Combustion, Explosion, and Shock Waves, Vol. 46, No. 6, pp. 712–718, 2010

Detonation of PETN Single Crystals Initiated by an Electron Beam

B. P. Aduev,[1] **G. M. Belokurov,**[1]
S. S. Grechin,[1] **and A. V. Puzynin**[1]

UDC 544.454

Translated from *Fizika Goreniya i Vzryva*, Vol. 46, No. 6, pp. 111–118, November–December, 2010.
Original article submitted July 2, 2009; revision submitted March 30, 2010.

Luminescence in the volume of PETN (tetranitropentaerytrite) single crystals exposed to an electron beam (duration 20 nsec) with an energy density of 15 J/cm^2, which exceeds the threshold of explosive decomposition, was investigated in real time. Exposure to the ionizing pulse causes radioluminescence and emission related to the critical electron emission from a dielectric which is transformed to a vacuum discharge. The emission zone propagates from the surface into the vacuum at a speed of 5000–6500 m/sec. The absorption of electron beam energy in the irradiated layer (0.25 mm) causes the formation and propagation of a shock wave enhanced by the chemical reaction in the crystal. When the shock wave is reflected from the target on the rear side of the sample, its amplitude increases. This leads to detonation accompanied by emission which propagates from the backside to the irradiated surface of the sample at a speed of 7500–8500 m/sec with the subsequent expansion of the explosive decomposition products into the vacuum.

Key words: PETN, detonation, electron beam, emission.

INTRODUCTION

Recently there has been increased interest in noncontact methods of initiation of explosives such as laser and electron beam exposure.

Our previous studies in which PETN crystals were initiated by nanosecond electron beams and exposed to picosecond pulsed electron beams in a subcritical mode and stationary x-rays revealed a number of regularities of physicochemical processes occurring during irradiation. It has been shown that irradiation in a subcritical mode leads to emission from excitons and the primary products — excited NO_2 radicals; the characteristic emission time does not exceed the time resolution of the recording channel (2 nsec) [1, 2]. NO_2 radicals are also recorded by the ESR method after γ-irradiation and are unstable at room temperature [3, 4]. Stable NO_2^- nitrite ions are also recorded in optical absorption spectra [3, 4].

According to quantum-chemical calculations [5, 6], the formation of NO_2 radicals is accompanied by release of energy, which, as follows from experiments [2], is largely expended in radiation and does not lead to the further development of the exothermic chemical reaction.

Upon exposure to a nanosecond electron beam with energy density exceeding the threshold of explosive decomposition, the emission spectra, already in the radioluminescent stage, contain not only the emission from excitons and NO_2 radicals but also an additional emission band with a maximum at 1.5 eV [2, 5, and 7]. In the emission spectra in the subsequent stages of explosive decomposition of PETN, only this band is observed, which, unfortunately, was not definitely identified. However, it has been found that the emission spectrum of this band is not thermal and, hence, it has a luminescent nature [7]. Measurements of optical nonstationary absorption spectra of PETN exposed to an electron beam with energy density below and above the threshold of explosive decomposition revealed that in the first case, at the moment of electron beam expo-

---

[1] Kemerovo Branch of Institute of Solid State Chemistry and Mechanochemistry, Siberian Division, Russian Academy of Sciences, Kemerovo 650099; lira@kemsu.ru.

0010-5082/10/4606-0712

sure, the absorption band of NO_2 radicals is recorded, and in the second case, along with NO_2 radicals, the absorption band due to NO_3 radicals [8] is recorded. A comparison of the results suggests that the emission band at 1.5 eV can be assigned to NO_3 radicals.

According to our estimates, already in the stage of thermalization of hot electrons and holes, the heating of the irradiated area of the crystal reaches at least the melting temperature [2]. At high temperature, thermally activated separation of the NO_3 radical from the ionized PETN molecule is possible, which has been confirmed experimentally [8]. This process requires a relatively small expenditure of energy — 44.7 kJ/mole (0.45 eV), according to quantum-chemical calculations [5, 6].

According to [9], the primary carbocation formed rearranges to a tertiary cation with an energy release of 96 kJ/mole. This leads to an increase in the temperature and pressure amplitude in the shock wave forming and propagating from the irradiated area of the crystal, and, apparently, initiates the further exothermic decomposition of PETN molecules [2]. It has been found experimentally that one of the final decomposition products of PETN molecules is molecular nitrogen in an excited state, which is manifested in emission spectra of the explosion products [2, 7].

Such is, in our view, the picture of primary physicochemical processes in PETN crystals exposed to electron-beam initiation, which leads to the development of an exothermic chemical reaction and explosion.

Since, in the accelerator used in our experiments, the extrapolated electron path in PETN single crystals is about 0.25 mm [2], the question arises of the nature of physicochemical processes in the unirradiated area of the crystal, or, at least it would be desirable to determine the explosion characteristics: normal detonation, adiabatic explosion, etc.

Attempts to answer this question have been made previously [10–12] using pressed PETN samples. The main conclusions are as follows: exposure to an electron beam leads to a volume electrical breakdown of PETN from the irradiated area of the crystal, with the breakdown paths playing the role of hot spots, at which the chemical reaction starts. This process is accompanied by gas-dynamic discharge and dispersion and ejection of ablation products toward the electron beam. In the process, the shock wave generated in the irradiated zone causes detonation of the sample at a velocity of $D \approx 10^4$ m/sec, followed by expansion of the detonation products at a velocity of $v \approx 5 \cdot 10^3$ m/sec [10].

From our point of view, these conclusions are general in nature and are not sufficiently supported by experiment. In particular, in experiments [10–12], volume breakdown of the sample was not observed. The shock wave velocity is obviously overestimated; according to [13], with a density of samples close to the density of single crystals cannot exceed $D \approx 8500$ m/sec. In this case, the velocity of expansion of detonation products into the vacuum should exceed the detonation velocity [13].

We believe that the experimental technique used in [10–12] is not accurate enough for space-time dimensions. In particular, the observed duration of the emission may be smaller than the actual duration of the explosive decomposition process because of reabsorption of the emission by the chemical reaction products.

In the present study, we measured the rate of explosive decomposition of PETN single crystals using an improved technique which provides a more unambiguous interpretation of the results on the nature of explosive decomposition processes in the crystal volume.

OBJECTS OF RESEARCH AND EXPERIMENTAL TECHNIQUE

In this study, we used PETN single crystals 1.1–1.8 mm thick and with transverse dimensions of $\approx$3–5 mm. PETN was initiated using a GIN-600 electron accelerator. The cathode was a stainless steel tube 3 mm in diameter, and the anode was a steel plate with a hole 3 mm in diameter for extraction of the electron beam. The beam parameters were: effective electron energy 0.25 MeV, and pulse duration 20 nsec. The total energy of the electron beam measured by a calorimetric method was $\approx$1 J. At the location of the test sample, the diameter of the irradiated area measured from the impression on the brass plate is approximately 3 mm, and, hence, the energy density acting on the sample is 15 J/cm^2. With such parameters, explosive decomposition of PETN single crystals occurs with a probability $P \approx 1$.

To determine the threshold of the explosive decomposition, it is necessary to measure the dependence of the probability of explosion on the energy density. However, such an experiment using an electron beam is extremely laborious, and so the following estimation was performed. The energy density was reduced by increasing the distance between the anode and the sample. Already with its small decrease to values of 12–13 J/cm^2, the probability of explosion was $P < 1$. Sometimes, the explosion was incomplete. In this case, on the walls of the vacuum chamber there was a deposit of PETN powder in the form of a narrow ring lying in the plane of the sample. This indicates that the gaseous products propagated mostly perpendicularly to the electron beam direction, scattering unexploded residue of the sample. These data, taken together, suggest, that the electron beam density $W = 15$ J/cm^2 used in the experiments is close to the critical energy density $W_{0.99}$.

The emission of the crystals resulting from the electron beam exposure was recorded by a streak camera based on a Vzglyad electron-optical converter. The experimental setup is described in detail in [14].

The samples were glued by the backside to a grounded copper plate and placed in the vacuum chamber of the electron accelerator. The distance between the irradiated surface and the anode of the accelerator was ≈3 mm.

The image of the sample was projected on the photocathode of the streak camera using an optical system. Then, a slit 0.1 mm wide was placed in the optical system, which bounded a zone at the center of the sample in the direction of the electron beam. The time sweep of the streak camera is perpendicular to the axis of the radiation input. Since the electron beam is absorbed in a crystal layer ≈0.25 mm thick [2], this geometry is suitable for observing the temporal evolution of the electron beam induced emission over the thickness of the sample.

RESULTS AND DISCUSSION

The most typical time sweeps of emission for two samples are shown in Fig. 1.

Upon exposure to the electron beam, radioluminescence in the irradiated crystal layer and an emission zone from the irradiated surface propagating into the vacuum at a velocity v_1 are observed (see Fig. 1).

After, as a rule, during a certain time interval, emission is not detected. In the next stage, emission begins to propagate from the backside of the sample glued to the copper plate to the outer surface at a velocity v_2. Upon reaching the surface, the emission propagates into the vacuum gap between the sample and the vacuum diode of the electron accelerator (see Fig. 1).

To collect statistical data on the velocities v_1 and v_2, we initiated explosion of 40 samples. In all cases, the processes in the time sweeps of the emission agree qualitatively with processes in the samples presented in Fig. 1. However, a correct processing of the records to determine the velocities v_1 and v_2 was possible only for 9 samples because in most cases the emission brightness during explosion exceeded the dynamic range of measurements. In such cases, due to the specificity of streak camera operation, the glowing area expands, which leads to an overestimation of the measured velocity. The results of data processing for 9 samples are given in Table 1. The error in determining the velocities v_i is caused by certain arbitrariness in drawing lines 1 and 2 in Fig. 1 due to blurring of the emission and is ≈5%. The calibration errors of the temporal and spatial axes are less significant — about 1%.

TABLE 1

Results of Processing of the Records

Sample number	Thickness, mm	Mass, mg	v_1, m/sec	v_2, m/sec
10	1.25	21	5000	8100
20	1.1	16	6500	8300
22	1.25	22	4900	8400
23	1.2	25	6300	8600
25	1.1	22	6400	7500
28	0.9	14	5000	8000
29	1.6	32	4500	8300
31	1.4	20	5500	7500
38	1.6	26	6500	8000

The observed picture can be interpreted as follows.

At the depth of penetration of the electron beam, as mentioned above, radioluminescence is observed whose spectral composition and the identification of the emission centers responsible for the luminescence are described in the introduction.

The emission propagating into the vacuum can be attributed to the flow of chemical reaction products, which begins immediately during the action of the ionizing pulse and leads to an explosion of the irradiated area of the crystal. To test this hypothesis, we performed a similar experiment using a CsI–Tl crystal in which the chemical reactions typical of explosives do not occur. In this crystal exposed to the electron beam, we also observed emission which propagated into the vacuum at a velocity of 5000 m/sec (Fig. 2).

In this connection, the following interpretation seems to be more true. During exposure to the electron beam pulse, a charge with a density $q > 10^{-5}$ C/cm^2 is introduced into the crystal. If a charge drain is not provided, the electric-field strength, as shown by simple estimates, should reach a value $E > 10^7$ V/cm. In practice, this should lead to electrical breakdown at the edge of the irradiation pulse in the direction with the lowest electrical strength. In particular, electrical breakdown of the crystal is possible. In the case of explosives, the breakdown channels can be regarded as hot spots from which the explosive decomposition reaction develops, as proposed in [10–12]. However, the emission related to the volume electrical breakdown of the crystal was not observed in the experiment.

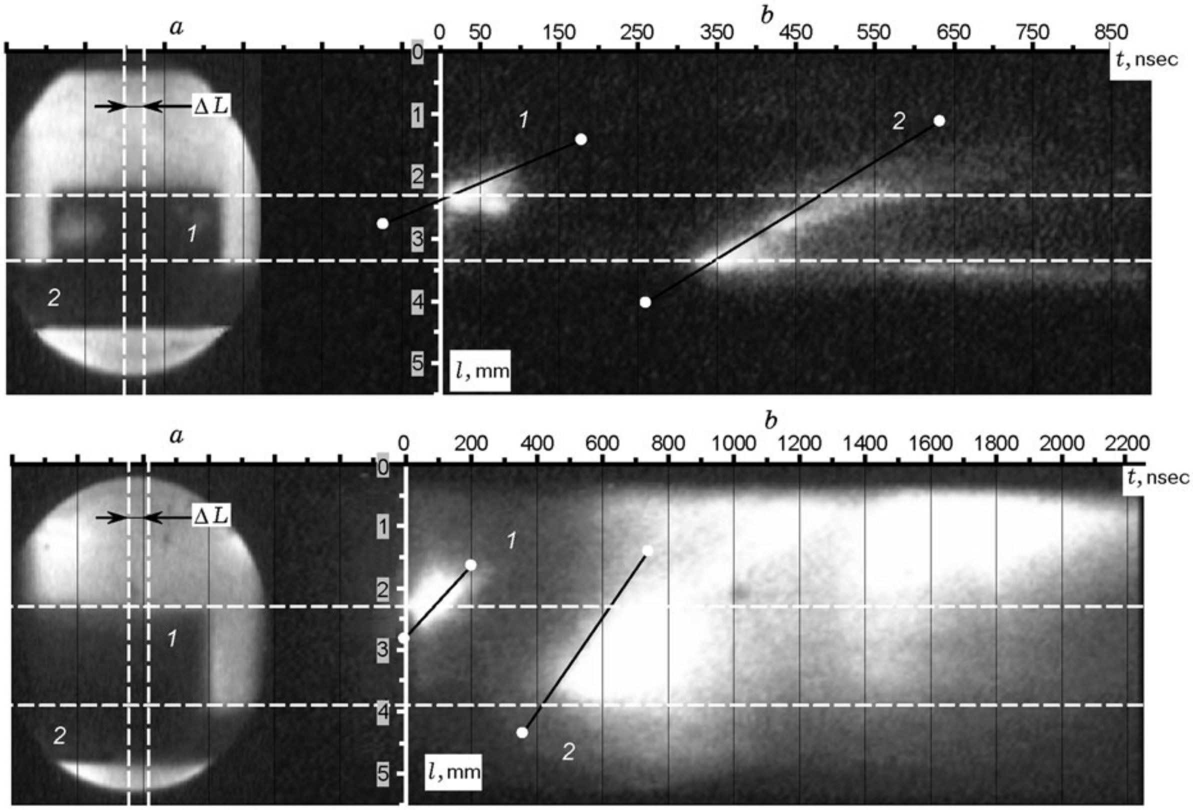

Fig. 1. Static image and time sweep of the emission from the sample Nos. 31 (at the top) and 38 (at the bottom) recorded by the streak camera at $W = 15$ J/cm^2: (a) static images of sample Nos. 31 and 38 on the output screen of the streak camera without an optical slit under illumination by a light source; 1) sample; 2) copper support; ΔL is the crystal area bounded by the optical slit; (b) time sweep of the emission from the crystal area bounded by the optical slit after exposure to an electron pulse with an energy density $W = 15$ J/cm^2, electron beam exposure of the sample corresponds to the time $t = 0$; 1) propagation of the emission into the vacuum (for sample No. 31, $v_1 = 5500$ m/sec and and for sample No. 38, $v_1 = 6500$ m/sec); 2) propagation of the emission resulting from the detonation (for sample No. 31, $v_2 = 7500$ m/sec, and for sample No. 38, $v_2 = 8000$ m/sec).

In our opinion, the excess charge injection in this experiment results from the vacuum breakdown of the gap between the crystal and the electron accelerator anode. This causes emission of the residual gas in the vacuum chamber of the accelerator.

It is also possible that the observed phenomenon is related to the critical electron emission from a dielectric that becomes a vacuum discharge, which has been studied for a number of stable crystals [15, 16]. According to the cited studies, exposure to a pulsed electron beam with a charge density $>10^{-6}$ C/cm^2 leads to an explosion of the surface with the formation of a plasma and a charge emission approximately equal to the introduced charge.

Let us consider the nature of the emission that begins on the backside of the sample. For most of the samples, the measured velocity of propagation of the emission v_2 is close to the normal velocity of detonation propagation in PETN crystals (see Table 1). The calculated detonation velocity of PETN single crystals is $D = 8500$ m/sec [13]. Consequently, in this stage, the emission is related to the explosive decomposition of the sample resulting from the detonation process. The occurrence of detonation is suggested by the destruction of the copper plate, in which the explosion produces a hole, whose shape and size approximately correspond to a sample with a mass 25–30 mg. In experiments with a sample of mass ≈40 mg, destruction of the optical windows of the experimental chamber at a distance of 45 mm from the sample was observed, and the anode was deformed.

It is noteworthy that detonation develops from the back surface rather than from the irradiated area of the crystal. This allows us to judge the nature of the initiation of explosive decomposition of thin single crystals of PETN.

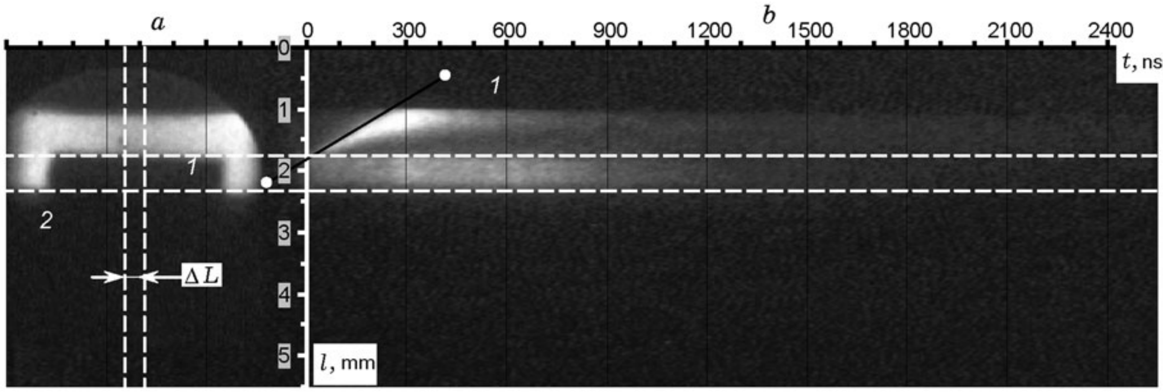

Fig. 2. Static image and time sweep of the emission from the CsI–Tl crystal: (a) static image of the sample at the output screen of the streak camera without an optical slit under illumination by a light source; 1) sample; 2) copper support; ΔL is the crystal area bounded by the optical slit; (b) time sweep of the emission from the crystal area bounded by the optical slit after exposure to an electron pulse with an energy density $W = 15$ J/cm^2, the exposure corresponds to the time $t = 0$; the ionizing pulse is followed by volume luminescence of the crystal for 1 sec excited by x-ray bremsstrahlung; 1 shows propagation of the emission into the vacuum ($v = 5000$ m/sec).

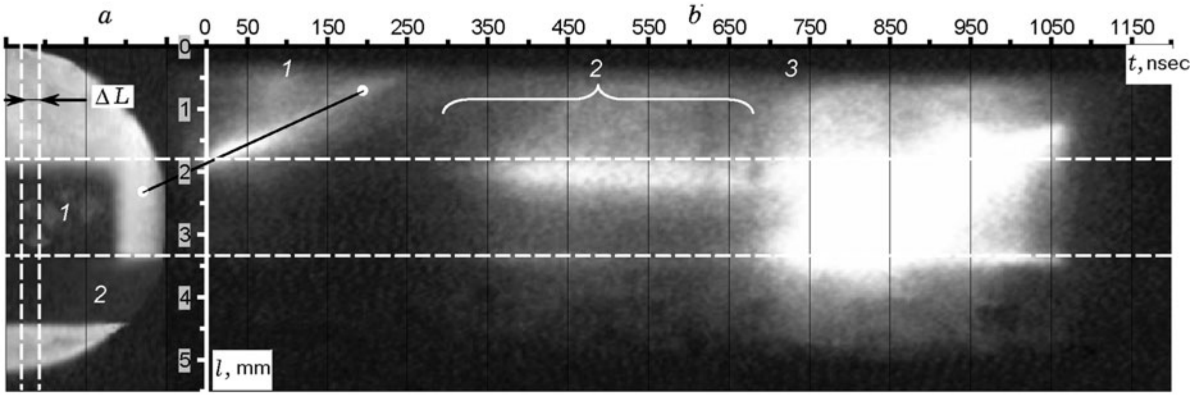

Fig. 3. Static image and time sweep of the emission recorded by the streak camera for $W = 13$ J/cm^2: (a) static image of the sample at the output screen of the streak camera without an optical slit under illumination by a light source from the backside; 1) sample; 2) copper support; ΔL is the area of the crystal bounded by the optical slit; (b) time sweep of the emission area of the crystal bounded by the optical slit after exposure to an electron pulse with energy density $W = 13$ J/cm^2 (the exposure corresponds to the time $t = 0$); 1) propagation of emission into the vacuum; $v_1 = 5900$ m/sec; 2) predetonation luminescence; 3) propagation of the emission resulting from detonation.

During exposure of the sample to an electron beam with a density of 15 J/cm^2, radiation defects were formed in the irradiated crystal layer (see Introduction). In addition, the absorption of electron beam energy causes the formation and propagation of a shock wave with a velocity $v = 3000 \pm 300$ m/sec, measured in [17] using a piezoacoustic converter. For an energy density of 15 J/cm^2, the volumetric energy density in a 0.25 mm thick layer is $Q_v = 750$ J/cm^3, and in the layer of the maximum energy release at a depth of 60–80 μm from the crystal surface, $Q_v \approx 900$ J/cm^3 [2].

The Grüneisen coefficient G for single crystals is unknown; therefore, the amplitude of the shock-wave pressure $p \approx 1$ GPa can be estimated using the known value of G for pressed PETN G = 1.15 [18] and the expression $p = \mathrm{G}Q_v$ [1].

Actually, the shock wave amplitude can increase due to the thermally activated detachment of the NO_3 radical from the ionized PETN molecule and the rearrangement of the primary carbocation to the tertiary one (see Introduction) caused by the additional energy release.

Reflection from a target (copper) with a greater acoustic stiffness than the explosive leads to a further increase in the shock wave amplitude (for an absolutely stiff target — by a factor of 2.74 [13]). As a result, the pressure becomes sufficient for shock-wave initiation of detonation in the sample.

The development of explosive decomposition in the case where the energy density is lower than or equal to the critical value can be more complicated than described above. Figure 3 shows the time sweep of the emission from a 39 mg sample exposed to an electron beam with an energy density of $\approx$13 J/cm^2. It is notable that it was possible to observe preexplosion luminescence which developed as a result of the chemical reaction in the irradiated crystal layer. The luminescence intensity reaches the recorded value in $\approx$300 nsec. In this case, above the crystal surface there is a faint luminous background related to the expanding gaseous reaction products. The explosion of the crystal volume is recorded with a delay of $\approx$700 nsec relative to the initiating pulse. The rate of development of the reaction in the volume is difficult to estimate from the given record because the emission brightness exceeded the dynamic range of the recording system. Nevertheless, the explosion caused destruction of the structural elements, as in the cases described above, which indicates a detonation nature of the explosion. Unfortunately, we were unable to record a clearer picture of explosion at a nearly critical energy density in a series of 10 experiments because the process has a statistical nature and requires longer sweeps of the streak camera, whose time resolution is insufficient to estimate the rate of development of the chemical reaction.

We note that shock-wave initiation of detonation of a sample 1 mm thick requires a pressure amplitude $>$4 GPa [13]. The shock-wave amplitude resulting from the adiabatic heating of the irradiated crystal area due to absorption of the electron beam energy was estimated above as about 1 GPa. Even with allowance for the pressure increase upon reflection from the copper plate, this is not sufficient for detonation initiation.

This fact confirms the conclusion that the exothermic chemical reaction leading to an increase in the initial pressure starts in the irradiated crystal layer already during exposure to the electron beam.

This work was supported by the Russian Foundation for Basic Research (Grant No. 07-02-96009).

REFERENCES

1. B. P. Aduev, D. R. Nurmukhametov, and V. N. Shvaiko, “Fast processes in subcritical excitation of PETN by picosecond electron pulses,” in: *Proc. of the II Russian Conf. on Energetic Condensed Systems*, Chernogolovka (2004), pp. 154–155.
2. B. P. Aduev, G. M. Belokurov, S. S. Grechin, and V. N. Shvaiko, “Investigation of the early stages of explosive decomposition of PETN crystals initiated by pulsed electron beams,” *Izv. Vyssh. Uchebn. Zaved., Fiz.*, **50**, No. 2, 3–9 (2007).
3. B. P. Aduev, N. V. Nelyubina, and V. Kh. Pak, “Radical products in gamma-irradiated PETN,” *Fund. Probl. Sovr. Materialoved.*, No. 3, 17–19 (2008).
4. B. P. Aduev, N. V. Nelyubina, and V. Kh. Pak, “Formation and destruction of products in gamma-irradiated PETN,” *Izv. Vyssh. Uchebn. Zaved., Fiz.*, **52**, No. 8/2, 307–309 (2009).
5. B. P. Aduev, B. M. Belokurov, V. K. Golubev, and S. S. Grechin, “Initial stages of explosive decomposition of PETN initiated by an electron beam,” in: *Proc. X Int. Conf. on Physicochemical Processes in Inorganic Materials*, Vol. 1, Kemerovo (2007), pp. 192–193.
6. B. P. Aduev and V. K. Golubev, “Effect of electronic excitation and ionization of PETN molecules on the initial stage of its decomposition upon exposure to an electron beam,” in: *Zababakhin Scientific Readings*, Proc. of the IX Int. Conf. (September 10–14, 2007), Inst. of Tech. Phys., Russian Federal Nuclear Center, Snezhinsk (2007), pp. 79–80.
7. B. P. Aduev, G. M. Belokurov, S. S. Grechin, and E. V. Tupitsyn, “Explosive luminescence of PETN initiated by an electron beam,” *Pis’ma Zh. Tekh. Fiz.*,, **30**, No. 15, 91–95 (2004).
8. B. P. Aduev, G. M. Belokurov, S. S. Grechin, and A. V. Puzynin, “ Transient optical absorption spectra of PETN crystals exposed to a pulsed electron beam,” *Izv. Vyssh. Uchebn. Zaved., Fiz.*, **51**, No. 11/2, 104–106 (2008).
9. Z. A. Dreger, Y. A. Gruzdkov, et al., “Shock wave induced decomposition chemistry of pentaerythitol tetranitrat single crystals: Time-resolved emission spectroscopy,” *J. Phys. Chem. B*, **106**, No. 2, 247–256 (2002).
10. V. I. Korepanov, V. M. Lisitsyn, V. I. Oleshko, and V. P. Tsipilev, “Initiation of PETN detonation by a powerful electron beam,” *Pis’ma Zh. Tekh. Fiz.*, **29**, No. 16, 23–28.
11. V. I. Oleshko, V. I. Korepanov, V. M. Lisitsyn, and V. P. Tsipilev, “Destruction and gasification of PETN on exposure to an electron beam,” in: *Zababakhin Scientific Readings*, Proc. IX Int. Conf. (September 10–14, 2007), Inst. of Tech. Phys., Federal Nuclear Center, Snezhinsk (2007), pp. 58, 59.

12. V. I. Oleshko, V. I. Korepanov, V. M. Lisitsyn, and V. P. Tsipilev, "Nature of glowing generated by irradiation of pentaerythrite tetranitrate by an electron beam," *Combust., Expl., Shock Waves*, **43**, No. 5, 572–574 (2007).
13. L. P. Orlenko (ed.), *Physics of Explosion* [in Russian], Vol. 1, Fizmatlit, Moscow (2004).
14. V. N. Shvaiko, A. G. Krechetov, B. P. Aduev, et al., "An experimental complex for investigation of spectral-kinetic and spatial-dynamic characteristics of explosive decomposition of energetic materials," *Zh. Tekh. Fiz.*, **75**, No. 6, 59–62 (2005).
15. I. N. Balychev, D. I. Weissburd, and G. I. Gering, "Strong emission during pulsed irradiation of dielectrics by high-density electron beams," *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 3, 157–158 (1975).
16. I. N. Balychev, D. I. Weissburd, and G. I. Gering, "Powerful threshold emission of dielectrics on exposure to nanosecond electron beams of high density," *Pis'ma Zh. Tekh. Fiz.*, **2**, No. 7, 327–330 (1976).
17. B. P. Aduev, G. M. Belokurov, and S. S. Grechin, "Acoustic characteristics of explosive decomposition of tetranitropentaerytrite single crystals initiated by an electron beam," in: *Physicochemical Processes in Inorganic Materials*, Proc X Int. Conf., Vol. 1, Kemerovo (2007), pp. 193–196.
18. A. A. Borisov (ed.), *Detonation and Explosives* (collected scientific papers) [Russian translation], Mir, Moscow (1981).