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Study of the piezoelectric properties of rubidium acid phthalate crystals by time-resolved three-crystal X–ray diffractometry

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Using the method of time-resolved X-ray diffractometry in a three-crystal scheme, the lattice deformation of a rubidium biphthalate ($C_8H_5RbO_4$) crystal was measured in an external electric field. Under the action of an external pulsed electric field along the [001] polar direction, the piezoelectric moduli d_{31}, d_{32}, and d_{33} were determined independently using three reflections 400, 070, and 004; the obtaind values are -32.8 ± 0.6, 12.8 ± 0.3, and 21.8 ± 1.2 pC/N, respectively. A good agreement was found between the values of the piezoelectric moduli obtained in this work and the values obtained earlier by the quasi-static method.

Keywords: piezoelectric effect, time-resolved X-ray diffractometry, three-crystal diffraction scheme, acid phthalate crystals, external electric field.

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1. Introduction

Studying strain-controlled behavior of materials and changes in their structural organization is of interest for the creation of new energy-saving systems of information recording and storing, as well as other components of microelectronics [1,2].

One of the possible methods to control strains in acentric crystals is the application of an external electric field. Piezoelectric materials become widely used in micro- and nanoelectronics, photonics, and sensorics, but at the new stage of development of such fields as straintronics [3] and defect engineering [4], these studies have become important again.

One of the promising objects for these purposes are crystals of rubidium biphthalate. Compounds of the biphthalate family draw attention due to the unique combination of optical, electrical, and mechanical properties ensuring their different applications in optoelectronics and acoustooptics [5,6], in converters of laser radiation [7], electro-optic modulators [8], soft X-ray monochromators [9]. At the same time biphthalate crystals are strong piezoelectrics that, in particular, have record high values of sensitivity of acoustic signal reception [10].

Piezoelectric characteristics of rubidium biphthalate were studied earlier by the method of quasistatic mechanical loads [11] and method of resonance-antiresonance [12]. However, there are significant differences between the values of piezoelectric moduli obtained in the above-mentioned studies.

Currently, along with traditional electrophysical and mechanical methods of studying piezoelectric properties, methods based on X-ray diffraction are actively developed. X-ray radiation is a convenient and high-precision tool for contactless strain studying. Methods of X-ray diffraction in different schemes are widely used to study piezoelectric properties of various crystalline materials due to their highest sensitivity to changes in parameters of a crystalline lattice.

At the same time, X-ray diffraction measurements of piezoelectric properties carried out using synchrotron [13,14] and laboratory sources [15,16], as a rule are implemented in a static mode that makes it difficult to separate the piezoelectric effect from other accompanying effects, for example, caused by the reconstruction of the defect structure creating mechanical strain under the impact of an electric field [17,18]. For this purpose the use of quick-acting techniques is required, such as time-resolved X-Ray diffractometry [19,20], in combination with high-resolution scanning schemes to distinguish strains of different types.

In this study a laboratory diffractometer was used to measure mutually normal piezoelectric strains in a metalorganic crystal of rubidium biphthalate using the modified technique of time-resolved high-resolution X-ray diffractometry (HRXRD) in a triple-crystal scheme in $\theta - 2\theta$ scanning mode with the synchronization of pulsed supply of the electric field.

2. Studied samples

Crystals of rubidium biphthalate ($C_8H_5RbO_4$, RBP) belong to space group $Pca2_1$. Lattice parameters for RBP are $a = 10.064$ Å, $b = 13.068$ Å, $c = 6.561$ Å [21]. There

are several crystalline physical setups described in literature. The setup used in this study has crystalline direction [100] corresponding to X, [010] — Y, [001] — Z. Polar axis of crystals coincides with [001] direction.

In the matrix of piezoelectric moduli 5 independent coefficients are represented, three of which correspond to tension-compression strains d_{31}, d_{32}, d_{33}; another two components, d_{15} and d_{24}, are related to shear strains. Dielectric permittivity of crystal is $\varepsilon_{33} = 4.37$.

The crystals for this study were grown from an aqueous solution in the Crystallography and Photonics Federal Research Center of RAS following the technique described in [10]. Prepared parallel-sided plates of (001) cut with transverse dimensions of $9 \times 6\,\text{mm}^2$ and a thickness of 2.54 mm were etched in an aqueous solution to remove the disturbed layer. Then colloidal silver solution was applied on their face sides to create conductive contacts and to form a uniform electric field in the volume. Thin ($50\,\mu$m) conductive leads were soldered to the samples, then the samples were mounted in a special crystal holder on the diffractometer.

3. Technique and equipment for measurements of piezoelectric moduli

X-ray diffraction method to determine piezoelectric moduli is based on the measurement of the change in interplane distance in crystals by the shift of diffraction reflection curve (DRC).

A relative change in the interplane distance is a function of the Bragg angle θ and its change $\Delta\theta$:

$$\frac{\Delta d}{d} = -\cot\theta\Delta\theta, \quad (1)$$

On the other hand, the strain is proportional to the strength of the applied external electric field E with a factor of proportionality equal to the appropriate piezoelectric modulus

$$\frac{\Delta d}{d} = d_{ij}E_i, \quad (2)$$

Thus, piezoelectric moduli of the crystal can be derived from the results of X-ray diffraction measurement of the DRC peak shift position in the case of inverse piezoelectric effect with pre-defined strength of the electric field.

Measurements were carried out in a triple-crystal X-ray diffraction scheme that features the use of one more crystal-analyzer in addition to the monochromator. This component functions as a narrow gap in front of the detector with an angular aperture corresponding to the FWHM (Full Width at Half Maximum) of its DRC. The use of this scheme makes it possible to perform precision measurements of the Bragg angle variations in the process of experiment, distinguishing only the strain contribution, which is responsible for the change in the interplane distance in the direction of a scattering vector.

Measurement of DRC in the triple-crystal diffraction scheme is carried out in the $\theta - 2\theta$ mode, where the sample is rotated over θ angle in a stepwise manner and the analyzer-detector system is rotated over 2θ angle with double steps in the pre-defined angular range near the diffraction maximum.

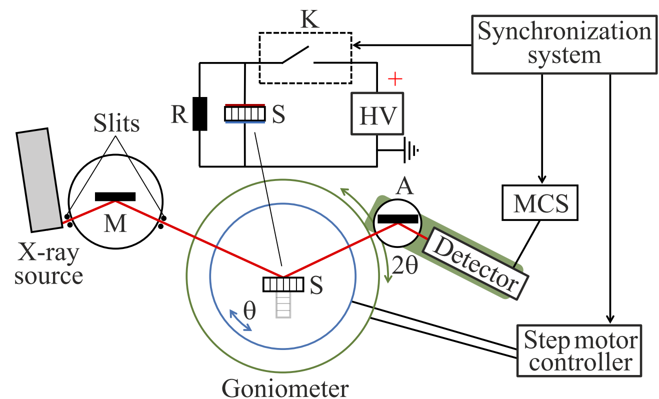

Figure 1. Schematic diagram of the experimental setup to implement time-resolved X-ray diffractometry in a triple-crystal geometry. The setup includes a molybdenum source of X-ray radiation, a monochromator (M), a set of collimating slits, a goniometer with a step motor controller, a crystal-analyzer (A), a detector with a multichannel intensity analyzer (MCS), a system to supply electric field to the sample. The synchronization system controls the multichannel analyzer and the system of electric field supply, which electric circuit includes a high-voltage source (HV), a solid-state switch (K), and a resistor (R) connected in parallel to the sample (S).

The method of X-ray diffractometry is based on the mechanical rotation of the goniometric system, and one scanning cycle can take several minutes. In the process of measurement in the conditions of exposure to electric impact, due to migration of charge carriers and charged defects their accumulation can take place near the electrode, that results in the screening of the external electric field and obtaining incorrect values of piezoelectric moduli. This restriction can be avoided by means of time-resolved technique of X-ray diffractometry. When measuring DRC, the time scanning of intensity is recorded in every angular point in the process of pulsed electric field impact on the sample synchronized with the multichannel analyzer of intensity. See [22,23] for the detailed description of this technique. An important condition of applicability of this technique is the reversibility of the process under study with repeated external impact.

As a result, the data set recorded under pre-defined conditions and made-up in coordinates of time–angle–intensity reflects a DRC set, that then is approximated by a Pseudo-Voigt function in order to obtain information about dynamics of DRC parameters: angular position of peak, integral intensity, and FWHM.

The technique of piezoelectric moduli measurement is implemented in a setup of a triple-crystal X-ray spectrometer (TXS) equipped with an X-ray tube with a molybdenum anode with a maximum power of 2.5 kW. Schematic diagram of the setup is shown in Fig. 1. To

monochromate the radiation and to distinguish the spectral line of λ [Mo$K_{\alpha 1}$] = 0.70932 Å a perfect single crystal of Si 220 was used with a Bragg angle of $\theta_M = 10.644°$ and a FWHM of its DRC equal to 2.1829 arcsec, a similar crystal was used as an analyzer. After the monochromator, a slit collimator was installed with an aperture of 0.2×5 mm, that also defined the size of the beam on the sample. The intensity of diffracted radiation was recorded using a point detector (Radicon SCSD-4) with a dynamic range of $5 \cdot 10^5$ cps, coupled with the multichannel intensity analyzer (ORTEC Easy-MCS). The measuring equipment was synchronized with the pulsed electric field impact on the sample by means of TTL-pulses (Transistor–transistor Logic) using a synchronization system on the basis of a generator (Tektronix AFG 3022B) and oscilloscope. The electric impact on the sample was implemented by means of a quick-acting solid-state TTL-switch (Mantigora HVS-F-10-35) that allows applying a pulsed electric field with a frequency of up to 10 kHz with a short build-up time of pulses ($\sim$ 40 ns). A shunt resistor with a resistance of $R = 10\,\text{M}\Omega$ was connected to the electric circuit in parallel to the sample. This resistor defines the time ($\tau = RC$) of crystal discharge (calculated value is $\sim 8\,\mu$s), which is much less that the time resolution of the experiment.

In the process of experiment, DRC of reflections 400, 070, and 004 were measured in three mutually normal directions. The presence of rubidium atoms in the crystal structure provides quite a strong absorption, which made it impossible to measure reflections 400 and 070 in Laue geometry (in transmission mode). The above-mentioned reflections, as well as 004, were measured in Bragg geometry (in reflection mode) from appropriate ends of the crystal.

Bragg angles of appropriate reflections of the crystal under study are: $\theta_{400} = 8.104°$, $\theta_{070} = 10.951°$, $\theta_{004} = 12.487°$. Calculated extinction depth for the reflection 400 is $L_{400} = 15.9\,\mu$m, for the reflection 070 it is $L_{070} = 28.2\,\mu$m, for the reflection 004 it is $L_{004} = 49.9\,\mu$m.

In all cases the applied electric field was [001]-oriented. The length of the electric pulse was 5 s. Measurements were carried out at an electric field strength of 900 V/mm in both polarities. Time resolution in each case was set on the basis of the diffracted signal intensity and was 100 μs for the reflection 400, 200 μs for the reflection 070, 500 μs for the reflection 004. An angular step of scanning was 0.25 arcsec for the reflection 070 and 0.5 arcsec for reflections 400 and 004.

The measurement of three orthogonal reflections made it possible to observe strain behavior of the crystal in space for three mutually normal directions and to determine appropriate piezoelectric moduli: d_{31}, d_{32}, d_{33}. Values of piezoelectric moduli were determined on the basis of peak shifts by means of averaging the points over three equal time intervals of 5 s: before the start of the impact, with field switch on, and after the field is switched off. Statistical error of the measurement was determined as a root-mean-square deviation from the mean value.

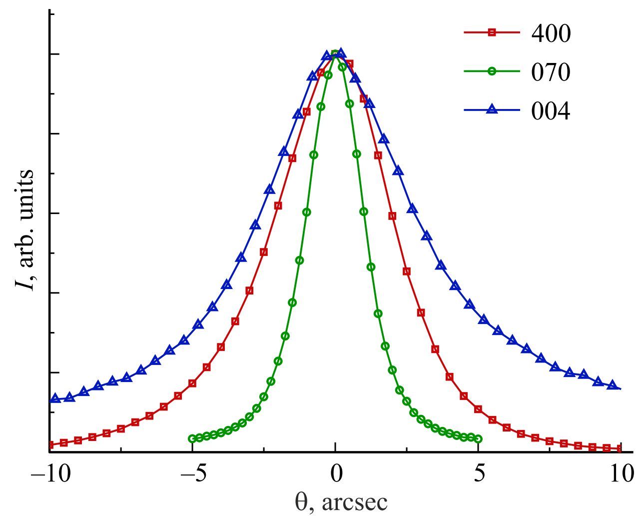

Figure 2. DRCs of reflections 004, 400, and 070 of the RBP crystal obtained in the triple-crystal scheme of diffraction.

4. Experimental results

In the process of preliminary analysis of the crystalline structure degree of perfection, the X-ray diffraction method was used to obtain DRCs for three reflections of both crystals. Peaks were approximated by an analytic Pseudo-Voigt function.

The experimentally determined *FWHM* (Full Width at Half Maximum) values of DRC of the sample in a triple-crystal scheme were: $FWHM_{400}$=5.0 arcsec, $FWHM_{070}$=2.4 arcsec, $FWHM_{004}$= = 6.3 arcsec (Fig. 2). FWHM of DRC of the reflection 070 is the lowest due to nearly absent dispersion in the scheme, while two other peaks are almost equally broadened due to a slight dispersion, i.e., the difference in the Bragg angles of crystals in the scheme (not more than 2°). Narrow curves with a regular, symmetric Gaussian shape in the triple-crystal scheme are indicative of high degree of structural perfection of samples.

Then DRCs were scanned in the time-resolved mode for three reflections 400, 070, and 004 under a pulsed external electric field. As a result, time dependencies of DRC parameters were obtained. The stepwise shift of diffraction peaks under the application of electric pulse corresponds to piezoelectric response of the crystalline structure. Shifts at switching the electric field on and off are identical. These shifts were converted to a relative change of lattice parameter by formula (1) and averaged over polarity. The dependence of relative strain vs time in the process of electric pulse supply is shown in Fig. 3. The error of relative strain was determined by the error of peak approximation. It was found that such parameters as FWHM of peaks and their intensity remain unchanged in the process of electric field supply (Fig. 4).

In [24] it was found in crystals of potassium biphthalate that application of external electric field results in emergence

of two strain types: fast strain — due to piezoelectric effect, and relaxation strain — due to migration of potassium ions under the field. It was shown, that the second mechanism is characterized by a threshold value of field strength exceeding 500 V/mm, which is defined by the energy of potassium ions activation.

As can be seen from Figs. 3 and 4, for rubidium biphthalate only a stepwise change in DRC peak position is observed, and there are no slow changes observed for potassium biphthalate. The electrical conductivity of rubidium biphthalate was measured in the [001] direction, that was $\sigma = 3.8 \cdot 10^{-12}$ S/m under a constant field of 200 V/mm, which is by an order of magnitude less than the electrical conductivity of potassium biphthalate.

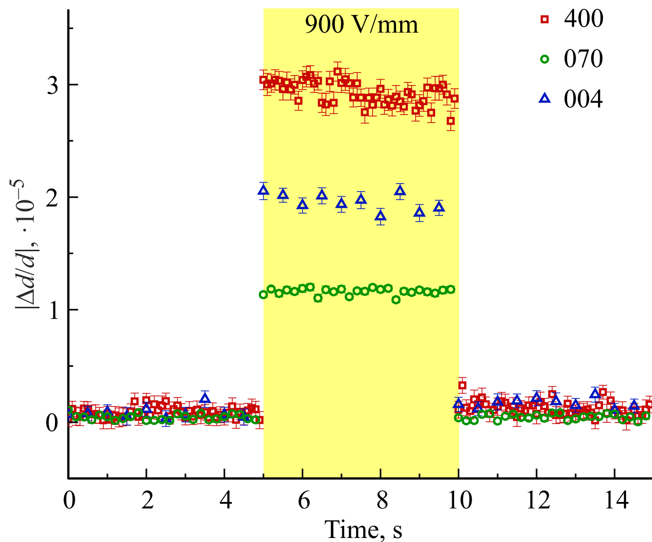

Figure 3. Time dependencies of the interplane interval change along directions of [100], [010], and [001] as measured by the DRC shift of reflections 400, 070, and 004 of the RBP under pulsed electric field impact with a strength of 900 V/mm with averaging over polarity. Values are taken in absolute magnitude. Yellow color highlights the time interval corresponding to an electric pulse of 5 s.

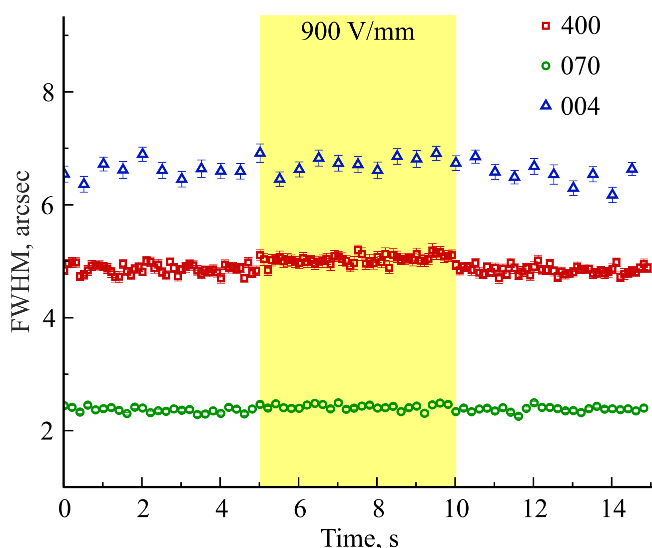

Figure 4. Time dependencies of DRC FWHM of reflections 400, 070, and 004 for RBP under pulsed impact of electric field with a strength of 900 V/mm with averaging over polarity. Yellow color highlights the time interval corresponding to an electric pulse of 5 s.

Piezoelectric moduli for RBP obtained in this study by X-ray diffractometry and comparison with literature data

Piezoelectric modulus	Experimental values (this study)	Literature data	
		[11]	[12]
d_{31}, pC/N	-32.8 ± 0.6	-32.6	-24.3
d_{32}, pC/N	12.8 ± 0.3	13.7	12.0
d_{33}, pC/N	21.8 ± 1.2	26.1	10.2

5. Discussion of results

Values of piezoelectric moduli d_{31}, d_{32}, and d_{33} were calculated by formula (2). For a more precise determination of piezoelectric coefficients, strain values at electric field switching on and off were averaged between each other.

Values of the obtained piezoelectric moduli are listed in the table with comparison against literature data.

The experimental values obtained in this study match well the values obtained by the method of applying quasi-static mechanical loads in [11] and considerably differ from the data obtained by a resonance method [12]. In the method of resonance-antiresonance piezoelectric moduli are determined through the excitation of an electro-mechanical resonance in the crystal with characteristic frequencies in a range of several kHz. In the case of quasi-static method, mechanical loads are applied to the crystal that have much less frequency of the impact, i.e., about units of Hz, and induced charge is detected to serve as the basis to calculate piezoelectric moduli of the material.

The technique used in this study has a quasi-static low-frequency type of impact. The difference between the data of this study and [11] from the data reported in [12] probably is due to the significant difference in impact frequencies.

The fact that he rubidium biphthalate is free from the charge carrier migration effects found in potassium biphthalate is presumably connected with the considerably higher activation energy of rubidium ions, which is confirmed by an order of magnitude difference in resistances of the above-mentioned crystals [24].

6. Conclusion

In this study the time-resolved X-ray diffraction technique was modified in order to apply it in the field of studying the piezoelectric effect in metalorganic crystals of phthalic acid. Using the triple-crystal scheme of X-ray diffraction the dynamics of DRC of reflections 400, 070, and 004 of

rubidium biphthalate crystal was studied under the impact of an external electric field with a strength of 900 V/mm along [001] polar axis of the crystal.

Piezoelectric moduli of rubidium biphthalate d_{31}, d_{32}, and d_{33}, corresponding to three mutually normal strains in the crystal are determined at a high precision. The results are averaged over polarity and over DRC shifts at electric pulse on and off, which are identical in each case.

At the same time the character of DRC change is defined only by piezoelectric strains and no any relaxation processes are observed, that were previously found in potassium biphthalate when threshold values of electric field strength were achieved.

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Conflict of interest

The authors declare that they have no conflict of interest.

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