A study into light scattering and absorption by aluminum nanoparticles in PETN

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Abstract. The paper is devoted to experimental and theoretical research into nanoparticles’ optic properties in pentaerythritol tetranitrate (PETN) matrix. A photometric sphere was applied for the transmittance and sum of transmittance and reflectance measurement of PETN pressed pellets containing aluminum nanoparticles at the light wavelength 643 nm. The theory of light propagation in terms of spherical harmonics solution of radiative transfer equation in the slab geometry with Fresnel boundary conditions was developed. The properties of aluminum nanoparticles were evaluated in terms of Mie theory. The absorbed energy distribution inside the sample was calculated. It was shown that the Beer’s type law is applicable approximately. The apparent light absorption cross section determined, which takes into account both scattering and absorption, is bigger than the geometrical one. The aluminum refractive index value, estimated during comparison of theory with the experimental data, agrees well with the handbook’s data.

1. Introduction
A lot of studies have been devoted to research into optical properties of metal nanoparticles [1-6] because they could be utilized in many fields including optical detonators [7-10] solar cells [1,2] design, hyperthermia cancer therapy [5] and nanophotonics devices development [3]. As the light interaction with nanoparticles concerned on both the effects of scattering and absorption, the problem is a challenging one. The effect of multiple scattering was pointed out in [11]. Though there are a lot of papers discussing the optical properties of nanometals, most of the results were obtained using simple spectral approaches where there were no differentiation of scattering and absorption. In the present paper we developed a new approach of the optical results obtained with an integrating sphere processing that made possible to estimate the scattering and absorption parameters of metal nanoparticles.

2. Experimental section
The pressed pellets of pentaerythritol tetranitrate (PETN) contained aluminum nanoparticles were used as the experimental samples because they are perspective explosive materials for optic detonators. The grains’ average size of the PETN powder was 1 – 2 μm [7,8]. The aluminum nanoparticles were synthesized in the Institution of Physics of Metals with the gas-phase method. The size distribution of the nanoparticles showed the maximum at 100 – 120 nm. The aluminum oxide (Al₂O₃) content
estimated with electron microscope JEOL JSM63901A equipped with a JEOL JED2400 feature for the element analysis was 24 wt%.

The samples were prepared as follows. The weighted amounts of aluminum and petn were mixed, than the substance was ultrasonificated in hexane, which leads to uniform distribution of the nanoparticles inside the sample. After that the hexane was evaporated and the mixture dried. The weighted amount of the mixture was pressed into the pellets with the diameter \( 3 \pm 0.01 \) mm and variable thicknesses. The pressure increased up to 1.8 GPa during 30 min when a pellet was being pressed. This procedure allowed us to obtain samples with density value of the monocrystal \((1.73 \pm 0.03 \text{ g/cm}^3)\). The pellets did not have any visible defects which were able to contribute to the scattering [7]. An integrating photometric sphere was used to determine the reflectance and transmittance. In the first blank experiment the intensity inside the sphere \( I_0 \) was measured without the sample. Then the sample was placed on the entrance hole and inside the sphere in order to measure transmitted intensity \( I_T \) and sum of the transmitted and reflected intensity \( I_{T+R} \) correspondingly. These values divided by \( I_0 \) gave \( T \) and \( T+R \) correspondingly. The method was tested with the standard glass light filters [12] and its consistency was verified.

3. Theoretical section

The scattering medium is characterized by scattering phase function \( \chi(\hat{s}',\hat{s}) \) and linear coefficients of extinction \( k \), absorption \( k_{abs} \) and \( k_{sca} \) scattering [13]. The albedo of every light-medium interaction is \( \Lambda = k_{sca}/k \). The radiative transfer equation, describing the light propagation in scattering and absorbing medium, is:

\[
(\hat{s},\nabla)I(r,\hat{s}) - kI(r,\hat{s}) = \frac{k\Lambda}{4\pi} \int I(r,\hat{s}')\chi(\hat{s}',\hat{s})d\hat{s}' + q(r,\hat{s})
\]  

(1)

where \( I(r,\hat{s}) \) is specific intensity of light in the direction \( \hat{s} \) at the coordinate \( r \), \( q(r,\hat{s}) \) is the sources function. This equation could be simplified in the one dimensional case to

\[
\mu \frac{dI(\tau,\mu)}{d\tau} - I(\tau,\mu) = \frac{\Lambda}{2} \int I(\tau,\mu')\chi(\mu',\mu)d\mu' + q(\tau,\mu)
\]

(2)

where \( \mu \) is cosine of the spherical angle, \( \tau = kz \) is dimensionless coordinate.

The radiation transfer equation was solved with the spherical harmonics approach requiring splitting of the radiance into scattered \( I_s \) and incident \( I_0 \) parts [14]:

\[
I = I_0 + I_s
\]

(3)

The incident part obeys the Beer’s law. One is able to write the following formula for \( I_0 \) taking into account the reflectance from the bottom boundary of the sample (slab):

\[
I_0 = J \cdot (\exp(-\tau) + R_f \exp(\tau - 2L))
\]

(4)

where \( J = J_0 (1 - R_f) \), \( R_f \) is the Fresnel reflectivity from the upper sample’s surface, \( J_0 \) is the intensity of the incident irradiation outside the sample. The equation system describing spatial dependence of the spherical harmonics expansion coefficients of the intensity (\( C_m \)) reads as [14]:

\[
\frac{1}{2m+1} \left[ (m+1)\frac{dC_{m+1}}{d\tau} + m\frac{dC_{m-1}}{d\tau} \right] + \left( 1 - \frac{x_m}{2} \right) C_m = \frac{JAx_I}{2} \left[ \exp(-\tau) + R_f \exp(\tau - 2L) \right]
\]

(5)

where \( x_I \) are expansion coefficients of the scattering phase function into spherical harmonics series.

The boundary conditions for the equation (5) are the Fresnel ones [15]:

2
\[ I_s(0, \mu) = R(\mu)I_s(0, -\mu), \quad 0 \leq \mu \leq 1 \]  
(6)

\[ I_s(L, -\mu) = R(\mu)I_s(L, \mu), \quad -1 \leq \mu \leq 0 \]  
(7)

where \( R(\mu) \) is angular dependence of the Fresnel reflectivity coefficient, \( \mu = \cos \theta \) is cosine of the spherical angle. Formulae (9) and (7) give the conditions for the upper and bottom sample’s surfaces. One obtains the boundary conditions for the harmonics’ contributions applying the \( R(\mu) \) expansion into Legendre polynomials:

\[ \sum_{m=0}^{N} \left( N_{lm} - R'_{lm} \right) C_m(0) = 0 \]  
(8)

Where the matrix elements read as:

\[ R'_{lm} = (-1)^m \frac{2m+1}{2} \int P_m(\mu)R(\mu)P_l(\mu) d\mu \]  
(9)

\[ N_{lm} = \frac{2m+1}{2} \int P_m(\mu)P_l(\mu) d\mu \]  
(10)

The solution of (5) is represented as:

\[ C_m(\tau) = \sum_{i=0}^{N} a_{mi} \tilde{C}_i \exp(y_i \tau) + C_p^1 \exp(-\tau) + C_p^2 \exp(\tau) \]  
(11)

Where coefficients \( C_p^1 \) and \( C_p^2 \) are:

\[ C_p^1 = -JA \cdot \sum_{m=0}^{N} \left[ \delta_{pm} + A_{pm} \right]^{-1} B_m \]  
(12)

\[ C_p^2 = JAR_f \cdot \exp(-2L) \cdot \sum_{m=0}^{N} \left[ \delta_{pm} - A_{pm} \right]^{-1} B_m \]  
(13)

where the upper index -1 denotes the matrix inversion.

The coefficients \( \tilde{C}_i \) were determined from the boundary conditions (8) forming an overdetermined system, so the least squares method was used. The following equation written in matrix form was derived for the coefficients \( \tilde{C}_i \):

\[ \tilde{C} = [Z^T Z]^{-1} Z^T b \]  
(14)

where \( Z = \begin{pmatrix} (N - R') d \tau \\ (\tilde{N} - \tilde{R}) \mu \exp(\gamma L) \end{pmatrix} \) and \( b = \begin{pmatrix} (N - R')\left[C_p^1 + C_p^2\right] \\ (\tilde{N} - \tilde{R})\left[C_p^1 \exp(-L) + C_p^2 \exp(L)\right] \end{pmatrix} \) are auxiliary matrixes.

For the comparison with the experiment, the values of absorption coefficient (\( A \)), reflectivity (\( R \)) and transmittance (\( T \)) were evaluated:

\[ A = (1 - \Lambda) \cdot \frac{1}{L} \int_0^L C_o d\tau + (1 - R_f) \cdot \int_0^L \left[ 1 - \exp(-L) + R_f \exp(-L) \cdot (1 - \exp(-L)) \right] \]  
(15)
\[
T = \left( \frac{1}{J_0} \sum_{m=0}^{N} C_m(r) \xi_m + (1 - R_f) \exp(-L) \right)
\]  
(16)

\[
R = \left( \frac{1}{J_0} \sum_{m=0}^{N} (-1)^m C_m(0) \xi_m + R_f + R_f \left( 1 - R_f \right) \exp(-2L) \right)
\]  
(17)

where the vector \( \xi_m \) is

\[
\xi_m = \frac{2m+1}{2} \int_{0}^{1} P_m(\mu) \left[ 1 - R(\mu) \right] \mu \: d\mu
\]  
(18)

The theoretical results were compared with the experiment in assumption that the Mie theory of light scattering is applicable. The details of the absorption and scattering coefficients as well as the scattering phase function evaluation could be found in [8,10,13].

### 4. Results and discussion

Two series of measurements were carried out. In the first one the samples of width 0.13 ± 0.01 mm containing different weight percentage of nanoparticles were used. In the second one the sample width was varied at constant weight percentage of aluminum 0.017%. The results a shown on the figures 1 and 2 correspondingly. The light wavelength was 643 nm.

The reflectivity value for the pure samples was 0.10, which is close to the monocrystal’s one. The theoretical margin in the case of Fresnel refraction at \( n=1.54 \) (petn) is 0.09. Thus the petn matrix is a transparent medium.

The samples having some aluminum content showed the increasing in the reflectivity up to 15%. This value does not depend on the nanoparticles’ weight percentage and the sample’s width at the level of the experimental accuracy. The increasing in the reflectivity is the consequence of the light scattering inside the sample.

The theoretical dependencies of the reflectivity and sum of the reflectivity and transparency are also presented on the figures 1 and 2. The aluminum refractivity index was varied during the calculations.

It is evident from the data presented on the figures 1 and 2 that the theory matches experiment at the refractive index value 1.28-5.90i.

**Figure 1.** The dependence of transmittance (1,3) and sum of the transmittance and reflectance (2,4) on the sample’s width (the weight percentage of aluminum was 0.017%). 1,2 – experiment, 3,4 – calculation.

**Figure 2.** The dependence of transmittance (1,3) and sum of the transmittance and reflectance (2,4) on the aluminum weight percentage (the sample’s width was 0.13 mm). 1,2 – experiment, 3,4 – calculation.
The handbook [16] gives the values of \((1.14 \pm 0.16) - (6.54 \pm 0.57)i\) for the aluminum refractive index at the wavelength 650 nm which agrees well with the margin obtained in the present paper. Thus the bulk metal properties, such as refractive index, could be extrapolated into the range of small particles’ sizes. The average values of the aluminum nanoparticles absorption and scattering effectiveness at the light wavelength 643 nm are 0.6614 and 2.1561 correspondingly. At the histogram’s maximum (50 nm) these values are 0.7022 and 1.8506 correspondingly. The difference is concerned on the finite size distribution width. The calculated absorption energy distribution inside the sample (1) in relative units is shown on the figure 3 in the case of weight percentage of aluminum nanoparticles equal to 0.05%. The contributions of the incident (2) and scattered (3) light are also presented. It is worth mentioning that they are comparable near the sample’s surface. As the distance from surface increases, the contribution of the scattered part becomes more significant. The maximum on the scattered light contribution in the absorbed energy is a typical one. It arises because the scattered light partly penetrates the sample’s boundary. The absorbed energy distribution inside the sample is nearly exponential, so the law of the Beer’s type is applicable. The apparent absorption coefficient is determined by both scattering and absorption processes in the medium. The substantial deviation from the Beer’s type law during the simulations was observed in the case of the very thin samples only, where the refraction from the bottom sample’s surface is pronounced.

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The apparent absorption coefficient dependence on the aluminum weight percentage is shown in figure 4. The experimental (1) and calculated (2) apparent absorption coefficients dependent on the aluminum weight percentage. The experimental margins were estimated as \(d^{-1} \ln [(1 - R)/T]\). The theoretical ones were calculated as the energy distribution curve slope in the semilogarithmic coordinates. The experimental and calculated results agree well (figure 4). Thus the Beer’s type dependence of the apparent absorption coefficient on the aluminum concentration arises in terms of the both experiment and theory (figure 4).

The assumption that the light scattering is able to provide substantial increasing in the energy absorbed by the nanoparticles in the transparent medium was suggested in [11]. The apparent nanoparticle light absorption cross section could be estimated as \(k/C = 1.52 \times 10^{-10}\). The obtained value incorporates the scattering effects. The geometrical cross section of the 50 nm nanoparticle corrected by the refraction from the upper sample’s surface is \((1 - R) \cdot k/\pi r_{eff}^2 C = 1.64 (R \approx 0.15)\). Thus, the multiple scattering is able to increase the amount of energy absorbed by a nanoparticle, so it becomes bigger than falls on its surface. Though the effect is not as substantial as it was predicted earlier (12 – 24 times) [11], if one...
assumes the small values of the absorption effectiveness there is 2.48-fold increasing in the absorbed energy.

5. Conclusion
A photometric sphere was applied for the transmittance and sum of transmittance and reflectance measurement of petn pressed pellets containing aluminum nanoparticles at the light wavelength 643 nm. The theory for these values calculation in terms of spherical harmonics solution of radiative transfer equation in the slab geometry with Fresnel boundary conditions was developed. The Mie theory was applied for nanoparticles properties evaluation. The absorbed energy distribution inside the sample was calculated. It was shown that the Beer’s type law is applicable approximately. The apparent light absorption cross section determined, which takes into account both scattering and absorption, is bigger than the geometrical one. The obtained aluminum refractive index agrees well with the handbook’s data.

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