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**TlBr CRYSTAL OPTICAL, ELECTRICAL AND
SURFACE PROPERTIES INVESTIGATION;
X-RAY AND γ -RAY DETECTORS
DEVELOPMENT**

Summary of the Doctoral Thesis

Promotion to the Degree of Doctor of Physics

Subbranch: Solid State Physics

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Abstract

TlBr crystals are used as room temperature radiation detectors which are applicable for x- and γ - ray detectors. The detectors are used in energy range from 5 keV to 1 MeV. These detector characteristics give an opportunity to apply them in space applications, medicine and also for radionuclide analysis. In spite of the achieved progress of the detector production technology the several problems of the TlBr detector production still take place. Due to these problems the detectors produced on TlBr crystal bases cannot be used as commercial production. At the present moment the several companies try to improve the technology of TlBr crystal growth to get a qualitative crystal for using in the optical devices in infrared spectral range and as radiation detectors. The electronic processes are poorly investigated and the information about interaction between electronic excitation and crystal intrinsic defects is insufficient. The general aim of this work is to obtain and summarize the information usable for producing the radiation detectors based on TlBr crystals of good quality. Therefore the investigation of electronic properties the TlBr crystals have been carried out and compared with properties of radiation detectors made from the same crystals. In the present work the obtained results have been described and discussed. The correlation between the crystal optical properties (absorption, luminescence) and the radiation detectors spectrometric characteristics was found. The recommendations have been elaborated for the crystal growth improvement. Also the processing of TlBr crystal surface for radiation detector fabrication has been improved.

1. Introduction

Two types of devices are used mainly for x- and γ -ray radiation registration. The first type of the detectors (I) is scintillation detectors. In these detectors the energy of ionizing radiation are transformed to visual light and then photo sensitive detector are converted to electric signal. The second type (II) of the detectors is the detectors which directly converts ionizing radiation to electric signal. The second type has some advantages in comparison to the first type. In the first type detectors the optical signal should be converted to electrical signal and responding time are limited by the luminescence center excited state lifetime. In the second type of the detectors the electric signal is obtained immediately and provides response in a very short time. Using the solid state crystals as the radiation detectors the charge carries are appeared in conductive and valent zones and the life time of the charge carries is very small. Due to this reason the second type detectors are widely used. The materials for this detector type are germanium, silicon or CdZnTe (CZT) crystals. All type of these crystals has relatively small band gap width (0.67 eV Ge, 1.12 eV Si and 2 eV CZT). Due to this reason the concentration of free charge carries induced by thermal energy is relatively high at room temperature and ionizing radiation registration is complicated or even impossible. The detectors are cooled down often to liquid nitrogen temperature. Now there is an intensive search for detector materials with opportunity to operate at room temperature without deep cooling. The band gap width of this material should be wide but not too much because the charge carries generation should be sufficiently effective.

The thallium bromide (TlBr) crystals meets these requirements and is very promising material for uncooling radiation detector operation. Good quality detectors for x- and γ -radiation in energy range from 5 keV to 1 MeV have been produced sometimes from these crystals [1]. But till now the radiation detectors production from TlBr crystals with good spectrometrical performance (energy resolution) is still problematic.

1.1 Motivation

The suitable TlBr crystals as a detector material should have the following properties: relatively high density (7.56 g/cm³), and high average atomic number [2] which define the electromagnetic ionizing radiation stopping efficiency and high generation electron-hole pair efficiency. The thermodynamically balanced concentration of charge carrier is relatively low at room temperature due to wide gap band. But till now the material is not fully investigated for detector production and the several unsolved problems, which prevent the

fabrication the ionizing radiation detectors as serial product take place. One of these problems is as follows: sometimes TlBr detectors have good quality high efficiency and energy resolution, but sometimes the fabricated detectors do not operate at all. The reasons probably may be in unsatisfactory quality of the crystal impurity. The second reason may be the presence of the dislocations or morphology of monocrystal – the crystal could have different blocks. The systematic results of this properties investigation cannot be found in literature therefore one brunch of this investigation is relating to resolve this problem. The next important problem is the contact quality. The crystal obtained after cutting from big grown monocrystal boule is not suitable for the contact deposition. To solve this problem the crystal surface treatment studies have been done. The crystal processing impact studies was made to solve this problem. By contrast charge carrier generation and the charge carrier collection efficiency of the material processes of electronic processes – charge carrier trapping levels in the band gap, chargecarrier scattering on defects, chargecarrier mutual recombination. The qualitative detector fabrication requires the search how and what are electronic processes in the material and the details of these processes in the scientific literature are pretty stingy, then turning to the exploration of the problem. These three issues are very important for the development of TlBr high-quality production of ionizing radiation detectors. In conclusion it should be mentioned that the quality of the TlBr radiation detectors are promising for application in space medicine and radionuclide detection and analysis

1.2 The aim of this work

The general aim of this work is to obtain and summarize the information that would be used to produce the high-quality ionizing radiation detector based on TlBr crystals.

1. Clarify at least some of the criteria for assessing the suitability of a good crystal TlBr radiation detector manufacturing.
2. Develop techniques in TlBr single crystal surface processing in order to provide high-quality electrical contact creation.
3. Clarify how the TlBr crystal electronic properties correlate with the radiation detector spectroscopic properties.

To achieve this aims the following things have been done:

1. The optical properties study of TlBr crystals (the fundamental absorption edge position, luminescence spectra and kinetics, short lived absorption induced).
2. TlBr crystal surface properties study (surface etching, microhardness determination and optical microscopy).

3. Electric properties study (volt-amps curves, resistivity).
4. Ionizing radiation detector fabrication from the TlBr crystals and its spectroscopic properties.

1.3 Author's contribution

In the framework, the author together with the company BSI Ltd. staff participated in the TlBr crystal grow in initiating and organizing the crystal growth in GIREDMET (Moscow Institute), as well as in Korth Crystal Company (Germany). The feedback was made between the crystal-growing companies and researchers, which could modify the crystal growth to produce crystals with predictable crystal optical properties and spectrometric characteristics. The author has carried out the preparation of the detector samples (sample cutting and surface treatment), experiments (luminescence and absorption spectra recording and processing of results, the crystal surface of optical imaging and volt-amps characteristic registration). Detectors from the TlBr crystals were manufactured and tested in the company BSI Ltd. The work has been presented at the several International conferences as posters and oral presentations. The results are published in 11 scientific journals, including 10 international journals

1.4 Scientific novelty

The scientific novelty of this work is that for the first time we compared the results obtained in the TlBr crystal optical properties studies in the radiation detection properties, which are made of these crystals. The correlations between optical properties and TlBr radiation detector spectrometric properties have been found.

The work is also important for improvement of radiation detector technology production. Detector manufacturing technology cycle is proposed. A new surface treatment technology and methods of quality control (microhardness method and visual inspection using optical microscopy) were used. The recommendations of TlBr crystal manufacturers for the improvement of detector crystal quality (spectrometric parameters) have been done.

2. Literature review

2.1 Defects, electronic excitations, luminescence mechanisms and fundamental absorption edge of thallium halides

Thallium halide crystals were used in infrared spectroscopy (lenses, windows, fiber optic) [3] and for the production of ionizing radiation detectors [4].

The question of intrinsic defects structure, impurities and radiation induced defects is very important in all thallium halide practical application directions as well as different electronic excitation and their interaction with mentioned defects. This is significant due to optical absorption, luminescence, electrical conductivity and electronic relaxation processes dependence on defects.

Impurities can take cationic or anionic sites in thallium halides replacing the thallium or halogen ions. The Cl^- and I^- anions are homogenous impurities in TlBr . Since TlCl and TlBr crystals have the same crystalline structure the TlCl - TlBr continuous solid solutions are possible. The TlI and TlBr crystals have different crystal structure and therefore can only be a partial substitution of Br ion with I ions, the iodine concentration of TlBr crystals cannot exceed 10%.

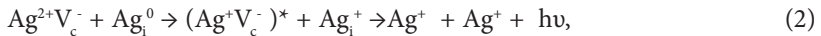
For the studies of the radiation defects and processes in TlBr crystals the analogy with silver halides was used since the defects formation is widely studied and there are more data in the literature. It is known that the structural point defects – vacancies and interstitial ions – mainly are formed in cationic sublattice (Tl^{++} and V_{Tl}^0) [5]. Radiation-induced primary defects (Frenkel pairs), the model and the possible formation mechanism are described in [6], there are shown that the primary defect pair consist from the interstitial thallium (Tl_i) atom and the vacancy ($\text{Tl}^{++}\text{V}_{\text{Tl}}$) nearest hole located at thallium ion with nearest cation vacancy. It is assumed that the defect pair can be formed as a result of unradiative decay of electronic excitation – exciton. Similar processes are the primary defects and the formation of silver halide. The main argument is that the defect pair could be formed by annihilation of electronic excitation is seen in experiments, colloidal silver or silver and the formation of thallium thallium halides ultraviolet or even visible light exposure. It is known that Colloidal point for effective formation of the silver halide grain surfaces and facilitate the emergence of specially recorded impurities – sensitizers [7].

The defect studies use both luminescent and absorption spectroscopy. For example, silver chloride has been widely studied photoluminescence 2.5–2.6 eV spectral region [6, 8] and it is shown that this luminescence band is due to selftrapped exciton decay. The process is described by the reaction:



where Ag^{2+} is selftrapped hole and $(\text{Ag}^+)^*$ selftrapped exciton. Selftrapped hole in AgCl crystal form complexes $\text{Ag}^{2+} \text{Cl}_6^-$; the existence and the center has been studied by electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) techniques. To center corresponding absorption band is at 1.2 eV [9]. In thallium halides EPR signal of Tl^{2+} has not been observed so far, but just short living absorption is observed in the spectral region, which is close to 1 eV [5] and it is concluded that of the thallium halides hole can be localized in the thallium ion.

AgCl crystal luminescence decay kinetics is explained by diffusion-controlled recombination process model, which is theoretically described in [7]. According to this description the process is as follows:



Probably in thallium bromide primary defect pair formation and exciton annihilation is similar to that described in the reaction (2), only the silver instead of the thallium. The diffusion controlled recombination model, for the theoretical description of the TlBr crystals luminescence still should be developed.

Thallium halide luminescence studies are described at a number of works [5, 10, 11]. At low temperatures, as well as under the excitation pulse the luminescence band at 2.2 – 2.5 eV region was observed. The luminescence band maximum shifts to a high-energy side of the row of solid solutions $\text{TLI} - \text{TlBr} - \text{TlCl}$. In the all thallium halides luminescence nature are similar to (exciton annihilation) and luminescence band peak shift caused by Tl ion surroundings change – one halogen ion replacement by another.

In the stationary luminescence studies of TlBr crystals the band at 1.8 eV are well-observed, which according to existing point of view are associated with interstitial Tl ions or aggregates [7]. A similar luminescence band was observed in TlCl crystal at 1.9 eV and it was concluded that it could be related to unstechiometric Tl ions excess of the crystal [12], while [13] concluded that the luminescence from the electron and hole recombination at the center, containing the cation vacancy. In [14] concluded that the 1.9 eV band is associated with thallium colloidal particle formation thallium chloride. Primacy of thallium atoms can be ionized as a result of light absorption and conductivity zone electrons recombine these centers to observed luminescence.

Summarizing the previous description, we can conclude that the luminescence of 1.8 – 1.9 eV spectral region TlBr crystals is probably associated with interstitial thallium atoms, or by the atomic units, in experiments with the use of thallium-enriched crystals makes the unlikely possibility that the luminescence center of

the composition could have a cation vacancy. The above-mentioned possibility that the thallium atoms in the unit one of the atoms are ionized and the reunion of an electron is observed luminescence is not the only cause. The other option: if the crystal is thallium colloids or smaller units, then there is the possibility that the crystals are also more certain, implements and void, thallium interstitial atoms and the thallium concentration in interstitial atom can be localized hole, which constitute a unique adhesion electron interstitial existing exciton $(\text{Tl}_i^0)^*$. The emitting photons such can also be exciton decay:



Thallium bromide zone structure studies [15, 16] show that for the fundamental absorption edge the indirect electron transition is responsible (~ 2.67 eV). However the indirect transitions region overlap with the direct electron transition (~ 3.02 eV). For this reason, the fundamental absorption edge of the area spectrum is observed in the step [17]. The excited luminescence near absorption edge define the both processes indirect exciton formation (~ 2.67 eV) and the direct exciton formation (~ 3.02 eV).

Fundamental absorption edge shift was described by Urbah's law [18], which is a universal law for various substances, regardless of band type (ionic, covalent), and structural arrangement (glass, crystal). Usually increasing the temperature, the fundamental absorption edge shifts to lower energy side (the forbidden zone width decreases). The law could not be realized for thallium halides. The exciton absorption peak shifts to high energy side with temperature increases. The effects mentioned cause is not clear, but it could be exciton-phonons specific cooperative process due to, for example, special phonons frequency distribution function dependence on temperature, or the whole complex phonons interaction process (for example, optical branch of phonons unharmonical interaction with phonons states continuum). There are not experimental facts to show the benefit of any of the above mentioned possible causes.

2.2 Ionizing radiation semiconductor detector operation principle

The semiconductor detectors have an important in nuclear physics leads in apparatus arsenal and its role on elementary particles (quantum) physics is growing. The semiconductor radiation detector has the following principal advantages:

- 1) The energy required for a single electron-hole pair formation is small (silicon, germanium ~ 3 eV, TlBr ~ 9 eV).

- 2) Ionizing radiation penetration depth on solid-state detectors is significantly higher than for the gas filled ones.
- 3) In solid state detectors the charge carriers mobility of electrons and holes should be approximate equal, it means that the charge collection time of the electrodes are close and do not result in serious difficulties of the registration of quantum or particle with different penetration depths.
- 4) Despite the fact that the semiconductor detector resolution is lower than magnetic detectors it is possible to obtain whole spectrum simultaneously by using semiconductor detectors.

The energy (E) higher than the band gap (E_g) is required to form electron-hole pairs. If the band gap width is large enough, then a small electric field does not cause the electrical current of detector. Conversely, if the band gap width is small, the part of the valent zone electrons due to thermal fluctuations can transit to conduction zone and it is appeared current, called leakage current or the dark current.

Under ionizing radiation in semiconductors the valent zone electrons or electrons from deeper energy levels transfer to conduction band or to higher level empty energy bands. As a result at the beginning the electrons appear in free bands and the holes at the beginning complete the valent band. After secondary interactions and the energy dissipation by fonons emission during a very short time (~ 10 – 12 s), all the electrons relax to the bottom of conduction zone but holes to the valent band top. Due to the fact that part of energy is spent to fonons excitation, the process of energy required for electron-hole pair formation is above the band gap width (2 – $3 E_g$).

Semiconductor detectors are essentially analogous to the gas ionization chamber, where the operating media – the gas is replaced by a solid state environment. As in any device, based on the ionization principle, the information on the about particle (quantum) energy gives the electric charge, which was created during a particle (quantum) and the detector material interaction - the larger particles (quantum) energy, the higher the charge is created in the detector material. The following conditions have to be copleted for ensure the radiation spectrometry:

- 1) The quantum of irradiated energy should trap the detector to the sensitivity region (i.e. the strong field areas);
- 2) Quantum generated electron-hole pairs must be fully collected on the electrodes to provide an electrical signal proportionate absorbed quantum energy;
- 3) To ensure sufficient energy resolution the output noise should be minimal.

Let us look what characteristics of the material must correspond for producing of ionizing radiation solid-state (semiconductor) detector.

First, it is necessary for high-energy particles or photons to interact with a substance creating a lot of electron-hole pairs. Electron-hole pairs in semiconductors concentration are linearly related to the quantum energy that is absorbed matter, however, the more electron-hole pair formation energy is lower, the easier it is registration of low-energy quanta.

Second, the detector circuit shown in the external power signal, charge carrier mobility in outer electric field must be large enough. In order to be fulfilled linearity between the absorbed quantum energy and the current pulse amplitude, charge carrier should be unwanted catch of the trap. This means that charge carrier trapping probability of the traps should be the minimum possible, if the trap concentration is small, and both electrons and holes have high mobility.

Third, the detectors registered a weak signal, then the detector leakage (dark) current should be minimized at the detector added to high electric voltage required for operation of the detector.

And finally, the material must be appropriate for relatively small detector of ionizing radiation or particle radiation should be completely absorbed. The free length is depend on the nature of the substance: the substance is denser and higher Z , the smaller size detector can be used [19].

Detector energy resolution is one of the main detector characteristics. Energy resolution mainly determines the ionization loss of statistical fluctuations. These fluctuations are the reason of the energy peak, corresponded to a falling monoenergy beam is spread. Energy resolution is defined as the shift of the quadratic average amplitude maximum from the amplitude value. In other words, the energy resolution(ΔE) is defined as the peak (corresponding to energy E) width on half maximum (FWHM).

was used to initiate electron beam pulse of 10 ns and halfwidth motion energy 270 keV. Xenon lamp, which operated on a pulsed mode was applied as the probing light source. Sample temperature in the experiments was possible from 80 K to 600 K. Registration of the channel time resolution is determined by photomultiplier tube (PMT).

The time resolution is 12 ns via PMT-100. PMT-100 signal recorded in a given memory oscilloscope TEKTRONIX TDS – 5052B, the time resolution is 0.7 ns. Facility for diffraction monochromator MDR-2 the spectral range is 200-2500 nm. Equipment can also be used with electron beam induced fluorescence spectral-kinetic studies. Luminescence radiation is focused on the monochromator entrance slit and the xenon lamp is applied.

3.1.2 Luminescence spectroscopy

Luminescence registration was also used by two methods – spectrum registration, the continuous motion of sources (stationary luminescence spectra), and luminescence spectra and decay kinetics of the registration, the impulsive Initiative (luminescence with a time resolution). For source of excitation in stationary luminescence experiments x-rays irradiation was used. Fluorescent intensity of the registration has made photon counting mode.

Sample temperature in the experiments was possible from 80 K to 600 K. Prism monochromator SPM-1 was applied. X-ray tube anode voltage was 50 kV, current up to 10 mA. Mercury lamp was used to create a model of colloidal samples irradiated with unfiltered light of this lamp.

Luminescence with a time resolution of recorded has used two systems – the equipment already described above where the luminescence suggested electron beam pulses and other equipment, as proposed by the luminescence of YAG: Nd laser radiation of the fourth harmonic (266 nm, or 4.66 eV) pulses. In this facility, in difference from the equipment in which the luminescence is excited by an electron beam, the sample temperature experiments can be vary from 12 K to 350 K. Intensity of luminescence shall be executed by the photon counting method, the kinetics of the registration provides a wider dynamic range than oscilloscopic method. Impulse length at half width is 2 ns, the resolution time of registration channel is 0.25 ns.

3.2 Sample surface hardness and optical microscopy equipment

For the surface quality control the microhardness method (Vickers) and optical microscopy methods have been chosen. The methodology of the microhardness measurements are shown in Fig. 2.

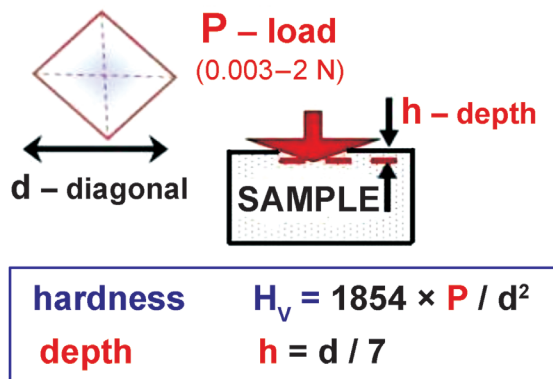


Fig 2. The operation principle of equipment for microhardness (H_v) measuring

Experiments were used by Bridgman-Stockbarger method grown TlBr single crystals. Different series of samples (A, L and S), with a thickness of 2 mm square and 5x5 mm² were analyzed. Microhardness measurements were used for microhardness meter PMT-3 (LOMO, Russia) with improved loading node, using the Vickers pyramid as indenter. Microhardness HV was calculated in $1.854 P/d^2$, where P is load and d is the pyramids left by indentation diagonal length, measured in the optical microscope.

3.3 Radiation detector spectroscopic properties

TlBr crystals produced from the radiation detectors of spectroscopic parameters were determined and the detector performance was examined using a device with a functional scheme seen in Fig.3.

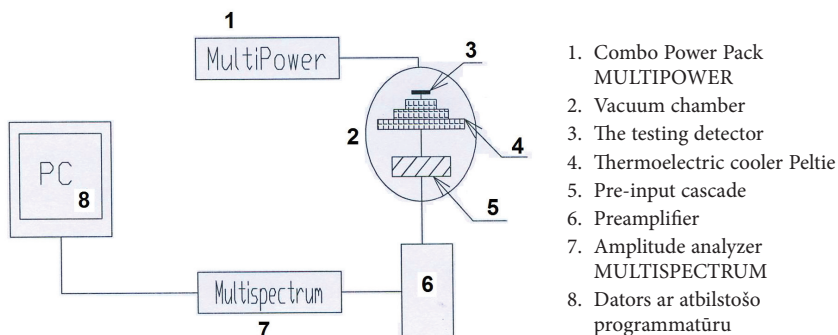


Fig. 3. The functional scheme for testing the radiation detector spectrometric parameters

The facility for the radiation detector testing with different gamma-ray energy is shown on Fig. 3. Gamma rays in the vacuum chamber go from Be window not shown in Fig. 3. The radioisotopes that give monochromatic gamma rays, namely, Fe-55, Am-241, Co-57 and Cs-137 were used for gamma-ray sources. Such isotopes emit gamma radiation energy of 5.9 keV, 59.6 keV, 122 keV and 662 keV. It was possible to verify the detector performance broad gamma-ray energy region applying these sources.

3.4 Investigated samples

The samples used for the study are cut out of plates in the form of large array of single crystals, which are supplied by two organizations, which grow TlBr single crystal. One of the organizations is Russian GIREDMET (Moscow), which has many years of experience in the treatment of thallium halide impurities and the single crystal growing. Purified TlBr was used for large, bulky single crystal grown by Bridgman-Stockbarger method. The other organization is German Korth Crystal where TlBr crystal growth is newly launched process and it operates traveling molten zone method for TlBr purification and obtaining an array of single crystal. In the work described studies the numbers of samples and the growth method are described below.

Investigated crystals:

- grown by Bridgman-Stockbarger method : M12, M13, M14, A8a, A8b, A8c, Z3a, Z3b, Z4a, Z4b, A1(B1), L, S;
- grown by travelling molten zone method: 4R, 4RB1

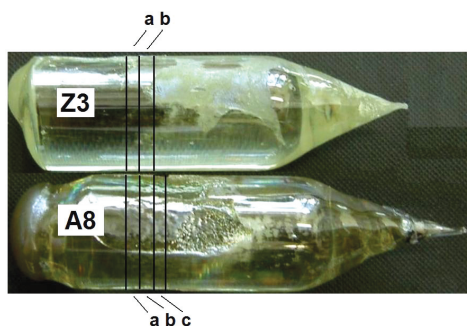


Fig. 4. TlBr crystals grown by Bridgman-Stockbarger method.

The largest numbers of studies of the crystal were grown by Bridgman-Stockbarger method in the Moscow organization GIREDMET. The picture of the TlBr crystals grown by Bridgman-Stockbarger method is shown on Fig. 4.

Bridgman-Stockbarger method has been widely distributed in various laboratories for crystal growth [20]. This method is almost the only one that allows growing of thallium halide crystals for using them in industrial uses. The main advantage of this crystal growth method is the possibility to grow the large-diameter (~ 4 cm) thallium halide crystals. Fig. 4 shows TlBr single crystal wafers grown by this method. Figure demonstrates that the crystals are different in visual appearance and that it is very difficult to obtain identical crystals [21].

3.5 Crystals growing in Germany by the traveling molten zone methode

For the TlBr crystals grown used the traveling molten zone method in the German company Korth Crystal GmbH. The traveling molten zone method is commonly used as for raw material purification from impurities and as the method for crystal growth. As a result, material purification and crystal growth occur in the same ampoule, preventing against additional impurities, in a difference removing material from the ampoule to ampoule as in Bridgman-Stockbarger method. The traveling molten zone method has two disadvantages, namely, (I) the crystal could not be grown as large as the diameter of the crystals like in Bridgman-Stockbarger method and (II) there were growth in refined crystal part and the part with high impurity content was not separated [1, 22].

4. Results and discussion

4.1 Thallium bromide optical properties

4.1.1 Luminescence excited by electron beam and short living absorption of TlBr crystals

Luminescence irradiated by electron beam and induced absorption have been studied in three TlBr crystals (M12, M13 and M14) prepared from the large, massive single crystals, grown by Bridgman-Stockbarger method. The results of these experiments and analysis have been published [1]¹. Luminescence spectra recorded at liquid nitrogen temperature (at room temperature luminescence has been extinguished), irradiating the samples by an electron beam. The spectra are shown in Fig. 5. By analyze of the spectra we can distinguish two fluorescent spectrum of areas – at 1.8 eV and 2.2–2.4 eV. The comparison of the spectra shows that for the samples M13 and M14 luminescence band position of the

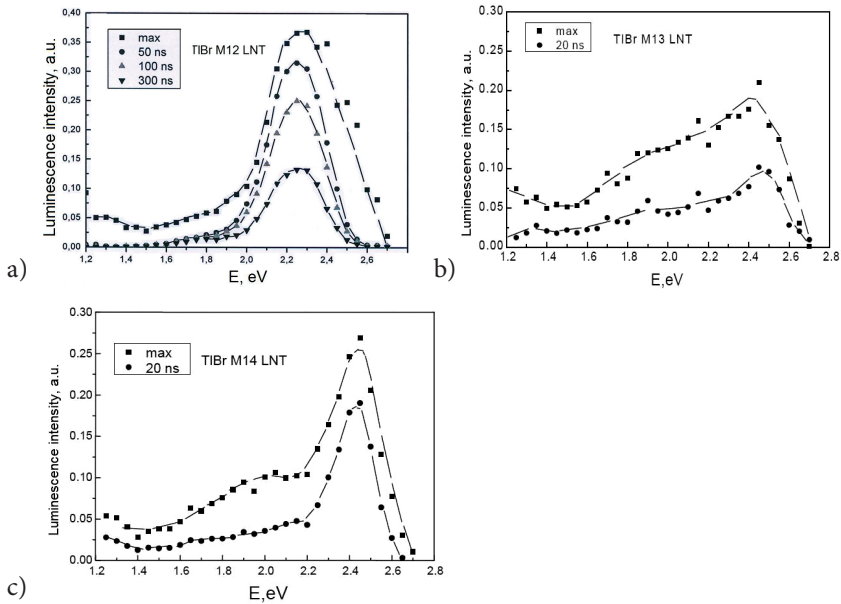


Fig. 5. Luminescence spectra of samples M12, M13 and M14, the images a, b and c accordingly excited by electron beam pulses. The term "max" corresponds to spectra recorded during the drive pulse. The other spectra recorded after the excitation pulse, the corresponding delay in the sketch.

¹ Hereinafter referred to as the author publications citing use of sign {}

spectrum are high-energy region at ~ 2.45 eV and the luminescence band shape and position during time change a little. Specimen M12 luminescence band spectrum of high-energy region is different – the peak of the band at ~ 2.25 eV and the first 50 ns after the excitation pulse of the band shape is changing, disappearing part of the luminescence band high-energy side.

The differences in luminescence spectra show that the samples have different luminescence centers, so the samples are of different random impurities or have different intrinsic defects. Accompanied by verifiable sample composition (Tab. 1) showed that the M12 sample containing elevated concentrations of iodine. It can be concluded that the high iodine concentration is responsible for the luminescence bands shift to low energy side of the model M12. Luminescence kinetics decay recorded at 2.3 eV, the samples M13 and M14 are very similar, while the M12 luminescence kinetics decay changes greatly, as shown in Fig. 6.

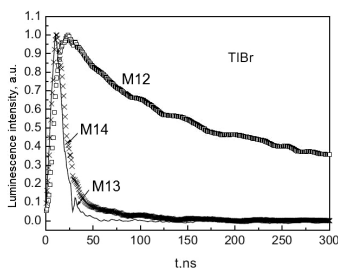


Fig. 6. Samples M12, M13 and M14 luminescence kinetics decay at 2.3 eV.

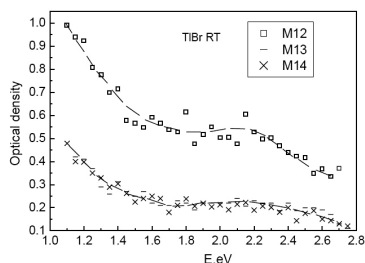


Fig 7. Induced absorption spectra at room temperature.

Samples M13 and M14 fluorescent intensity in the first 50 ns decreases in ~ 10 times. M12 sample fluorescence decay kinetics is longer, but the spectral changes during the first 50 ns (see Fig. 5.) indicates that the sample M12 luminescence is 2.45eV band contribution and the observed spectral change is a consequence of luminescence band disappeared at 2.45 eV. So for the sample M12 is the addition luminescence band and it is the opportunity for additional charge carrier trapping. Charge carrier trap can occur not only in luminescence centers, but also in the defect, that is not participating in luminescence. For this reason registration of short-lived induced absorption was studied and the spectra were shown in Fig. 7.

The registration of induced short-lived absorption have been done in a way that probe light optical path for the different samples would be identical. Therefore, induced optical density values are comparable between the samples.

The observed absorption bands in two spectral regions (<1.1 eV and at 2.2 eV). Samples M13 and M14 have a short-lived absorption spectra of the

same, but the sample M12 has short-lived absorption the optical density is at least twice as large as the whole spectrum. We can conclude that short living radiation defect effectively formed in the sample M12. Possible cause is the stabilization of the crystal defects existing materials. If the sample of M12 is a large concentration of iodine (see Table 1.), it is conceivable that other defect concentration in this sample is high. The specific type of defect in charge of short-lived absorption increased in samples M12, is not possible to clarify.

Table. 1. **Comparison of some characteristics of TlBr samples M12, M13 and M14.**

	M12	M13	M14
$R(\Omega \cdot \text{cm})$	1.2×10^{10}	1.3×10^{10}	1.6×10^{10}
$\mu\tau_e(\text{cm}^{-1})$	---	5×10^{-5}	3×10^{-5}
$\mu\tau_h(\text{cm}^{-1})$	---	Initially $\approx \mu\tau_e$, followed by degradation	Initially $\approx \mu\tau_e$, followed by degradation
$Cl(\text{ppm})$	300	100	---
$I(\text{ppm})$	6000	40	---
Δt	300 ns+ slow μs component	22 ns	28 ns+ slow μs component

Table 1. summarizes the sample of M12, M13 and M14 for some characteristics, namely resistivity R , chargecarries mobility-lifetimes of electrons and holes – $\mu\tau_e$ and $\mu\tau_h$, homologous anion Cl^- and I^- chargecarrier concentration and collection time Δt . The table shows that the model M12 charge carriers collection time is much longer than other samples. Fabrication and testing of radiation detection from samples M12, M13 and M14 found a correlation between the optical properties studies and detector spectrometric properties. The detector made of sample M12 does not work at all – it was not possible to collect charge carries on the electrodes. Apparently homologous anionic iodine admixture, which is the highest concentration in the sample M12, created good conditions for trapping of the chargecarries and thus the charge carriers collection on the electrodes is complicate in the detector. For this reason, it was not possible to evaluate $\mu\tau$ products for this sample.

4.1.2 X-ray luminescence of TlBr crystals

Light influence of thallium halides can form colloids [7], which could affect the charge carriers collection efficiency for the manufactured radiation detector from the crystal. For this reason, a number of samples grown by Bridgman-Stockbarger method were tested by the luminescent method. The method can detect the concentrations of colloids of TlBr crystal. Results of these studies have been published in [2]. The TlBr crystals were irradiated with unfiltered light of mercury lamp to create colloids. Part of the samples has different luminescence spectra before irradiation with light from mercury lamps, indicating different defect content in crystals. The biggest differences have the samples A8A and

Z4a. The initial luminescence spectra of these samples are shown in Fig 8. They are different, the sample A8a main luminescence band is at 2.25 eV and the low intensity band at ~ 1.5 eV, while the sample is Z4a two approximately equal-intensity luminescence bands whose maxima are at ~ 2.0 eV and 1.5 eV. In both samples the observed luminescence is related to the defect. Experimental conditions and evaluation results of the analysis show that the sample A8A has less structural defects than in the sample content Z4a, so it is likely that the defect types in the two samples are similar if not identical ones and the difference spectra associated with different concentrations of defects in these samples.

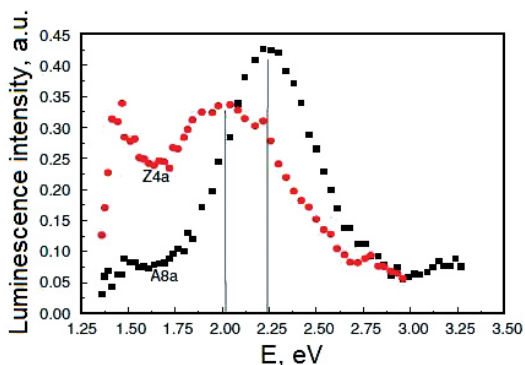


Fig. 8. Stationary X-rays luminescence spectra of samples A8a Z4a at room temperature.

Two different samples Z3a and A8c were selected to check the possible effects on the colloidal sample luminescence. After the initial registration X-ray luminescences spectrum, samples without removing them from the plant, irradiated for four hours with the unfiltered light of mercury lamps and after irradiation the luminescence spectra were re-recorded.

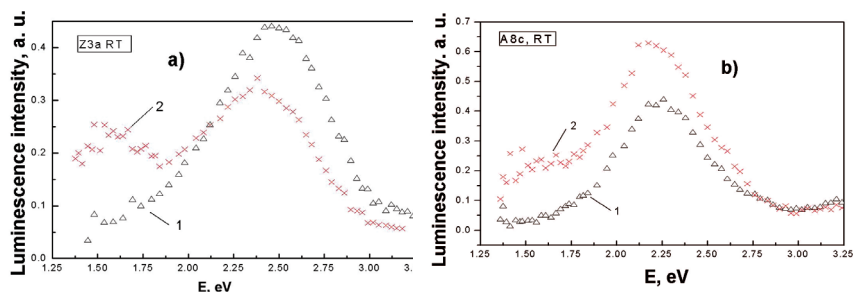


Fig. 9. X-ray luminescence spectra of TlBr samples before (1) and after (2) irradiation by mercury lamp; a) Z3a and b) A8c sample.

In the sample Z3a creates radiation defects effectively, than the sample A8c. The sample Z3a has less intensive luminescence band at ~ 1.5 eV already before the irradiation with mercury lamp light. This band is related to the presence of colloidal crystal and band intensity of a significant increase in the sample irradiated with mercury lamps light, suggesting that this sample has a positive colloid formation conditions.

4.1.3 The fundamental absorption edge at room temperature

The fundamental absorption edge is very sensitive to the crystal composition and homological impurities. For example, TlBr-I case, the edge shifts to lower energy side, but TlBr-Cl – to high-energy side. Therefore, the fundamental absorption edge position and shape can provide information on impurities and other defects presence in crystal structures. Our research results of the fundamental absorption edge of TlBr crystals are publications {1.2}, which have shown correlation between the fundamental absorption edge position (and shape) and the crystals produced from these radiation detection properties. Registration of absorption of the fundamental absorption edge of the area investigated samples was carried out at room temperature. The Fig. 10 shows spectra of absorption edge for the TlBr samples M12, M13 and M14.

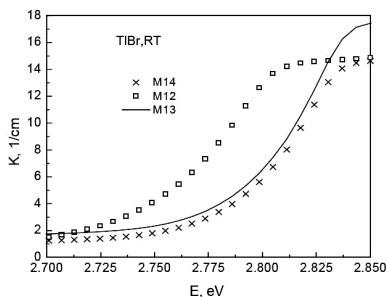


Fig. 10. Fundamental absorption edge of three different TlBr crystals.

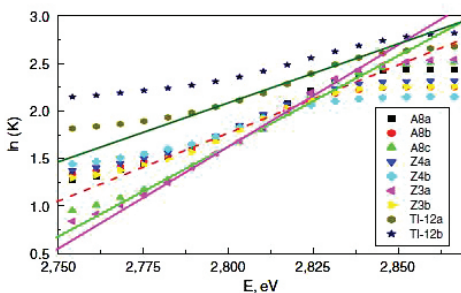


Fig. 11. The fundamental absorption edge of a number of TlBr crystals.

As shown in Fig. 10, sample M12 fundamental absorption edge is shifted to the low energy side compared with the samples M13 and M14. As has been shown above, the sample M12 has been increased with concentration of iodine, which forms the fundamental absorption edge shift. Fundamental absorption edge position was analyzed in a series of TlBr samples and the results were

shown in semilogarithmic coordinates, as they are quite extensive area of the fundamental absorption edge approximated with a straight line. These line position and the slope makes easier the comparison of the results in different samples. Figure 11 shows the results for the 9 samples of the fundamental absorption edge.

Based on the experimental results, we conclude that the five samples, which are the fundamental absorption edge position coincide with the dashed red line, composition and structure of defects is about the same and we can assume that it is a composition according to TlBr. Samples A8c Z3a and gradients do not coincide with the red line what means that the sample composition differs from the TlBr stock. Samples A8c and Z3a are cut from the same A8 and Z3 monocrystalline blocks with TlBr composition, but homologous to the impurity concentration can vary single crystal blanks at the ends. It could be assumed that the samples have a small homologous ions impurity such as chlorine. The sample TL-12A has about the same fundamental absorption edge of the slope, observed in the rest of TlBr crystals, but is an additional absorption at lower energies by 2.7 eV. This absorption may be related to 1) the colloid center-wide band 2) with structural defects that cause probing light scatter, for example, block structure, so that it can be concluded that the sample has poor quality. It confirms that even the samples made of one single crystal wafers could have different impurities and other structural defects. From these studies, the conclusion comes that the samples made of one single crystal wafers have different impurities and defects in the composition.

4.1.4 Photoluminescence at liquid helium temperature

TlBr exciton luminescence decay is observed at temperatures below liquid nitrogen temperature. However, the exciton luminescence is highly dependent on the quality of the crystal – crystals with large defect content the intensity of the exciton luminescence less than in crystals with low defect content. To obtain more details on TlBr luminescence spectra (direct and indirect exciton), we use the facilities for spectrum registration with possibility cooling sample close to liquid helium temperature (~ 14 K).

Luminescence spectra were recorded in TlBr crystals at various stages of processing. First, the spectra were recorded after the sample cut – “as Grown” (Fig. 12.). Then by pressing the sample and etching – “Pressed”. The model A1B2 spectrum was recorded after annealing the sample – “Pressed and annealed”. Extrusion was chosen in the light of observations that TlBr is a plastic material, which can be obtained by pressing a smooth surface, but pressing the crystal is deformed and changes the defect content.

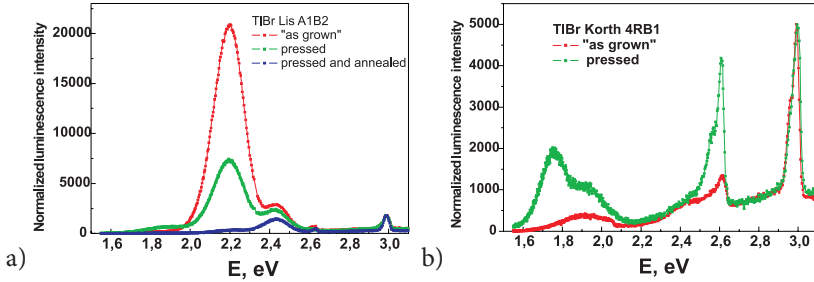


Fig. 12. Luminescence spectra at liquid helium temperature for TlBr crystals grown a) by Bridgman-Stokbarger method, b) by traveling molten method.

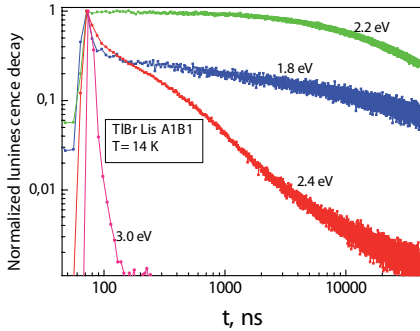


Fig. 13. Luminescence kinetic decay at liquid helium temperature for TlBr crystal A1B1 grown by Bridgman-Stokbarger method.

The Figure 12 shows luminescence spectra normalized on the direct exciton luminescence band, which makes possible to assess the relative contributions of defect luminescence. We can distinguish some baseband in luminescence spectra: 1) the band at 3.0 eV is a direct (straight passes) exciton luminescence, 2) band at 2.6 eV is indirect (transition bias) exciton luminescence, 3) band at 2.4 eV is related to the defect luminescence, 4) band at 2.2 eV – impurity luminescence and 5) the band at 1.8 eV associated with colloidal thallium centers. The research results show that the crystal deformation increases the concentration of colloidal centers but after annealing crystal the concentration of the center reduces significantly. It is known that colloidal centers are formed at dislocations and grain boundaries. Deformation significantly increases the number of dislocations and thus efficiency of to the colloid formation. After annealing the luminescence intensity of colloidal band decreases, which means that the annealing leads to dislocations (possibly other defects) reduction.

Figure 9 shows the luminescence decay kinetics model A1B1. The picture shows that the exciton luminescence kinetics (3.0 eV) is a fast (<20 ns), but kinetic defect bands (1.8, 2.2, 2.4 eV) is nonexponential and slower. The nonexponential kinetics decay means that the luminescence is raised from the recombinative process that permits charge carries migration inhibition. As a result quality of ionizing radiation detector is deteriorating because chargecarries collection time increases and it cause deterioration of the radiation detector resolution – at least part of the radionuclides cannot be detected. It was found that the detector, made of crystal-M12, does not work at all.

4.2 Surface properties of TlBr crystals

Ionizing radiation detector manufacturing technology includes crystal surface preparation procedures – crystal cutting, polishing, etching and so on. The electrical contacts could be qualitatively applied to the crystal surface and these contacts should be ohmic. It is necessary to produce high-quality detector contact surface sputtering. The results of this section are published in papers {3, 4, 5,10}. To make the TlBr radiation detector materials need be machined. TlBr is a soft material, so mechanical working within the materials is significant and material deformation is generated in a variety of surface and volume structural defects – dislocations, vacancies, and others. Depending on the processing technologies, highly defective surface layer depth can vary from 10 micrometers to one millimeter, or even deeper. Therefore, one of the specific objectives was developing a surface treatment technology, which permits the production of indefected surface, what is very urgent problem in detector crystal preparation. Microhardness measurements and optical microscopy method has been selected for the surface quality control. Microhardness is structuresensitive method, which senses the presence of defects.

The experiments applied TlBr single crystal samples of series A, L and S grown by the Bridgman-Stockbarger method. The samples thickness was 2 mm and square was 5×5 mm². The Vickers pyramid was used for the microhardness measurements as the indenter. Microhardness H_v was calculated according to the methodology described in section 3.2. The studied crystals were cut by a diamond wire. The sample surface after cutting is shown in Fig. 14a, which are visible cutting traces of streak form. The surface microhardness measurements after cutting indicated that the surface of the specimen is cut, microhardness increased and reached 160 MPa, compared with 75-80 MPa deformation model (Fig. 15). The results show that after cutting hardened layer depth is at least 20 μ m, but with the defect-rich layer of depth is even larger. Our experiments defective layer was removed by chemical etching. Etchant was prepared, consisting of ethyl alcohol and bromine ratio of 10:1.

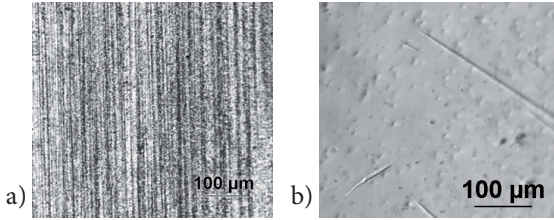


Fig. 14. The images of TlBr crystals in optical microscope after etching (a) and before chemical etching (b).

Results of the solidified layer thickness depending on the chemical etching steps are shown in Fig. 15 after 6 and 12 minute etching reduced the microhardness. After this etching the crystal surface of the defective layer had not been fully removed. Completely defective layer removal requires a 20-minute long etching. Etched surface is smooth and just a few microscopic defects are visible (Fig. 14 b). The results showed that the proposed method of surface treatment of different series of samples (A, L and S) allows obtaining a high-quality topographical surface and homogeneous hardness with good surface quality repeatability.

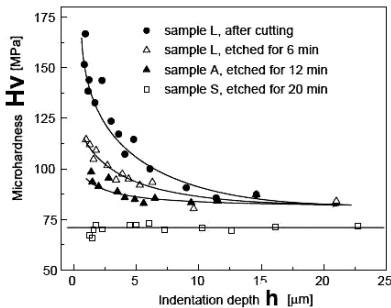


Fig. 15. The surface hardness of TlBr as a function of the indentation depth after different surface treatments.

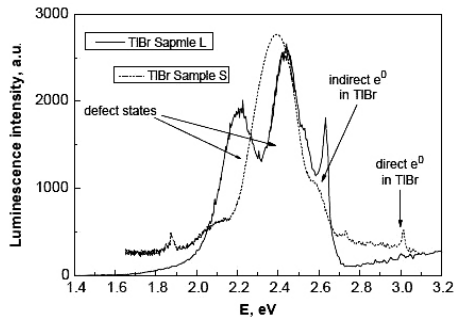


Fig. 16. Luminescence of TlBr samples L after 12 min and S after 20 min of the etching.

It is known that luminescent method is sensitive and is being used in various types of faults [10]. 12 and 20 minutes long chemically treated TlBr crystal luminescence spectra are shown Fig. 16. Spectra were recorded at 14 K temperature of the sample excited by a laser (4.66 eV). It is evident from the spectra that the sample S is observed due to direct exciton luminescence (3 eV), but the sample L is not, what explain the fact that sample L has no completely

corrode defective surface layer and the excitones appearing into this layer recombine without radiation process.

The practical result of the study is a TlBr crystal surface processing technology, which allows production of crystals with good topological surfaces of detector production. Mechanically defective layer may be almost entirely removed by chemical etching, surface quality control of the microhardness and optical microscopy method. The comparison of different samples (A, L and S) shows that the differences of microhardness values for different single crystal series are not decisive role in detector characteristics. However, the increased hardness of the defective surface layer removal is a necessary preparatory step in the production of radiation detection equipment. For example, the surface quality is a critical parameter for high-quality gold evaporated contacts. To ensure ohmic contacts with good adhesion requires there should be no any surface contamination and the surface has to be optically smooth. This requirement is met by application of chemically etched TlBr.

4.3 Electrical properties of TlBr crystal

Electrical properties of the material are very important for the detector operation. The study of the electrical properties of TlBr was by Bridgman-Stockbarger method grown crystal samples, as well as samples grown in a traveling molten zone method. Before the deposition of gold contacts in the sample surface processing was made – the sample was first pressed and then its surface was etched. Before contact deposition the samples were annealed. Before pressing the sample thickness was 2 mm, but the result of pressing down to 0.5 mm and all samples were equal. However, one sample in each series has also evaporated contacts, in order to compare the characteristics of the samples before and after extrusion. Volt-amps curves were measured at room temperature before and after pressing the samples. Gold contacts were evaporated to the samples and with gold weir-probes a voltage bias was applied. The whole measurement procedure was implemented in a “black box” – the sample was in the dark to avoid photocurrent appearance during the measuring. In Fig. 17, 18 show volt-amps characteristic for the manufactured radiation detection from TlBr crystal. Before press all volt-amps curves of the samples were nonlinear (Fig. 17a, 18a), but after pressing, annealing and etching volt-amps curve for all the samples became linear (Fig. 17b, 18b). However, the curve of 4R sample is steeper and puncture voltage is 170 V, at the same time with the same thickness puncture voltage of sample A1B2 is 400 V. The detector crystal resistivity was calculated in order to assess the impact pressing of the sample electrical properties of the resulting volt-amps characteristic curves, the results are shown Table 2.

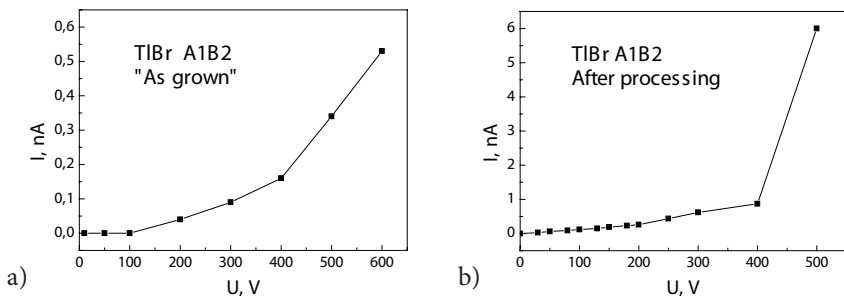


Fig. 17. Volt-ampere characteristics of the TlBr crystals grown by Bridgman-Stockbarger method a) unpressed and b) pressed.

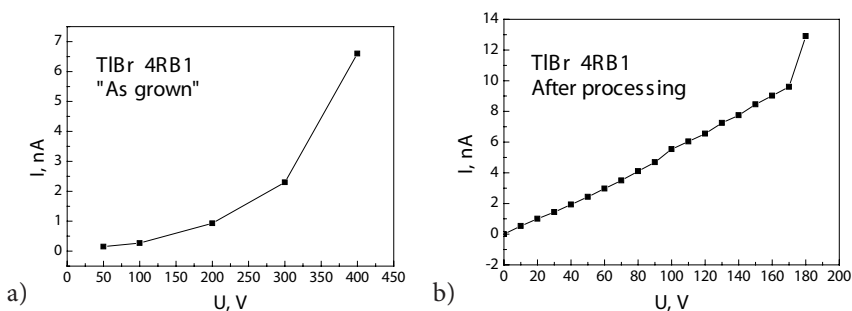


Fig. 18. Volt-ampere characteristics of the TlBr crystals grown by traveling molten zone method a) unpressed and b) pressed.

Table 2 shows that the model A1B2 resistivity practically has not changed after the pressing, but the model 4RB1 resistivity changed by one decimal round. We can assume that the sample 4RB1 contains structure defects such as dislocations, cracks, grain boundaries, which causes “black” current leakage as before the treatment, as well as after treatment.

Table 2. The sample resistivity (ρ , $\Omega \cdot \text{cm}$)

Paraugs	A1B2	4RB1
Pirms apstrādes	$8,2 \times 10^{12}$	$3,7 \times 10^{11}$
Pēc apstrādes (presēšana, kodināšana)	2×10^{12}	$4,5 \times 10^{10}$

Crystal pressing before etching and extrusion coating contacts has a significant impact on radiation detection crystals and changes the characteristic volt-amps of resistivity values.

5. Ionizing radiation detector fabrication from TlBr crystals

The testing of ionizing radiation detector properties and the estimation of the potential application were published in papers {8, 9, 11}. The detector fabrication technology and testing of the spectrometrical properties were described.

5.1 The detector fabrication technology

The technological processes for ionizing radiation detector producing the several operations have been carried out. The sequence of the detector manufacturing technology is following:

- Initial preparations for slicing monocrystalline wafers
- Cutting to the pieces with the required configuration and the sizes
- Polishing
- Etching
- Annealing
- Gold contact vacuum deposition
- Photolithography (if necessary complicate contacts)

5.2 Spectrometric properties of gamma ray detectors made from TlBr crystals grown by Bridgman-Stockbarger method

Ionizing radiation detector was made from Bridgman-Stockbarger method grown crystal A1 and the spectrometric properties recorded were demonstrated in Fig. 19. During testing, the following results were obtained for the detector spectrometric properties (energy resolution): 0.8 (13.6%), 1.4 (2.3%), 2.1 (1.7%) and 7.1 keV (1.1%) respectively at the energies 59.6, 59.6, 122, and 662 keV. Detector contact area was 12.56 mm² and a crystal thickness was 2 mm. As we can see in the figures, the background level is increased in all spectra, what happen due to incomplete contact coverage on the crystal area. The electric field is inhomogeneous at the contact edges and therefore charge carries collection time increases. This effect is more pronounced, for the detection high energy quanta when chargecarries are collected from the whole detector volume not only from the near-surface region as at low energies quanta. Such effect has been observed in CdZnTe (CZT) detector as with fully deposited contacts, as well as not. If the detector surface contacts are deposited in full – a background level decreases.

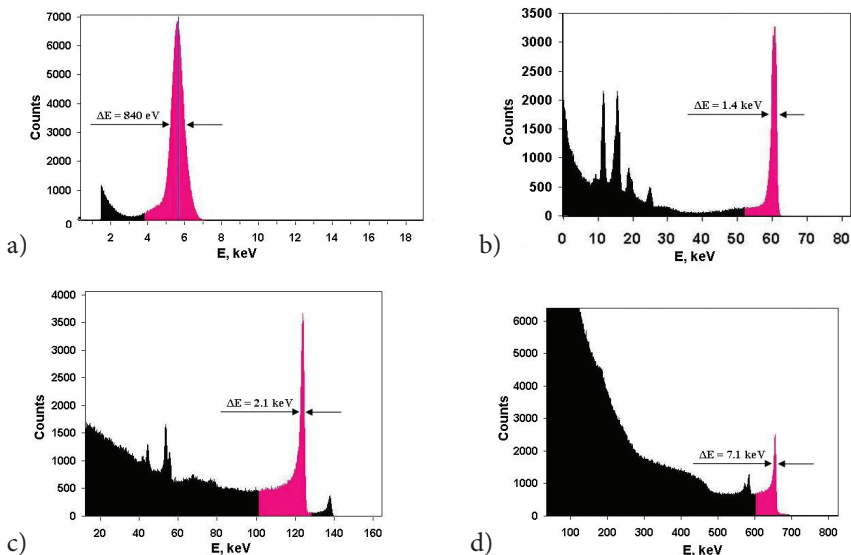


Fig. 19. Ionizing radiation spectra obtained by the TlBr crystal detectors grown by Bridgman-Stockbarger method a) Fe-55, b) Am-241, c) Co-57, d) Cs-137

Spectrometric parameters of A1 crystal made detector are summarized in Table 3. Currently, the best results were obtained from the A1 crystal manufactured by Planar TlBr detectors [20 – 25].

Table 3. Comparison of spectrometric properties (FWHM) of several radiation detectors made from TlBr and CdZnTe crystals

Crystal	5.9 keV	59.6 keV	122 keV	662 keV
	FWHM, keV			
TL-1	0.5	2.7	4.4	29
Lis25	0.85	1.8	3.1	21.1
A1	0.8	1.4	2.1	7.1
4R		4.8	13	
CdZnTe	1.1	1.9	3	12

These spectrometric parameters demonstrate that good and acceptable results were achieved because of the growing crystal and detector manufacturing technology improvements. For example, BSI Ltd some time ago has produced the planar TlBr detectors [23] from the crystal TL-1 (Tab.1), which at that

time was the best in the world. But now, as can be seen from Table 3, detector made from the crystal A1 is better than mass-produced CdZnTe detectors [4]. This means that in the production of the TlBr detector some progress has been done, due to the crystal growing and detector manufacturing technology improvements [10]. The fabricated detectors produce repeatable characteristics from the recently obtained crystals. Resistivity is about $(3 - 5) \times 10^{11} \Omega \cdot \text{cm}$ and mobility-lifetime ($\mu\tau$) parameter values for electrons and holes is $\sim 10^4 \text{ cm}^2 / \text{V}$.

5.3 Spectrometric properties of gamma-ray detector from TlBr crystal grown by traveling molten zone method

The ionizing radiation detectors also were made from TlBr crystals grown by traveling molten zone method. The spectrometric characteristics of these detectors were tested. The obtained results are shown in Fig. 20.

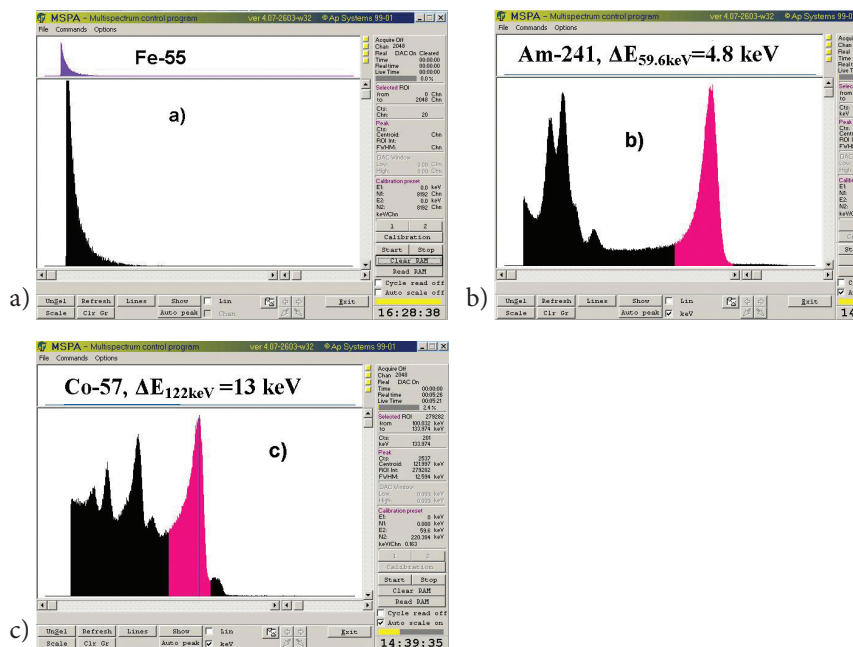


Fig. 20. Ionizing radiation spectra obtained by the TlBr crystal detectors grown by traveling molten zone method, sample 4R a) Fe-55, b) Am-241, c) Co-57

The testing of spectrometric characteristics has been done at a temperature of -10°C , and applied bias voltage 580 V. The following energy resolutions

were obtained: 4.8 keV at 59.6 keV and 13 keV at 122 keV. Compared to detectors made from crystals grown by Bridgman-Stockarger method (Tab.3) the conclusion comes that the detector resolution is not sufficient for the widely used detectors, however, crystals are spectrometric. In this case, the main role of crystal quality improvement is based on the development of traveling molten zone method for TlBr crystal growth. It is possible that traveling molten zone could be repeat several times, each time removing uncontrolled impurities to the ends of the grown crystal. Probably the further development of ionizing radiation detector manufacturing technology might be such special treatment as the annealing, or other modification of technological process are possible as well.

6. Optical and electrical properties correlation with radiation detector characteristics

During these studies the optical properties and spectrometric characteristics were compared for some crystals. The following conclusions were obtained from the comparison:

- Iodine and other homological impurities deteriorate ionizing radiation detector characteristics and such crystals are not suitable for the manufacture of the detectors. Homological impurities may be determined by the fundamental absorption edge position and the crystal luminescence.
- Detectors made from the crystals with high colloid creation efficiency have a short operation time.
- Linearity of volt-amps characteristics and a crystal high specific resistance ($\sim 10^{12} \Omega \cdot \text{cm}$) are the detector operating necessary conditions. The volt-ampere curve is steeper and puncture voltage is lower for crystals grown by Traveling molten zone than that for crystals grown by Bridgman-Stockbarger method.

7. Main theses

1. It is demonstrated that some optical properties correlate with ionizing radiation detector spectrometric characteristics. Therefore it is possible to make the control of crystal optical properties and to determine the crystal adaptability for radiation detector producing {1, 2}.
2. The procedure of TlBr crystal surface processing was proposed and applied for detector manufacturing. Those procedures assured the qualitative electrical contact properties in system Au-TlBr. The procedures comprised surface etching, crystal annealing and surface quality control by optical microscopy and microhardness measurements {3, 4}.
3. It is revealed that volt-ampere characteristic depends on TlBr crystal grown method and surface treatment procedure. It is shown that high specific resistivity and linearity of volt-ampere characteristic determine the TlBr detector spectrometric characteristics {8}.
4. The ionizing radiation (x-ray, γ -ray) detectors have been manufactured from TlBr crystals grown by two different methods and its spectrometric characteristics have been compared. The best detectors have the spectral energy resolution of 0.8 (13.6%), 1.4 (2.3%), 2.1 (1.7%) and 7.1 keV (1.1%) for 5.9, 59.6, 122 and 662 keV energies accordingly. The obtained characteristics are better than that ones obtained with widely used CdZnTe detectors {8, 9}.

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8.1 Authors' publications related to this work. {}

1. L. Grigorjeva, D. Millers, M. Shorohov, I. S. Lisitskii, M. S. Kuznetsov, S. Zatoloka, V. Gostilo, Optical investigations of TlBr detector crystals, *Nucl. Instrum. Methods in Phys. Res. A*, **531**, 1-2, (2004), 197–201.
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8.2 Other authors' publications.

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2. A. Bulycheva, M. Shorohov, A. Lupilov, V. Gostilo, W. Inui, M. Funaki, CdTe linear arrays for registration of hard gamma-ray fluxes, *Nucl. Instrum. Methods in Phys. Res. A*, **607**, 1, (2009), 107–109.

9. Participation in conferences

- 5th International Workshop on Radiation Imaging Detectors, Riga, Latvia September 7–11, 2003.
- 7th International Workshop on Radiation Imaging Detectors, Grenoble, France, July 4–7, 2005.
- 8th International Workshop on Radiation Imaging Detectors, Pisa, Italy, July 2–6, 2006.
- 9th International Workshop on Radiation Imaging Detectors, Erlangen, Germany, July 22–26, 2007.
- 10th International Workshop on Radiation Imaging Detectors, Helsinki, Finland, June 29 – July 3, 2008.
- 12th International Workshop on Radiation Imaging Detectors, Erlangen, Germany, July 11–15, 2010.
- 16th Room Temperature Semiconductor Detector Workshop, Dresden, Germany, October 19–25, 2008
- LU CFI, 22.–25. Zinātniskās konferences.

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