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INSTRUMENTS AND METHODS OF INVESTIGATION

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Time-resolved X-ray reciprocal space mapping of a crystal in an external electric field

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Contents

1. **Introduction** 179
2. **Technique of time-resolved reciprocal space mapping by triple-crystal diffraction** 180
3. **Experimental facility** 181
4. **Sample under investigation** 181
5. **Results and discussion** 182
6. **Conclusions** 183
References 184

Abstract. **A reciprocal space mapping technique with the use of triple-crystal time-resolved X-ray diffractometry has been developed and implemented using a laboratory X-ray source for the first time. This technique allows studying fast processes that occur in a sample under external influences that cause reversible deformations of its crystal lattice. It also allows distinguishing these processes in time and distinguishing different types of crystal deformations caused by these actions. The essence of the technique is to measure time dependences of the intensity for each point of the reciprocal space in the vicinity of the diffraction maximum in three-axis diffraction geometry by subjecting the sample to repeated and structurally identical action of a strong electric field, with the subsequent construction of the time evolution of the two-dimensional reciprocal space map. The time resolution is achieved with the use of a high-speed multichannel intensity analyzer synchronized with a high-voltage source. The results of measuring the reciprocal space maps with a laboratory radiation source with a time resolution of up to 10 ms are demonstrated for a piezoelectric crystal of lanthanum gallium silicate subjected to an external electric field with the field strength 3.08 kV mm^{-1}, which is close to the sample breakdown value.**

Keywords: time-resolved technique, reciprocal space map, triple-crystal X-ray diffractometry, external electric field, piezoelectric effect, langasite

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1. Introduction

The development of approaches to in situ X-ray investigations of the processes occurring in crystal materials due to external influences is presently a topical problem in the area of structural diagnostics. The existing time-resolved techniques make it possible to study the dynamics of structural changes and thereby distinguish different physical processes in time by their different flow rates. At present, time resolution in the area of X-ray structural diagnostics can be achieved by only a few techniques. A high time resolution (up to tens of femtoseconds) of the pump-probe method [1] is achieved with the use of specialized high-intensity X-ray sources, for instance, with the free-electron lasers developed in several countries. This approach is based on the temporal characteristics of the beam (on its pulse duration) determined by the design of the radiation source, which requires expensive detection and auxiliary instrumentation and imposes certain requirements on the object under investigation and the character of the processes occurring.

Another technique [2] involves the use of fast-response adaptive X-ray optics with bending resonance vibrations, which permits varying the angle of beam incidence on a sample with a high frequency (up to tens of thousands of times per second). An alternative way of implementing time-resolved diffractometry was proposed by a group from Siegen University (Germany) [3]. Based on the use of fast-response recording instruments for measuring diffraction peaks with the time resolution up to several microseconds, it has been implemented with synchrotron [4] and laboratory [5] radiation sources.

A wealth of papers are concerned with the investigation of the effect of external influences on crystals by X-ray diffractometry with laboratory radiation sources. Nonequilibrium processes in crystals under the action of an electrostatic field were studied in Refs [6, 7]; the applicability of X-ray topography for studying the distribution of electromechanical deformations in quartz resonators was demonstrated in Ref. [8].

The methods of high-resolution X-ray diffractometry (HRXRD) and, especially, reciprocal space mapping (RSM)

have long been established as the main tools for structural diagnostics and have gained widespread acceptance in the analysis of the characteristics of epitaxial layers and films [9] and heterostructures [10–12]. In particular, the quantitative analysis of reciprocal space maps allows characterizing different features of the real structure of the object under study (the degree of crystallinity, the type and magnitude of mechanical lattice stress) and obtaining a detailed description of the defect structure: dislocations [13], inclusions [14], and mosaic structure [15].

Here, we propose an approach realizable using a laboratory diffractometer, which combines the capabilities of classical RSM and the cumulative intensity measuring technique with time scanning. This combination was implemented and tested for the first time. It permits a clear visualization of the behavior of a real structure under external influence. Specifically, it allows separating the contribution of this action to the variation of the position and shape of X-ray reflection (Bragg peak) along different directions of the reciprocal space and hence determining the character of emergent deformations. The use of this technique permits separating the influence of physical processes of different nature, which are excited in a sample by the external influence, on the total crystal lattice deformation due to the difference in their flow rates.

2. Technique of time-resolved reciprocal space mapping by triple-crystal diffraction

As a rule, reciprocal space maps are measured in a triple-axis X-ray diffraction geometry with a crystal analyzer placed in front of the detector. The analyzer has a narrower angular acceptance aperture (up to several arc seconds, depending on the analyzer in use) than an ordinary slit collimator and permits precision measurements of the angular intensity distribution of the radiation scattered by the sample. The RSM is performed for different angular deviations of the sample and the analyzer–detector system from the position corresponding to the strict satisfaction of the Wolf–Bragg condition, with the subsequent conversion of the angular coordinates to the reciprocal space coordinates $\mathbf{q}$. The deviation vector $\mathbf{q}$ is the difference between the scattering vector $(\mathbf{k_h} - \mathbf{k}_0)$ and the reciprocal lattice vector $\mathbf{h}$ (Fig. 1) and has two components in the diffraction plane: one, q_z, is aligned with the reciprocal lattice vector and the other, q_x, is directed perpendicular to the reciprocal lattice vector. In this case, ω-scanning in a small angular range corresponds to the coordinate q_x of the reciprocal space (Fig. 1a), and the $\theta/2\theta$-scanning geometry corresponds to the q_z direction (Fig. 1b). Measuring the radiation intensity diffracted by the sample for different combinations of the angular positions of the sample and the analyzer–detector system in the neighborhood of the exact Bragg position allows constructing the entire two-dimensional map of the reciprocal space. For a symmetric reflection, the projections of the $\mathbf{q}$ vector are related to the crystal sample deviation $\alpha = \theta - \theta_{\mathrm{B}}$ from the exact Bragg angle and the analyzer–detector system deviation $\Delta\theta$ by the equations [16, 17]

$$q_z = k_0 \Delta\theta \cos\theta_{\mathrm{B}} \,, \tag{1}$$

$$q_x = k_0 (2\alpha - \Delta\theta) \sin\theta_{\mathrm{B}} \,, \tag{2}$$

where $k_0 = 2\pi/\lambda$ and λ is the X-ray wavelength.

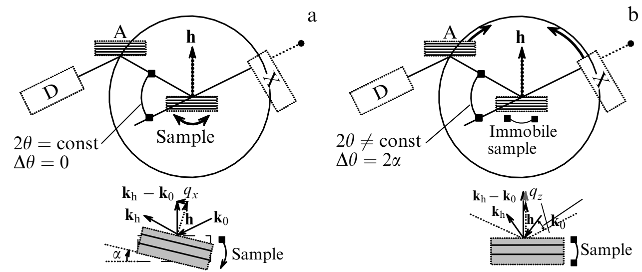

Figure 1. (a) ω-scanning scheme: sample rotation by an angle α (the source and detector are immobile). (b) $\theta/2\theta$-scanning scheme: synchronous rotation of the source and detector by an angle $\Delta\theta$ relative to the immobile sample. Shown under both diagrams is a change in the scattering vector modulus. X — source of the low-divergence monochromatic X-ray beam; A — analyzer; D — wide-aperture detector.

The essence of time-resolved RSM is that the resultant three-dimensional reciprocal space map $I(q_x, q_z, t)$ is assembled from the temporal dependences of the radiation intensity diffracted by a sample, which is measured at each point of the map. To state it in different terms, when the variation of the real structure induced by external influence (for instance, by an external electric field) proceeds in a similar way under the same recurring events of this action, it is possible to measure the temporal dependence of the radiation intensity diffracted by the sample for each point of the reciprocal space $I(q_{xi}, q_{zi}, t)$ in the neighborhood of a reciprocal lattice node and then numerically assemble the resultant experimental data into the entire picture of the reciprocal space map variation in time. Therefore, the method under discussion can be used to investigate only those actions that cause reversible structural changes in the sample, while the action itself can be of any nature: mechanical, light, electromagnetic, etc.

The study of fast processes under external influence invites the use of a fast-response multichannel intensity analyzer, which permits separating the intensity of the signal arriving at the detector into short accumulation time intervals. A purpose-oriented timing system is a generator of electric transistor–transistor logic (TTL) synchronizing pulses applied at well-defined time instants to control a high-voltage source, the multichannel intensity analyzer, and a goniometer. First, the synchronizing pulse triggers the accumulation of signals recorded with a scintillation detector, which the multichannel intensity analyzer distributes over channels of predefined duration (time resolution). Then, at a certain instant, electric voltage of a given magnitude and duration is applied to the crystal due to the synchronizing pulse. After a lapse of time during which the sample is under the external influence, the action is turned off and the goniometer turns the crystal and the analyzer–detector system to a new angular position. On completing the experiment, the resultant data are of the form of time dependences of the radiation intensity scattered by the sample, which are measured under identical events of external influence at each point of the reciprocal space inside some two-dimensional range of the angular scanning mesh. The resultant four-dimensional data array (I, q_z, q_x, t) comprise the time picture of the behavior of the reciprocal lattice node on the diffraction plane prior to and after the application of the external electric field.

3. Experimental facility

An experiment to measure time-resolved reciprocal space maps was carried out on a laboratory triple-crystal X-ray spectrometer (TXS) [18, 19]. This unique laboratory instrument permits carrying out experiments, including those to study the effect of external influences. A special feature of this facility is its unique modular structure, which makes it possible to implement a wide range of X-ray diffraction methods. Furthermore, the diffractometer design provides an accuracy of $0.1''$ for the angular positioning of the object under investigation.

The diffractometer diagram is schematized in Fig. 2. As the radiation source, an X-ray tube is used with a molybdenum anode with the power up to 2.5 kW. The monochromatic incident radiation of low angular divergence (several dozen arc seconds) is prepared with a unit for radiation monochromatization and collimation (a high-perfection Si single crystal whose surface is cut parallel to the system of (110) atomic planes, and a system of aperture slit collimators). Sample rotation about three mutually perpendicular axes, lateral translation of the sample in two directions, and detector positioning are effected with a multiple-circle precision goniometer. To determine the angular position of the radiation diffracted by the sample with high accuracy, an analyzer–detector unit is used, which comprises a high-perfection crystal analyzer similar to the monochromator and a NaI scintillation SDSC-4 detector (Radicon Ltd., Russia) with a dynamic range of 5×10^5 pulse s^{-1}. To investigate the action of an electrostatic field, the facility is additionally equipped with a high-voltage source (up to 5 kV) and auxiliary instruments for implementing time-resolved methods: a timing system based on a Tektronix (USA) clock generator with an oscilloscope and the fast-response multichannel intensity analyzer ORTEC Easy MCS based on a semiconductor field-programmable gate array (FPGA) with a high-frequency input for detector signals. The shortest gating time (time resolution) of the multichannel analyzer is limited by hardware to an interval of 100 ns, because the accuracy of response of the timing system is characterized by a much shorter time ($\sim$ 20 ns). The spatial (angular) resolution is determined by the goniometer accuracy and the stability of the X-ray optical system.

4. Sample under investigation

The object of our investigation is the crystal of lanthanum gallium silicate ($La_3Ga_5SiO_{14}$: LGS, or langasite). The crystals of the lanthanum gallium silicate family are piezoactive materials with a trigonal crystal lattice with the *P*321 symmetry group. Although this crystal family was initially synthesized for the frequency tuning of solid-state lasers, langasite, owing to its properties and a high electromechanical coupling coefficient, is currently finding increasing application in many sensors as a substitute for quartz, which has been traditionally used in piezo-engineering. Among the virtues of this material is also the absence of hysteresis in the physical properties and of phase transitions up to the melting temperature. Because of high demand, this crystal material is frequently used in extreme conditions: at high temperatures and in strong electromagnetic fields. However, the effect of external influence on the real structure and functional characteristics of langasite is barely described in the literature.

It is noteworthy that langasite-family crystals are multicomponent (Fig. 3a), and therefore the study of external influence on the structure of these crystals is of practical interest from the standpoint of determining the relation between the structure and physical properties of these crystals.

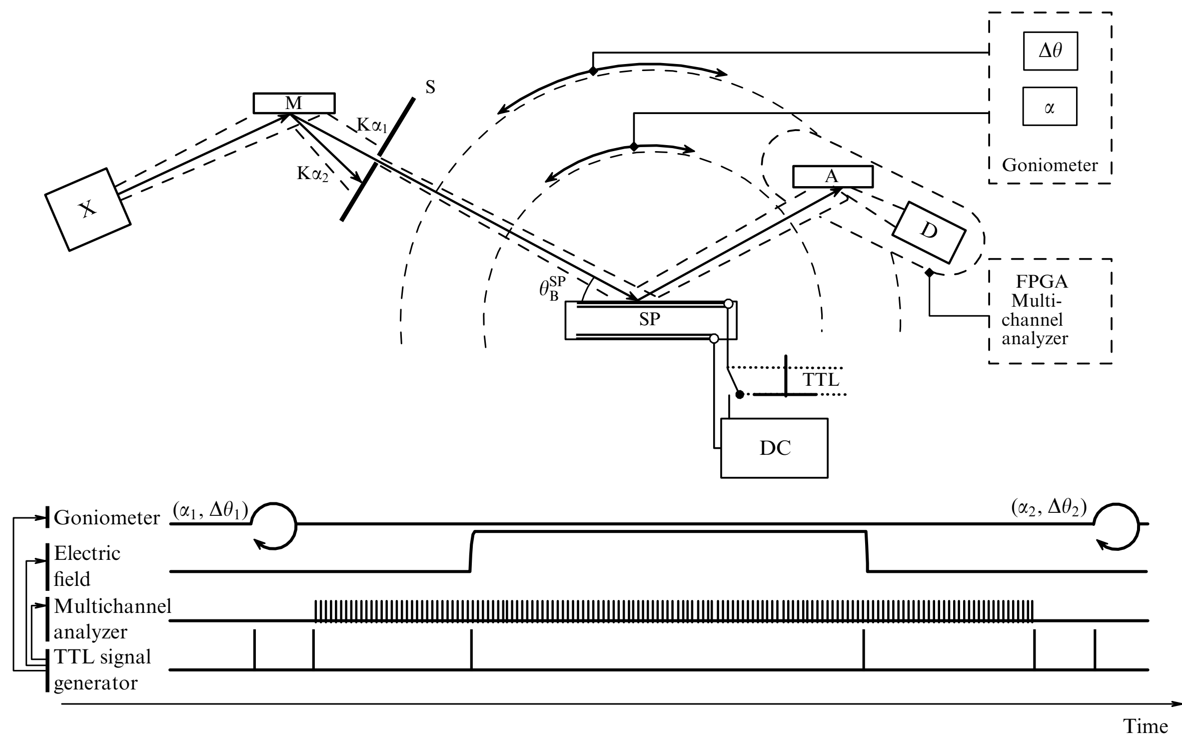

Figure 2. Diagram of experimental facility intended for time-resolved diffractometry and measurement of triple-crystal diffraction reciprocal space maps with the use of a multichannel detection and timing system. X — X-ray source (X-ray tube), M — monochromator, S — collimating slit, SP — sample, A — analyzer, D — detector, DT — high-voltage DC source, TTL — transistor-transistor logic.

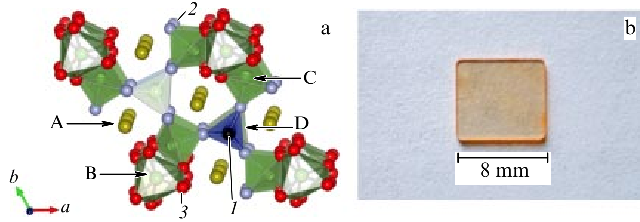

Figure 3. (a) (Color online.) Combination of coordination polyhedrons in a langasite crystal lattice cell: projection *a–b* [20]. Ga atoms are shown in green (B, C, and a half of D positions), Si atoms are located in blue polyhedrons (half of D positions), and La (A) atoms are indicated in yellow. O1 oxygen positions are marked in black (*1*), O2 in blue (*2*), and O3 in red (*3*). The LGS crystal under investigation before deposition of current conducting contacts.

The piezoelectric modulus matrix of the crystal consists of four components. On applying an electric field in the crystal direction [110], three components of the piezoelectric tensor are active: d_{11}, d_{12}, and d_{14}.

To study a sample, we prepared and preliminarily polished a plate $8 \times 8 \times 0.65$ mm in size. To remove the damaged layer by chemical etching, a 3:1 mixture of a 32% aqueous solution of hydrochloric acid HCl and a 66% aqueous solution of HNO_3 was used. Upon etching, on the sample surface corresponding to the [110] crystallographic orientation, we deposited 70 nm thick Ag electrodes with a 30 nm Cr sublayer to improve adhesion.

Preliminarily determined for the crystal sample studied in this work were the values of electrophysical constants, which agree nicely with the data found in the literature [21, 22]. The resistivity of the sample, equal to about 10^{14} Ω mm, characterizes it as a good dielectric. By and large, the ion–electron type of conduction is characteristic of pure langasite: for high values of specific partial oxygen pressure, ion conduction prevails [23] owing to the mobility of oxygen vacancies, while for its low values, electron conduction prevails, which is attributable to the appearance of electrons due to reduction.

5. Results and discussion

An experiment to study the dynamics of the crystal structure of lanthanum gallium silicate in a high-intensity electrostatic field was performed in a triple-crystal quasi-dispersionless scheme in a reflection geometry. The area of sample X-ray irradiation, which was limited by the 0.2×8 mm slit aperture, was selected so as to optimize the relation between the intensity of incident radiation and its divergence.

To gain information from different depths of the surface layer, our experiment was carried out using two orders of symmetric reflection: 220 reflection (the Bragg angle $\theta_B = 10.0°$, and the extinction depth $L_{ext} = 4.59$ μm for the $MoK\alpha_1$ line radiation) and 440 reflection ($\theta_B = 20.3°$ and $L_{ext} = 15.34$ μm). For each of the above reflection orders, we used the corresponding reflection orders of a silicon monochromator and analyzer crystals, 220 ($\theta_{M1} = 10.6°$) and 440 ($\theta_{M2} = 21.2°$), in order to minimize the magnitude of dispersion in the quasi-parallel diffraction scheme. The halfwidths of the 220 and 440 diffraction peaks, which were preliminarily measured by double-crystal diffractometry, were 3.7″ and 3.1″, respectively. Their good agreement with the calculated values (3.2″ and 3.0″) is an indication of high structural perfection and suggests that the surface damage layer is hardly present.

In the execution of the time-resolved experiment to measure the reciprocal space map of the langasite crystal, measurements were made by mechanical rotation of the sample at increments of 0.5″ and the analyzer–detector system at doubled increments of 1″ within angular ranges such that the two-dimensional mesh size was 21×21 points.

For each combination of the angular position of the sample and the analyzer–detector system corresponding to a separate point of the reciprocal space, we measured the time dependence of the radiation intensity diffracted by a sample exposed to the external electric field of fixed magnitude and duration. The electric field was applied to the crystal in the first second after the start of intensity measurements by the multichannel analyzer. The field was removed in 2.5 s, after which 2.5 s more was allocated for relaxation prior to the passage to the next reciprocal space coordinate. The applied voltage was 2.00 kV; in view of the sample thickness, this is equivalent to the field strength of 3.08 kV mm^{-1} in the bulk.

The duration of the analyzer channel during the intensity recording cycle, which determines the time resolution, was specified such that the intensity accumulated in the experiment was sufficient for an unambiguous approximation of reflection by a two-dimensional analytic function. For the 440 reflection, the time resolution was equal to 50 ms. For the 220 reflection, which exhibits a high reflectivity (including that from the monochromator and analyzer crystals), it was possible to achieve a time resolution of 10 ms. Considering the ranges of two-dimensional angular scanning mesh and the time of accumulation at each point, the overall duration of the experiment for one reflection order amounted to about 45 min. Critically important for the successful execution of the experiment is a good thermostating of the environment.

From the resultant time dependences of the intensity, we formed a four-dimensional data array, which was next converted, in accordance with relations (1) and (2), to reciprocal space coordinates q_x and q_z to obtain a diffraction 'movie' — a set of reciprocal space-map-frames depicting the reciprocal lattice node at each instant. Figure 4 shows the reciprocal space maps of the 220 reflection at the instant of electric field imposition on the crystal. Figure 5 corresponds to the 440 reflection order with a narrower peak. Subsequently, each such map was processed using a two-dimensional pseudo-Voigt function approximation algorithm written in the Python programming language. Based on these approximations, for the 440 reflection order we constructed the cross sections of the lattice node in the reciprocal space for the crystal prior to the field imposition (Figs 6a and 6b) and the time dependences of the peak position during the imposition of the electric field on the sample (Figs 6c and 6d).

The resultant data clearly demonstrate the behavior of the reciprocal lattice node in time when the crystal is exposed to an electrostatic field. For the electric field strength of 3.08 kV mm^{-1}, which is close to the breakdown value, lanthanum gallium silicate manifests itself as a piezoelectric with a high resistivity. In the course of experiment, the diffraction peak shifts along the q_z axis, which is caused by a variation in the interplanar spacing due to the inverse piezoelectric effect (of the piezoelectric modulus d_{11}) in the crystal under the action of an external field. An analysis of the resultant experimental data shows the absence of relaxation broadening effects [5, 6] and of variations in the integral reflection spot intensity characteristic of the motion of charged macrodefects to the surface region, which testifies to a high structural perfection of the crystal element. The

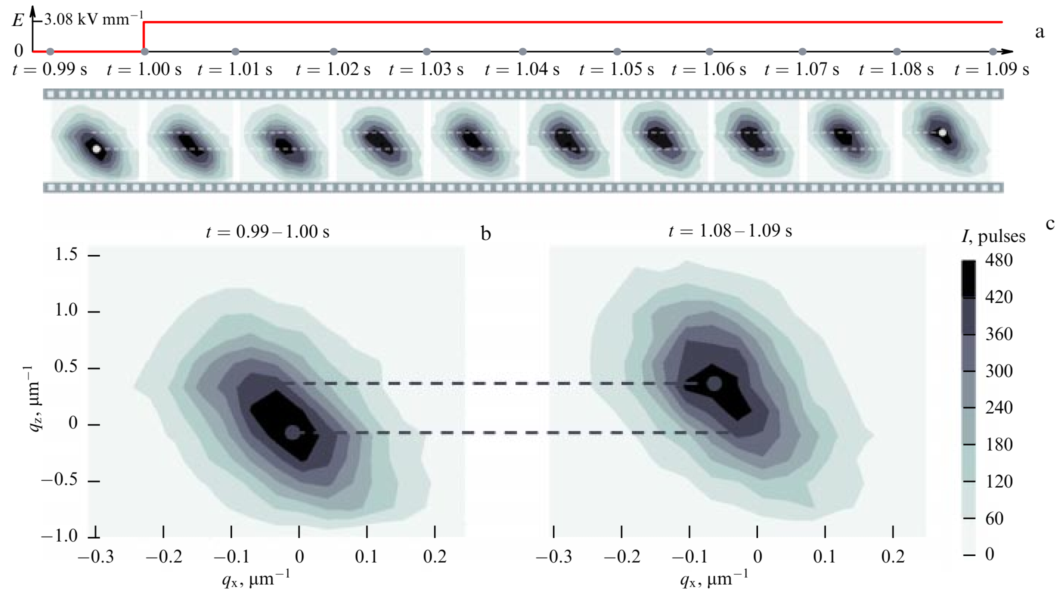

Figure 4. Reciprocal space mapping in the vicinity of the 220 reflection of a langasite crystal. (a) Dynamics of the reciprocal lattice node variation at the instant of electric field imposition. The indicated time coordinate corresponds to the beginning of exposure, whose duration determines the time resolution and is equal to 10 ms for each frame. Image of the reciprocal lattice node (b) prior to the imposition and (c) after the electric field with the strength 3.08 kV mm^{-1} sets in within the crystal volume. The high-voltage source is engaged in the first second.

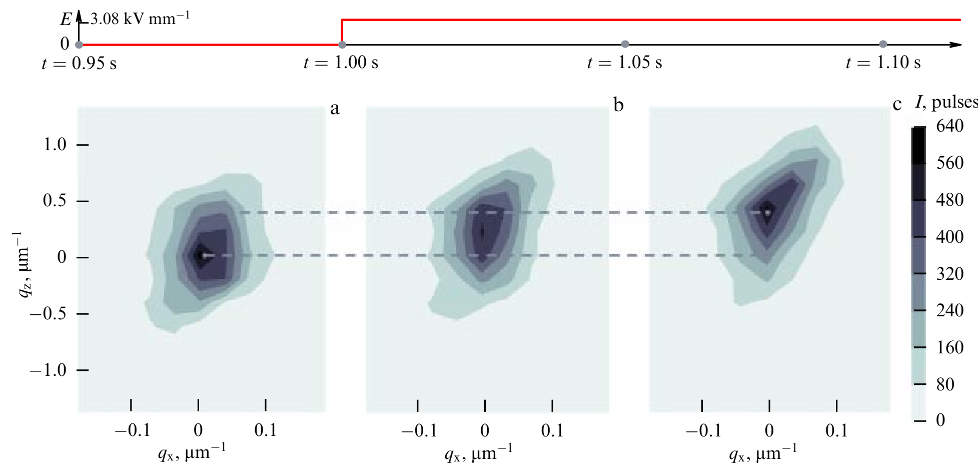

Figure 5. Reciprocal space map in the vicinity of the 440 reflection of langasite: position of the reciprocal lattice node (a) prior to and (b, c) after the imposition of the 3.08 kV mm^{-1} electric field on the crystal. The electric field is turned on in the first second. The exposure of each frame (time resolution) is equal to 50 ms.

effect of a short (several microseconds) inertia in the angular shift of diffraction peaks at the instants of imposition and removal of the external field is due to the temporal characteristics of the voltage source actuation. Furthermore, the displacement of the reflection spot along the q_x direction after the imposition and removal of the electric field whose magnitude varies exponentially with time suggests that charge carriers moving in the bulk of the sample are redistributed nonuniformly, partly compensate the external field, and are responsible for the bending of the sample.

Proceeding from the shift of diffraction peaks, we calculated the average relative lattice deformation $\varepsilon = 1.4 \times 10^{-5}$, which corresponds to the piezoelectric coefficient $d_{11} = 4.5 \pm 0.2 \times 10^{-12}$ C N^{-1}. To verify this result, the piezoelectric modulus was also determined by a direct quasistatic technique, which involved measurements of the induced charge versus the applied force. The value $d_{11} = 4.62 \times 10^{-12}$ C N^{-1} obtained with this technique agrees nicely with the X-ray measurement data. The piezoelectric modulus given in Ref. [24] is 6.16×10^{-12} C N^{-1}. This difference may arise from the conditions of crystal growth, in particular, from the oxygen atmosphere, which may exert an appreciable effect on the real structure of the crystal and its properties.

6. Conclusions

In this paper, we developed and for the first time implemented a technique for time-resolved reciprocal space mapping with the use of a fast-response multichannel intensity analyzer and a laboratory X-ray source. We demonstrated the possibility of using this technique to investigate the influence of a strong electric field (up to 3.08 kV mm^{-1}) on a piezoelectric crystal of

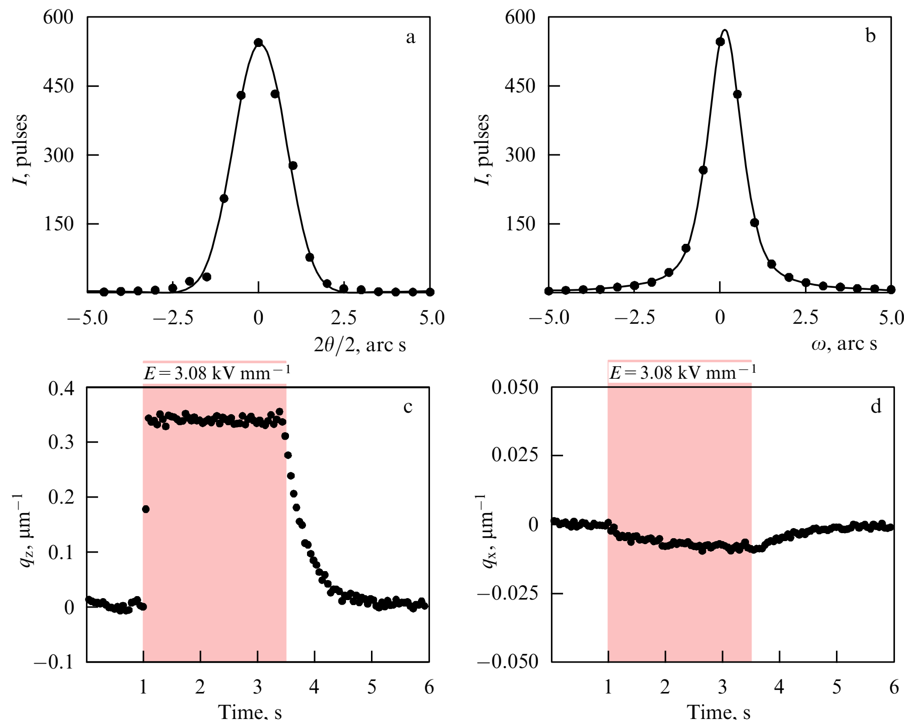

Figure 6. Cross section of the 440 langasite reflection spot in coordinates (a) q_z and (b) q_x prior to field imposition, and (c, d) the corresponding dynamics of the reciprocal lattice node position measured in the triple-crystal diffraction scheme after the imposition of an electric field with the field strength 3.08 kV mm^{-1} on the crystal. The electric field is turned on in the first second and turned off after 3.5 s. The time resolution is 50 ms.

lanthanum gallium silicate. The time resolution that was possible to achieve with a laboratory radiation source was 10 ms for the 220 reflection and 50 ms for the 440 reflection of the langasite crystal. The variation in the lattice node position in the q_z direction of the reciprocal space corresponds to the crystal lattice deformation caused by the piezoeffect in lanthanum gallium silicate on imposing of the electric field along the [110] direction. A small change in the node position in the q_x direction, which corresponds to the possible bending or rotation of atomic planes, may result from a redistribution of charge carriers in the bulk of the crystal, which compensate the external field nonuniformly. This kind of separation of different deformation types is impossible with the use of classical double-crystal diffractometry.

A further enhancement of the proposed approach for obtaining higher-quality experimental data is possible by upgrading the experimental equipment. First, the use of a synchrotron source would greatly increase the intensity of incident radiation, which would permit the total experiment duration to be significantly shortened. Second, an improvement in the signal-to-noise ratio due to vacuum channels would permit operating with weaker reflections. Furthermore, the use of avalanche photodiodes broadens the dynamic intensity range, which, in view of the above improvements, allows improving the time resolution to several nanoseconds. Unfortunately, there is no way of studying irreversible processes with the use of this technique: in this case, it is necessary to record the entire reciprocal space map at each instant, which can only be realized with the use of a bright synchrotron radiation source and a two-dimensional detector, whose present-day count rate is limited to a few milliseconds.

Acknowledgments

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