Refractive indexes and piezooptical effect in the $Ca_2Pb(C_2H_5CO_2)_6$ crystals

[1,2]Vlokh R.O., [2]Gotra Z.Yu., [1]Andrushchak A.S., [1]Mys O.G., [1]Kaidan M.V.

[1] Institute of Physical Optics, 23 Dragomanov Str., Lviv, 79005, Ukraine,
e-mail: vlokh@ifo.lviv.ua
[2] National University "Lviv Politechnik", 12 S.Bandera Str., Lviv, 79013, Ukraine

Received 16.01.2001

Abstract

The $Ca_2Pb(C_2H_5CO_2)_6$ organic crystals of good optical quality were obtained by a slow evaporation method. The temperature dependencies of refractive indexes and piezooptical coefficients were investigated at the region of ferroelectrical phase transition. The coefficients of the quadratic electrooptical as well as piezo-electrooptical effect induced by spontaneous polarization were calculated. The obtained results are discussed on the base of the optical indicatrix equation.

Key words: ferroelectrics, organic crystals, piezoelectrooptical effect, $Ca_2Pb(C_2H_5CO_2)_6$ crystals.

PACS: 07.60; 64.70.Hz; 77.84.Fa; 78.20Jq

Introduction

The crystals $Ca_2Pb(C_2H_5CO_2)_6$ (DLP) belong to the propionate organic crystals family as well as $Ca_2Sr(C_2H_5CO_2)_6$ (DSP) and $Ca_2Ba(C_2H_5CO_2)_6$ (DBP) [1]. DBP crystals undergo the phase transitions with the change of point group of symmetry m3m ↔422↔4 at T_{c1}=267K and at T_{c2}=203K, respectively [2]. The phase transition at T_{c2} is ferroelectrical but at T_{c1} probably - higher order ferroical. DLP and DSP crystals possess the same ordering of phase transitions with the change of symmetry 422 ↔4→ ? at T_{c1}=332K and T_{c2}=191K (for DLP) and T_{c1}=281K and T_{c2}=104K (for DSP) [3,4]. The phases below T_{c1} are ferroelectrical and phases below T_{c2} are probably monoclinic (point group of symmetry – 2) and ferroelastical. The mechanical stress which appear on the phase boundary at T_{c2} in DLP and DSP usually leads to the cracking of crystals. Such optical properties as optical activity and electrooptical effect have been already studied in these crystals [5,6]. In our previous paper we have reported about the investigations of gyrotropy and linear electrooptical effect in the DLP crystals at ferroelectric phase transition [7]. As it is seen from our results the change of gyration at T_{c1} in the DLP could be described as quadratic electrogyration effect induced by spontaneous polarization. It was also shown that at T_{c1} the coefficient of linear electrooptical effect $n_3^3r_{33}$-$n_{13}r_{13}$ undergo diffusion maximum and at $T>T_c$ gradually decreases to zero. From another point of view latter investigations show that organic crystals can possess great nonlinear optical effects as well as parametrical crystallooptical effects [8]. From these data it follows that in organic crystals, particularly in propionate crystal group, such effects as second harmonic generation, electrooptical and piezooptical effect etc., could be greater than in inorganic one. We should note that such principle constants as refractive indexes were not yet studied in DLP crystals. The aim of present studies is the investigation of refractive indexes and piezo-optical effect in DLP crystals at ferroelectrical phase transition.

Experimental

DLP crystals of good optical quality were grown by a slow evaporation method at T=308K. The salts of calcium propionate and lead propionate were mixed in molar ratio 2:1. The duration of crystal growth was 40–50 days. The size of obtained crystals was 20×20×15 mm^3. The piezooptical effect was investigated by Senarmount method and refractive indexes - by prism method. The samples were set in the optical furnace or optical cryostat. The control of the temperature was not worse than 0.1K.

Results and discussion

As it is shown on Fig.1 refractive indexes possess the kink temperature dependence on ferroelectric phase transition. At room temperature (T=295K) the values of refractive indexes are n_3=1.550 and n_1=1.544. The change of refractive indexes at T_{c1} is proportional to the quadratic of spontaneous polarization taking from [4] (Fig.2).

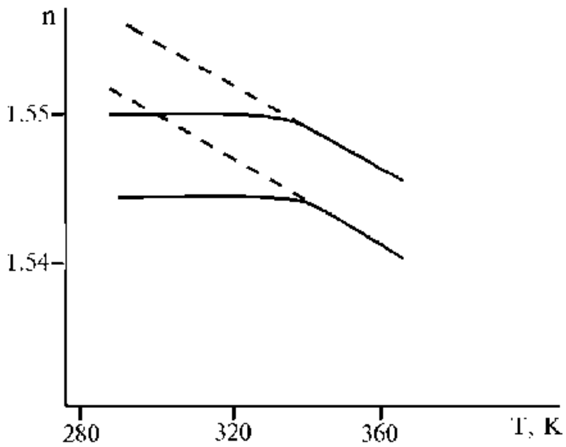

Fig. 1. The temperature dependencies of refractive indexes of the DLP crystals (λ=546 nm, dashed lines are the linear approximation of refractive indexes to the ferroelectrical phase region).

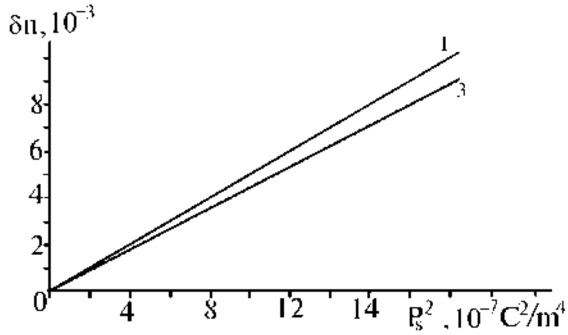

Fig. 2. The dependencies of the change of refractive indexes on the square of spontaneous polarization (1 and 3 - for refractive indexes of n_1 and n_3 respectively).

Such temperature behavior of indexes of refraction could be described as quadratic electrooptical effect induced by spontaneous polarization. In this case the equation of optical indicatrix could be written as:

$$(a_{11}+M_{13}P^2_{s3})x^2+(a_{11}+M_{13}P^2_{s3})y^2+ +(a_{33}+M_{33}P^2_{s3})z^2=1 \quad (1)$$

where a_{ij} - components of polarization constants tensor, P_{sm} – spontaneous polarization, M_{rm} – tensor of quadratic electrooptical effect. From (1) follows that the change of refractive indexes in ferroelectric phase could be written as:

$$|\Delta n_1|=2M_{13}P^2_{s3}n_1^3 \text{ and } |\Delta n_3|=2M_{33}P^2_{s3}n_3^3 \quad (2).$$

From (2) one can calculate the coefficients of quadratic spontaneous electrooptical effect M_{13}=6.7x$10^2m^4/C^2$ and M_{33}=6.8x$10^2m^4/C^2$.

As it is shown on Fig.3 piezooptical coefficient $\pi^*_{23}=n_3^3\pi_{33}-n_1^3\pi_{13}$ possess quite weak temperature dependence. It undergoes only a little maximum at T_{c2}. It was found out that DLP crystals possess significant piezooptical coefficient $\delta\pi^*_{23}$=3.5x$10^{-12}m^2/N$ (T=295K, λ=632.8nm). Besides, the temperature dependence of this coefficients is insufficient in the temperature range T=280K–380K. This fact makes these materials perspective for using as sensors of mechanical strain and as elements of acoustooptical devices. The change of piezooptical effect at T_{c1} (Fig.4) could be described as spontaneous crossflow piezo-electrooptical effect – the effect which consists of changing piezooptical constants at the appearance of spontaneous polarization:

$$\Delta\pi_{ijkl}=N_{ijklm}P_{sm}+R_{ijklmn}P_{sm}P_{sn} \quad (3)$$

where - N_{ijklm} and R_{ijklmn} are fifth rank and sixth rank tensors, respectively. From the symmetry appears that coefficients $N_{11333}=N_{33333}=0$ for the point group of symmetry 422. It means that spontaneous crossflow piezoelectrooptical effect could be proportional only to the square of spontaneous polarization. As it is seen from Fig.5 the dependence of piezooptical constants on square of the spontaneous polarization is linear. From this dependence one can calculate the coefficient of spontaneous crossflow piezo-electrooptical effect $R=(aR_{113333}+bR_{333333})= =\delta(n_3^3\pi_{33}-n_1^3\pi_{13})/P_{s3}^2=1.3^x10^{-6}m^6/NC^2$.

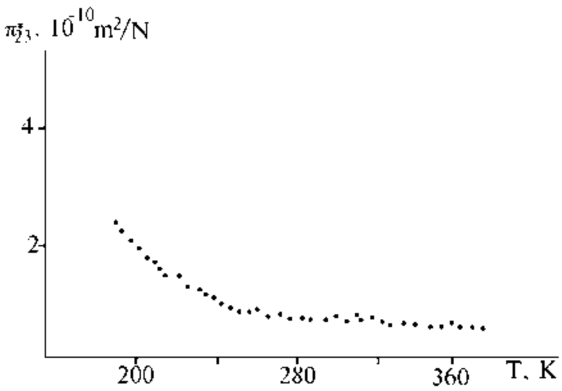

Fig. 3. The dependencies of piezooptical coefficient on the temperature.

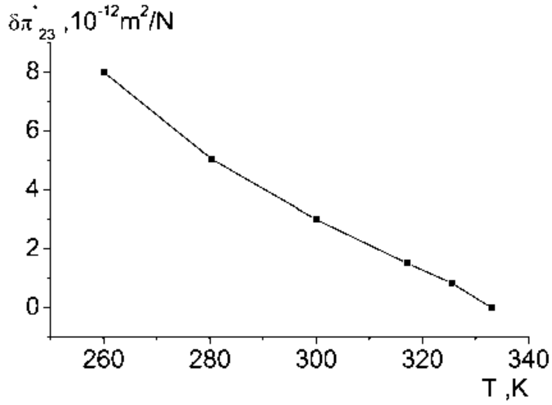

Fig. 4. The dependencies of change of piezooptical coefficient on the temperature at phase transition.

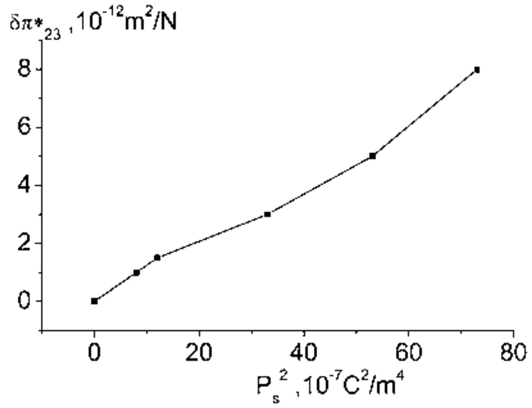

Fig. 5. The dependencies of the change of piezooptical coefficient on the quadratic spontaneous polarization.

Conclusions

1. The organic $Ca_2Pb(C_2H_5CO_2)_6$ crystals of good optical quality were obtained by a slow evaporation method.
2. The temperature dependencies of refractive indexes and piezooptical coefficients of the $Ca_2Pb(C_2H_5CO_2)_6$ crystals were investigated in the region of ferroelectrical phase transition. It was shown that the change of refractive indexes and piezooptical coefficients at ferroelectrical phase transition could be described as electrooptical effect and crossflow piezo-electrooptical effect induced by spontaneous polarization, respectively.
3. The coefficients of quadratic electrooptical effect induced by spontaneous polarization of the $Ca_2Pb(C_2H_5CO_2)_6$ crystals were calculated ($M_{13}=6.7^x10^2m^4/C$ and $M_{33}=6.8^x10^2m^4/C$) as well as coefficient of spontaneous piezo-electrooptical effect $R=(aR_{113333}+bR_{333333})= = \delta(n_3^3\pi_{33}-n_1^3\pi_{13})/P_{s3}^2=1.3x10^{-6}m^6/NC^2$).

References

1. Sawada A., Ishibashi I., Takagy Y. Izv. AN USSR, ser. phys., **41**, (1977) 509. (in Russian)
2. Sawada A., Kikugawa T., Ishibashi I. J.Phys.Soc.Jap., **46**, (1979) 871 .
3. Gesi K., Ozawa K. Phys.Letters, **49A**, (1974) 283 .

4. Takashige M., Iwamura H., Hirotsu S., Sawada S. Ferroelectrics, **11**, (1976) 431.
5. Kobayashi J., Bouillot J., Kinoshita K. Phys.Stat.Sol. (b), **47**, (1971) 619.
6. Kobayashi J., Uesu Y., Hosokava T. Izv. AN USSR, ser. phys., **41**, (1977) 460.
7. Vlokh R.O., Biletsky I.N. Ferroelectrics, **90**, (1989) 183.
8. Bosshard Ch. Abs. of EMF-9, Praha, (1999) 275.