SECOND HARMONIC GENERATION IN TRIGLYCINE SULFATE CRYSTALS

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A phenomenological description of the nonlinear polarizabilities responsible for second harmonic generation in ferroelectric crystals is considered. A ruby laser is used to investigate the temperature dependences of the nonlinear polarizabilities $\chi_{14}^{2\omega}$, $\chi_{25}^{2\omega}$, $\chi_{23}^{2\omega}$, and $\chi_{34}^{2\omega}$ of triglycine sulfate single crystals between 20° and 90°C. Above the Curie point (49°C) and up to 90°C, where the nonlinear polarizabilities should vanish from symmetry considerations, an intense second harmonic has been detected which cannot be due to magnetic dipole absorption or to the electric quadrupole moment. An experimental investigation of how an electric field affects the second harmonic intensity suggests that residual domains are present in the given region.

THE Ginzburg-Devonshire thermodynamic theory[1], which is the basis for expanding crystal free energy in powers of the polarization, is known to describe satisfactorily many experimental results obtained for ferroelectric crystals in low-frequency investigations. Miller,[2] assuming the correctness of this expansion for the nonlinear polarizabilities that are responsible for second harmonic generation in lasers, obtained agreement with experiment for barium titanate crystals far from the Curie point.

In the present work we measured the nonlinear polarizabilities for ferroelectric crystals of triglycine sulfate (TGS) $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ and their temperature dependence within the broad interval 20°—90°C, which includes the Curie point 49°C. We also discuss phenomenologically the behavior of the nonlinear polarizabilities, which are responsible for the generation of the second harmonic in ferroelectric crystals.

When discussing the temperature dependence of nonlinear polarizability in a general form it is convenient to utilize the nonlinear coefficients in the expansion of the second harmonic electric field $E^{2\omega}$[2] (producing a linear polarization $P^{2\omega}$ at the frequency of the second harmonic; this polarization, in turn, generates an experimentally determinable electromagnetic wave at the frequency 2ω) in terms of the induced linear polarization P^{ω} at the fundamental emission frequency:

$$E_i^{2\omega} = \delta_{ijk}^{\omega} P_j^{\omega} P_k^{\omega}. \qquad (1)$$

The existence of spontaneous polarization is equivalent to the presence of a high static electric field in the crystal; in the terms of the field expansion with respect to the polarization we can take into effect the influence of spontaneous polarization on the generation of the second harmonic as follows:

$$E_i^{2\omega} = \delta_{ijk}^{2\omega} P_j^{\omega} P_k^{\omega} + \delta_{ijkl}^{2\omega} P_j^{\omega} P_k^{\omega} P_l^0 = (\delta_{ijk}^{2\omega} + \delta_{ijkl}^{\omega} P_l^0) P_j^{\omega} P_k^{\omega}, \qquad (2)$$

where P_l^0 is the spontaneous polarization in the direction of the l axis, and $\delta_{ijkl}^{2\omega}$ is a fourth-rank tensor. Equation (2) shows that spontaneous polarization is taken into account by the term of the next order of smallness.

In ferroelectric crystals second harmonic generation is therefore determined by nonlinear coefficients of the form

$$\delta_{ijk}^{\prime 2\omega} = \delta_{ijk}^{2\omega} + \delta_{ijkl}^{2\omega} P_l^0, \qquad (3)$$

The temperature dependence of $\delta_{ijk}^{\prime 2\omega}$ is determined only by the temperature dependence of the spontaneous polarization.

If the paraelectric phase of the crystal lacks a center of symmetry the temperature dependence of the nonlinear coefficients will be described by (3). Since $\delta_{ijkl}^{2\omega}$ is much smaller than $\delta_{ijk}^{2\omega}$, the nonlinear coefficients[1)] may be practically independent of temperature, exhibiting a discontinuity at the Curie point.

In the case of crystals with centrosymmetrical paraelectric phases the first term in (3) vanishes and the temperature dependence of the nonlinear coefficients is governed only by the temperature dependence of the spontaneous polarization.

The nonlinear coefficients of TGS crystals were measured by the customary technique[3] using a 20—30 kW ruby laser. In the ferroelectric phase (class 2) the components of nonlinear polarization in these crystals are, in matrix form,

$$\begin{aligned} P_1^{2\omega} &= \chi_{14}^{2\omega} E_2^{\omega} E_3^{\omega} + \chi_{16}^{2\omega} E_1 E_2^{\omega} \\ P_2^{2\omega} &= \chi_{21}^{2\omega} (E_1^{\omega})^2 + \chi_{22}^{2\omega} (E_2^{\omega})^2 + \chi_{23}^{2\omega} (E_3^{\omega})^2 + \chi_{25}^{2\omega} E_1^{\omega} E_3^{\omega}, \\ P_3^{2\omega} &= \chi_{34}^{2\omega} E_2^{\omega} E_3^{\omega} + \chi_{36}^{2\omega} E_1^{\omega} E_2^{\omega}. \end{aligned} \qquad (4)$$

When Kleinman's[4] supplementary symmetry conditions are applicable the following equalities hold between the nonlinear coefficients:

$$\chi_{21}^{2\omega} = \chi_{16}^{2\omega}, \quad \chi_{14}^{2\omega} = \chi_{25}^{2\omega} = \chi_{36}^{2\omega}, \quad \chi_{23}^{2\omega} = \chi_{34}^{2\omega}. \qquad (5)$$

A direct experimental test of the symmetry conditions in multidomain samples is meaningless, because in repeated measurements values of the nonlinear coefficients were reproduced to within a factor of one-half to two; we have shown in[5] that these results can be attributed to the domain structure.

A single-domain sample was produced by applying a static field of 1.5 kV/cm up to 70°C and then cooling slowly to room temperature. It should be noted that

[1)] The nonlinear coefficients $\delta_{ijk}^{2\omega}$ are related to the nonlinear polarizability $\chi_{ijk}^{2\omega}$ as follows: $\chi_{ijk}^{2\omega} : \chi_{ijk}^{2\omega} = \varkappa_{ii}^{2\omega} \varkappa_{jj}^{\omega} \varkappa_{kk}^{\omega} \delta_{ijk}^{2\omega}$. Since the linear polarizabilities change very slowly as the temperature is varied, the temperature dependences of these two coefficients are similar.

electric fields up to 3 kV/cm without temperature change did not produce satisfactory single-domain samples.

We obtained the following values of the nonlinear coefficients (expressed, as is customary, in relative units with $\chi_{36}^{2\omega}$ of KDP crystals taken as unity): $\chi_{14}^{2\omega} = 3.6 \times 10^{-3}$, $\chi_{25}^{2\omega} = 3 \times 10^{-3}$, $\chi_{36}^{2\omega} = 4 \times 10^{-3}$, $\chi_{23}^{2\omega} = 3 \times 10^{-3}$, $\chi_{34}^{2\omega} = 2.7 \times 10^{-3}$, $\chi_{22}^{2\omega} = 7.5 \times 10^{-3}$. The coefficients $\chi_{21}^{2\omega}$ and $\chi_{16}^{2\omega}$ are at least one order smaller. The effect produced by the domain configuration on the experimental values of the nonlinear polarizabilities is indicated by the fact that we previously obtained 70×10^{-3} for $\chi_{23}^{2\omega}$, having applied a static field of 2 kV/cm.

It is clear from the foregoing that for TGS crystals with central symmetry in the paraelectric phase the temperature dependence of the nonlinear coefficients will be given by

$$\delta_{ijk}'^{2\omega} = \delta_{ijkl}^{2\omega} P_l^0 \tag{6}$$

or, in terms of the polarization expansion with respect to the field,

$$\chi_{ijk}^{2\omega} = \chi_{ijkl}^{2\omega} E_l^0. \tag{7}$$

Here $\chi_{ijkl}^{2\omega}$ represents the nonlinear polarizabilities and $E_l^0 = P_l^0/\chi_l^0$, where χ_l^0 is the static linear polarizability per unit volume, measured in a high static field. For TGS crystals $\chi_l^0 = 2.7$ esu,[7] and $P_2^0 = 9 \times 10^3$ esu; then $E_2^0 = 3.3 \times 10^3$ esu. With these values and those of the nonlinear coefficients $\chi_{ijk}^{2\omega}$ that were obtained experimentally we easily derive from (7) the nonlinear coefficients $\chi_{ijkl}^{2\omega}$ describing the second harmonic generation induced by an external electric field (spontaneous polarization): $\chi_{1232}^{2\omega} = 10.9 \times 10^{-7}$, $\chi_{2132}^{2\omega} = 9 \times 10^{-7}$, $\chi_{3122}^{2\omega} = 12 \times 10^{-7}$, $\chi_{2332}^{2\omega} = 9 \times 10^{-7}$, $\chi_{3232}^{2\omega} = 8.2 \times 10^{-7}$, $\chi_{2222}^{2\omega} = 22.7 \times 10^{-7}$.

The thermodynamic formalism leads to the following relation between the coefficients $\chi_{ijkl}^{2\omega}$ and $\delta_{ijkl}^{2\omega}$:

$$\chi_{ijkl}^{2\omega} = \kappa_{ii}^{2\omega} \kappa_{jj}^{\omega} \kappa_{kk}^{\omega} \kappa_{ll}^{0} \delta_{ijkl}^{2\omega}, \tag{8}$$

where $\kappa_{ii}^{2\omega}$, κ_{jj}^{ω}, κ_{kk}^{ω}, κ_{ll}^{0} are the linear susceptibilities at the frequencies 2ω, ω, and 0 in a high static electric field (in the principal coordinate system).

Since the nonlinear polarizabilities of TGS crystals are greatly reduced as the Curie point is approached, it is very difficult to investigate their temperature dependence. We therefore investigated the temperature dependences of the nonlinear polarizability coefficients that are involved in second harmonic generation, in three directions of synchronism—at $\theta_0 = 48^\circ$ and 64° to the ferroelectric axis ⟨010⟩ in the (001) plane, and at $\theta_0 = 32^\circ$ to the ⟨010⟩ axis in the (100) plane.[8]

The first synchronism with $\theta_0 = 48^\circ$ results from the interaction type

$$2\mathbf{k}_1^o = \mathbf{k}_2^e, \tag{9}$$

where $\mathbf{k}_1^0$ and $\mathbf{k}_2^e$ are the wave vectors of the ordinary and extraordinary waves in second harmonic laser emission. In this case the coefficient $\chi_{23}^{2\omega}$ participates in generation of the harmonic.

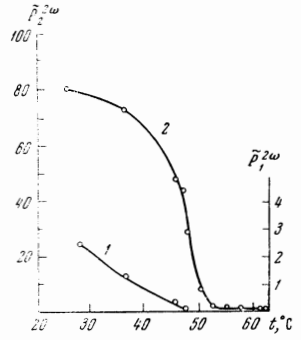

FIG. 1. Temperature dependence of second harmonic power for synchronism with $\theta_0^\circ = 32$ (arbitrary units). 1—for multidomain sample; 2—with an external static 1.5-kV/cm field along the ferroelectric axis.

The second pair of synchronisms with $\theta_0 = 64^\circ$ and 32° result from the interaction type

$$\mathbf{k}_1^o + \mathbf{k}_1^e = \mathbf{k}_2^e. \tag{10}$$

Here the coefficients $\chi_{14}^{2\omega}$, $\chi_{25}^{2\omega}$, and $\chi_{34}^{2\omega}$ participate, respectively. Temperature-associated changes of intensity in the directions of synchronism result only from changes in the corresponding nonlinear polarizabilities, since the dispersion characteristics in the investigated temperature range vary very little and exhibit small anomalies in the phase transition region.[9] Consequently, in the synchronism direction the coherence length[10] is practically independent of the temperature.

Figure 1 shows the temperature dependence of second harmonic power for multidomain and single-domain TGS crystals with synchronism of the type of (10) with $\theta_0 = 32^\circ$. Second harmonic generation is here observed above the Curie point at 49° C. Bass et al.[11] and we ourselves[6] had previously not observed generation of the harmonic above the Curie point when a laser beam propagated along the ⟨100⟩ axis. Our failure seems to have resulted from the low power of the harmonic in directions far from synchronism.

The reduced yield of the second harmonic in multidomain crystals is accounted for by the energy-degrading effect of domain structure,[2,5] especially in the direction of synchronism, where the following condition is satisfied:

$$l_d / l_c \ll 1. \tag{11}$$

Here l_d is the domain thickness and l_c is the coherence length for the given direction in the crystal. When (11) is fulfilled the second harmonic power is given by

$$\tilde{P}^{2\omega} = K(l_d^+ - l_d^-)^2, \tag{12}$$

where the quantity in parentheses is the difference between the total thicknesses of domains with opposite signs and K is the proportionality constant. The degree of degradation of the harmonic in the direction of synchronism will increase as the ratio in (11) is reduced.

The degrading effect of the domains is not uniform within the aperture of the fundamental radiation beam, and is maximal only within a narrow 1′—3′ cone where the inequality (11) is well satisfied. However, according to[10] more than 90% of the total second harmonic intensity for a crystal several times thicker than its coherence length will be concentrated in the central cone with an apex angle of a few minutes.

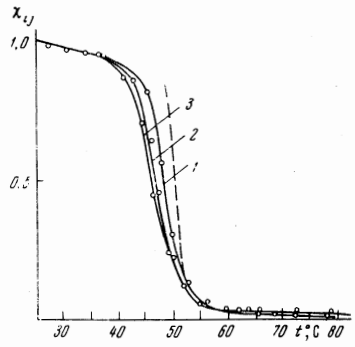

FIG. 2. Temperature dependence of the nonlinear polarizabilities (1) $\chi_{14}^{2\omega}$ and $\chi_{25}^{2\omega}$, (2) $\chi_{36}^{2\omega}$, and (3) $\chi_{23}^{2\omega}$ (arbitrary units). The dashed line represents the behavior of the spontaneous polarization when an external static 1.0-kV/cm field was applied.[12]

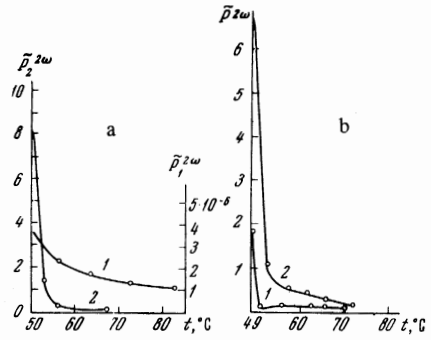

FIG. 4. Temperature dependence of second harmonic power in the parelectric phase (arbitrary units): a–synchronism with $\theta_0 = 64°$; b–synchronism with $\theta_0 = 48°$. 1–without an external field, 2–in a 1.5-kV/cm static external field.

Figure 2 shows the temperature dependences of the nonlinear coefficients for single-domain samples with a static 1.5-kV/cm electric field along the ⟨010⟩ axis. We observe that in accordance with (6) there is a resemblance to the behavior of the spontaneous polarization in the presence of a high static field.[12] The agreement is especially good at the Curie point, where the external field is strong enough to produce a single-domain structure. At lower temperatures the small difference between the behaviors of the polarization and nonlinear polarizabilities appears to result from the presence of a few residual domains that were not destroyed by the applied field. Like the spontaneous polarization in a high perturbing field, the nonlinear polarizabilities do not vanish at the Curie point; however, while the spontaneous polarization vanishes at about 3°–5° above the Curie point, the nonlinear coefficients are still of appreciable magnitude at 90°C.

We have also investigated second harmonic generation in the (2/m) centrosymmetrical paraelectric phase of TGS crystals.

Figure 3 shows the temperature dependence of the synchronism angle in the (001) plane for interactions (9) and (10) when an external 1.5-kV/cm field is applied along the ferroelectric axis. Synchronism is observed from the Curie point to 90°C. Figure 3 shows that the angle-change curves are bent at the Curie point.

Generation in a medium possessing a center of symmetry and in the presence of a static field can be caused by[13] magnetic dipole absorption, the quadrupole electric moment, and the reduction of crystal symmetry to a non-centrosymmetric class by the external field (an induced harmonic). The nonlinear coefficients describing these processes are several orders smaller than those describing harmonic generation in a medium that lacks a center of symmetry,[7] and they are independent of temperature.

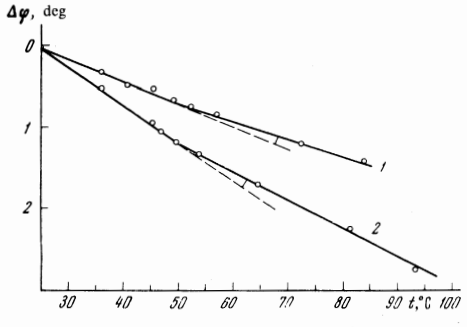

FIG. 3. Temperature dependence of the synchronism angle. $1-\theta_0 = 48°$; $2-\theta_0 = 64°$.

Figure 4 shows the temperature dependence of second harmonic power in the paraelectric phase. For single-domain samples this power in the presence of a static electric field diminishes by four orders of magnitude in the interval 25°–90° (by three orders up to 55°C and by one order from 55° to 90°C).

Figure 4 shows that in the absence of the field the second harmonic power in the paraelectric phase changes by less than one order for type (9) synchronism with $\theta_0 = 48°$ and is reduced by six orders for synchronism of type (10) with $\theta_0 = 64°$, as compared with the power in a static field. [For type-(10) synchronism with $\theta_0 = 32°$ the temperature dependence is similar to that in the case of $\theta_0 = 64°$.] The pronounced temperature dependence in the centrosymmetrical phase can be accounted for only by assuming that in the investigated 50°–90° range the paraelectric phase contains residual domains, and that in this case the nonlinear coefficients responsible for second harmonic generation have the form given in (6) or (7).

It is noteworthy that in the absence of an external electric field the second harmonic power for both type-(10) synchronisms in the experimental temperature interval is several orders lower than for type (9). This can be understood if we consider that the mismatch $\Delta\mathbf{k}$ of the phase velocities,[13] which is zero in the exact direction of synchronism, will change for both types of synchronism upon departing by an angle $\delta\theta$ from that exact direction, as follows:

$$\delta(\Delta k) = \frac{\partial k_2^e}{\partial\theta}\delta\theta, \quad \delta(\Delta k) = \frac{\partial[k_2^e(\theta) - k_1^e(\theta)]}{\partial\theta}\delta\theta. \qquad (13)$$

Using the dispersion characteristics of TGS crystals,[10] we learn from (13) that near type-(10) synchronism $\Delta\mathbf{k}$ will increase three to four times more slowly with the deviation from the synchronism direction. Therefore the inequality (11) will be satisfied more severely for a large apex angle of the laser radiation cone, thus increasing greatly the degradation of second harmonic power. We can also assume that in

(12) the total thicknesses of domains of opposite signs will become equal with great accuracy above the Curie point ($l_d^+ \sim l_d^-$). Since the domains have almost no influence on the second harmonic yield in the direction of type-(9) synchronism with $\theta_0 = 48$, which has ~0.6-mm coherence length, we can infer that in the paraelectric phase the residual domain thickness is of the order 1—2 mm. An additional proof that residual domains exist in the TGS paraelectric phase is found in the fact that when a static field is applied in the direction of type-(10) synchronism with $\theta_0 = 64^\circ$ and 32° the second harmonic power grows by several orders, whereas the power remains practically unchanged in directions far from synchronism. We can account for this by considering that the domains have a degrading effect in the synchronism directions where (11) holds true.

The rise and decay times of the harmonic as the field is switched on and off, are of interest. With increasing temperature these times decrease from 7—10 minutes at 50°C to several seconds at 80°C; this effect is obviously associated with increased mobility of the domain boundaries.

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