

HETEROGENEOUS CHAIN MECHANISM OF LEAD AZIDE INITIATION BY A LASER PULSE IN THE TRANSPARENCY REGION OF A CRYSTAL

A.V. Khaneft

Department of physics
Kemerovo State University

Krasnaya, 6, Kemerovo State University, Kemerovo, 650043, Russia

The heterogeneous-chain mechanism of low-threshold initiation of heavy azides metal (HMA) is suggested. The recombination of azides-radicals on a HMA surface leads to generation of electron-hole pairs. Azide radicals are formed at trapping of holes surface levels of azide anions. The computer simulation of this mechanism is carried out. The computing were performed at different length and density of energy of a laser pulse. The initiation delay depends on the characteristic time within which traps are filled by holes.

The effect of low-threshold initiation of heavy metal azides (HMA) by pulse radiation is widely known in physics of explosion. The essence of this effect is as follows. The energy absorbed by a sample is much less than the energy needed for HMA explosion according to the thermal mechanism of explosion [1]. Recently, an opinion has appeared that the effect of HMA low-threshold initiation in the crystal transparency region is due to the development of a chain reaction. However, the problem in what way holes needed to form azide radicals, i.e. for chain reaction startup are generated in HMA (thermal band gap width $E_g \sim 3,5$ eV) under absorption of light quantum of laser radiation with energy $h\nu_0 \sim 1,17$ eV has been ignored in a number of works. It should be noted that in terms of common considerations the chain mechanism of low-threshold HMA initiation should:

1) satisfy to Einstein law of quantum equivalence according to which each quantum, absorbed by molecule or solid causes single elementary excitation [2]. For HMA the critical concentration of nonequilibrium holes p^* in impurity area ($\alpha_0 \sim 1 \text{ cm}^{-1}$) can not be more than concentration of absorbed photons

$$p^* \leq n_f = \alpha_0 (1-R) W^* / h\nu_0 \sim 10^{15} \text{ cm}^{-3}$$

2) be nonlinear, otherwise there will be no initiation threshold [3].

Earlier [4], in order to explain low-threshold initiation of lead azide by pulse radiation it has been assumed that the azide-radicals N_3 are formed in HMA under photoionization of surface azide-anion levels. At the same time for better understanding the physics of chain process development, the simplified system of the differential equations for mechanism of initiation of lead azide was considered. In the present work, the system of the kinetic equations for free localized holes and electrons in a bulk of a solid was numerically solved

$$\frac{\partial p}{\partial t} = 3\alpha k_2 m^2 \exp(-\alpha x) - k_3 p (P_t - p_t) - k_7 np + D_p \frac{\partial^2 p}{\partial x^2}, \quad (1)$$

$$\frac{\partial n}{\partial t} = 3\alpha k_2 m^2 \exp(-\alpha x) - k_4 np_t - k_5 n (N_t - n_t) - k_7 np + D_n \frac{\partial^2 n}{\partial x^2}, \quad (2)$$

$$\frac{dp_t}{dt} = k_3 p (P_t - p_t) - k_4 np_t, \quad (3)$$

$$\frac{dn_t}{dt} = k_5 n (N_t - n_t), \quad (4)$$

with the following boundary conditions on a surface and in the center of a crystal

$$D_p \frac{\partial p(0,t)}{\partial x} = k_1 p(0,t)(M - m),$$

$$D_n \frac{\partial n(0,t)}{\partial x} = k_6 n(0,t)(K - k),$$

$$\frac{\partial p(t,L)}{\partial x} = 0, \quad \frac{\partial n(t,L)}{\partial x} = 0.$$

The kinetics of a trapping of holes and electrons by surface levels of azide-anions and lead cations and bimolecular recombination of azide-radicals, resulting in a formation of molecular nitrogen N₂ was determined from the solution of the following system of the differential equations:

$$\frac{dm}{dt} = \sigma_f (M - m)(1 - R)I(t) + \quad (5)$$

$$+ k_1(M - m)p(0,t) - m/\tau_D - 2k_2m^2,$$

$$\frac{dk}{dt} = \sigma_f (K - k)(1 - R)I(t) + \quad (6)$$

$$+ k_6n(0)(K - k) - k/\tau_K,$$

$$\frac{d[N_2]}{dt} = 3k_2m^2. \quad (7)$$

The initial concentrations of electrons and holes (both free and localized) were supposed to be equal to zero. In the present work, the following labels are accepted: σ_f is the cross section for photoionization of azide anion surface level; R is the diffuse reflectance coefficient of lead azide ($R = 0,9$ [1]); $I(t)$ is the laser radiation intensity; M , P_t are the initial concentrations of azide anion surface levels and hole traps, respectively; p_t , m are the concentrations of trapped holes and azide radicals; K , N_t are the initial concentrations of surface levels of lead cations and electron traps; k , n_t are the electron concentration on surface and bulk centers, respectively; k_1 is the constant of a trapping of a hole by anion surface level; k_2 is the constant for recombination of azide radicals; k_3 is the constant for a trapping of a hole in the crystal bulk; k_4 is the constant of recombination of an electron with trapped hole; k_5 is the constant for a trapping of an electron in crystal bulk; k_6 is the constant of a trapping of an

electron by surface cation level; k_7 is coefficient of interband radiation recombination; τ_D is the characteristic time of desorption of azide radical; τ_K is the characteristic time of reconstruction of a cationic sublattice on a crystal surface. The time τ_K was supposed to be equal to the time of radical recombination $(k_2m)^{-1}$. The constants of a trapping of electrons and holes were determined by expression $k_i = v_{th}\sigma_i$, where v_{th} is the thermal velocity of a hole (electron); σ_i is the capture cross-section of the relevant process. The intensity of laser light radiation as a function of a time is given in the form

$$I(t) = \frac{W}{4! h \nu_0 t} \left(\frac{4t}{t_f} \right)^5 \exp(-4t/t_f),$$

where t_f is the duration of the pulse leading edge, which is connected with the duration of a pulse measured by equation $t_f = \tau/1,19$ at its half-height.

The first term in the equations (1) and (2) reflects the effect of multiplication of electron-hole pairs in near-surface area ($\alpha^{-1} = 10^{-5}$ cm width) under recombination of radicals on HMA surface [5,6]. According to [5] a vibratory-excited dipole under radical recombination appears, whose interaction with Bloch valence band electrons results in generation of electron-hole pairs. The yield of the given process can be close to unity [5]. In addition, in the case of a formation of electronic – excited molecules of nitrogen on a surface, their lifetime can decrease up to $5 \cdot 10^{-15}$ s. This results in fast exchange by the energy of a nitrogen molecule with a solid, forming electron - hole pairs in near-surface area of a crystal [6]. The recombination of electrons with holes results in so-called radically-recombination luminescence [5,7]. It is possible, that the pre-explosive luminescence detected for HMA for the first time in the work [8] is radically -recombination luminescence.

The diffusion equations for electrons and holes were solved by a chaser method with a

variable step on coordinate at $D_n = D_p = 0,25$ cm²/s. The system of the ordinary differential equations (ODE) for electron-hole trapping centers in a bulk and on a solid surface was solved by half-implicit method of the second order of accuracy. To increase the accuracy of calculations, in view of the fact that the system of equations is nonlinear, some iterations were carried out on each step, first the ODE system was solved and then diffusion equations were solved.

A numerical modeling was carried out at the following initial concentrations of electron-hole trapping centers: $P_t = 4 \cdot 10^{17}$ cm⁻³, $N_t = 10^{18}$ cm⁻³, $M = 0,886 \cdot 10^{15}$ cm⁻², $K = 0,443 \cdot 10^{15}$ cm⁻² and their cross-sections: $\sigma_1 = 2 \cdot 10^{-14}$ cm², $\sigma_3 = 10^{-13}$ cm², $\sigma_4 = 10^{-16}$ cm², $\sigma_5 = 10^{-14}$ cm², $\sigma_6 = 10^{-15}$ cm², $\sigma_7 = 10^{-19}$ cm². The recombination constant for radicals was supposed to be equal to $k_2 = 10^{-5}$ cm²/s, photoionization cross-section for surface azide anion levels was $\sigma_f = 4,9 \cdot 10^{-18}$ cm², time was $\tau_D = 4 \cdot 10^{-7}$ s and thermal velocity was $v_{th} = 10^7$ cm/s.

The calculations were carried out under different densities of energy W and laser pulse duration τ . Functional connection of a delay time of initiation t_i as a function of a density of energy W agrees well with experimental data [1] obtained for lead azide (Figure. 1). The delay time t_i no longer depends on τ at $\tau < 10^{-7}$ s (Figure. 2), this qualitatively agrees with experimental data [9]. The critical density of initiation energy for lead azide as a function of a laser pulse duration is due to a competition of two processes being desorption of radicals (breaking of a chain) and recombination of radicals on a crystal surface (branching of a chain). The calculations have shown (Figure. 3), that explosive growth of a hole concentration and, correspondingly, the growth of heterogeneous reaction velocity of molecular nitrogen formation begins under completing of

hole centers, which are also recombination centers. The delay time of initiation for lead azide in this case is provided by the characteristic time of the trap completing $t_i \sim (k_3 p_0)^{-1}$, where p_0 is the hole concentration on completion of a laser pulse. It should be noted that recombination centers in lead azide are two-charging cationic vacancies V_k²⁺ [10]. However, in view of the fact that the capture cross-section of an electron by a repelling center V_k⁻ is much less than the capture cross-section of a hole by V_k²⁺ center, the given center may be considered mainly as a hole trap up to a particular level of completing.

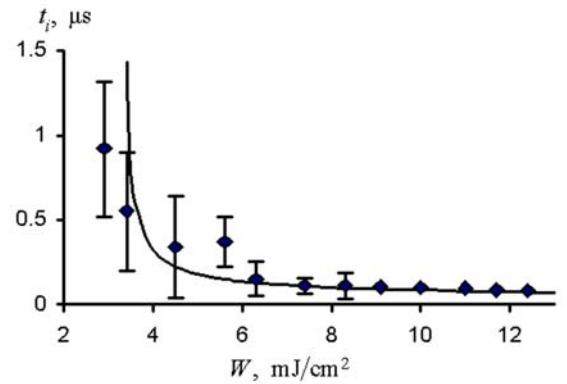


FIGURE. 1

FIGURE. 1. DELAY TIME OF LEAD AZIDE INITIATION AS A FUNCTION OF THE LASER ENERGY (DENSITY SOLID CIRCLES) EXPERIMENT [1], (CURVE) CALCULATIONS.

The calculations of photoluminescence kinetics due to radiation interband recombination I_{cv} and recombination level I_p, I_n are carried out by the formulas [11]

$$I_{cv}(t) = k_7 \int_0^L npdx,$$

$$I_p(t) = k_3 \int_0^L p(P_t - p_t)dx,$$

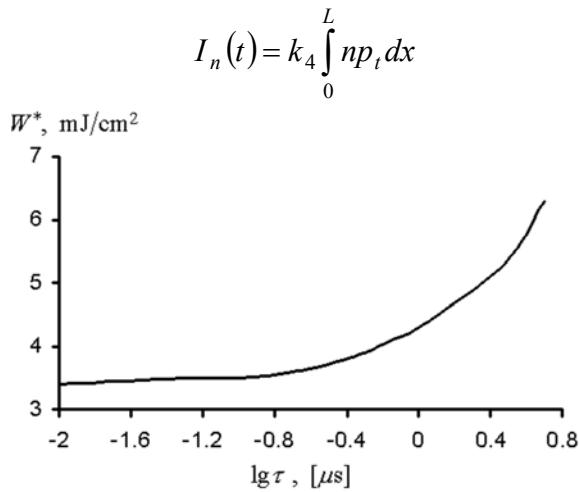


FIGURE. 2

FIGURE. 2. CRITICAL DENSITY OF ENERGY OF INITIATION OF LEAD AZIDE AS A FUNCTION OF LASER PULSE DURATION.

The results of the pre-explosive photoluminescence kinetics calculation are given in Figure. 4 (curves 1-3). As it can be seen from Figure. 4 the most intensive process is the trapping of holes on recombination center (curve 1). As the level completes by holes the recombination rates of electrons and holes begin to equalize (curves 1, 2). The intensity of interband recombination of electron-hole pairs (curve 3) is much less than the rate of recombination through a recombination level.

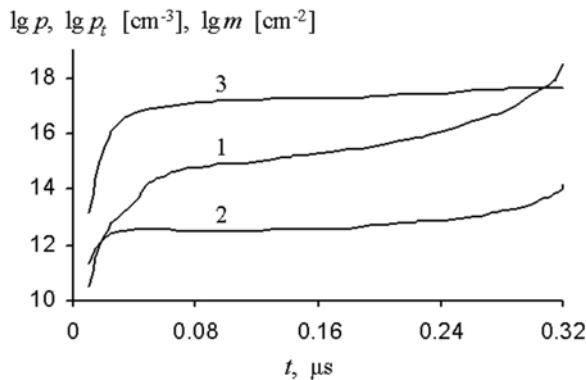


FIGURE. 3

FIGURE. 3. TIME HISTORIES OF THE CONCENTRATIONS OF (1) HOLE, (2) AZIDES RADICALS, AND LOCALIZED

HOLES FORMED UNDER THE EFFECT OF A LASER PULSE.

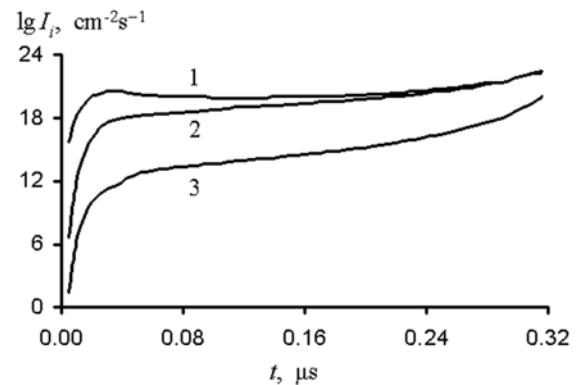


FIGURE. 4

FIGURE. 4. PRE-EXPLOSIVE PHOTOLUMINESCENCE KINETICS OF LEAD AZIDE: 1 - $I_p(t)$, 2 - $I_n(t)$, 3 - $I_{cv}(t)$.

The kinetic curves from Figure. 3 and Figure. 4 are calculated at the following parameters of a laser pulse: $W = 4 \text{ mJ/cm}^2$, $\tau = 30 \text{ ns}$.

Critical density of initiation energy for lead azide depends not only on duration of a laser pulse, but also on a diameter of a laser beam. The critical energy increases with decrease in beam diameter [12]. This dependence is more abrupt one than that derived from the theory of the thermal explosion (in particular, $W^* \sim d^{-1.7}$ for lead azide [12]) [14]. It is supposed that one of the possible reasons for the dependence of initiation threshold on a diameter of a laser beam is the fast hydrodynamic expansion of electron-hole plasma formed in near-surface area of a crystal. Assuming that an electron-hole “gas” is an ideal gas and a profile of plasma expansion does not change for some time, free expansion of electron-hole plasma is described by the following equations in cylindrical coordinates:

$$\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} = -\frac{\partial P}{\partial r},$$

$$\frac{\partial v_z}{\partial t} + v_z \frac{\partial v_z}{\partial z} = -\frac{\partial P}{\partial z},$$

where P is a pressure of plasma. The following solution of the equations above has been obtained for rates of plasma expansion in radial and normal directions:

$$v_r = 4v_0 r/d, \quad v_z = v_0 \sqrt{2\alpha z}, \quad v_0 = \sqrt{k_B T/m},$$

where m – effective mass of electron-hole pair, k_B – Boltzman constant, T –temperature of plasma. From the solution above it is obvious that the less is diameter of a beam, the more is the radial velocity of electron-hole pair drift from “reaction zone” and, consequently, the more should be threshold density of energy of a laser pulse. It should be noted that the interaction of expanded plasma with phonons will result in generation of an acoustic pulse [17] before explosive decomposition of lead azide.

In the present work, the opportunity of a formation of hole and initiation of lead azide under two-photon impurity absorption of a laser pulse has been also considered. This was caused by the fact that the critical hole concentration needed for starting up the energy-branched chain reaction is not too large: $p^* \sim 10^{12} \text{ cm}^{-3}$ [4]. However, the overstated value of a cross-section of two-photon absorption ($\sigma^{(2)} \sim 3 \cdot 10^{-40} \text{ cm}^4 \cdot \text{s}$) and stronger functional dependence of the delay time for chain reaction development on a density of a laser pulse energy nearby threshold allows one to conclude that the primary holes are not generated under two-photon laser beam absorption in HMA. In conclusion, it should be noted that the positive aspect of the model suggested consists in the fact that the explosive and sluggish thermal decomposition of lead azide are considered from united positions [4,15,16].

REFERENCES

1. E.I. Aleksandrov, A.G. Voznyuk. Fiz. Gorenija i Vzryva. 14. No.4, 86 (1978).
2. Artemiev Yu.M., Riabchuk W.K. Introduction in heterogeneous photocatalysis. – SPb:SpbGU. 1999.
3. V.V. Barelko, Yu. E. Wolodin. Kinetika i kataliz. XVII. No.3, 683 (1976).
4. A.V. Khaneft. Khim. Fiz. 17.No.4, 100 (1998).
5. Yu.N. Tyurin. Poverkhnost. No.9, 115 (1986).

6. O.V. Krylov , B.R. Schyb. Neravnovesnye protsessy v katalize. – Moscow: Khimia. 1990.
7. F.F. Vol'kenshtein. Elektronnye protsessy na poverkhnosti poluprovodnikov pri khemosorbsii. – Moscow: Nauka. 1987.
8. B.P. Aduev, E.D. Aluker, A.G. Krechetov. Pisma JTF. 1996. 22. No.6, 24 (1996).
9. E.I. Aleksandrov, A.G. Voznyuk A.G. Fiz. Gorenja i Vzryva. 20. No.6, 104 (1984).
10. A. V. Khaneft. Zh. Fiz. Khim. 69. No.3, 433 (1995).
11. A.B. Petrenko, M.N. Stoliarov, V.Yu. Timoschenko. Poverchnost. No.5-6, 14886 (1999).
12. E.I. Aleksandrov, V.P. Tsipilev. Fiz. Gorenja i Vzryva. 17. No.5, 77 (1981).
13. V.I. Krascheninin, L.V. Kusmina, V.Yu. Zakharov. Khim. Fiz. 1997, 16. No.4, 74 (1997).
14. A.V. Khaneft. Khim. Fiz. 17.No.10, 67 (1998).
15. A.V. Khaneft. Zh. Fiz. Khim. 66. No.7, 1772 (1992).
16. A.V. Khaneft. Zh. Fiz. Khim. 70. No.4, 651 (1996).
17. V.E. Gusev. Fiz. tverdogo tela. 31. No.5, 97 (1989).