Optical Characterization of Organic-Inorganic $[(CH_2OH)_3CNH_3)]H_2PO_4$ Crystals

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Abstract

The results of studies for the refractive indices dispersion, optical activity, electro- and piezooptic effects, thermal expansion and ultrasonic wave velocities in $[(CH_2OH)_3CNH_3)]H_2PO_4$ crystals are presented. It is shown that the above crystals represent good electrooptic materials.

Key words: $[(CH_2OH)_3CNH_3)]H_2PO_4$ crystals, refractive index, electrooptic and piezooptic coefficients, thermal expansion, ultrasonic wave velocities

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Introduction

$[(CH_2OH)_3CNH_3)]H_2PO_4$ crystals (TDP) represent a crystalline material containing tris(hydroxymethyl)aminomethane $[(CH_2OH)_3CNH_2]$ (abbreviated as TRIS) and phosphoric acid. Pure TRIS crystallizes in noncentrosymmetric space group $Pn2_1a$ [1,2]. Some TRIS compounds are also noncentrosymmetric and so might be expected to show nonlinear or electrooptic properties [3,4]. Moreover, $[(CH_2OH)_3CNH_3]_2SiF_6$ undergoes a feroelastic phase transition at T_c=177K [5]. According to [6], the space symmetry group of TDP crystals is $P2_1$. Most of the mentioned crystals are characterized by a monoclinic symmetry and comparatively large parameters of unit cell. This can lead to essential polarizability and electrooptic figure of merit, so that the materials under consideration seem to be attractive from the viewpoint of nonlinear optics and, in particular, electrooptics. As far as we know, the Pockels effect has not yet been studied in the TDP-type compounds. Thus, the present paper is devoted to studies of some crystal physical properties of TDP crystals, especially electrooptic ones.

Experimental

Dispersion of the refractive indices was studied with the standard index-matching technique. Alpha-monobromine naphthalene with kerosene or iodine methane were used as index-matching liquids. Crystal plates with the faces perpendicular to principal crystallographic planes and the average thickness of few millimetres were prepared from the bulk single crystals grown from aqueous solution. Optical activity was determined, using the methods for measuring rotation of polarization plane of the light (λ=632.8nm) propagated along one of the optical axes. Electrooptic and piezooptic effects in the TDP crystals were measured at the same wavelength with the Senarmont method, the interference method utilizing Mach-Zender

interferometer and the method for measuring optical indicatrix rotation under the action of electric field or mechanical stress.

Measurements of the velocity of longitudinal and transverse ultrasonic waves were performed on single crystals, using the pulse-echo overlap method. The accuracy of the absolute velocity determination was about 0.5%. The acoustic waves were excited in samples with $LiNbO_3$ transducers (the resonance frequency f=10MHz, the bandwidth Δf=0.1MHz and the acoustic power P_a=1–2W). Finally, thermal expansion was studied in both cooling and heating temperature runs (the temperature scan rate $\partial T/\partial t$=1K/min) with the aid of capacity dilatometer (the sensitivity 2nm).

Results and discussion

The dispersion of the refractive indices for TDP is represented in Fig.1. The TDP crystals are optically biaxial, with their optic axes lying in *ab* plane, where *a* axis is a bisector of the acute angle between the optic axes. The crystals are "optically negative", i.e. $n_g - n_m < n_m - n_p$ (with n_g, n_m and n_p being respectively the largest, intermediate and the least refractive indices). The measured acute angle between the optic axes is equal to $2V = 64.84°$ at the wavelength of 632.8nm.

The point symmetry group of the TDP crystals permits the existence of optical activity. We have found out that the optical rotatory power is equal to $\rho = -1.45 \deg/mm$ for the light propagating along one of the optic axes. The sign "minus" means that the crystals are laevorotary for the direction of light propagation mentioned above.

Temperature dependences of the thermal expansion for TDP crystals obtained at cooling and heating temperature runs are presented in Fig.2. We did not observe any anomalous behaviour of thermal expansion in this crystal down to the liquid-nitrogen temperature. Instead, we revealed a noticeable anisotropy in the thermal expansion: the thermal expansion coefficient $\alpha_{22} = 52.8 \times 10^{-6} K^{-1}$ at room temperature is essentially larger than $\alpha_{11} = 19.1 \times 10^{-6} K^{-1}$ and $\alpha_{33} = 15.2 \times 10^{-6} K^{-1}$. It can be easily explained by the fact that *b* axis corresponds to the polar direction. The propagation velocities of the ultrasonic waves in TDP crystals have quite large values: $v_{11} = 4580 m/s$, $v_{22} = 4660 m/s$, $v_{33} = 4150 m/s$, $v_{12} = 2675 m/s$, $v_{13} = 2025 m/s$ and $v_{23} = 2225 m/s$. Along with inessential magnitudes of piezooptic coefficients,

$$n_2^3 \pi_{22} - n_1^3 \pi_{12} = 16.2\, pm^2/N,$$

$$n_3^3 \pi_{32} - n_2^3 \pi_{22} = 12.7\, pm^2/N,$$

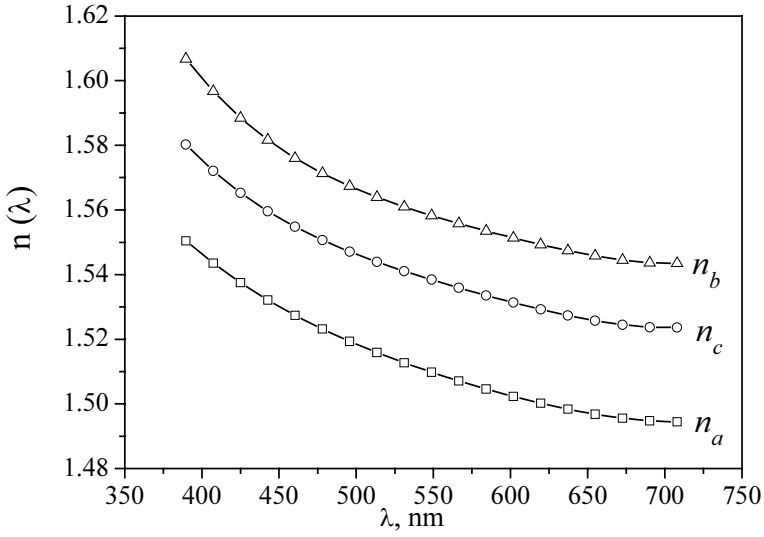
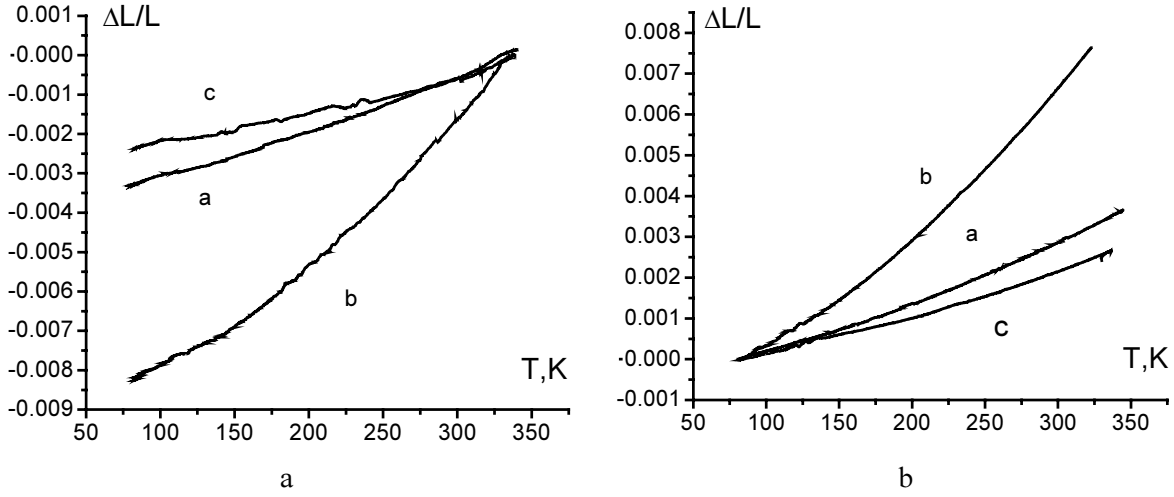


Fig. 1. Dispersion of refractive indices for the TDP crystals at



a b

Fig. 2. Temperature dependences of thermal expansion for the TDP crystals at cooling (a) and heating (b).

$$n_1^3\pi_{13} - n_3^3\pi_{33} = 5.72\,pm^2/N,$$

$$n_3^3\pi_{31} - n_1^3\pi_{11} = 4.38\,pm^2/N,$$

$$n_3^3\pi_{33} - n_2^3\pi_{23} = 7.03\,pm^2/N,$$

$$n_1^3\pi_{11} - n_2^3\pi_{21} = 10.4\,pm^2/N,$$

this should lead to low values of acoustooptic figures of merit. On the other side, some of electrooptic coefficients achieve high enough magnitudes. For example, the modules of the electrooptic coefficients are as follows: $r_{63} = 11\,pm/V$, $r_{61} = 21.4\,pm/V$, $r_{52} = 15\,pm/V$, $r_{43} = 45\,pm/V$, $r_{41} = 38\,pm/V$, $r_{22} = 30.8\,pm/V$, $r_{12} = 3.5\,pm/V$ and $r_{32} = 9.6\,pm/V$. It implies that the crystals under test can be used as electrooptic materials. Summarizing electrooptic properties, let us write out the modules of the electrooptic tensor:

	E_1	E_2	E_3	
ΔB_1	0	3.5	0	
ΔB_2	0	30.8	0	
ΔB_3	0	9.6	0	$\times 10^{-12}\,m/V$.
ΔB_4	38	0	45	
ΔB_5	0	15	0	
ΔB_6	21.4	0	11	

Conclusions

In this paper we have studied a number of physical properties of the TDP crystals, in particular, the refractive indices, the optical activity, electrooptic and piezooptic coefficients, the thermal expansion and the velocities of ultrasonic waves. On the basis of the presented results, one can conclude that the TDP crystals may be treated as a good electrooptic material.

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