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TEMPERATURE DEPENDENCE OF THE KERR CONSTANT OF FOMBLIN M03

The Kerr constant B of perfluoropolyether Fomblin M03 has been determined within the temperature range 295-370K. At 300K the constant B was found to be equal to $2.8\cdot 10^{-15}$ *m/V*^{2}*. The measurements indicate that B varies inversely with temperature. Relatively low electro-optic response of the perfluoropolyether shows its usability in measurements of the quadratic electro-optic effect and the electrostriction in crystals.*

Keywords: perfluoropolyether Fomblin M03, Kerr effect, quadratic electro-optic effect.

1. INTRODUCTION

In centrosymmetric crystals and liquids phenomena described by a third-rank polar tensor, like the linear electro-optic effect, are vetoed by symmetry and the lowest-order electro-optic effect is the quadratic one [1]. In liquids changes in the refractive index quadratic with electric field are often called as the Kerr effect. According to the frequency of involved electric field one can consider the electro-optic and optical Kerr effects for the static or low-frequency and optical frequency fields, respectively. The nature and, therefore, magnitude of nonlinear interactions responsible for the electro-optic and optical Kerr phenomena are very different. This work is devoted to measurements of the electro-optic Kerr effect.

The Kerr effect can be described in terms of various coefficients. In this work we follow the phenomenological theory of linear and quadratic electro-optic effects developed by Pockels [2] who introduced electro-optic coefficients defined in terms of changes in the optical impermeability tensor η_{ij} which are induced by the low-frequency electric field **E**. In a principal axes system the quadratic electro-optic coefficient is defined as

$$g_{iijk} = \frac{1}{2}\frac{\partial^2 \eta_{ii}}{\partial E_j \partial E_k} . \tag{1}$$

It follows from equation (1) that the changes in the refractive index due to the applied low-frequency field are given by [2]

$$\Delta n = \frac{1}{2} n^3 g_{iijk} E_j E_k , \tag{2}$$

where *n* is the field free refractive index. Pockels coefficients are commonly employed in investigations of electro-optic properties of crystals. In liquids the induced birefringence Δn is usually described in terms of the factor *B* known as the Kerr constant

$$\Delta n = B \lambda E^2 , \tag{3}$$

where λ is the light wavelength.

Up to now the linear electro-optic effect in many noncentrosymmetric crystals has been precisely measured. The quadratic electro-optic properties of the most crystals are, however, still not well recognized (see, e.g., [3-9]). This is despite the fact that the quadratic electro-optic effect in crystals attracts attention as related to numerous nonlinear phenomena (see, e.g., [3]).

Coefficients of the quadratic electro-optic effect in crystals usually need very sensitive experimental techniques to be determined. In some compounds the coefficients measured by different authors differ even by three orders of magnitude. For example, such spread can be observed for the quadratic electro-optic coefficients in the KH_2PO_4 (KDP) family of crystals. The reasons of the discrepancy have been discussed in [3,4], where a necessity of remeasurements of the quadratic electro-optic coefficients in many crystals, especially these which lack a center of inversion, have been shown.

To increase the accuracy of measurements of the quadratic electro-optic coefficients, or even sometimes to make them possible, it is necessary to apply to the sample the electric field of relatively high strength. This is often difficult to do. Many crystals under interest, are grown from solutions and are hygroscopic. To reduce the risk of electric breakdown the sample can be placed in a bath containing a liquid which does not solve the crystal (see, e.g., [3,5,10]). In measurements of electro-optic properties based on interferometric methods the use of two immersion media with different refractive indices makes also possible to evaluate changes in the optical path due to the electrostriction [11]. Any liquid is, however, a source of an additional contribution to the modulation of the light beam related to the fringing electric field and the Kerr constant of the liquid. When the Kerr constant is large enough, there appear difficulties in distinguishing between contributions due to the modulation of the light by the crystal sample and that of the liquid. Usually the constant B lay in the range from 10^{-12} m/V^2 to 10^{-15} m/V^2. For example, the values of B determined at room temperature for nitrobenzene, water and metylosilicone oils are roughly; $2{\cdot}10^{-12}$ m/V^2, $5{\cdot}10^{-14}$ m/V^2 and $2{\cdot}10^{-15}$ m/V^2, respectively. By taking into account equations (2) and (3), the quadratic electro-optic coefficient as defined by Pockels may be related to the Kerr constant B by the relation

$$g = \frac{2\lambda B}{n^3}\,. \tag{4}$$

Thus, the values of B listed above correspond roughly to the Pockels quadratic electro-optic coefficient equal to $1{\cdot}10^{-18}$ m^2/V^2, $3{\cdot}10^{-20}$ m^2/V^2 and $1{\cdot}10^{-21}$ m^2/V^2 for nitrobenzene, water and metylosilicone oils, respectively. One notes that despite the fact that metylosilicone oils are known for low electro-optic response, their quadratic electro-optic coefficients are close to that expected in KDP-type crystals [3-5].

The aim of this work is to test a possibility of application of perfluoropolyether oxide Fomblin M03 as an immersion liquid to increase the sensitivity of measurements of quadratic electro-optic and electrostrictive coefficients in crystals. Investigations of electro-optic properties of crystals are often performed at different temperatures (see, e.g., [5]). Therefore, in our work we present the Kerr constant of the Fomblin M03 as a function of the temperature as well.

2. SOME PROPERTIES OF PERFLUOROPOLYETHERS

Perfluoropolyethers (PFPEs) are the family of polymers composed entirely of carbon, fluorine and oxygen atoms. These compounds are liquids over very wide temperature range (–100ºC to 450ºC) and posses high thermal oxidative stability, low volatility, non flammability, excellent lubrication properties, biological inertness, etc. [11-13]. Purified PFPEs are ultra-transparent materials and are promising media for optical lithography. They are employed in a number of diverse and demanding applications such as: high vacuum pump fluids, lubricants for jet-engines, turbines, nuclear reactor cooling pumps, satellite instrumentations as environmental coatings, electrical insulators and, recently, for magnetic recording media.

Optical properties of perfluoropolyethers have not been yet investigated in details. The refractive index of many PFPEs has been measured and found to increase with the molecular weight. The refractive index of the compounds is only slightly sensitive to the oxygen/carbon ratio in the macromolecule.

Perfluoropolythers can be homopolymers or copolymers (linear or branched). The most common PFPEs are non polar and exibit very low dielectric constant. The second generation of the polymers with terminating functional groups shows slightly increased polarity [11, 12].

In the present work, the perfluoropolyether Fomblin M03, product of Solvay Co., used as received, is investigated. The compound is a nonpolar linear copolymer with chemical structure:

$$CF_3O-\left[CF_2CF_2O-\right]_n[CF_2O-]_m CF_3 .$$

3. EXPERIMENTAL

We have used the dynamic method the basis of which is the harmonic analysis of light modulated by an electric field $E(t)=E_0\sin(\omega t)$. The intensity of the light passed through a cell containing a birefringent medium placed between the polarizer and analyzer is given by [13]

$$I=I_0\left[\cos^2(\alpha)-\sin(2\rho)\sin\left[2(\rho-\alpha)\right]\sin^2\left(\frac{\Gamma}{2}\right)\right], \tag{5}$$

where I_0 is the incident light intensity, α is the angle between the plane of polarization in polarizer and analyzer, ρ is the angle between the plane of polarization and the principal axis of the elliptical cross-section of the optical indicatrix. The induced birefringence which is due to the Kerr effect in liquids is of such symmetry that the directions of the principal axis of the cross-section of the indicatrix are parallel and perpendicular to the direction of the applied electric field. In equation (5) Γ is the phase difference between the ordinary and extraordinary beams

$$\Gamma=\Gamma_0+kl\Delta n, \tag{6}$$

where Γ_0 is that part of Γ which is independent of the electric field, $k = 2\pi/\lambda$ and l denotes the path length of the light beam in the liquid. In our measurements, the polarizers were crossed, i.e. $\alpha=\pi/2$ and oriented in such a way that $\rho=\pi/4$. A quarter-wave plate provided the optical bias $\Gamma_0 = \pi/4$. For such optical bias equation (5) may be rewritten in the form

$$I=\frac{I_0}{2}\left(1+\sin\left(kl\Delta n\right)\right). \tag{7}$$

By employing a lock-in technique, we determined the modulation index $m(2\omega) = I(2\omega)/I_0$, where I_0 and $I(2\omega)$ is the intensity of the constant component and the second harmonic of the light transmitted by the system, respectively. A computer controlled data acquisition and processing system was used in our measurements. As in earlier measurements performed for crystals (see, e.g., [6]), we employed the He-Ne laser (λ = 0.633 μm) and the electric field of frequency 417 Hz. Following previous measurements (see, e.g., [14]), the Kerr constant as defined by equation (3) was determined by employing the following expression

$$B = \frac{m(2\omega)d^2}{\sqrt{2}\pi U^2 l}, \tag{8}$$

where d is the distance between electrodes and U is the rms voltage applied to the electrodes. Shown in Fig. 1 is a schematic diagram of the optical and electronic equipment used in the measurements.

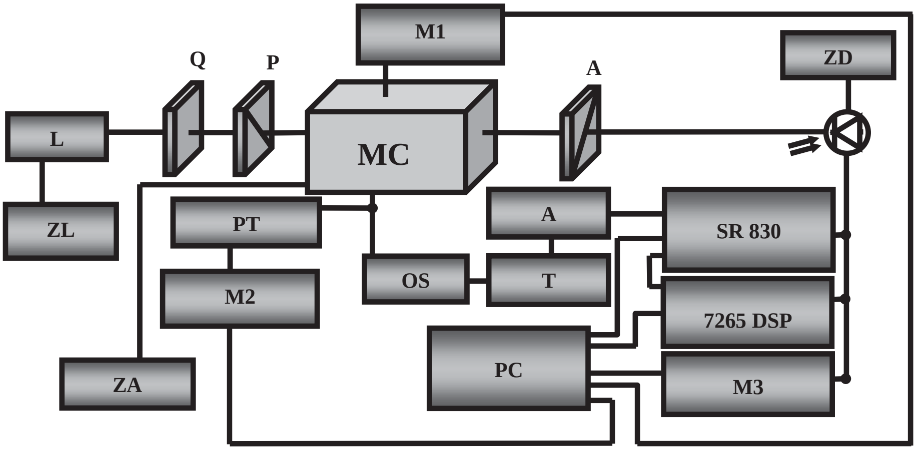

Fig. 1. Diagram of the optical and electronic components used in the polarimetric method: L – laser, ZL – power supply, Q – quarterwave plate, P – polarizer, A – analyser, M1 – multimetr Metex M-4650CR, Zd – power supply, MC – measuring chamber, PT – probe Tektronix P6015A, M2 – Multimetr Fluke 45, OS – overcurrent system, A – amplifier, T – transformer, PC – personal Computer, SR830-Lock in Stanford SR830 DSP, 7265 DSP-Lock in EG&G 7265 DSP, M3 – Multimetr Keithley 2000 DMM, ZD – power supply, ZA – power supply Amrel LPS 305

4. RESULTS AND DISCUSSION

At 300K the constant B was found to be equal to $2.8\cdot10^{-15}$ m/V^2 being comparable to the metylosilicone oils employed previously in our measurements of the quadratic electro-optic effect and electrostriction of crystals. The results obtained indicate that the Kerr constant decreases slightly with temperature. Such behavior, i.e. the decrease in B with temperature is typical for many liquids.

The temperature dependence of the Kerr constant of the perfluoropolyether under investigation plotted against the $1/T$ is shown in Fig. 2. It is known that the Kerr constant of non-polar liquids varies inversely with temperature. The perfluoropolyether Fomblin M03 is non-polar and its Kerr constant possesses the typical value of non-polar liquids, i.e. 10^{-15} m/V^2. The temperature dependence of B, as shown in Fig. 2, fits expected linear dependence on $1/T$.

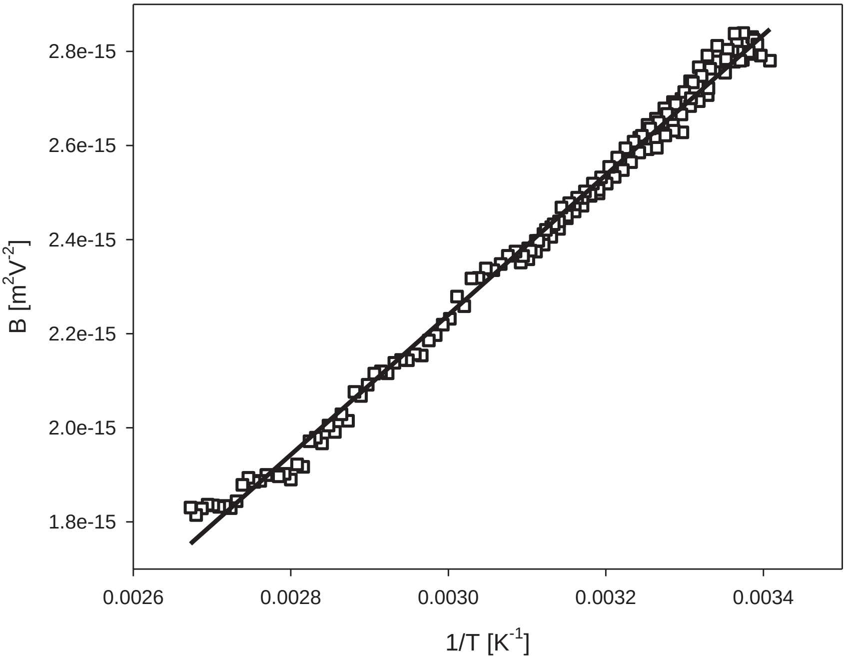

Fig. 2. The temperature dependence of the Kerr constant B in perfluoropolyether Fomblin M03 plotted against $1/T$. The frequency of modulating field is 417 Hz

In conclusion, the electro-optic response of the Fomblin M03 is of the same order of magnitude as that observed in transformer mineral and silicon oils employed previously as immersion liquids [15]. The low-value of the Kerr constant of Fomblin M03 along with the high electric strength of the liquid, allow to use the perfluoropolyether as the immersion liquid in measurements of the quadratic electro-optic effect in crystals. Moreover, Fomblin M03 possesses very low refractive index which is close to 1.3. In interferometric investigations of electrostriction of crystals in transmission, it is very useful to perform measurements employing different immersion liquids with their refractive indices as different as possible [3, 10]. The low refractive index of Fomblin M03 and its relatively low electro-optic response confirm the usability of the perfluoropolyether in measurements of the electrostriction in crystals by the transmission interferometric method.

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TEMPERATUROWA ZALEŻNOŚĆ STAŁEJ KERRA FOMBLINU M03

Streszczenie

W zakresie temperatur 295- 323 K przeprowadzono pomiary stałej Kerra B polimeru Fomblin M03. Stwierdzono, że stała B jest odwrotnie proporcjonalna do temperatury. W temperaturze 300 K jej wielkość wynosi $2.8\cdot10^{-15}$ m/V^2. Wyniki pokazują, że ze względu na małą wartość stałej Kerra Fomblin M03 może być wykorzystany jako ciecz immersyjna w pomiarach współczynników kwadratowego efektu elektrooptycznego oraz elektrostrykcji w kryształach.

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