Temperature Behavior of the Coefficients of Combined Piezoelectrooptical Effect at the Proper Ferroelectrical Phase Transition in $Pb_5Ge_3O_{11}$

R.Vlokh, O.Mys, M.Kostyrko

Institute of Physical Optics, 23 Dragomanov Str., Lviv, 79005, Ukraine

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Abstract

The article is devoted to the study of a combined piezoelectrooptical effect induced by a bias electric field and external mechanical stress in the $Pb_5Ge_3O_{11}$ crystals at the proper ferroelectrical phase transition. The measurements were carried out on the application of electrical field and of mechanical stress σ_{33} along *z* axis. The electrooptical "butterfly" like hysteresis loops were obtained at different temperatures in the range of the ferroelectric phase on the application of different magnitudes of mechanical stress. On the base of dependencies $\Delta n=f(E_3,\sigma_{33})$ the temperature behavior of the electrooptical coefficient of Pockels effect $n_3^3r_{33}-n_1^3r_{13}$, Kerr effect $n_3^3R_{33}-n_1^3R_{13}$ and coefficients of combined piezoelectrooptical effect $n_3^3N_{333}-n_1^3N_{133}$ were obtained. Phenomenological analysis of the temperature dependence of these coefficients have been made. It was shown that temperature dependence of combined bilinear piezoelectrooptical effect coefficients in the ferroelectrical phase follow the temperature dependence of dielectric permitivity. The Curie-Weiss constant has been calculated on electrooptical measurements ($C=1.21\times10^4$K) and on piezoelectrooptical measurements ($C=1.22\times10^4$K) and it is in good agreement with the value obtained from dielectric measurements ($C=1.04\times10^4$K).

Key words: combined piezoelectrooptical effect, ferroelectrics, electrooptical effect, $Pb_5Ge_3O_{11}$ crystals.

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Introduction

In our previous papers [1,2] we reported the finding of a combined piezoelectrooptical effect induced by external mechanical stress and spontaneous polarization at proper ferroelectric phase transitions in $Pb_5Ge_3O_{11}$ and $Ca_2Pb(C_2H_5CO_2)_6$ crystals. This effect is described by the relation

$$\Delta\pi_{ijkl}=\underline{N}_{ijklm}P^s_m+N_{ijklmn}P^s_mP^s_n , \tag{1}$$

where $\Delta\pi_{ijkl}$ - is the change of the piezooptical coefficient at proper ferroelectric phase transition in respect to it value in the paraelectric phase, N_{ijklm} , N_{ijklmn} – the fifth and six rank polar tensor, respectively, P^s_m, P^s_n - spontaneous polarization; which is difined by the change of piezooptical coefficients at phase transition proportionally to the spontaneous polarization. The determined coefficients of the combined piezoelectrooptical effect and accuracy of available polarimetric methods of measuring show that this effect could be detected on condition of mutual influence of a bias electric field and external mechanical stress. The next experiment suggests this assumption and we successfully detected the induced effect at room temperature in $LiNbO_3$ and $LiTaO_3$ crystals [3] the measuring the birefringence increment in the presence of an external electrical field and mechanical stress:

$$\Delta B_{ij}=N_{ijklm}\sigma_{kl}E_m, \qquad (2)$$

where $\Delta B_{ij}\propto 1/\Delta n^2$ - is the increment of the optical polarization constants, σ_{kl} - mechanical stress tensor. The aim of the present investigation is to study the temperature dependence of an induced piezoelectrooptical effect at a proper ferroelectric phase transition. It is interesting to note that a similar effect which consists of a change of optical activity at a mutual influence of the electric and magnetic field (Faraday effect in the presence of an electric field) was already observed in $Pb_5Ge_3O_{11}$: Cd^{3+} and $Pb_5Ge_3O_{11}$: Nd^{3+} crystals [4] and explained [5].

Experimental

The lead germanate crystals possess a proper ferroelectric phase transition with a change of the point group of symmetry $\bar{6}F3$ at T_c=450K [6,7]. The $Pb_5Ge_3O_{11}$ single crystals with flat parallel faces perpendicular to z and x crystallophysical axis were polished by diamond powders and paste. The He-Ne laser radiation with a wavelength of 632.8nm propagated along y-axis. On electric field using was copper electrodes was applied along z-axis as well as mechanical stress. The crystal was seated in a specially designed furnace with the accuracy of temperature stabilization 0.1K. The temperature dependence of the birefringence change on the application of an electric field was measured at different magnitudes of applied mechanical stress.

Results of measurement

In Figure 1 the electrooptical "butterfly" like hysteresis loops obtained at different temperatures in the ferroelectric phase are presented. As it is clear the field dependence of the increment of birefringence is linear for the field values greater than coercive but domain switching does not lead to the change of the sign of birefringence as well as the electrooptical effect induced by spontaneous polarization is quadratic due to the symmetry of paraelectric phase (Fig. 2).

From data presented on Figure 1,2 and other obtained field dependencies of birefringence at different temperatures the temperature dependence of the electrooptical coefficient at σ_{33}=0 can be calculated.

The optical indicatrix equation in the presence of an electric field E_3 can be written as

$$\begin{aligned}&(B_{11}+r_{13}E_3)x^2+(B_{11}+r_{13}E_3)y^2+\\&+(B_{33}+r_{33}E_3)z^2=1 \qquad \text{at}\, T<T_c\end{aligned} \qquad (3)$$

and

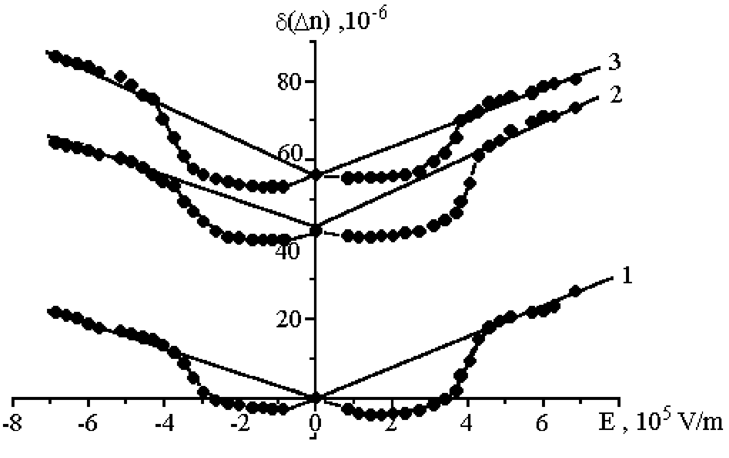

Fig. 1. Electrooptical hysteresis loops of $Pb_5Ge_3O_{11}$ crystals (λ=632.8nm, T=293K, 1-σ_{33}= 0; 2-σ_{33}=1.9 $\cdot 10^6$ N/m^2; 3-σ_{33}=3.8 $\cdot 10^6$ N/m^2).

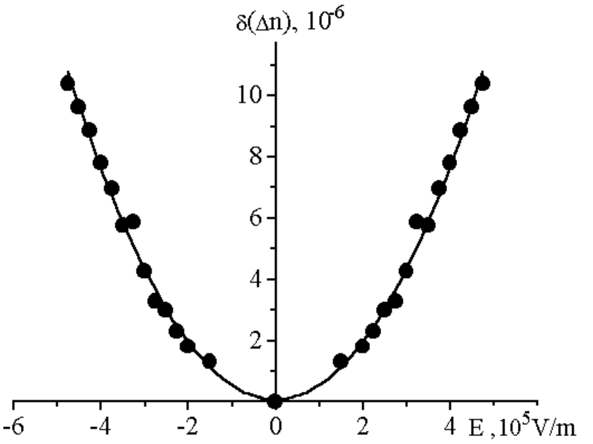

Fig. 2. Dependence of the increment of birefringence versus electric field in paraelectric phase of $Pb_5Ge_3O_{11}$ (λ=632.8nm, T=454K).

$$\begin{aligned}&(B_{11}+R_{13}E_3^2)x^2+(B_{11}+R_{13}E_3^2)y^2+\\&+(B_{33}+R_{33}E_3^2)z^2=1 \quad \text{at}\,T>T_c.\end{aligned} \qquad (4)$$

From these equations one can easily derive the relations for the coefficients of linear and quadratic electrooptical effect

$$n_3^3r_{33}-n_1^3r_{13}=2\delta(\Delta n)_{23}/E_3, \qquad (5)$$

and

$$n_3^3R_{33}-n_1^3R_{13}=2\delta(\Delta n)_{23}/E_3^2. \qquad (6)$$

The temperature dependencies of Pockels and Kerr coefficients are presented in Figure 3.

The rewritten eq.(3) taking into account the piezooptical effect and the combined piezoelectrooptical effect are:

$$\begin{aligned}&(B_{11}+r_{13}E_3+\pi_{13}\sigma_{33}+N_{133}\sigma_{33}E_3)x^2+\\&+(B_{11}+r_{13}E_3+\pi_{13}\sigma_{33}+N_{133}\sigma_{33}E_3)y^2+\\&+(B_{11}+r_{13}E_3+\pi_{13}\sigma_{33}+N_{333}\sigma_{33}E_3)z^2=1\end{aligned} \qquad (7)$$

and if to eliminate the piezooptical and electrooptical effect one can obtain the relation for induced birefringence by a mutually applied electric field and mechanical stress

$$n_3^3N_{333}-n_1^3N_{133}=2\delta(\Delta n)_{23}/E_3\sigma_{33} \qquad (8)$$

or

$$n_3^3N_{333}-n_1^3N_{133}=\left(n_3^3r_{33}-n_1^3r_{13}\right)/\sigma_{33}. \qquad (9)$$

At room temperature the application of mechanical stress σ_{33} does not change the electrooptical coefficient magnitude that is proportional to the tangent of the angle of inclination of these linear dependencies to the coordinate axis E_3. But in the temperature range of $335K<T<T_c$ the electrooptical coefficient $n_3^3r_{33}-n_1^3r_{13}$ already depends on mechanical stress σ_{33} and this dependence increases approaching to T_c. The temperature dependencies of the electrooptical coefficient in the vicinity of phase transition temperature at different values of mechanical stress σ_{33} are presented in Fig. 4 (see insert). The temperature dependence of the coefficient of combined piezoelectrooptical effect was derived (Figure 4) from such dependencies obtained at different temperatures.

Discussion

The change of the optical polarization coefficients in the presence of an electric field is described by the well known relation

$$\Delta B_{ij}=r_{ijk}E_k+R_{ijkl}E_kE_l, \qquad (10)$$

where the first term of eq.(10) describes the Pockels effect as the second one – the Kerr effect. Let as show that the Kerr effect consists in the change of the Pockels coefficient proportional to the electric field:

$$r_{ijk}=R_{ijkl}E_l \Rightarrow R_{ijkl}=\partial r_{ijk}/\partial E_l. \qquad (11)$$

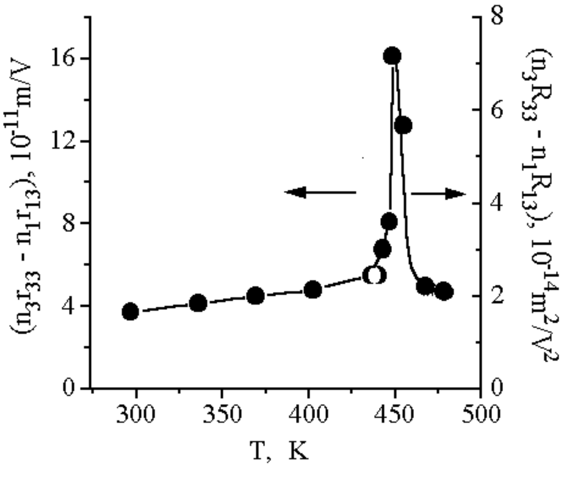

Fig. 3. Temperature dependencies of electro-optical coefficients of $Pb_5Ge_3O_{11}$ crystals (λ=632.8nm).

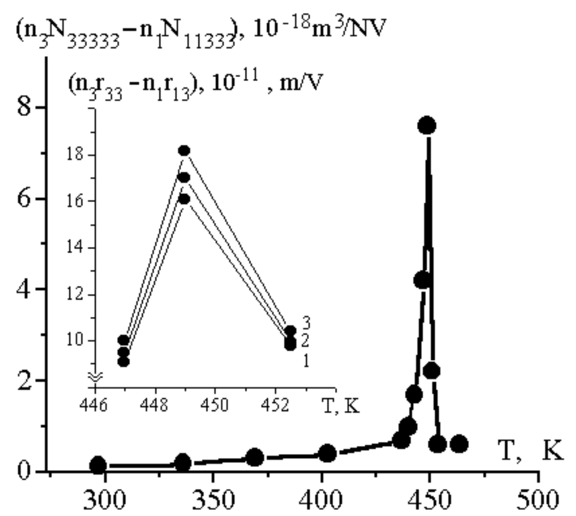

Fig. 4. Temperature dependence of the coefficient of the combined piezoelectrooptical effect at phase transition in $Pb_5Ge_3O_{11}$ crystals (λ=632.8nm). Insert: temperature dependencies of electrooptical coefficient in the vicinity of phase transition at 1-$\sigma_{33}=0$; 2-$\sigma_{33}=3.8\cdot10^6 N/m^2$; 3-$\sigma_{33}=7.6\cdot10^6 N/m^2$.

As well as

$$B_{ij}=r_{ijk}E_k \Rightarrow r_{ijk}=\partial B_{ij}/\partial E_k \qquad (12)$$

and

$$B_{ij}=R_{ijkl}E_kE_l \Rightarrow R_{ijkl}=\partial^2 B_{ij}/\partial E_k\partial E_l \qquad (13)$$

the relation (11) taking into account (12) can be rewritten as

$$R_{ijkl}=\frac{\partial r_{ijk}}{\partial E_l}=\frac{\partial\left(\partial B_{ij}/\partial E_k\right)}{\partial E_l}=\frac{\partial^2 B_{ij}}{\partial E_k\partial E_l}. \qquad (14)$$

It means that coefficients R_{ilkl} in eq.(11) and (13) are the same.

In such a case the appearance and the temperature change of Pockels coefficients at the proper ferroelectric phase transition from the centrosymmetrical paraelectric phase to the noncentrosymmetrical ferroelectric one, at the first blush should be determined by the temperature dependence of spontaneous polarization $r`_{ijk}=R`_{ijkl}P_l^s$ that lead to the lowering of symmetry and appearance of a linear electrooptic effect, and only after this by the temperature dependence of dielectric permitivity $r``_{ijk}=r^*_{ijk}\varepsilon_o(\varepsilon^{f.p.}-1)$. Thus the temperature change of Pockels coefficients can be described by the relation

$$r_{ijk}=r`_{ijk}+r``_{ijk}=R`_{ijkl}P_l^s+r^*_{ijk}\varepsilon_o(\varepsilon^{f.p.}-1)=$$
$$=\varepsilon_o(\varepsilon^{p.p.}-1)R`^*_{ijkl}P_l^s+r^*_{ijk}\varepsilon_o(\varepsilon^{f.p.}-1), \qquad (15)$$

where ε_o - permitivity of free space, $\varepsilon^{p.p.}$ and $\varepsilon^{f.p.}$ - dielectric constants of paraelectric and ferroelectric phases, respectively, $R`^*_{ijkl}$ – the fourth rank polar tensor for the paraelectric phase determined through the electric field and polarization and r^*_{ijk} - Pockels coefficients for ferroelectric phase determined through polarization. It is necessary to note that the Kerr effect tensor in eq.(11),(13) and (14) possesses the symmetry $[V^2][V^2]$ as well $R`_{ijkl}$ and $R`^*_{ijkl}$ tensors possess the symmetry $[V^2]V^2$ because the

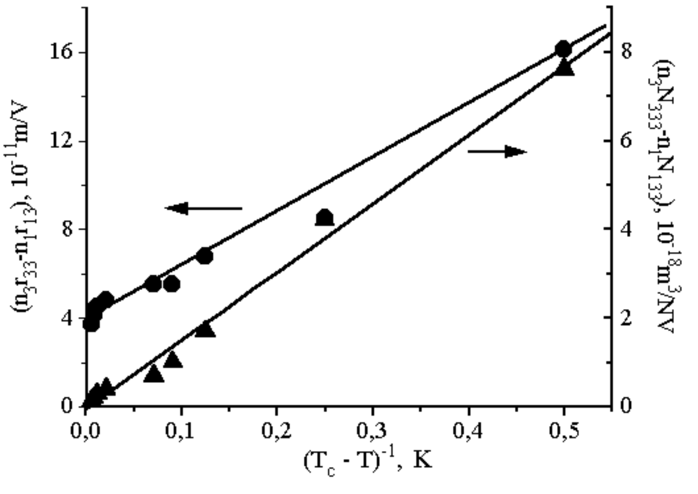

Fig. 5. Temperature dependencies of the ($n_3^3r_{33}$-$n_1^3r_{13}$) and ($n_3^3N_{333}$-$n_1^3N_{133}$) coefficients for $Pb_5Ge_3O_{11}$ crystals versus $(T_c-T)^{-1}$.

transposition of the electric field E_k and spontaneous polarization P_l^s do not lead to the same result.

Let us consider the simple thermodynamic potential in the case of the second order proper ferroelectrical phase transition (case of lead germanate crystals):

$$F=F_o+\alpha(T-T_c)P^2+\beta P^4+\gamma P^6+... \qquad (16)$$

From eq.(10) it follows that $P^2(T)=-\alpha(T-T_c)/\beta \propto (T-T_c)/C$ as well as dielectric susceptibility and permitivity obey the well known Curie-Weiss law (see for example [8]):

$$\varepsilon=4\pi\chi=C/(T-T_c) \text{ for } T>T_c, \qquad (17)$$

and

$$\varepsilon=4\pi\chi=C/2(T_c-T) \text{ for } T<T_c. \qquad (18)$$

where C- is a Curie-Weiss constant. It is quite difficult to determine the $R`^*_{ijkl}$ coefficient in the paraelectric phase and separate contributions of $r`_{ijk}=R`_{ijkl}P_l^s$ and $r``_{ijk}=r^*_{ijk}\varepsilon_o(\varepsilon^{f.p.}-1)$. A similar equation to (15) can be written for $(n_3^3N_{333}-n_1^3N_{133})$ coefficients. To analyze the relation (15) one can use the graphical method. If to plot the dependence of the electrooptical and combined coefficients versus $(T_c-T)^{-1}$ it is evident that these dependencies are linear (Fig. 5). It means that the morphotropic effect described by $r`_{ijk}$ and $N`_{ijklm}$ terms does not contribute sufficiently to the temperature dependence of these coefficients. Following from the relations

$$\left[\frac{n_3^3r_{33}-n_1^3r_{13}}{2\varepsilon_0\left(n_3^3r_{33}^*-n_1^2r_{13}^*\right)}\right]=\frac{C}{(T_c-T)} \qquad (19)$$

and

$$\left[\frac{n_3^3N_{333}-n_1^3N_{133}}{2\varepsilon_0\left(n_3^3N_{333}^*-n_1^2N_{133}^*\right)}\right]=\frac{C}{(T_c-T)}, \qquad (20)$$

one can calculate the Curie-Weiss constant.

If to compare the Curie-Weiss constant calculated from electrooptical measurements (C=1.21×10^{4}K) and from piezoelectrooptical measurements (C=1.22×10^{4}K) it is clear that their values are in good agreement. On the other hand the calculated Curie-Weiss constant from dielectric measurements [9] equal C=1.04×10^{4}K which is almost equal to the values obtained by us.

Conclusions

The temperature dependencies of the electrooptical coefficient of Pockels effect $n_3^3r_{33}$-$n_1^3r_{13}$, Kerr effect $n_3^3R_{33}$-$n_1^3R_{13}$ and coefficients of combined piezoelectrooptical effect $n_3^3N_{333}$-$n_1^3N_{133}$ were obtained. The temperature dependence of these coefficients has been analyzed phenomenologycally. It was shown that temperature dependence of the coefficients of combined bilinear piezoelectrooptical effect in the ferroelectrical phase follows the temperature dependence of dielectric permitivity. The Curie-Weiss constant has been calculated from electrooptical measurements (C=1.21×10^{4}K) and from piezoelectrooptical measurements (C=1.22×10^{4}K) and it is in good agreement with the value obtained from dielectric measurements (C=1.04×10^{4}K).

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