

# Effect of nanosecond UV laser irradiation on luminescence and absorption in silver- and copper-containing phosphate glasses

A.A. Murashov, A.I. Sidorov, M.V. Stoliarchuk

**Abstract.** Experimental evidence is presented that nanosecond UV laser irradiation of silver- and copper-containing barium phosphate glasses leads to luminescence quenching in the visible range. Subsequent heat treatment induces an absorption in the range 350–500 nm. These effects are due to the ionisation and fragmentation of subnanometre molecular clusters by laser radiation and subsequent (heat treatment-induced) formation of nanoparticles possessing plasmon resonance. Our numerical modelling results demonstrate the feasibility of producing stable  $Ag_nCu_m$  hybrid molecular clusters in glass. Local modification of the optical properties of glass by laser light can be used for optical information recording.

**Keywords:** laser irradiation, glass, molecular cluster, nanoparticles.

## 1. Introduction

Advances in photonics and optoelectronics are highly dependent on the ability to produce new functional optical materials with tailored optical properties and develop new techniques for modifying their properties. Promising systems for these purposes are inorganic glasses containing silver and/or copper. Silver and copper can be present in glass in the form of ions, neutral atoms, charged or neutral subnanometre molecular clusters [1] and nanoparticles possessing plasmon resonance [2]. Laser or electron beam irradiation makes it possible to transform the state of a metal in glass, thereby drastically changing the optical properties (refractive index, absorption coefficient and luminescence) of the glass [1, 3–7]. One important advantage of laser or electron beam irradiation is that it allows the optical properties of glass to be modified locally, in particular in a submicron region. This offers the possibility of producing volume holograms in glass [8], optical waveguides [7] and submicron light sources [4] and enables optical information recording, in particular in higher order codes [4, 5].

One mechanism underlying the modification of optical characteristics of glass under laser irradiation is free-electron photogeneration, which leads to a charge redistribution between its components. If a low-power cw UV laser radiation is used, a photosensitiser (e.g.  $Ce^{3+}$ ) whose absorption

band coincides with the He–Cd laser wavelength ( $\lambda = 325$  nm) is introduced into glass [8]. In the case of pulsed lasers, free electrons can be generated through multiphoton ionisation of glass components by femtosecond IR laser pulses [3, 9–11] or single-photon photoionisation of glass components and glass network defects by nanosecond UV laser pulses [4, 5]. One advantage of the latter approach is the possibility of laser beam focusing to a submicron spot size.

The optical characteristics of silver- and copper-containing glasses after laser irradiation are influenced by not only laser processing parameters, such as laser fluence [4], but also the prior history of the glass (glass preparation conditions, UV irradiation [12], heat treatment and others). Glass composition also has a significant effect on the results of laser irradiation [1, 3]. Varying the parameters in question, one can obtain glass with optimal and desired optical characteristics.

The purpose of this work is to study the effect of nanosecond UV laser irradiation and subsequent heat treatment on luminescence and absorption in silver- and copper-containing barium phosphate glasses. We also examine the feasibility of the formation of  $Ag_nCu_m$  hybrid molecular clusters in the glass.

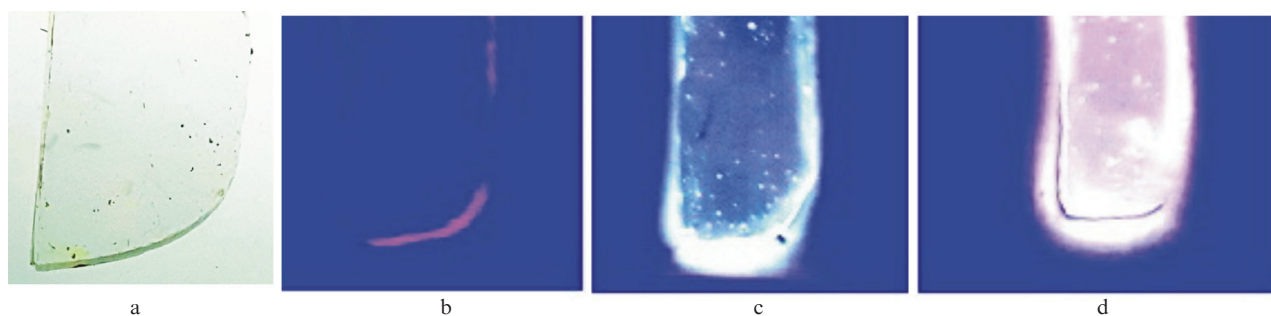
## 2. Experimental procedure

In our experiments, we used polished plates of barium phosphate glass with the composition  $Al_2O_3(5)-Ba(PO_3)_2(75)-NaPO_3(20)$ , prepared at the ITMO University. The glass was doped with  $Ag_2O$  (0.2) and/or  $Cu_2O$  (0.2) (the numbers in round brackets indicate concentrations expressed as a mole percent). To ensure reducing conditions,  $SnO_2$  (0.7) was added to the glass batch. The glass transition temperature of the glasses, measured with a Netzsch STA 449 F1 Jupiter differential scanning calorimeter, was 400–410 °C, depending on their composition. Figure 1 shows the appearance of a sample (Fig. 1a) and luminescence images of silver-doped (Fig. 1b), copper-doped (Fig. 1c) and silver–copper codoped (Fig. 1d) samples before laser irradiation. It is seen that the as-prepared glasses are transparent and colourless. The silver-doped glass has a very low luminescence intensity in the visible range. The luminescence intensity in the copper-doped glass is higher, and the highest luminescence intensity is offered by the glass codoped with silver and copper. Clearly, the last glass is the most attractive for practical applications, so samples of this glass were used in further work.

The glasses were irradiated at room temperature by the third harmonic ( $\lambda = 355$  nm) of an LS-2131M multimode Nd:YAG laser (Lotis TII) at a pulse energy of 30 mJ, pulse duration of 5 ns and pulse repetition frequency of 1 Hz. The beam spot diameter on the sample surface was 1.5 mm for

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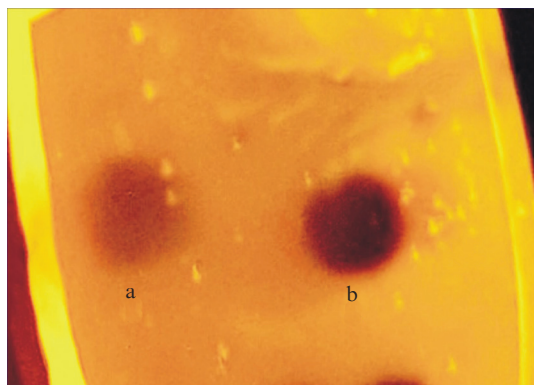
**Figure 1.** Photograph of a sample (a) and luminescence images of silver-doped (b), copper-doped (c) and silver-copper codoped (d) samples before laser irradiation. The luminescence excitation wavelength is 365 nm.

convenience of measurements. The laser fluence was varied by changing the irradiation time. After the laser irradiation, some of the samples were heat-treated in air for 2 h at a temperature of 450 °C (above the glass transition temperature).

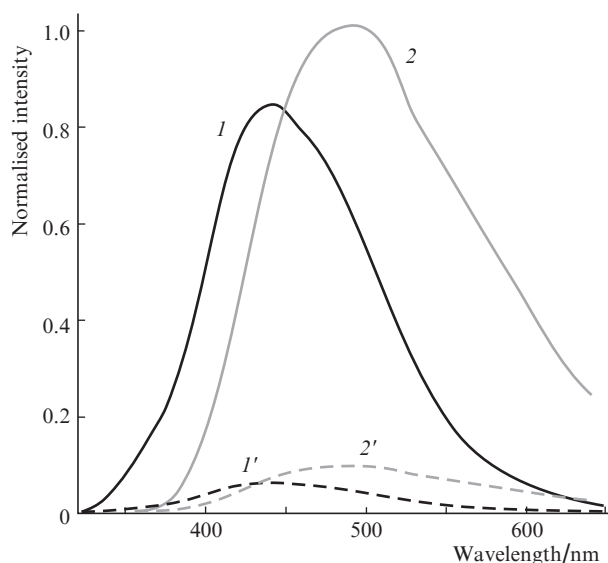
Optical density spectra were measured on a PerkinElmer Lambda 650 spectrophotometer, and luminescence spectra, on a PerkinElmer LS-55 spectrofluorometer. The spectroscopic measurements were made at room temperature.

### 3. Experimental results

The as-prepared silver- and copper-containing phosphate glasses were colourless and showed bright visible luminescence under UV excitation (Fig. 1). UV laser irradiation leads to luminescence quenching in the irradiated zones (Fig. 2). Raising the laser fluence leads to a stronger luminescence quenching. Figure 3 illustrates the effect of laser fluence on the luminescence spectrum of a sample after laser irradiation. It is seen that the luminescence spectrum obtained under excitation with 260-nm laser radiation consists of two bands, centred at 440 and 470 nm. Under excitation with 330-nm laser radiation, the luminescence spectrum also consists of two bands, centred at 480 and 550 nm. The luminescence spectra of unirradiated areas on the glass surface have a similar structure, but the luminescence intensity is higher. Increasing the laser irradiation time from 1 to 10 min leads to a reduction in peak luminescence intensity by about ten times.

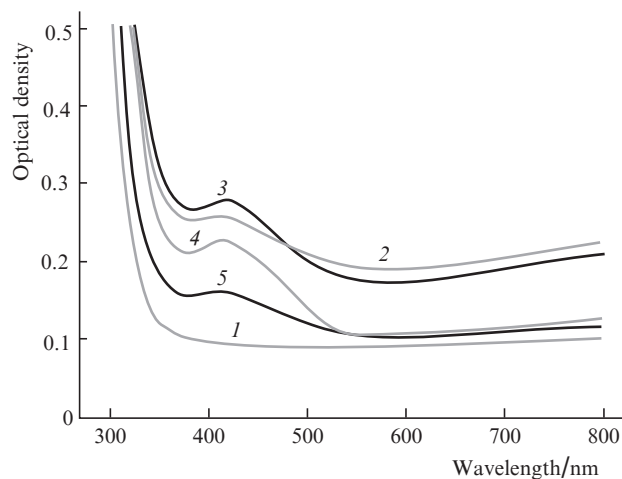


**Figure 2.** (Colour online) Luminescence image of the silver-copper codoped phosphate glass sample after laser irradiation. Irradiation time of (a) 1 and (b) 10 min. The luminescence excitation wavelength is 365 nm.



**Figure 3.** Luminescence spectra of irradiated areas of a sample. Irradiation time of (1, 2) 1 and (1', 2') 10 min; luminescence excitation wavelength of (1, 1') 260 and (2, 2') 330 nm.

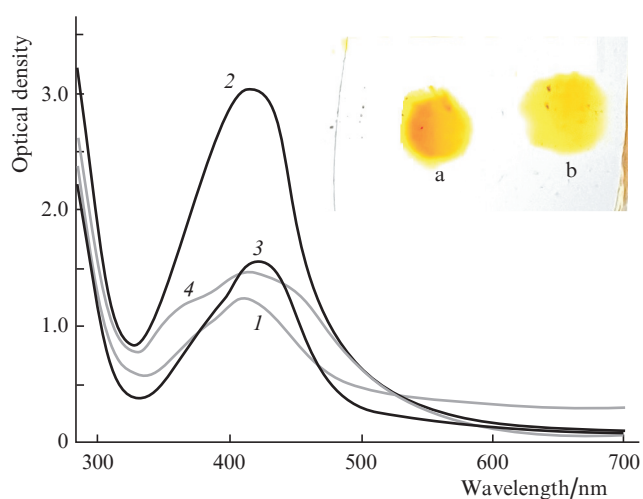
Laser irradiation produces a light pale yellow colour in the irradiated areas of the glass. In addition, an absorption band emerges in its optical density spectrum in the range 380–530 nm, peaking at  $\lambda = 415$  nm (Fig. 4). It is seen from



**Figure 4.** Optical density spectra of a sample before (1) and after laser irradiation for 1 (2), 3 (3), 5 (4) and 10 min (5).

Fig. 4 that, with increasing irradiation time, the peak absorption first rises and then falls off. In addition, laser irradiation for 1–3 min leads to a uniform increase in absorption in the range 380–800 nm and produces a broad absorption band in the range 600–800 nm.

Heat treatment of the laser-irradiated glasses above their glass transition temperature produces a bright yellow-orange colour in the irradiated areas and a strong absorption band in the range 350–500 nm (Fig. 5). With increasing irradiation time, the peak absorption first rises and then falls off. Moreover, increasing the irradiation time increases the peak absorption wavelength of the band from 410 to 425 nm. At an irradiation time of 10 min, the absorption band broadens and can be decomposed into three components, centred at 360, 410 and 445 nm. It is also seen from Fig. 5 that heat treatment eliminates the broad absorption band in the range 600–800 nm.



**Figure 5.** Optical density spectra of a sample after laser irradiation and heat treatment; irradiation for (1) 1, (2) 3, (3) 5 and (4) 10 min. Inset: (colour online) photograph of glass areas irradiated for (a) 3 and (b) 5 min.

## 4. Discussion

Before laser irradiation, the silver- and copper-containing glass shows bright visible luminescence (Fig. 1). Such luminescence is typical of neutral molecular clusters of some metals, including silver [1]. In this study, a neutral state of molecular clusters is ensured by the reducing conditions of glass preparation. Comparison of the luminescence images of the samples in Fig. 1 leads us to the following conclusions: (1) Since the silver-doped glass has low luminescence intensity, the luminescence of the silver–copper codoped glass is unrelated to molecular silver clusters. (2) Since the luminescence intensity in the silver–copper codoped glass is considerably higher than that in the copper-doped glass, it is unrelated to the luminescence of molecular clusters of copper or  $\text{Cu}^+$  ions. It is thus reasonable to assume that the silver–copper codoped glass contains  $\text{Ag}_n\text{Cu}_m$  neutral hybrid molecular clusters (this possibility is analysed below).

Consider the main processes induced in glass by nanosecond UV laser irradiation. One process is the photoionisation of glass components, which produces free electrons in the

glass. After a laser pulse, the electrons are captured by glass components and network defects. Another process is the breaking of chemical bonds in the glass network, resulting in the formation of radiation-induced point defects. Yet another process is the heating of the glass by laser radiation. Below we describe additional processes that allow the observed effects to be accounted for.

The silver–copper codoped glass has structured luminescence bands peaking at  $\lambda = 440, 470\text{--}480$  and 550 nm (depending on the excitation wavelength). These bands can be compared to  $\text{Ag}_1, \text{Ag}_2 + \text{Ag}_4$  and  $\text{Ag}_3$  luminescence bands, respectively [13, 14]. The luminescence in the range 470–480 nm can be contributed by  $\text{Cu}_n$  ( $n < 8$ ) neutral molecular clusters [15], and the 550-nm luminescence, by  $\text{Cu}^+$  ions and  $\text{Cu}^+\text{--Cu}^+$  dimers [16]. However, the presence of ions in the glass before laser irradiation is unlikely because of the reducing glass preparation conditions. Moreover, these assumptions are inconsistent with the luminescence intensities in the glasses of different compositions (see above). This provides additional evidence that the glass under investigation contains  $\text{Ag}_n\text{Cu}_m$  hybrid molecular clusters. In previous work [17–19], numerical simulation was used to describe the structural and electronic properties of several types of  $\text{Ag}_n\text{Cu}_m$  molecular clusters, but there are no data on their luminescence properties. Laser irradiation leads to luminescence quenching in the irradiated regions of the glass (Figs 2, 3). This is due to the photoionisation and fragmentation of the molecular clusters. As shown earlier [1], the luminescence intensity of charged molecular clusters is considerably lower than that of neutral ones.

Laser irradiation produces changes in the optical density spectrum of the silver–copper codoped glass. In particular, an absorption band emerges in the range 380–530 nm, peaking at  $\lambda = 415$  nm (Fig. 4). Such an absorption band is characteristic of plasmon resonance of spherical silver nanoparticles 2–20 nm in diameter [1, 2]. It is known however [20] that silver nanoparticles can only be formed in glass as a result of prolonged heat treatment above the glass transition temperature of the material, which differs from the laser irradiation conditions in our experiments. Moreover, as mentioned above, laser irradiation causes the photoionisation of the glass components, and positive silver ions cannot form nanoparticles because of the Coulomb repulsion. The band in question may be due to the presence of a high concentration of radiation-induced point defects characterised by absorption in the spectral region under consideration. Possible defects include phosphorus–oxygen hole centres (POHCs). As shown by Ebeling et al. [21], X-ray irradiation of phosphate glasses produces an absorption band in the range 350–550 nm, due to the formation of this type of radiation-induced defect. It is seen in Fig. 4 that, with increasing irradiation time, the absorbance first rises and then falls off. This may be due to laser-induced point defect annealing.

Heat treatment of the glasses above their glass transition temperature causes changes in their optical density spectra, producing absorption bands characteristic of spherical silver nanoparticles 2 to 20 nm in diameter [1, 2] [Fig. 5, spectra (1)–(3)]. After irradiation for the longest time, the absorption band has a complex shape and can be represented as three components [Fig. 5, spectrum (4)]. Such a shape of the absorption band is characteristic of plasmon resonance of silver nanoparticles in the shape of a generalised ellipsoid [2]. The three constituent absorption bands correspond to vibrations along the three axes of the ellipsoid. One possible reason

for the observed changes in the shape of the silver nanoparticles with increasing laser fluence is that irradiation of the glass to high laser fluences produces not only point defects but also groups of associated defects in the form of broken chemical bonds in the glass network. Such defects cannot be eliminated by heat treatment, and the corresponding ‘loosened’ regions may contain more complex shaped nanoparticles. It follows from Fig. 5 that increasing the irradiation time first increases the height of the plasmon absorption band and then reduces it. This means that, after irradiation to low laser fluences, heat treatment increases both the concentration and size of silver nanoparticles, whereas at high laser fluences these parameters decrease. The cause of this effect is that increasing the laser fluence leads to not only defect formation in the glass network but also the disintegration of the molecular silver clusters. Since the neutral molecular silver clusters act as nucleation and growth centres for silver nanoparticles during heat treatment, reducing the concentration of molecular clusters leads to a decrease in both the concentration and size of the nanoparticles. Thus, even though the optical density spectra in Figs 4 and 5 are similar and undergo similar changes, the observed effects are related to different objects and the underlying processes follow different mechanisms.

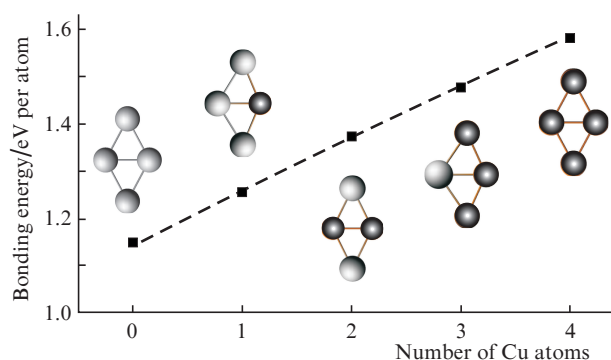
It is of interest to analyse the possibility of the formation of  $\text{Ag}_n\text{Cu}_m$  neutral hybrid molecular clusters in the glass. A condition for their existence is their stability, which is in turn determined by the intramolecular bonding energy. The bonding energy was evaluated by numerical modelling using density functional theory calculations and the Amsterdam Density Functional program (ADF2014.11) [22]. Modelling was performed for  $\text{Ag}_n\text{Cu}_m$  ( $n + m = 4$ ) neutral hybrid tetramers. In the initial stage, we identified the structures of the most stable molecular clusters. Next, their bonding energy was calculated. In all the calculations, we used the Perdew–Burke–Ernzerhof (PBE) exchange–correlation semilocal functional and an all-electron triple-zeta basis set of Slater-type orbitals (TZ2P). The bonding energy  $E_b$  of ‘pure’ and hybrid molecular clusters was evaluated as follows:

$$E_b(X_n) = [(n-1)E(X) + E(X) - E(X_n)]/n,$$

$$E_b(\text{Ag}_n\text{Cu}_m) = [nE(\text{Ag}) + mE(\text{Cu}) + E(\text{Cu}) - E(\text{Ag}_n\text{Cu}_m)]/(n+m).$$

Here  $X$  stands for Ag or Cu and  $E$  is the total energy of an isolated atom or molecular cluster.

The structures and bonding energies of stable  $\text{Ag}_n\text{Cu}_m$  neutral molecular clusters are presented in Fig. 6. It is worth noting that the lines between the atoms do not represent chemical bonds, but only indicate the relative positions of the atoms involved and the interatomic distances. It is seen from Fig. 6 that the stable hybrid tetramers have a planar structure and that increasing the number of copper atoms in them increases their bonding energy and, accordingly, improves their stability. This increases the probability of the formation of hybrid molecular clusters in the phosphate glass, in comparison with  $\text{Ag}_n$  ‘pure’ molecular clusters.  $\text{Cu}_4$  ‘pure’ molecular tetramers have the highest bonding energy. At the same time, it follows from Fig. 4 that laser irradiation converts some of the copper ions into a divalent state ( $\text{Cu}^{2+}$ ). This reduces the probability of the formation of ‘pure’ neutral molecular copper clusters.



**Figure 6.** Bonding energy against the number of copper atoms for  $\text{Ag}_n\text{Cu}_m$  ( $n + m = 4$ ) neutral tetramers. Inset: structures of the stable tetramers.

Since molecular clusters act as nuclei for the growth of metallic nanoparticles, it might be expected that heat treatment would produce nanoparticles of a silver–copper alloy in the glass. The question that arises in this context is what is the material of the nanoparticles obtained in our experiments? The absorption bands shown in Fig. 5 correspond to plasmon absorption bands of silver nanoparticles [1, 2]. The plasmon absorption bands of copper nanoparticles lie in the range 550–570 nm. As pointed out above, laser irradiation converts some of the copper ions into a divalent state. The thermal diffusion coefficient of divalent copper ions is two orders of magnitude smaller than that of monovalent copper ions. Moreover, during heat treatment the oxygen dissolved in glass oxidises the copper to form copper oxides. At the same time, silver oxides are thermally unstable and readily decompose on heating. It is, therefore, reasonable to expect that the nanoparticles produced in the glass by heat treatment contain only minor amounts of copper, which has a weak effect on the permittivity of the alloy and, hence, on the spectral position of the plasmon resonance of the nanoparticles.

## 5. Conclusions

The present experimental data demonstrate that nanosecond UV laser irradiation of silver- and copper-containing barium phosphate glasses leads to luminescence quenching in the visible range and defect formation in the glass network. Subsequent heat treatment induces an absorption in the range 350–500 nm. These effects are due to the ionisation and fragmentation of subnanometre molecular silver clusters by laser radiation and subsequent (heat treatment-induced) formation of silver nanoparticles possessing plasmon resonance. The present numerical modelling results demonstrate the feasibility of producing stable  $\text{Ag}_n\text{Cu}_m$  hybrid molecular clusters in glass. Local modification of the optical properties of glass by laser light can be used for optical information recording.

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## References

1. Dubrovina V.D., Ignatiev A.I., Nikonov N.V., Sidorov A.I., Shakhverdov T.A., Agafonova D.S. *Opt. Mater.*, **36**, 753 (2014).
2. Klimov V.V. *Nanoplasmonics* (Singapore: Pan Stanford, 2010; Moscow: Fizmatlit, 2009).

3. Klyukin D.A., Dubrovin V.D., Pshenova A.S., Putilin S.E., Shakhverdov T.A., Tsyarkin A.N., Nikonorov N.V., Sidorov A.I. *Opt. Eng.*, **55**, 067101 (2016).
4. Gorbiak V.V., Sidorov A.I., Vasilyev V.N., Dubrovin V.D., Nikonorov N.V. *Opt. Eng.*, **56**, 047104 (2017).
5. Klyukin D.A., Khmelev A.Yu., Pshenova A.S., Sidorov A.I., Fedorov Yu.K. *Quantum Electron.*, **46**, 930 (2016) [*Kvantovaya Elektron.*, **46**, 930 (2016)].
6. Ignat'ev A.I., Nashchekin A.V., Nevedomskii V.M., Podsvirov O.A., Sidorov A.I., Solov'ev A.P., Usov O.A. *Tech. Phys.*, **56**, 662 (2011) [*Zh. Tekh. Fiz.*, **81**, 75 (2011)].
7. Podsvirov O.A., Sidorov A.I., Churaev D.V. *Tech. Phys.*, **59**, 1674 (2014) [*Zh. Tekh. Fiz.*, **84**, 96 (2014)].
8. Glebov L.B., Nikonorov N.V., Panysheva E.I., Petrovskii G.T., Savvin V.V., Tunimanova I.V., Tsekhomskii V.A. *Opt. Spectrosc.*, **73**, 237 (1992).
9. Dai Y., Hu X., Wang C., Chen D., Jiang X., Zhu C., Yu B., Qiu J. *Chem. Phys. Lett.*, **439**, 81 (2007).
10. Bourhis K., Royon A., Papon G., Canioni L., Makria N., Petit Y., Cardinal T. *J. Non-Cryst. Solids*, **377**, 142 (2013).
11. Klyukin D.A., Sidorov A.I., Ignat'ev A.I., Nikonorov N.V., Silvennoinen M., Svirko Yu.P. *Opt. Spektrosk.*, **119**, 122 (2015).
12. Klyukin D.A., Sidorov A.I., Ignatiev A.I., Nikonorov N.V. *Opt. Mater.*, **38**, 233 (2014).
13. Fedrigo S., Harbich W., Buttet J. *J. Chem. Phys.*, **99**, 5712 (1993).
14. Felix C., Sieber C., Harbich W., Buttet J., Rabin I., Schulze W., Ertl G. *Chem. Phys. Lett.*, **313**, 105 (1999).
15. Lu Y., Chen W. *Chem. Soc. Rev.*, **41**, 3594 (2012).
16. Dedecek J. *J. Phys. Chem.*, **99**, 16327 (1995).
17. Kilimis D.A., Papageorgiou D.G. *Eur. Phys. J. D*, **56**, 189 (2010).
18. Zhao S. *Commun. Theor. Phys.*, **57**, 452 (2012).
19. Li W., Chen F. *Physica B*, **451**, 96 (2014).
20. Nikonorov N.V., Sidorov A.I., Tsekhomskii V.A., in *Silver Nanoparticles*. Ed. by D.P. Perez (Croatia, Vukovar: In-Tech., 2010) pp 177–200.
21. Ebeling P., Ehrt D., Friedrich M. *Opt. Mater.*, **20**, 101 (2002).
22. ADF2014, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands (2014), <http://www.scm.com>.