*Proceedings of the International Conference*
*Nanomaterials: Applications and Properties*
Vol. 4 No 1, 01NNPT03(3pp) (2015)

# Determination of Sizes of Ag Nanoparticles in Glass $Li_2B_4O_7$:Ag,Gd

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(Received 29 May 2015; published online 27 August 2015)

Annealing in air and vacuum were obtained glass samples $Li_2B_4O_7$:Ag,Gd with Ag NPs. Three methods: the half-width strip plasmon resonance, X-ray diffraction and Small-angle X-ray scattering, in these samples by size NPs Ag. Revealed that the size of NPs Ag, defined by half-widths plasmon resonance band much smaller than obtained by other methods. It is concluded that the methods of X-ray diffraction and small-angle X-ray scattering give results closer to reality than the method plasmon resonance.

**Keywords:** Botate glasses, Ag nanoparticles, Plasmon resonance, Small-angle X-ray scattering.

PACS numbers: 61.46. – w, 64.70.ph

## 1. INTRODUCTION

High attention was recently paid to metal nanoparticles (NPs) primarily due their property of light induced collective excitation of free electrons, or so-called localized surface plasmon resonance (LSPR) and also due to their extremely fast nonlinear response. Usually the LSPRs are seen in extinction spectra of metal nanoparticles embedded in a dielectric matrix as a wide band, the position of which depends on nature of the metal, the size of NPs and dielectric properties of the enviroment surrounding the nanoparticles. Bands of plasmon absorption for nanoparticles of noble metals (Au, Ag, Cu) in dielectric enviroment are observed in the visible range of spectrum, making them especially attractive for application in a variety of optical and nonlinear optical devices.

Promising dielectric material for embedding of Ag nanoparticles in it is borate glass $Li_2B_4O_7$, which was demonstrated in our previous paper [2]. However, some ambiguities have been documented, when determining the amount of Ag NPs, formed by annealing under reducing atmosphere doped with silver glass $Li_2B_4O_7$:Ag. For example, it turned out, that the diameter of Ag NPs determined from atomic force microscopy falls within the range of D = 7 - 40 nm [3] with a maximum at about 14-18 nm, whereas from the half-width strips plasmon resonance it does not exceed 10 nm.

At the same time, control of the size of Ag NPs in the dielectric matrix is very important, since the size of nanoparticles influences the relevant parameters of the composite Ag NPs in glass matrices. It is therefore interesting to perform a comparative study to determine the size of Ag NPs for the same sample, but with different techniques. After all, to determine the size of metal nanoparticles one can also use other methods such as x-ray diffraction [4] and angle x-ray scattering was [5-7].

The goal of this work is a comparative study of the size of Ag NPs in the same glass samples $Li_2B_4O_7$:Ag,Gd annealed in air and vacuum, determined by X-ray diffraction, small-angle X-ray scattering and by the half-width strips plasmon absorption.

## 2. EXPERIMENTAL TECHNIQUE

For fabrication of $Li_2B_4O_7$:Gd,Ag glass, lithium carbonate $Li_2CO_3$, we use boric acid $H_3BO_3$, gadolinium oxide $Gd_2O_3$, and silver nitrate $AgNO_3$ of high purity. The mixture of chemical reagents corresponding to the stoichiometric composition of $Li_2O \cdot 2B_2O_3$ was placed in a ceramic crucible. Employing the method of multistage temperature synthesis and the following the chemical reaction:

$$Li_2CO_3 + 4H_3BO_3 \rightarrow Li_2B_4O_7 + CO_2\uparrow + 6H_2O\uparrow$$

the $Li_2B_4O_7$ powder with $T_{melt}$ = 1198 K was obtained. Then 2 mol.% of $AgNO_3$ and 1 mol.% $Gd_2O_3$ were added. Glass was fabricated by melting the powder in an $Al_2O_3$ crucible at the temperature of 1270 K in the air environment. The melt was homogenized for 0.5 h. First, it was quenched down to the temperature of about 670 K and then left freely cooling down to room temperatures. Plates of about 10×7×1 mm$^3$ in dimension were cut out from the obtained glass, and their surfaces were ground and polished. In order to form Ag NPs, the specimens were annealed at a temperature of 710±5 K for 1–2 h in the air environment or in vacuum (<$10^{-4}$ mm Hg with a titanic getter).

X-ray studies of resulting composite material were conducted using X-ray complex STOE Transmission Diffractometr System STADI P and by tilted shooting (small-angle X-ray scattering) on DRON-3 diffractometer (Cu $K_\alpha$-radiation, $\lambda$ = 1,5418 Å).

The transmission spectra were measured on a setup created on the basis of an MDR-23 monochromator and a personal computer. An incandescent halogen lamp was used as a light source. A photoelectron multiplier PMT-79 operating in the quantum counting mode played the role of a detector, which provided the linearity of signal registration in the range of $10^2$–$10^6$.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

Determination of Ag NPs was conducted by three methods.

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*X-ray diffraction.* X-ray studies of the prepared composite material were conducted using X complex STOE Transmission Diffractometr System STADI P. On the diffraction pattern (Figure 1, b) registered for the glass one finds a semi-amorphous halo corresponding to maxima of theoretically expected diffraction reflections for $Li_2B_4O_7$. Pure gadolinium is not fixed, but the reflex at 38,68° 2θ corresponds to the reflection from the 111 face-centered cubic lattice of pure silver. From the value of the half-width of the reflection we have estimated the size of coherent scattering domains. Assuming that the metallic nanoparticles formed during annealing are completely crystalline, the latter can be considered as an estimation for the typical size of grains in the phase.

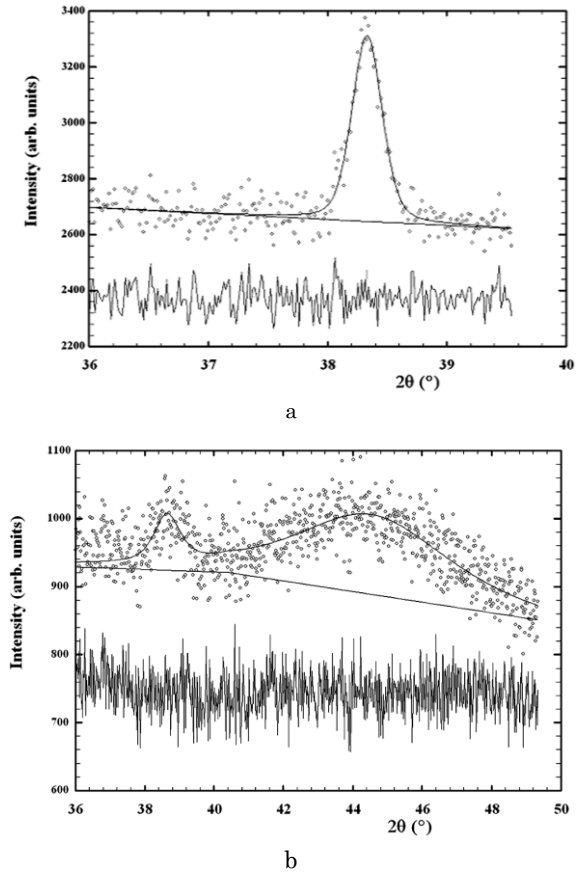


**Fig. 1** – Profiles of diffraction peak (111) Ag in samples $Li_2B_4O_7$:Gd,Ag, annealed in vacuum (a) and annealed in air (b).

Comparison of diffraction for two samples annealed in vacuum and in air (Figure 1, b) shows that in these cases metal nanoparticles are formed of different sizes, such that, for glass, annealed in vacuum the coherent domain size was found to be D = 26,9 nm, whereas for glass, annealed in air it was of 7.5 nm in diameter (Table 1). The concentration of formed nanoparticles was found to be also different, namely: it appeared to be higher for annealing in vacuum and much lower when annealing in air.

*Small-angle X-ray scattering.* For samples $Li_2B_4O_7$:Gd,Ag, annealed in vacuum, the size of metallic nanoparticles on the surface was evaluated also by small-angle X-ray scattering (Figure 2). A standard mounted at an angle α = 3° with respect to the direction of the primary beam. Registration profile of the diffraction peak (111) Ag was measured in a discrete mode with step 0,05° and exposure time of 25 sec. Technical Ag was used as the standard sample.

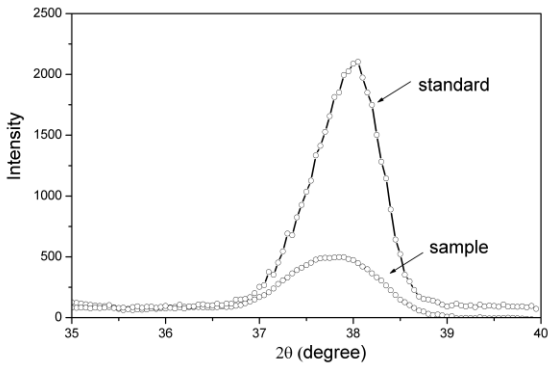


**Fig. 2** – Profiles of diffraction peak (111) of the sample $Li_2B_4O_7$:Gd,Ag, annealed in vacuum and standard technical Ag.

To determine the half-width maximums profiles they were fitted by the Lorentz function. In this case, the average size of the nanocrystals can be defined as follows: $D = \lambda/(\beta - \beta_0)\cos\vartheta$, where $\beta_0$, $\beta$ are half-width maximums for the standard and studied sample respectively, 2ϑ is the diffraction angle of (111) Ag reflection.

Analysis of profile maxima Ag (111) for the sample and standard gives $\beta_0 = 0.698\pm0.020°$, $\beta = 1.052\pm0.150°$. After some calculations, the average size of Ag NPs was found to be $D = (26.0 \pm 3.0)$ nm (Table 1).

Results obtained with the two methods of X-ray analysis for samples annealed in a vacuum lead to the same size of silver nanoparticles. We have to note that the concentration of nanoparticles in the glass, annealed in air was too small to obtain reliable results for sizes of nanoparticles by small-angle X-ray scattering in our experiments.

*The half-width of the plasmon absorption band* can be used to estimate the Ag NPs sizes $D$: $D = 2V_F/\Delta\omega_{1/2}$ [8], where $V_F$ is the Fermi velocity, and Δω is the half-width of the plasmon absorption band. In metallic Ag, the Fermi velocity is $V_F = 1.39\times106$ m/s [9].

Sizes of Ag NPs appeared to be of 2.3 nm, which is much smaller (Table 1), although they are fairly well correlated with the size of 2.0 - 6.0 nm obtained for Ag NPs in various glasses by other authors [9, 10].

As shown in Table 1, there is quite a big difference in sizes of Ag NPs, determined with different methods. Moreover, the size values of Ag NPs for samples annealed in air and measured from the half-width of the plasmon absorption band and from X-ray diffraction differ by about 2 times, whereas for the samples annealed in vacuum the results are different almost by an order of magnitude. Therefore, if we take into account that the size values for annealed in vacuum sample of Ag NPs, obtained by X-ray diffraction and small-angle X-ray scattering, are practically identical (26.0 and 26.9 nm), one can accept that they are more accurate and closer to the real values than those obtained from the value of the half-width of the plasmon absorption band. The obtained by X-ray diffraction difference in sizes Ag NPs in samples annealed in air (7.5 nm) and vacuum (26.0 nm) can be explained very simply: in

glass $Li_2B_4O_7$:Gd,Ag, which is annealed in air, the Ag NPs are formed inside the matrix just under its surface (since they are not fixed Small-angle X-ray scattering method), but when annealed in vacuum the Ag NPs are formed on the top of the sample surface [11]. Since the mechanisms of Ag NPs in the same glass matrix and its surface are definitely different, the differences in sizes are quite understandable.

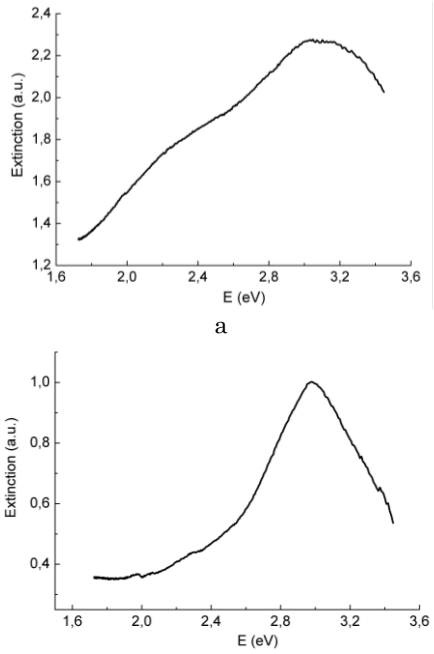


**Fig. 3** – Absorption difference spectrum $Li_2B_4O_7$:Ag,Gd glass: (a) annealed in vacuum; (b) annealed in air atmosphere.

**Table 1** – Dimensions Ag NPs in glass $Li_2B_4O_7$:Gd,Ag, determined by different methods

| Annealing | The method of determining | *D*, nm |
|---|---|---|
| In air atmosphere | Plasmon resonance | 2,8 |
| | X-ray diffraction | 7,5 |
| In vacuum | Plasmon resonance | 1,8÷3,0 |
| | Small-angle X-ray scattering | 26,0 |
| | X-ray diffraction | 26,9 |

## 4. CONCLUSION

The samples of glass $Li_2B_4O_7$:Ag,Gd Ag NPs, formed by annealing in air and vacuum were obtained. The results of the investigations of sizes of Ag NPs by means of different methods, namely: half-width of the plasmon resonance band, X-ray diffraction and small-angle X-ray scattering, show significantly different results. It turns out that from the method of half-widths of the plasmon resonance band the Ag NPs size is much smaller than the size obtained by other methods. In conclusion, the methods of X-ray diffraction and small-angle X-ray scattering give results closer to reality than the method of plasmon resonance.

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