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The Size Effects and Before-Threshold Mode of Solid-State Chain Reaction

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In this work size effects and before-threshold mode of the solid state reaction in silver azide crystals were experimentally and theoretically researched. It was shown that if the crystal's size decreases the critical initiation energy density considerably increases. This is because of the bigger speed of the electron-carriers' recombination on the crystal surfaces in comparison with the same value for the bulk. Before-threshold mode of the solid state branched chain reaction can be observed if the energy of the initiation is smaller than the critical value; and the carriers' diffusion length is comparable with the sample sizes or with the area there the initiating irradiation absorbed. The results of the research are necessary to work out the details of optical detonator.

Keywords: explosive decomposition, solid-state chain reaction, size effects, before-threshold mode, kinetics, laser initiation.

Размерные и допороговые эффекты твердофазных цепных реакций

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В работе экспериментально и теоретически исследованы размерные и допороговые режимы разветвленных твердофазных цепных реакций разложения кристаллов азида серебра. Показано, что с уменьшением размера кристалла пороговая плотность энергии перехода медленного разложения во взрывное существенно увеличивается. Причина проявления размерных

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эффектов связана с повышенной скоростью обрыва цепи на поверхности по сравнению с объемом. Допороговые эффекты разветвленных твердофазных цепных реакций наблюдаются в тех случаях, когда диффузионная длина носителей цепи сопоставима с размерами образца или с областью поглощения лазерного излучения, а энергия инициирующего импульса меньше соответствующей критической величины.

Ключевые слова: взрывное разложение, твердофазные цепные реакции, размерные эффекты, допороговые эффекты, кинетика, импульсное инициирование.

1. Introduction

One of the most important problems of the physical chemistry is the processes' mechanism identification in order to regulate their speed in case of different external actions. The importance of the presented research is determined by the necessity of working out the optical detonators based on the secondary explosives [1-3]. There are two main points of view using to explain the explosive process – thermal model [1-5] and chain model [6-8]. In terms of the thermal model it is supposed that the material decomposes according to the one-step reaction, which kinetic constant obeys the Arrhenius law [9-11]. At the same time it is supposed that the preexponential factor and the activation energy do not depend on the temperature. In terms of the chain model the self-accelerating decomposition relates to the multiplication of the electron and ion defects of lattice [12-13]. Using the chain model several regularities of the silver azide (SA) crystals' explosive decomposition initiated by the excimer laser were explained [14-17].

In spite of the fact that the chain model was experimentally and theoretically approved to be true for the SA [17], the common conception in the order of the elementary stages of the process are still absent in literature. The main difficulties of identification of the chain reaction's elementary stages (generation and evolution) occur because it was widely experimentally investigated only the self-accelerating mode of the explosive decomposition process. To work out the experimentally approved solid-state chain reaction it is necessary to investigate the kinetics of the before-threshold mode of the decomposition process and the regularities of the transition from the damped mode to the self-accelerating mode Aim of this work is to experimentally and theoretically investigate size effects and before-threshold mode of the solid-state branched chain reaction in the silver azide crystals.

2. Experimental section

The depiction of experimental set-up, which was used to research the regularities of the silver azide explosive decomposition, one can find in [18]. Silver azide macrocrystals with dimensions 1*1*0.3 mm^3 were used as experimental samples. The crystals had no visible imperfections. The main impurities' concentration was not exceed 10^{17} cm^{-3}.As a source of pulse influence, which initiates explosive decomposition, a Nd: Yag laser (λ = 1060 nm) was used. The initiation wavelength is in the area of the impurity absorption, this allowed to initiate the reaction homogeneous throughout the sample [19]. Maximum energy density of the laser was 20 J. Pulse duration was 30 ns.

It was experimentally shown that before-threshold mode, in which the initiated chain reaction decayed without reaching the self-accelerating mode, is observed in microcrystals initiated by the

pulses which energy density is smaller than the critical value $H_c(r)$. The dependence of the critical energy density on the crystal size for the silver azide crystal is shown on Fig. 1. The crystal size range for which the before-threshold mode might be observed is also shown on Fig. 1.

3. Model of the branched chain reaction

In the work [19] a new reason of increase of critical energy density (H_c) of azide heavy metals explosion initiated by pulse radiation was proposed. This reason is the result of the branched chain reaction and is the feature of all chain reactions. According to the model it is bound up with the increased rate of electron-hole (*e-h*) pairs (breaking chain stage) on crystal surface in comparison with the bulk recombination. It results in increase of H_c if the sample size is comparable with the free path of electron excitations – chain carriers. The proposed model is a solid-state analogue of the dependence of explosion initiation critical parameters on vessel dimensions of gas-phase reaction [20-21].

Let us consider the effect of laser 20ns pulse radiation on silver azide microcrystal. Taking into account the influence of surface on the reaction propagation the kinetics of the process will be described by the system of integro-differential equations [20-23]:

$$\begin{cases} dp/dt = G(t) - 2k_2 p^2 - k_r p + 3k_1 \beta A + D\Delta p, \\ dA/dt = k_2 p^2 - k_1 A, \\ dN_2/dt = 3k_1 A, \qquad D\dfrac{dp}{dx}_{x=0,\ x=l} = sp, \\ \beta = (L - p - 1{,}5[\mathrm{N_2}] - 2A)/L; \end{cases} \tag{1}$$

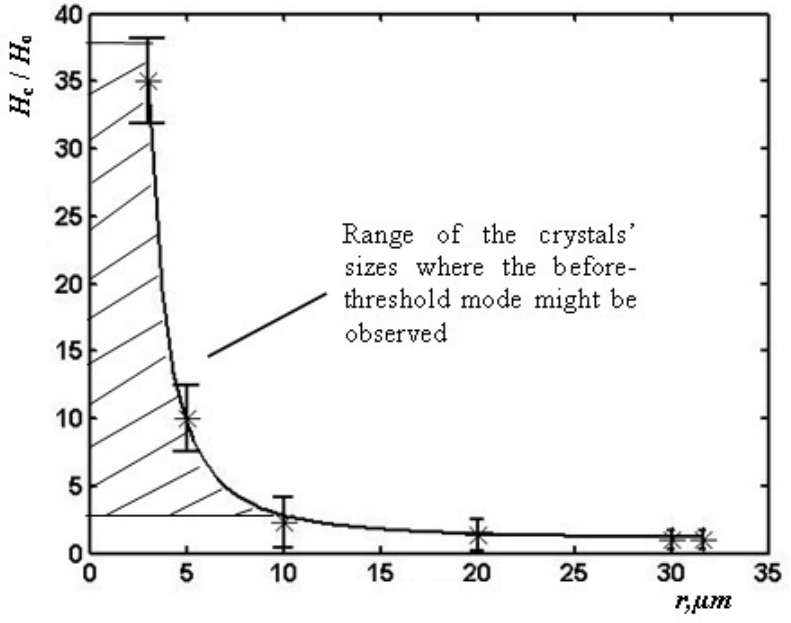

Fig. 1. Dependence of the initiation critical energy density of the silver azide crystals (relative units) on the crystal size. Points are experimental data, line is calculation. H_c – critical energy density necessary to initiated explosive decomposition of the microcrystal, H_0 – critical energy density of big crystals, r – crystal's size

where p, A, N_2 are concentrations of holes, N_6 complexes and molecular nitrogen in the bulk of the crystal; k_2, k_1, k_r are constants of generation, N_6 – complex destruction and *e-h* pair recombination rates in the bulk of the crystal; D is the diffusion constant of holes; s=5*10^{5}cm/s is the rate of surface recombination in silver azide crystals; *sp* is a boundary condition taking into account the recombination rate of charge carriers on the surface; β is the coefficient taking into account anion expenditure during the reaction; L is Loshmidt number.

The dependence of initiation energy critical density on the size of the crystal under short pulses might be presented as:

$$H_c = \left[k_r^* \Big/ k_2 + 2 \cdot (k_r^*)^2 \Big/ k_2 \cdot k_1 \right] \cdot \frac{E}{\alpha} \tag{2}$$

where $k_r^* = k_r + \pi^2 D \Big/ r^2$ is the effective constant of the recombination rate, which includes the inhibitory influence of the surface; E is the average energy of one *e-h* generation; α is the effective absorption coefficient.

In work [19] it is shown that increase of H_c will reveal itself in the most effective way if the size of the crystal is in following range

$$r_1 = \pi \left(\frac{6D^2}{k_1 k_2 L} \right)^{1/4} \le r \le r_2 = 2\sqrt{\frac{\pi^2 D}{k_r}} \tag{3}$$

With the reaction constants estimated in [23] these values are r_1 = 1μm, r_2 = 20μm.

If the crystal size is r> (2-3) $r_2 \approx$ 50μm the critical initiation energy density practically coincides with the bulk density H_c=H_o. If $r \le$ 1μm H_c increases in more than 10^3 times that practically corresponds to the total ionization of anionic sublattice. Finally, the branched-chain reaction is not realized and microcrystals are decomposed without explosion.

The results are presented in Fig. 1. From these results it follows that according to [23] H_c increases in more than 30 times if the crystal size decreases from 35 to 3μm, and tends to H_o if the crystal size increases. After the action of pulse radiation the large crystals (r > 50μm) either explode over exceeding initiation threshold or show no visible changes (including flash of light emission). The microcrystals with sizes r ≤ 1μm cannot be initiated up to the energy density $H \ge$ 10 J/cm^2. Under these H microcrystals are practically decomposed entirely under pulse duration, but the stage of exponential increase of the reagents' concentration is absent.

On Fig. 1 the experimental and calculated using equation (2) dependences of the explosion initiation critical energy density on the sizes of silver azide microcrystals are shown. The comparison with the experiment has allowed to determine the parameters k_r= 1,6 * 10^6 s^{-1} and k_1= 6,2 * 10^7 s^{-1} for silver azide microcrystals which do not much differ from the values obtained in [22] while studying other experimental explosive characteristics in silver azide.

Thus, the experimental results confirm the viewpoint [23] that the breaking chain stage is the recombination of electron excitations. High rate of this stage on the surface of the crystal is one of the main reasons for H_c increase if the sample sizes are comparable with the free path of electron excitations.

The obtained results also allow to estimate the mobility (diffusion constant) of electron excitations directly during explosive decomposition. The calculations were carried out with the diffusion constant of holes $D = 0.25$ cm^2/s which corresponds to their experimental mobility $\mu \approx 10$ cm^2/ V s.

The close coincidence calculated at D=0.25cm^2/s and experimental values $H_c(r)$ indicate firstly that the mobility (diffusion constant) of electron excitations during explosion decomposition slightly differs from the values determined with use of Hall effect, and secondly that the temperature rise is not the first cause of silver azide explosive decomposition.

4. Before-threshold behavior of silver azide chain explosive decomposition

The model described above allows to predict theoretically and to detect experimentally a new before-threshold mode of the chain reaction. This mode is observed in case of irradiation of the microcrystals with sizes $r_2 < r < r_2$ by pulses with the energy density $H_o < H(r) < H_c(r)$.

The before-threshold mode take place because the reaction after being initiated in the bulk of the crystal goes out on the crystal surface owing to the diffusion of electron excitations where the recombination process is very intensive. By increasing pulse energy density it is possible to fulfill the condition $H(r) \geq H_c(r)$ and the reaction process transforms from damping mode to self-acceleration mode resulting in the explosion of the sample. In «MATLAB» environment the software package was developed for mathematical modeling the kinetics of solid-state chain reactions in silver azide. The package allows to solve numerically the system of 1500–2000 integro-differential equations. The obtained solution allows to visualize the image of the reaction propagation at any moment of time and at any point of the crystal. Fig. 2 and 3 present the results of the reagent space distribution calculated for silver azide microcrystyals with sizes 5μm at different points of time. The initial rate of *e-h* pair generation is taken the same for the whole bulk of the sample. Fast decrease of holes' concentration owing to N_6 complex generation is realized directly after the ending of the pulse. In subsurface areas faster decrease of holes' concentration is realized owing to the high recombination rate on the crystal surface. The following growth of reagents' concentrations, especially in the central part of the crystal, is because of the multiplication of electron excitations during chain reaction (Fig. 2). The maximum concentration is achieved in 326 ns, and then the decrease of the reagent concentrations is realized owing to the sample burnout (Fig. 3).

On Fig. 4 the oscillogram of before-threshold illumination of the silver azide monocrystals is presented. When the initiating energy density was smaller than $H_c(r)$ the zonal photomultiplier in the spectral areas 800 ÷ 900 nm and 500 ÷ 550 nm registered a glow peak. This illumination is a result of the physic-chemical process in the initiated part of the sample. This glow might be the result of the reaction or the laser-induced breakdown.

Before-threshold glow one can observe for microcrystals which sizes are $r \leq 10$ mcm. The lowest value of the initiation energy density (H_p) for which the pre-threshold glow is observed for the microcrystals is about 60-65 mJ/cm^2. For 10μm crystals the values of H_p and H_c are almost equal and the before-threshold glow might be observed only in narrow area $H_p < H_0 < H_c$. The lowest value of the initiation energy density, for which the before-threshold glow might be observed, almost does not depend on the microcrystal size. H_p value is about doubled critical initiation energy density of the macrocrystals ($H_p \approx 2\ H_{\infty c}$). Although to prove experimentally that H_p is put and therefore depends on

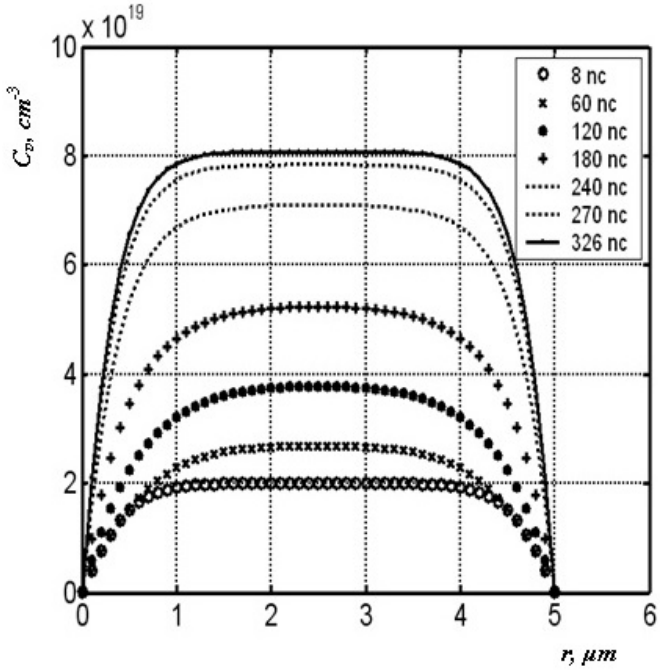

Fig. 2. Calculated distribution of reagents' concentration along microcrystal in 8, 60, 120, 180, 240, 270 and 326 ns time. C_p – concentration of the holes, main reagents of the solid –state chain reaction, axis r symbolizes the different places in the crystal

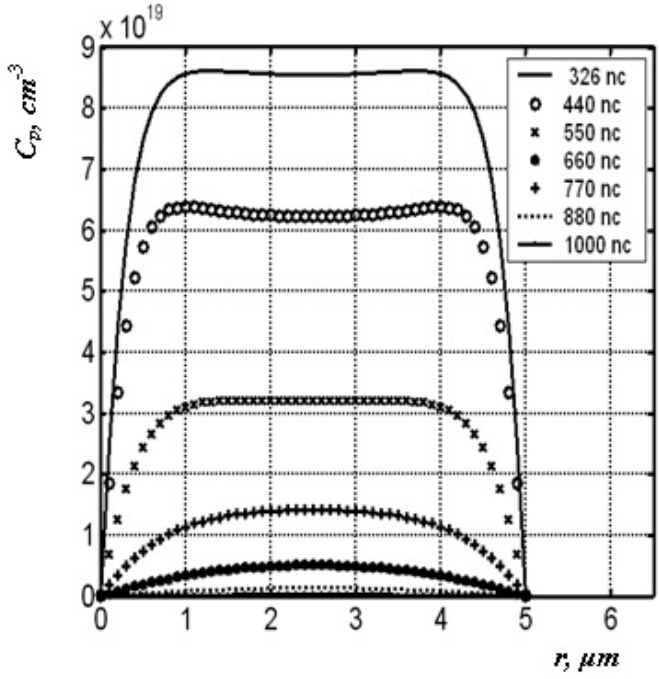

Fig. 3. The calculated kinetics of distribution of reagents concentration in microcrystal along crystal in 326, 440, 550, 660, 770, 880 and 1000 nc. C_p – concentration of the holes, main reagents of the solid –state chain reaction, axis r symbolizes the different places in the crystal

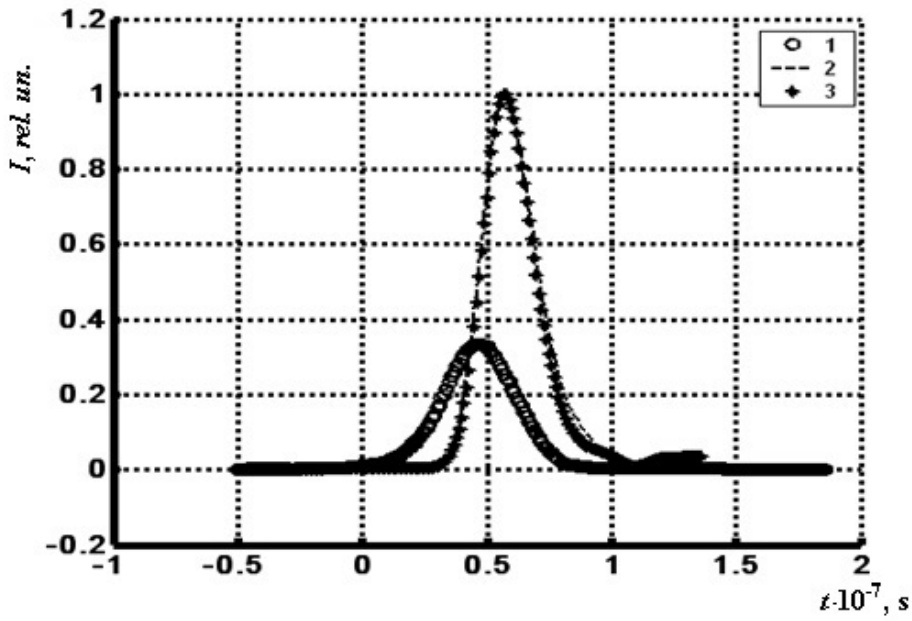

Fig. 4. Oscillogram of glow of silver azide microcrystal in case $H < H_c$: 1 – impulse, 2 and 3 – signals of the photomultipliers registered luminescence in the spectral areas 800 ÷ 900 nm and 500 ÷ 550 nm correspondingly. I – intensity of the signal, registered by the photomultiplier (relative units); t – time

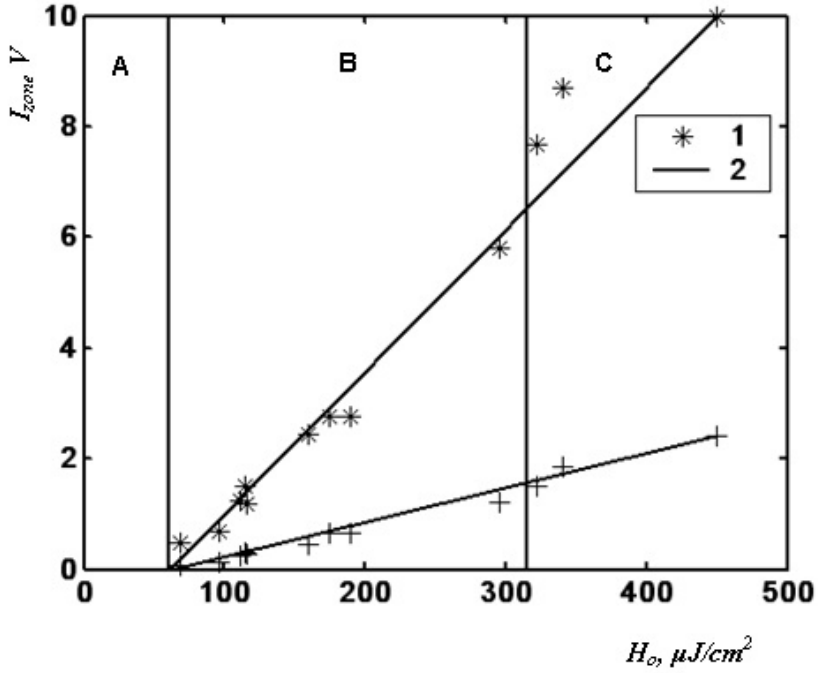

Fig. 5. Dependences of the peak value in the spectral areas 800 ÷ 900 nm and 500 ÷ 550 nm correspondingly for 5 mμ silver azide microcrystals on the initiation energy density. In part A crystal show no visible changes, in part B one can observe before-threshold mode of the solid-state reaction, C – explosive decomposition. H_o – energy density of the laser impulse

the critical initiation energy density of the macrocrystals it is necessary to make additional experiments and examine the dependence of H_p on the impulse duration and intensity and the spectrum of the preliminary irradiation.

The threshold of the laser-induced breakdown for a bulk of AgN_3 microcrystal is well known [18] ($H_b \sim 500$ mJ/cm^2) and exceeds in more than 8 times the value of the lowest energy density for which the before-threshold glow is observed ($H_p \approx 8\, H_b$). This allows to conclude that optical breakdown could not explain the fact of before-threshold glow in this experiment. The reason of the glow, registered by the zone photomultiplier while the initiation energy density is lower than H_c, is physic-chemical processes in individual microcrystals of silver azide. In this case there are two possible way of energy liberation – recombination of electrons and holes and decay of complex N_6 till N_2. We can suppose that the reaction is generated and then attenuates because the chain carriers' concentration decreases. The decrease occurs because of the recombination processes and the decomposition reaction.

The kinetic curves of before-threshold glow in spectral areas 800 ÷ 900 nm and 500 ÷ 550 nm are similar to each other and after being standardized on maximum almost coincide. Main parameters of the curves (constants of exponential growth and slop, peak values) also coincide. Small difference in the glow curves in these spectral areas is observed in the part of slope below the half of the amplitude. The difference is the slower decay of the signal in the area 800 ÷ 900 nm.

If the initiating energy density is bigger than its critical value H_c the kinetics of glow changes – it has two peaks. First peak of kinetics is similar to that of the before-threshold kinetics, for example has the same constant of exponential growth.

On Fig. 5 one can see the dependence of the kinetic curve maximum on the initiating energy density for the silver azide microcrystals with sizes 5μm. Each point is the averaging of 5 tests. The signal observed if the initiating energy density is equal to doubled critical energy density of the macrocrystals. On the figure the critical energy density of silver azide macrocrystals and microcrystals of examined sample party are marked with vertical lines. Regularities of the glow in case of initiating energy density growth till the critical value remain the same. The glow peak in both spectral areas depends linearly on the initiating energy density. In case of macrocristals initiation with the energy which is smaller than 60 μJ/cm^2, they show no visible changes. The intermediate area of energies (area B) is the area there the before-threshold mode in AgN_3 crystals.

The second peak on the kinetic curve in case of silver azide microcrystals initiation with energy bigger than H_c is observed in 100-300 ns. Its intensity is not equal to the intensity of the first peak. While the energy of the impulse growths the peak value almost does not change. The interval between the first and the second peak becomes smaller if the impulse energy growths. For impulse energy which is near to the critical value H_c the signal between two peaks might fall till zero.

5. Resume

In this work size effects and before-threshold behavior of the solid state reaction in silver azide crystals were experimentally and theoretically researched. It was shown that if the crystal's size decreases the critical initiation energy density considerably increases. This is because of the bigger speed of the electron-carriers recombination on the crystal surfaces in comparison with the same value for the bulk. Before-threshold effects of the solid state brainched chain reaction can be observed if the energy of the initiation is smaller than the critical value; and the carriers' diffusion length is

comparable with the sample sizes or with the area there the initiating irradiation absorbed. The results are necessary to work out the details of optical detonator. The authors thank Ministry of Education and Science of the Russian Federation (state order № 2014/64) and Russian Foundation for Basic Research for the financial support (grant №14-03-00534 A), prof. Kriger V. and prof. Tsipilev V. for help in experimental part of the work and useful discussion.

References

1. Aduev B.P., Nurmukhametov D.R., Furega R.I., Zvekov A.A., Kalenskii A.V. Vzryvchatoye razlozheniye TENa s nanodobavkami alyuminiya pri vozdeystvii impulsnogo lazernogo izlucheniya razlichnoy dliny volny. Khimicheskaya fizika, 2013, 32(8), 39–42.

2. Zykov I.Y. Accounting of the absorbance of nano-inclusions heated by laser impulse. International scientific periodical "Modern fundamental and applied researches", 2012, 3 (6), 42–48.

3. Ananyeva M.V., Zvekov A.A., Zykov I. Yu., Kalensky A.V., Nikitin A.P. Promising compounds for the cap of optical detonator. Perspektivnye materialy, 2014, 7, 5–12.

4. Kalenskii A.V., Zvekov A.A., Ananyeva M.V., Zykov I.Yu., Kriger V.G., Aduev B.P. Influence of the laser irradiation wavelength on the energetic materials' initiation critical energy. Fizika goreniya i vzryva, 2014, 50(3), 98–104.

5. Kriger, V.G., Kalenskii A.V., Zvekov A.A., Zykov I.Yu., Aduev B.P. Vliyaniye effektivnosti pogloshcheniya lazernogo izlucheniya na temperaturu razogreva vklyucheniya v prozrachnykh sredakh. Fizika goreniya i vzryva, 2012, 48(6), 54–58.

6. Kriger V.G., Kalenskii A.V., Zvekov A.A., Zykov I.Yu., Borovikova A.P., Grishaeva E.A. Opredeleniye shiriny fronta volny reaktsii vzryvnogo razlozheniya azida serebra. Fizika goreniya i vzryva, 2012, 48(4), 129–136.

7. Kriger V.G., Kalenskii A.V., Zvekov A.A. Relaksatsiya elektronno-vozbuzhdennykh produktov tverdofaznoy reaktsii v kristallicheskoy reshetke. Khimicheskaya fizika, 2012, 31(1), 18–22.

8. Kalenskii, A.V., Anan′eva M.V., Kriger V.G., Zvekov A.A. Koeffizient zahvata elektronnyh nositeley zaryada na ekranirovannom ottalkivaushyem centre. Khimicheskaya fizika, 2014, 33(4), 11–16.

9. Ananyeva M.V., Kalenskii A.V., Grishaeva E.A., Zykov I.Yu., Nikitin A.P. Kinetic regularities of the explosive decomposition of PETN containing nanosized inclusions of aluminium, cobalt, and nickel. Bulletin of Kemerovo State University, 2014, №1-1 (57), 194–200.

10. Aduev B. P., Nurmukhametov D. R., Belokurov G. M., Zvekov A. A., Kalenskii A. V., Nikitin A. P., and Liskov I. Yu. Integrating Sphere Study of the Optical Properties of Aluminum Nanoparticles in Tetranitropentaerytrite. Zhurnal Tekhnicheskoi Fiziki, 2014, 84(9), 126–131.

11. Kriger V.G., Kalenskii A.V., Zvekov A.A., Zykov I.Yu., Nikitin A.P. Protsessy teploperenosa pri lazernom razogreve vklyucheny v inertnoy matritse. Teplofizika i aeromekhanika, 2013, 20(3), 375–382.

12. Zhuravlev Yu. N., Lisitzin V. M. Izuchenie reakzionnoi sposobnosti azida serebra po dannim zonnych raschetov v ramkach teorii funkzionala plotnosti. Khimicheskaya fizika, 2014, 33(3), 3–12.

13. Kriger V.G., Kalenskii A.V., Zvekov A.A., Anan′eva M.V. Determination of Spatial Characteristics of the Chain Reaction Wave in Silver Azide. Khimicheskaya fizika, 2014, 33(8), 22–29.

14. Kalenskii A.V., Kriger V.G., Zvekov A.A., Grishaeva E.A., Zykov I.Yu., Nikitin A.P. The Microcenter Heat Explosion Model Modernization. Izvestia Vuzov Fizika, 2012, 8(11/3), 62–66.

15. Kriger V.G., Kalensky A.V., Zvekov A.A., Ananyeva M.V., Borovikova A.P. Diffuzionnaya model razvetvlennoy tsepnoy reaktsii vzryvnogo razlozheniya azidov tyazhelykh metallov. Khimicheskaya fizika, 2009, 28(8), 67–71.

16. Kriger V.G., Kalenskii A.V., Zvekov A.A. Opredeleniye nachala mekhanicheskogo razrusheniya kristallov azida serebra, initsiirovannykh lazernym impulsom. Fizika goreniya i vzryva, 2010, 46(1), 69–72.

17. Ananyeva M.V., Kriger V.G., Kalensii A.V., Zvekov A.A. Comparative analysis of energetic materials explosion chain and thermal mechanisms. Izvestia Vuzov Fizika, 2012, 55(11/3), 13–17.

18. Kriger V.G., Kalenskii A.V., Zvekov A.A., Tsipilev V.P. Explosive decomposition of silver azide single crystals for various diameters of the irradiated area. Fizika goreniya i vzryva, 2009, 45(6), 105–107.

19. Kalenskii A.V., Kriger V.G., Tzipilev V.P., Ananyeva M.V. Dependence of the critical initiation energy of the silver azide monocrystal on the diameter of the irradiation area. Polzunovskii vestnik, 2006, 2–1, 75–77.

20. Kriger V.G., Kalenskii A.V., Zakharov Yu.A., Tzipilev V.P. Mechanisms of the Solid state chain reaction. Materialovedenie, 2006, 9, 14–21.

21. Grishaeva E.A., Kalenskii A.V., Ananyeva M.V., Zvekov A.A. Non-isothermal model of branched chain explosive decomposition reaction in energetic materials. Fundamental'nye problemy sovremennogo materialovedenia, 2013, 10(1), 44–49.

22. Kriger V.G., Kalensky A.V. Initiation of heavy metal azides by pylse radiation. Khimicheskaya fizika, 1995, 14(4), 152–160.

23. Kriger V.G., Kalensky A.V. The effect of crystal size on initiation of decomposition of heavy metal azides by pulse radiation. Khimicheskaya fizika, 1996, 15(3), 40–46.