Abnormal photothermal effect of laser radiation on highly defect oxide bronze nanoparticles under the sub-threshold excitation of absorption

P Gulyaev¹, M Kotvanova¹ and A Omelchenko²

¹Physics and Chemistry Department, Ugra State University, 16 Chekhov St., Khanty-Mansiysk, 628012, Russian Federation
²Institute Photonic Technologies of Federal Scientific Research Centre “Crystallography and Photonics” of RAS, 2 Pionerskaya St., Moscow, 142190, Russian Federation

E-mail: p.gulyaev@ugrasu.ru

Abstract. The mechanism of abnormal photo-thermal effect of laser radiation on nanoparticles of oxide bronzes has been proposed in this paper. The basic features of the observed effect are: a) sub-threshold absorption of laser radiation by the excitation of donor-like levels formed in the energy gap due to superficial defects of the oxide bronze nano-crystals; b) an interband radiationless transition of energy of excitation on deep triplet levels and c) consequent recombination occurring at the plasmon absorption. K or Na atoms thermally intercalated to the octahedral crystal structure of TiO₂ in the wave SHS combustion generate acceptor levels in the gap. The prepared oxide bronzes of the non-stoichiometric composition NaₓTiO₂ and KₓTiO₂ were examined by high resolution TEM, and then grinded in a planetary mill with powerful dispersion energy density up to 4000 J/g. This made it possible to obtain nanoparticles about 50 nm with high surface defect density (10¹⁷–10¹⁹ cm⁻² at a depth of 10 nm). High photo-thermal effect of laser radiation on the defect nanocrystals observed after its impregnation into cartilaginous tissue exceeds 7 times in comparison with the intact ones.

1. Introduction

Photo-thermal effect of laser radiation on nanoparticles plays a key role in a number of medical technologies: laser hyperthermia, opto-acoustic diagnosis of tissues and laser tissue engineering. Photo-physics of this effect is related to the complex nature of photon energy transition of laser radiation in condensed media with photo absorbing nanoparticles. An abnormal photo-thermal effect of near IR-laser radiation on nanoparticles of oxide bronzes of the transition metals impregnated in cartilage has been observed in [1].

It is known [2,3] that the oxide bronze nanoparticle dispersions, as well as the magnetite ones have similar optical properties and intensive absorption in the near IR spectral band. Laser heating of both nanoparticles in aqueous media should result in an amounted temperature response, but the observed photo-thermal effect in biotissue is different [1]. The origin of this difference is still unknown. Note that the photo absorbing additives of the oxide bronze nanoparticles used for tissue impregnation have been produced by self-propagating high-temperature synthesis (SH-synthesis or SHS in brief) [4]. Solid products of the synthesis were grinded in a planetary mill into nano-sized particles [5].

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Optical absorption of oxide bronze nanoparticles dispersions in water has shown a plasmon resonance peak of absorption [1,2] that was observed for magnetite [3] and “core–shell” iron oxide nanoparticles [6], as well. Optical absorption behavior of these nanoparticles dispersions in the near IR spectral band is variously discussed [2,3, 6-10]. The mechanism of photo-thermal effect of the near IR-laser radiation on biotissues impregnated with these nanoparticles is not fully understood.

To elucidate the mechanism of this effect we studied the influence of defect structure and electronic zone states of nano-crystals of oxide bronzes produced by SHS and serial high energy ball milling on absorption of nanoparticle dispersions in the near IR spectral band.

In this paper, the photo-physical mechanism of the near IR-absorption of laser radiation by the nano-sized crystals of oxide bronzes of the transition metals (W, Mo, Ti) accounting for their semiconductor properties and explaining the high photo-thermal effect by high density of electronic states in zones of highly defect nanocrystals has been proposed.

2. Experimental route and Theoretical approach
As starting materials for SH-synthesis, we used ultra disperse powder metal oxides TiO$_2$, MoO$_3$ and WO$_3$, and alkali metal salts of NaI and KI, which are mixed with the oxides in the stoichiometric ratio, and the synthesis was conducted in accordance with the previously developed method [4]. In the works on SHS of the transition metal oxides and their bronzes [1,4] grinding of solid materials in ball mills [5] used for preparing nanopowders from the synthesis products is widely spread. This method is simple, high energy effective, and has high efficiency, as well as comparatively not high temperature of grinding (~ 250–350°C). Therefore, in this study it was used for fragmentation of Ti, Mo and W-bronze SH-synthesis, using methods [11] to determine the optimum modes of mechanical activation.

The solid products of synthesis were crushed in an agate mortar before grinding. The final stage of grinding was carried out in planetary mills of the "Activator-2SL" and AGO-3, developing centrifugal acceleration up to 120 g.

The change in physical and chemical properties of the powder particles was monitored by measuring the particle size and specific surface area of particles by laser diffraction instrument LA-300 (Horiba, Japan) and permeability was measured by the instrument PSH-11M ("Company Hodakova", Russia) using Karman-Kozeny method. The rating of the process of grinding the oxide bronzes was estimated by differential calorimetry of the grinding bodies and the powder after each time interval of mechanical activation. Mechanical activation time changed by doubling, and ratio of grinding body volume loading in the reactor are discrete (in the vicinity of the optimal theoretical value of 50%) at a constant ratio of the mass of the crushed product to the weight of grinding bodies equal to 1:50. Ambient temperature influence on the measurement results and the deformation of materials were taken into account in accordance with the previously developed methods [11,12].

The absolute size of nanoparticles and crystal structure were determined by high-resolution TEM images at a magnification of 10$^5$–10$^7$ times obtained with an electron microscope JEM-2500SE (JEOL, Japan). The samples of Na$_x$MoO$_3$ bronze for TEM were prepared by manual machining of the powder. A sample was triturated in an agate mortar for 5 minutes, after which it stuck to the walls of the mortar in the form of a thin layer. A small amount was taken from the walls and deposited on the substrate by ultrasonic disperser. During grinding, the substance changed from dark blue (almost black) to blue (Na$_x$MoO$_3$). Preparation of the crystals for TEM included processing to obtain the desired shape and thickness, and etching. Electron microscopic images and digital electronograms obtained after processing were analyzed via "IMAGEG" program (FFT algorithm).

Cooked bronze powders were used for preparing aqueous dispersions of nanoparticles. For this purpose, an equal amount of powder was dissolved in water, purified by reverse osmosis. Using centrifugation and sedimentation of the prepared solution, it was carried out separation of aqueous dispersion in nanoparticle size. The separation process was monitored for optical control of nanoparticle size in aqueous dispersions. The average size of the nanoparticles was estimated using a scattering and absorption photometry of the solutions in the UV-Vis and near infrared regions. For this
purpose, the spectrophotometers PE-5300B (EKROS, Russia) and U3600 (Shimadzu, Japan) were used to obtain the absorbance spectra of solutions in the wavelength range from 300 nm to 1700 nm.

Monochromatic coefficients of laser radiation attenuation were measured for wavelengths $\lambda = 1.45$ μm and 1.56 μm in the concentration range from 10 mg/ml to 30 mg/ml of the dispersed phase in aqueous dispersions of tungsten oxide, molybdenum, and titanium bronzes. The samples of aqueous dispersions of the bronzes were confined in the volume between the two glass-plates of thin slide. The slide with bronze was irradiated by the near IR monochromatic light. We used the Er-fiber laser, $\lambda = 1.56$ μm (IRE-Polus, Russia), and a solid-state diode laser, $\lambda = 1.45$ μm (Lakhta Milon, Russia), as a light source. Measurement of optical transmittance of the colloidal solution of nanoparticles was performed by measuring the power of laser radiation passed through the solution. An optical path in the solution was about 0.5 mm. Power meter Field Master (Coherent, USA) was directly behind the slide onto which the laser beam was directed. In measurements, Fresnel reflection losses from the slide windows were taken into account. At normal incidence of a narrow beam of radiation on the cartilage tissue, the intensity of light $I$ as it passes through the object varies according to the Bouguer-Lambert-Beer law:

$$I = I_0 \cdot e^{-\alpha l},$$

(1)

where $I_0$ is the intensity of the incident radiation, $\alpha$ is effective attenuation, $l$ is the path traversed by the radiation.

Based on the results of measurements of power intensity of the laser radiation transmitted by (1), the reduced absorption coefficient was calculated (neglecting scattering due to small particle size). Note that the measurements of power of laser radiation transmitted through the slide with the probe were carried out to satisfy the condition of optically thin layer ($d \ll 1$).

A photothermal effect of laser radiation on the oxide bronze nanoparticle for different wavelengths in the UV-Vis-NIR-region of the spectrum was evaluated using two approaches: the classical electron theory of Drude-Lorentz and the quantum theory of solids. [13]. The energy diagram illustrating sub-threshold absorption in semiconductor oxides is shown in Figure 1.

The frequency of the plasmon resonance of nanoparticles in water is determined by Langmuir formula:

$$\nu^2 = \frac{\pi e^2 n}{(m^* \varepsilon \varepsilon_0)},$$

(2)

where $e$ is charge, $n$ is density and $m^*$ is the effective mass of the conduction electrons. $\varepsilon$ is relative permittivity of water, and $\varepsilon_0$ is dielectric constant of free space.
Nanoparticles with dimensions not exceeding 10–100 nm of complex oxides represented the metallic oxide bronzes of the transition metals: W, Mo, and Ti have a density of conduction electrons close to the metal: \( n \sim 10^{23} \text{cm}^{-3} \).

The effective mass is \( m^* \approx m \), where \( m \) is the mass of free electrons \( 9.1 \times 10^{-31} \text{kg} \). In this case, the frequency of the plasmon resonance of the nanoparticles is determined by the concentration of free charge carriers, i.e. \( \nu \sim 1/\sqrt{n} \).

For nanoparticles with \( 10^3–10^5 \) atoms, it should be taken into account the quantum size effects [14], affecting the density of electron states in the band gap semiconducting oxide and oxide bronzes:

\[
\Omega(\varepsilon_f) = \frac{3N}{2\varepsilon_f},
\]

where \( N \) is the number of states, \( \varepsilon_f \) is Fermi energy.

The average distance between the levels of the electrons according to [14]:

\[
\Delta \varepsilon = 1/\Omega(\varepsilon_f) = \frac{2\varepsilon_f}{3N}.
\]

3. Results and Discussions

Table 1 shows the measured values of the aqueous solutions of monochromatic absorption coefficient of potassium-hydrogen, and -molybdenum bronzes of concentrations varying from 10 mg/ml to 35 mg/ml. The extinction values are also calculated for these solutions.

We failed to obtain the stable colloids of titanium bronze for concentrations over 1 mg/ml in an aqueous medium. Nanoparticles of these bronzes stick together and settle to the bottom.

**Table 1.** The absorption coefficient (attenuation constant) of laser radiation for different wavelengths in aqueous solutions of potassium-hydrogen and -molybdenum bronzes of various concentrations.

| Wave length, \( \lambda \), nm | Concentration, \( C \), mg/ml | Transmission, \( I_o/I_x \) | The absorption coefficient, \( \alpha \), \( \text{cm}^{-1} \) | Extinction*, \( \text{ml} / (\text{mg} \cdot \text{cm}) \) |
|-----------------------------|-------------------------------|-----------------------------|---------------------------------|-----------------|
| \( K_x MoO_3 \)             | \( H_2MoO_3 \)                | \( K_x MoO_3 \)             | \( H_2MoO_3 \)                  | \( K_x MoO_3 \) |
| 1560                        | 30                            | 540/90                      | 475/60                          | 35.8            | 39.6 |
|                             | 20                            | 480/145                     | 500/130                         | 23.9            | 58.6 |
|                             | 10                            | 440/240                     | 480/240                         | 12.1            | 25.4 |
| 1450                        | 35                            | -                           | 750/40                          | 58.6            | -    |
|                             | 25                            | -                           | 380/45                          | 42.7            | -    |

* Laser intensity \( (I) \) in mW/cm²

Figure 2 shows the nanoparticle absorption spectra of aqueous dispersions of potassium- and hydrogen molybdenum oxide bronze in a wide wavelength range from UV-Vis to the near-IR. A different behavior of optical density (OD) is observed at long-wavelengths of absorption spectrum in the visible and the near-infrared region. For hydrogen molybdenum bronze, a visible intense absorption band is observed in the range from 700 nm to 900 nm. For potassium bronze, absorption decreases with increasing wavelength, it is asymptotically is closed for absorption of water.
Figure 2. Absorption spectra of aqueous dispersions of nanoparticles NaTiO$_2$, and K, H molybdenum oxide bronzes.

Figure 3. The absorption peak in the field of plasmon resonance observed for nanoparticles of hydrogen molybdenum oxide bronze.

Figure 3 shows the absorption spectrum of an aqueous dispersion of nanoparticles of hydrogen molybdenum oxide bronze in the UV-Vis spectrum. There is a peak of the plasmon resonance at $\lambda = 340$ nm. Broad absorption bands are in the long-wavelength visible and near infrared regions of the spectrum.

Wide but less intense absorption bands in the infrared region are observed in aqueous solutions of tungsten bronzes $K_xWO_3$ [2]. In aqueous solutions of sodium and potassium titanium bronzes one can distinguish a plasmon resonance peak, but because of the low concentration of the colloids the marked absorption in the near-IR was not observed (Figure 2).

After machining of solid products of the synthesized Na and K titanium oxide bronzes the produced powders acquire magnetic properties. Thus, in the separation by sedimentation of the solutions with Na$_{0.2}$TiO$_2$ nanoparticles it was found that the sediment at the bottom of the sedimentation column contains nanoparticles with magnetic properties. This was revealed by the attraction of the sediment particles to the permanent magnet with a magnetic flux density of $\sim 0.2$ T. To study the magnetic properties of oxide bronze nanoparticles, magnetic separation of the magnetic components from the solution of nanoparticles in the sedimentation was carried out [15]. We used a magnetic trap with axially symmetric alternating magnetic field with a constant gradient of 2 T/m and field amplitude of 0.05 T [15].
Figure 4. Magnetic nanoparticles (left) and a magnetic trap (right) used for the separation of magnetic nanoparticles: trap circuit (a) and the magnetic field distribution in the interaction of nanoparticles with a magnetic field (b) with unidirectional (1) and opposite (2) magnet switched on.

The magnetic component was separated from the colloidal solution of nanoparticles of the titanium oxide bronzes with the magnetic trap (Fig. 4), and its elemental analysis was conducted. The atomic absorption analysis of magnetic sludge showed that the spectrum has a line of alkali metals K and Na. The paramagnetic properties of nanoparticles sediment were studied by ESR. Hydrogen bronze of the metal oxides of Ti, W and Mo markedly differ from K and Na-titanium bronzes in magnetic properties. The magnetic field did not affect them. They were deposited on the bottom of the column by gravity.

The results of the study of paramagnetic properties of K$_x$TiO$_2$ powder bronzes obtained after grinding of SH-synthesis products revealed that paramagnetic powder is present in the signal samples corresponding to different times of grinding. Moreover, the signal amplitude increases with increasing grinding time (Figure 5).

ESR-spectra showed free iron absorption lines observed under magnetic field of 3400 gauss with g-factor closed to 2. The presence of magnetic nanoparticles in a grinded product is apparently due to the wear of the steel balls used as milling bodies and high hardness of crystals K$_x$TiO$_2$. In grinding softer W and Mo oxides, the magnetic component in bronze milling is absent.
Figure 5. The ESR spectra of the K$_x$TiO$_2$ bronze powders obtained after SHS products grinding for different times of machining.

Structural studies a Na$_x$MoO$_3$ nanocrystals using a high-resolution TEM has shown the presence of high density of disturbed structures in the samples.

Figure 6. The images of nanocrystal (left) and electron diffraction (right) obtained for crystal structure of the Na$_x$MoO$_3$ -bronze with high resolution TEM.

The images in figure 6 present the structure of a highly defective bronze nano-crystal with varying degrees of layered single-crystal. The image of electron diffraction indicates the presence of the orthorhombic oxide bronze Na$_x$MoO$_3$ [16]. The image on the left (Figure 6) indicates high density of the surface defects at the boundaries of the crystals. In the body of the crystal, there are sufficient ordering areas with layered organization, which occupy the range from 60 to 70% of the total sample. Regions with one-dimensional ordering are distinguished. These areas determine the properties of semiconductor crystallites, namely the properties of photonic crystals: the absorption peak of the plasmon resonance and broad bands in the near IR. The density of surface defects in the limit of a 10
nm x10 nm aria of the crystal, as indicated by square at the Fig.6, is \( \sim 10^{17} - 10^{19} \text{ cm}^{-2} \). The high density of surface defects including non-stoichiometry defects, interstitial atoms and vacancies, as well as their number determines the intensity of the absorption bands, and the wavelengths of these bands are determined by the resonance properties of crystals caused by electron-phonon interaction. The broad absorption bands in the near infrared region of spectra (Figure 2) indicate a significant loss causing the photothermal effect.

Note that, the currently used metallic nanoparticles [17] (Au, Ag, etc.) have a lower photothermal effect of laser heating due to the narrow UV-Vis bands of plasmon absorption and weak electron-phonon interaction. As a result, to obtain photothermal effect of laser radiation on the nanoparticles based on plasmon resonance [17] it is needed to significantly increase the intensity of laser radiation (~10^5 W/cm^2 [17]). Using a shot pulse laser radiation, it is easy to reach high temperature \( T_e \) of electronic subsystem of nanocrystals. In this case, the equilibrium temperature of nanoparticle heating is not significant: \( T \approx m_e c_e / mc \cdot T_e \), since \( m_e << m \) and \( c / c_e = 2 \) [13], where \( m \) and \( m_e \), \( c \), \( c_e \) are the masses of the specific heat and the lattice and electron gas, respectively.

As shown in Figure 1, the average distance between electron levels \( \Delta \varepsilon \), in accordance with (4), depends on the Fermi energy \( \varepsilon_F \approx 1/2 E_g \) and high density of electron states [14], which is characteristic of the defective semiconductor oxides and oxide bronzes. As a result, the energy of the quantum of infrared laser radiation (\( h \nu \sim 0.5 \text{ eV} \)) is sufficient to generate the high density of electronic states in the conduction band causing high absorption, in contrast to the defect-free semiconductors, where high energy of excitation of interband transitions is required.

In pure semiconductor crystals, higher energy of the photons (\( h \nu > E_g \)) is required for excitation of interband transitions of electrons to overcome the threshold photoabsorption. The impurity (defects) of semiconductor oxides and oxide bronzes, as shown, provides sub-threshold absorption mechanism of excitation.

4. Conclusions
When using laser heating of nanoparticles of metal oxides and oxide bronzes it is required a lower intensity laser radiation and photon energy (\( h \nu \sim 0.5 \text{ eV} \)) than that for metal nanoparticles based on plasmon resonance. Accounting a sub-threshold laser absorption character in the near infrared region of the spectrum allows us to explain abnormally high photothermal effect [1]. Photothermal effect of laser heating of cartilage impregnated with nanoparticles of hydrogen molybdenum oxide bronze [1] is more than 7.5 times greater than the heating effect of intact (without nanoparticles) cartilage [18].

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