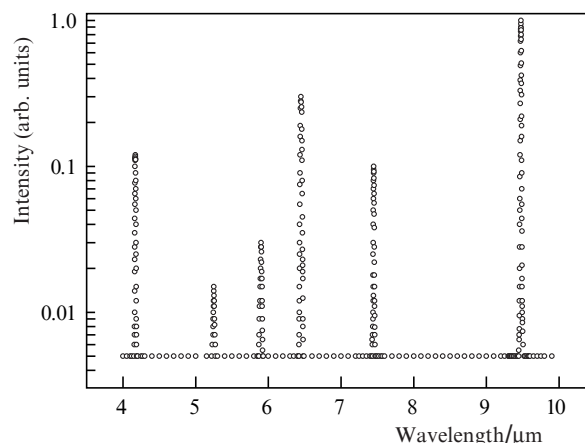
Figure 5. Spectrum of the difference-frequency radiation. The modulation frequency of argon laser radiation is 5 Hz, the output power is 200 mW, and the SLC cell thickness is 75 μm.

($\lambda = 9.4865$ μm). The resolution of the spectrum analyser at the wavelength ~10 μm is about 7 cm^{-1}; hence, the difference frequencies corresponding to the wavelengths of 9.4746 and 9.4865 μm cannot be separated.

The peaks at the wavelengths $\lambda = 7.45$, 6.45, 5.9, 5.25 and 4.17 μm correspond to the differences in the frequencies of spectral lines at 0.4880 and 0.4579 μm, 0.5145 and 0.4765 μm, 0.4965 and 0.4579 μm, 0.5017 and 0.4579 μm, and 0.5145 and 0.4579 μm, respectively.

The vibrational absorption bands of the SLCs under consideration lie in the range from 600 to 850 cm^{-1}. The absorption band at 645 cm^{-1} corresponds to fluorine vibrations in the chiral centre of SLC molecule. The bands at 770 and 838 cm^{-1} correspond, respectively, to the antisymmetric and symmetric vibrations of interacting benzene rings. The vibrational bands are due to the intermolecular interactions in SLC; hence, the absorption spectra barely depend on the boundary conditions and the SLC-cell thickness [9].

The difference frequency between the argon laser spectral lines at the wavelengths of 0.4765 and 0.4965 μm, which corresponds to the wavelength $\lambda = 11.829$ μm, lies in the SLC absorption band.

5.3. Efficiency of radiation energy conversion

5.3.1. Conversion efficiency for an SLC with a periodic structure of ferroelectric domains

If the spontaneous polarisation exceeds 70 nC cm^{-2}, the polarisation distribution over the SLC volume becomes spatially nonuniform in the direction orthogonal to smectic layers. This nonuniformity leads to periodic modulation of the azimuthal angle of director orientation φ in the same direction. As a result, the SLC becomes divided into ferroelectric domains: spontaneously ordered regions with different directions of the P_s vector. The period of the domain structure is inversely proportional to P_s^2 [10].

The formation of ferroelectric domains causes periodic changes in the refractive index of the SLC in the direction orthogonal to smectic layers. As in solid crystals (for example, MgO-doped lithium niobate [11]), choosing an appropriate inversion period of ferroelectric domains, one can increase the conversion efficiency for the difference-frequency generation. For example, for an SLC with a spontaneous polarisa-

tion P_s = 220 nC cm^{-2} (the period of the domain structure is 3 – 5 μm), the energy conversion efficiency for the generation of difference frequency, which corresponds to a radiation wavelength of 6.45 μm, increases by a factor of more than 1.5 in comparison with the conversion efficiency for an SLC with P_s = 70 nC cm^{-2}, where ferroelectric domains are not formed [Fig. 6, curves (1, 2)]. In both cases the SLC director was oriented homeotropically.
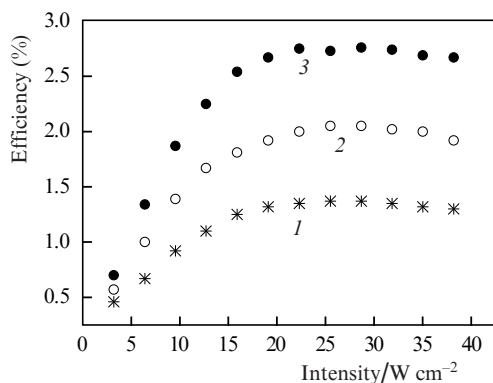

Figure 6. Dependence of the energy conversion efficiency in the case of generation of difference frequencies for the 0.5145- and 0.4765-μm Ar laser lines on the laser radiation intensity at the input of (1, 2) an SLC layer with a homeotropic director orientation and P_s = (1) 70 and (2) 220 nC cm^{-2} and (3) an SLC layer with a planar orientation, periodic deformation of smectic layers, and P_s = 70 nC cm^{-2}. The SLC layer thickness in the cells is 75 μm; the light-beam diameter is 1 mm.

For SLCs with ferroelectric domains the modulation depth of the azimuthal angle φ is 30° – 50° [10]. The significant local changes in the refractive index in the direction orthogonal to smectic layers do not make it possible to implement the phase-matching condition with a sufficient accuracy; this circumstance limits the energy conversion efficiency for difference-frequency generation.

5.3.2. Conversion efficiency in SLCs with periodic deformations of smectic layers

In nonhelicoidal SLCs with P_s < 100 nC cm^{-2}, the spatial nonuniformity of optical anisotropy is caused by periodic deformations of smectic layers [12]. They lead to periodic changes in the director (principal optical axis) orientation and, correspondingly, the refractive index along each smectic layer; i.e., in the direction orthogonal to the cell substrates. The presence of deformations of this type indicates that the SLC molecules in smectic layers, which made initially an angle θ_0 with the normal to a layer at a given point, deviate additionally by some angle ψ with respect to the z axis. Due to this, the director projection onto the xy plane changes (Fig. 7).

Thus, the periodic change in the refractive index in the volume of SLCs of this type is related to the continuous change in the direction of the principal optical axis along each smectic layer; note that the maximum deviation of the principal axis (maximum value of the angle ψ) does not exceed 15 – 17°.

The deformation period of smectic layers depends on the SLC molecular structure and may change from 2 to 7 μm. For SLCs with a deformation period of ~5 μm and P_s = 70 nC cm^{-2}, the energy conversion efficiency for generation of the difference frequency (which corresponds to a wavelength 6.45 μm)
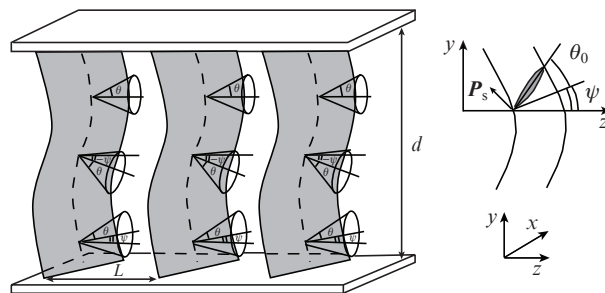

Figure 7. Deformation of smectic layers in a planarly oriented nonhelicoidal SLC (θ_0 is the angle of inclination of molecules in smectic layers, ψ is the angle on inclination of the smectic layer, d is the electro-optical cell thickness, and L is the smectic layer thickness).

was about 3%; the maximum conversion efficiency was attained at a total radiation power at the SLC-cell input of ~125 mW [Fig. 6, curve (3)]. In this case, the SLC director had a planar orientation.

The decrease in the energy conversion efficiency with an increase in the laser power (Fig. 6) is due to the thermal fluctuations of the director during the cell heating, which violate the phase-matching condition. When approaching the phase-transition temperature to the paraelectric phase, the conversion efficiency decreases several times.

6. Conclusions

The generation of difference frequencies in cells with nonhelicoidal ferroelectric LCs was experimentally investigated for the first time. The results obtained are as follows.

(1) The phase-matching conditions were experimentally determined for the planar and homeotropic director orientations in nonhelicoidal SLCs.

(2) The generation of six difference frequencies (corresponding to wavelengths 9.475, 7.45, 6.45, 5.9, 5.25, and 4.17 μm) was obtained for six argon laser lines at an output power of 25 – 300 mW and a modulation frequency of 5 Hz.

(3) It was shown that the energy conversion efficiency for generation of difference frequencies in the case of SLCs with a periodic structure of ferroelectric domains (with a period of the domain structure of 3 – 5 μm) increases by a factor of more than 1.5 in comparison with the conversion efficiency for the SLCs without ferroelectric domains.

(4) For SLCs with periodically deformed layers (deformation period ~5 μm) the maximum energy conversion efficiency for the generation of difference frequencies is about 3% at a total radiation power at the SLC–cell input of about 125 mW.

The energy conversion efficiency for the generation of each separately taken difference frequency can be increased by choosing properly the deformation period of smectic layers (or the inversion period for ferroelectric domains) and the laser power at the input of the SLC cell. The lower conversion efficiency (in comparison with that of periodically polarised lithium niobate) is compensated for by the simple technology and low cost of SLC cells.

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