ABSORPTION PROFILE OF LASER IMPULSE OF COMPOSITES BASED ON TRANSPARENT MATRIX AND METAL NANOPARTICLES

by

Andrey P. NIKITIN[a], Alexander A. ZVEKOV[a], Alexander V. KALENSKII[b*], Marina V. ANANEVA[b], and Denis R. NURMUKHAMETOV[a]

[a]Federal Research Center of Coal and Coal Chemistry,
Siberian Brunch of Russian Academy of Science, Kemerovo, Russia
[b]Kemerovo State University, Kemerovo, Russia

Original scientific paper
https://doi.org/10.2298/TSCI19S2553N

In this work the technique of modeling of optoacoustic signal initiated by laser pulse in composites based on transparent matrix and metal nanoparticles was proposed. It was shown that the time to achieve mechanical equilibrium is significantly lower than the pulse duration, and pressure is proportional to the augmentation of the nanoparticles' temperature. Testing of the modeling technique was carried out on the example of PETN – aluminum nanoparticles composite in two variant with and without taking into account the temperature dependence of the composites' optical properties. Comparison of calculated and experimental dependences of the effective absorption coefficient on the energy density of neodymium laser with pulse duration 14 ns was made. The modeling results are in good agreement with the experimental data only if the temperature dependence of the optical properties is taken into account.

Keywords: *metal nanoparticles, photoacoustic, non-linear absorption*

Introduction

The modeling of intensive light fluxes' influence on solids remains one of the main problems of applied physics. The arising effects could be used to determine the sample characteristics due to photothermal and photoacoustic effects. On the other hand, these intensive fluxes might initiate the destruction of the sample because of thermally induced stress [1]. The interaction of nanoparticles with laser radiation is accompanied by strong non-linear effects [2]. Composites based on the transparent matrix and metal nanoparticles exhibit the effects of non-linear absorption of laser radiation, which are widely used in optical switching devices [3, 4]. One is able to distinguish two main mechanisms of the non-linear light absorption by metal nanoparticles. First one is based on the properties' shift in the field of laser flux due to multi- and multiple-photon absorption, polarization of nanoparticles and so on [2]. In this case, the heating of the nanoparticle is not essential. The second mechanism is related to the heating of the nanoparticle and subsequent change in the refractive index. This drift caus-

* Corresponding author, email: kriger@kemsu.ru

es changes of light absorption efficiency factor, Q_{abs}, [5] and effective absorption coefficient of the sample during the laser exposure. As a result, one can expect the dependence of the observed absorption factor on the energy density.

In [6] the absorption coefficient, μ, of pressed pellet of PETN, containing aluminum nanoparticles, which diameters in maximum of distribution are 100-120 nm (0.03% by mass) in case of laser pulse with 1064 nm wavelength was studied. Using the optoacoustic method the dependence of absorption coefficient on the energy density, H, was determined. It was shown that if the energy density increases till 0.1 J/cm^2 the μ increases linearly from 20 to 110 cm^{-1}, further the absorption coefficient tends to stationary value 120 cm^{-1} [6].

In terms of the theory of optoacoustic effects [7] changes of the pressure of the sound wave is proportional to the increase in temperature of the substance. For the used mass concentration of nanoparticles [6] their pulse laser heating will lead to the rapid mechanical relaxation of the medium between the particles, and so the pressure growth will be proportional to the temperature change of the nanoparticles. The change in the temperature reflects the depth distribution of absorbed laser energy density [7].

Pressed pellets of secondary explosives, containing light absorbing particles, can be used to develop safe caps of optic detonators [8]. The temperature of the laser heated nanoparticle is a key value determining the evolution of the initial hot spots [9, 10]. Thus, the dependence of the absorption linear coefficient on the pulse energy density may change the particles' temperature.

The aim of this work is to formulate and test the modeling technique of the photoacoustic effect in composites, based on the transparent matrix and metal nanoparticles, heated by the laser pulse radiation.

Mathematical modelling

Consider the modeling technique of temperature distribution of heated metal nanoparticles by depth of the composite, based on the transparent matrix and metal nanoparticles heating by laser irradiation. Energy of the laser pulse, absorbed by the particle, transforms into thermal energy and causes the hearting of the particle and a layer of the matrix of a certain thickness, h.

Discussing on the qualitative level the initiation of the pressure wave in a transparent matrix containing metal nanoparticles we will consider the matrix as an inert one. Cases where the matrix was considered as an additional source of heat was discussed elsewhere, for example for the model of the laser explosion initiation [10-13], ignition of particles in the air flow [14], reaction initiation by particle's heating by microwaves [15], and propellant ignition by a hot particle [16]. The nanoparticles heating accompanied by heating of the matrix layer due to thermal conduction causes their thermal expansion. The typical temperatures of the nanoparticles are about 1000 K [10-13], which might cause the enormous expansion. On the other hand, the nanoparticles are inside the matrix, the most part of which keeps the initial temperature. Thus, the neating of nanoparticles make the cool part of the matrix compress. In order to estimate the typical time needed for the local mechanical relaxation of the matrix one estimates the average distance between nanoparticles as half of the cubic root of their concentration. The relaxation is done with the sound velocity. This way one obtains the following expression for relaxation time:

$$\tau \approx \frac{1}{c_s}\sqrt[3]{\frac{\pi R^3 \rho_{\mathrm{Al}}}{3\omega_{\mathrm{Al}}\rho_{\mathrm{PETN}}}} \tag{1}$$

where ρ_{PETN} and ρ_{Al} are densities of matrix (PETN) and nanoparticles, ω_{Al} – the mass fraction of aluminum nanoparticles in the sample, R – the radius of the nanoparticles, c_s = 2500 m/s – the sound velocity in PETN [6]. The typical local mechanical relaxation time for aluminum mass fraction 0.03% and nanoparticles' radius 50 nm is 0.35 ns, that is 40 times lower than full width at half maximum of the laser pulse (τ_i = 14 ns). For that reason, it is possible to assume that the local mechanic equilibrium is reached almost instantly and does not affect the photoacoustic response's kinetics. The pressure amplitude could be estimated if one neglects the mechanic relaxation of the sample as a whole, which is a limit of the sample confined in absolutely incompressible environment. The mechanical equilibrium implies that:

$$\begin{aligned} p &= \beta_{\mathrm{Al}}\left(T-T_0\right) - K_{\mathrm{Al}}\frac{V_{\mathrm{Al}}-V_{\mathrm{Al}}^0}{V_{\mathrm{Al}}^0} = \\ &= \beta_{\mathrm{PETN}}\left(T-T_0\right) - K_{\mathrm{PETN}}\frac{V_h-V_h^0}{V_h^0} = -K_{\mathrm{PETN}}\frac{V_1-V_1^0}{V_1^0} \end{aligned} \tag{2}$$

where $\beta_{\mathrm{PETN}} = 2.32\cdot10^{-4}$ K^{-1} [17] and $\beta_{\mathrm{Al}} = 22.58\cdot10^{-6}$ K^{-1} [18] are thermal expansion coefficients of matrix (PETN) and aluminum nanoparticles, respectively, $K_{\mathrm{PETN}} = 9.6\cdot10^{9}$ Pa [17] and $K_{\mathrm{Al}} = 7.1\cdot10^{10}$ Pa [18] are bulk modulus, V_{Al}, V_h, V_1 are volumes of the nanoparticle, heated and cool layers of the matrix per a nanoparticle, respectively. The balance equation for the whole volume per nanoparticle is:

$$V_{\mathrm{Al}} + V_h + V_1 = V_{\mathrm{Al}}^0 + V_h^0 + V_1^0 = \frac{4\pi R^3\rho_{\mathrm{Al}}}{3\omega_{\mathrm{Al}}\rho_{\mathrm{PETN}}} \tag{3}$$

The ratio in the right-hand side of the equation is the volume per a nanoparticle. Combining eqs. (2) and (3) one receives the expression for pressure estimation:

$$p = \left(T-T_0\right)\frac{\beta_{\mathrm{Al}}V_{\mathrm{Al}}^0 + \beta_{\mathrm{PETN}}V_h^0}{\dfrac{V_{\mathrm{Al}}^0}{K_{\mathrm{Al}}} + \dfrac{V_h^0+V_1^0}{K_{\mathrm{PETN}}}} \tag{4}$$

Assuming that the volume of the heated layer of the matrix is estimated with equation $V_h = 4\pi R^2[R + (\alpha\tau_i)^{1/2}]$ [11] and neglecting the difference of $V_1{}^0$ and $C_{\mathrm{Al}}{}^{-1}$ one receives the pressure about 1.5 MPa when the temperature is T = 900 K (initial temperature was taken as 300 K). The estimated pressure is typical for photoacoustic effects and significantly lower than pressure estimated without the assumption of local mechanic equilibrium, that is about $K_{\mathrm{Al}}\left(T-T_0\right) \approx 3$ GPa at the same conditions. According to eq. (4) the pressure depends linearly on the temperature augmentation. For that reason, in the following part of the paper we will pay our attention to the temperature only. This is reasonable providing that the temperature influence on the thermophysical properties is negligible. In the experimental paper [6] the uncalibrated pressure detector was used, so the relative values could be compared only.

An expression that allows one to calculate the thickness of the heated layer of the matrix around the particle was proposed in [11] and further validated in [12]. Its value determined by the duration of the laser pulse and thermal diffusivity of matrix α [$h=(\alpha\tau_i)^{1/2}$] and does not depend on the material of the inclusion [12]. Local absorption coefficient was calculated using expression $\mu(x)=\pi R^2 n_{\mathrm{Al}}Q_{\mathrm{abs}}[R,T(x)]$, where Q_{abs} is the efficiency factor of absorption, R – nanoparticle's radius, and n_{Al} – concentration of nanoparticles (cm^{-3}). Using the approximation of root dependence of the thickness of the heated layer of matrix on the

time of radiation one can get expression for the heating temperature of the nanoparticle at a depth x at a time t:

$$T(x,t) = T_0 + R\left\{4c_{\text{PETN}}\left[\alpha t + R\sqrt{\alpha t} + \frac{c_{\text{Al}}R^2}{3c_{\text{PETN}}}\right]\right\}^{-1}\int_0^t Q_{\text{abs}}(x,t')G(x,t')\,\mathrm{d}t' \tag{5}$$

$$G(x,t) = G_0\left\{1-\exp\left[-\int_0^x \pi R^2 n_{\text{Al}} Q_{\text{abs}}(y,t)\,\mathrm{d}y\right]\right\} \tag{6}$$

where $G(x,t)$ is the power density of laser radiation at depth x at time t. Expression (5) takes into account both the increase of thickness of heated layer of matrix over time and possible changes of the efficiency factor of absorption during the heating of nanoparticles. Expression (6) shows that the efficiency factor of absorption and local absorption coefficient can both depend generally on the co-ordinate and time, if the optical properties of the nanoparticle depend on temperature.

In this work the model (5) and (6) was used for modeling the temperature distribution of the heated nanoparticles with radius R = 60 nm by depth of composite. The PETN was used as a matrix. Sample was heated by the pulse of the first harmonic of neodymium laser with different pulse energy densities.

Simulated rectangular pulse with duration, τ, 16 ns was divided into 100 equal time intervals with the following calculation of its impact on the composite at each moment of time. Calculation was made on a regular grid in the co-ordinate, the thickness of the sample was 0.55 cm, which corresponds to a five-fold excess of the inverse absorption coefficient at the initial time. The spatial grid contained 200 cells of equal thickness.

Modeling results

Calculation results in case the efficiency factor of absorption does not depend on the temperature are presented in fig. 1(a). The surface of the composite is taken as the reference point on the x-axis. The Y-axis shows the temperatures of nanoparticles heating. The Bouguer law can satisfactorily describe calculated distribution of temperature of heated nanoparticles at the time of the termination of impulse. Exponential rate is proportional to the effective absorption coefficient, which can be estimated experimentally in the modeling samples by the photoacoustic methods [8].

According to [13, 19], dependence $Q_{\text{abs}}(T)$ for aluminum nanoparticles with radius 60 nm in temperature range 300 - 700 K is well interpolated by the expression:

$$Q_{\text{abs}}(T) = -0.102\theta^2 + 0.488\theta + 0.364, \quad \theta = \frac{T-300}{300} \tag{7}$$

If the energy of the laser pulse is low, the temperature in the composite decreases by a law close to exponential. As the energy density increases, the area with slight temperature change appear, followed by its sharp decrease in the sample depth. With a further increase in the energy density, the size of the area with a practically constant temperature increases. Distribution of temperature in the decay region can be combined with the same region for the lower energy density by using simple translation. In fig. 2 the corresponding absorption efficiency, Q_{abs}, distributions of aluminum nanoparticles by the sample depth at the time of the termination of impulse with different energy densities are presented.

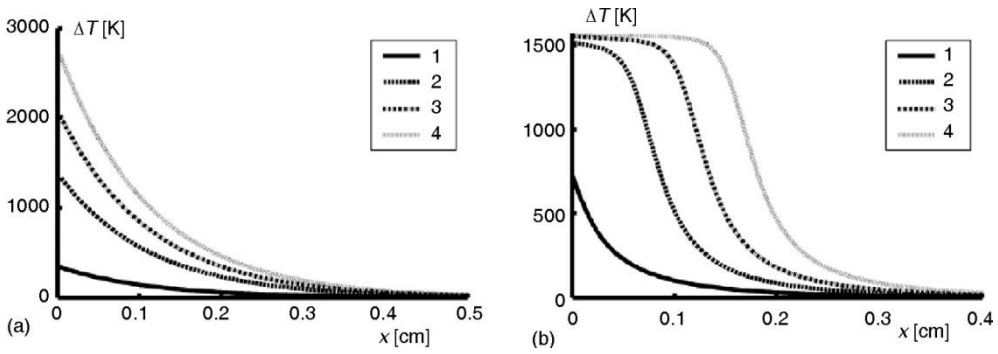

Figure 1. Distribution of nanoparticles' temperature by the sample depth; (a) Q_{abs} = const., (b) $Q_{abs} = f(T)$ in terms of eq. (3); values of energy density [J/cm^2] are 0.05 (1), 0.2 (2), 0.3 (3), 0.4 (4)

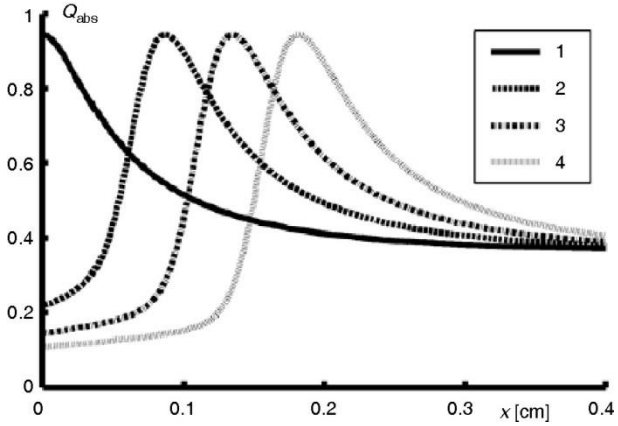

Figure 2. Calculated distributions of the efficiency factor of absorption of nanoarticles by the depth of PETN-Al sample under the laser heating; values of energy density [J/cm^2] are 0.05 (1), 0.2 (2), 0.3 (3), 0.4 (4)

Consider in terms of the model the processes in the sample in case of different values of the energy densities. If H is low, the temperature of heating of the particles is small and has little effect on the efficiency factor of absorption. If the energy density increases, the heating temperature of the particles in the surface area significantly increases, this causes the growth of the local efficiency factor of absorption (fig. 2, curves 1 and 2). The resulting positive feedback causes deviations from Bouguer law, which can be described as an increase in the effective absorption coefficient. Further increase in pulse energy leads to even higher heating temperatures of nanoparticles in the near-surface area, at which the contribution of the quadratic term in the eq. (7) becomes significant. As a result, the Q_{abs} starts to increase in the near-surface area (fig. 2, curve 3). For higher energy density a site with small and almost constant efficiency factor of absorption is formed, so that a site of weak temperature change is observed in the same area. Then the maximum of the efficiency factor of absorption is formed, its co-ordinate is determined by the energy density, and the temperature distributions behind the maximum are similar with a shift along the x-axis depending on the energy density (fig. 2, curve 4).

Observing effects are similar to the dye photobleaching in the field of high-power laser radiation. In both cases, at large values of the pulse energy density in the anterior region of the sample, an almost uniform distribution of the absorbed energy density occurs, what is against the Bouguer law. The most similar system, there one can observe the local maximum of absorption coefficient inside the sample is the dye solution with the multiple photon absorption in the four level system where the absorption cross-section from the second singlet state is higher than from the first one and the third singlet state is bleached due to triplet state.

Calculated dependence of the effective absorption coefficient on the energy density is presented in fig. 3. Behavior of calculated curve at the qualitative level coincides with the results of the optoacoustic experiment [6]. If the energy density is 10^{-3} J/cm^2 the observed absorption coefficient is 9.0 cm^{-1}. Then one can see the almost linear growth till 17.8 cm^{-1} for H = 0.09 J/cm^2. Local maximum on the dependence corresponds to the energy density 0.15 J/cm^2 with amplitude 18.4 cm^{-1}. Further growth of the energy density makes insignificant changes in μ, for example if H = 0.3 J/cm^2 μ = 18.1 cm^{-1}. In the examined model the following processes were not taken into account – melting of the nanoparticles under the action of high energy density of laser pulse, features of the light mode in the sample volume (multiple light scattering by nanoparticles), increasing of the radius of nanoparticles during heating, which also contributes to the intensity of the measured acoustic pulse. Taking into account these processes we will improve the agreement of the results of calculations and experiment.

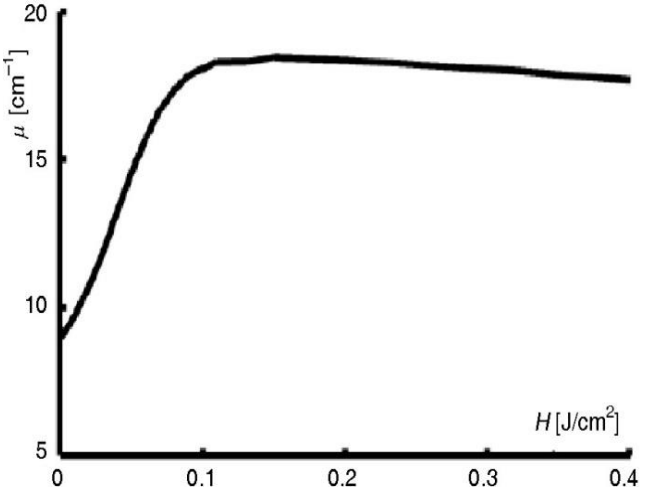

Figure 3. The calculated dependence of the effective linear absorption coefficient of PETN – Al (0.03 wt%) on the laser pulse energy density

Conclusion

In this work the modeling technique of optoacoustic signal, initiated by laser pulse in composite based on the transparent matrix with metal nanoparticles, was proposed. It is shown that in order to explain the experimentally dependence of effective absorption coefficient on the pulse energy density it is necessary to take into account the temperature dependence of the efficiency factor of absorption.

Acknowledgment

This work was partly supported by the Russian Foundation for Basic Research (project no. 18-03-00421A), State Assignment No. V.49.15, No. AAAA-A17-117041910150-2 for the Institute of Coal Chemistry and Chemical Material Science of FRC CCC SB RAS (supervised by Boris Aduev), and the Russian Ministry of Education and Science (state assignment no. 3.5363.2017/8.9).

References

[1] Shibib, Kh. S., *et al*., Analytical Solution of Transient Temperature in Continuous Wave End-Pumped Laser Slab, *Thermal Science*, *21* (2017), 3, pp. 1223-1230
[2] Panoiu, N. C., *et al*., Nonlinear Optics in Plasmonic Nanostructures, *J. Opt*. *20* (2018), 8, 083001
[3] Ros, I., *et al*., Femtosecond Nonlinear Absorption of Gold Nanoshells at Surface Plasmon Resonance, *Phys. Chem. Chem. Phys.*, *12* (2010), 41, pp. 13692-13698
[4] Ghambari, T., Dorranian, D., Measurement of Third-Order Nonlinear Susceptibility of Au Nanoparticles Doped PVA Film, *Optics and Spectroscopy*, *119* (2015), 5, pp. 838-848
[5] Sivan, Y., Chu, S.-W., Nonlinear Plasmonics at High Temperatures, *Nanophotonics*, *6* (2017), 1, pp 317-328
[6] Aduev, B. P., *et al*., Optiko-Akusticheskie Ehffekty V Tetranitrate Pentaehritrita S Vklyucheniyami Ultradispersnyh Chastic Alyuminiya Pri Impulsnom Lazernom Vozdejstvii, (Optoacoustic Effects in Pentaerythritol Tetranitrate with Ultrafine Aluminum-Particle Inclusions under Pulsed-Laser Action, – in Russian), *Optika i Spektroskopiya*, *124* (2018), 3, pp. 404-409
[7] Gusev, V. E., Karabutov, A. A., Lazernaya optoakustika (Laser Opto-Acoustics – in Russian), M: Nauka, 1991
[8] Gerasimov, S. I., *et al*., Vozmozhnost Iniciirovaniya Polimersoderzhashchego Ehnergonasyshchennogo Sostava Kompleksnogo Perhlorata Rtuti Luchom Lazernogo Dioda, (A Laser Diode Beam Initiates a High-Energy Mercury Perchlorate-Polymer Complex – in Russian), *Pis'ma v Zhurnal Tekhnicheskoi Fiziki*, *41* (2015), 7, pp. 66-72
[9] Aduev, B. P., *et al*., Osobennosti Lazernogo Iniciirovaniya Kompozitov Na Osnove TENa S Vklyucheniyami Ultradispersnyh Chastic Alyuminiya (Laser Initiation of PETN-Based Composites with Additives of Ultrafine Aluminium, Combustion – in Russian), *Fizika Goreniya i Vzryva*, *52* (2016), 6, pp. 104-110
[10] Burkina, R. S., *et al*., Iniciirovanie Reakcionno-Sposobnogo Veshchestva Potokom Izlucheniya Pri Ego Pogloshchenii Opticheskimi Neodnorodnostyami Veshchestva (Initiation of a Reactive Material by a Radiation Beam Absorbed by Optical Heterogeneities of the Material – in Russian), *Fizika Goreniya i Vzryva*, *47* (2011), 5, pp. 95-105
[11] Kalenskii, A. V., *et al*., Kriticheskie Parametry Mikroochagovoj Modeli Impulsnogo Lazernogo Iniciirovaniya Vzryvnogo Razlozheniya Ehnergeticheskih Materialov (Critical Parameters of a Micro-Hotspot Model of the Laser-Pulse Initiation of the Explosive Decomposition of Energetic Materials – in Russian), *Khimicheskaya Fizika*, *36* (2017), 9, pp. 45-52
[12] Kalenskii, A. V., *et al*., Kriticheskie Usloviya Iniciirovaniya Reakcii V TENe Pri Lazernom Nagreve Svetopogloshchayushchih Nanochastic (Critical Conditions of Reaction Initiation in the PETN During Laser Heating of Light-Absorbing Nanoparticles – in Russian), *Fizika Goreniya i Vzryva*, *53* (2017), 2, pp. 107-117
[13] Kalenskii, A. V., *et al*., Mikroochagovaya Model S Uchetom Zavisimosti Koehfficienta Ehffektivnosti Pogloshcheniya Lazernogo Impulsa Ot Temperatury (Micro-Hot-Spot Model Taking Into Account the Temperature Dependence of the Laser Pulse Absorption Efficiency Factor – in Russian), *Khimicheskaya Fizika*, *36* (2017), 4, pp. 43-49
[14] Glushkov, D. O., *et al*., Vliyanie Formy Chasticy Organovodougolnogo Topliva Na Usloviya I Harakteristiki Ee Zazhiganiya V Potoke Razogretogo Vozduha (Effect of the Shape of an Organic Water-Coal Fuel Particle on the Condition and Characteristics of Its Ignition in a Hot Air Flow – in Russian), *Khimicheskaya Fizika*, *35* (2016), 11. pp. 14-25
[15] Chumakov, Yu. A., Knyazeva, A. G., Iniciirovanie Reakcii V Okrestnosti Odinochnoj Chasticy Nagrevaemoj SVCH-Izlucheniem (Initiation of Reaction in the Vicinity of a Single Particle Heated by Microwave Radiation – in Russian), *Fizika Goreniya i Vzryva*, *48* (2012), 2, pp. 24-30
[16] Glushkov, D. O., *et al*., Zazhiganie Smesevogo Topliva Goryachej Chasticej V Usloviyah Neidealnogo Teplovogo Kontakta (Ignition of a Composite Propellant by a Hot Particle Under Conditions of a Nonideal Thermal Contact – in Russian), *Khimicheskaya Fizika*, *34* (2015), 7, pp. 39-45
[17] Olinger, B., Cady H. H., The Hydrostatic Compression of Explosives and Detonation Products to 10 GPa (100 KBars) and their Calculated Shock Compression: Results for PETN, TATB, CO_2, and H_2O, *Proceedings*, 6th Int. Detonation Symp., Coronado, Cal., USA, 1976, pp. 700-709
[18] Kaye, G. W. C., Laby, T. H., *Tables of Physical and Chemical Constants*, Franklin Classics, Lebanon, N. J., USA, 2018

[19] Kalenskii, A. V., *et al*., Vliyanie Temperatury Na Opticheskie Svojstva Kompozitov Prozrachnaya Matrica-Nanochasticy Serebra (Influence of Temperature on Optical Properties of Silver Nanoparticle–Transparent Matrix Composites – in Russian), *Zhurnal Prikladnoi Spektroskopii*, *83* (2017), 6, pp. 972-978

Paper submitted: September 6, 2018
Paper revised: October 31, 2018
Paper accepted: December 4, 2018