UV-VIS-NIR spectral optical properties of silver iodide borate glasses

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Abstract. We present a study of optical properties of a series of silver iodide borate glasses \((\text{AgI})_x(\text{Ag}_2\text{O} \cdot \text{B}_2\text{O}_3)_{1-x}\) by UV–VIS–NIR spectroscopy. The results show an increased absorbance in the whole analysed spectral range when the AgI concentration is augmented. In particular, the enhanced intensity of the wavelength band at 400-500 nm with silver iodine content suggests that this band arises from plasmon-related absorption, describing the formation of silver nanoparticles. With respect to this study, our results could motivate novel target designs consisting of ternary silver boron based bulk glasses for generating resonant absorption of laser light by plasma.

1. Introduction

The laser-plasma interaction that occurs when a high power laser pulse is focussed on a solid target is used for different applications and in particular for the ion acceleration. Over the last few years, significant attention has been paid to the improvement of the efficiency of the coupling between the laser pulse and the plasma obtained by the ionization of the target, aiming to enhance the ion acceleration. Enhanced energy absorption and ion acceleration to higher energies has been shown to occur in a number of configurations. In particular, if a target with a periodic surface modulation on the irradiated side is considered, a resonant coupling of the laser pulse with surface waves [1] can be achieved at a particular angle of incidence. Different strategies have been proved to be useful in producing increment of the laser absorption by resonance absorption at the critical surface. The insertion in dielectric target of absorbent nano- and micrometric particles with size comparable with the laser wavelength [2], the production of nano- and microscopic topological defects on the surface of the target by ion sputtering, rolling burnishing or chemical etching [3], the employment of nano-size foam target [4] or of targets consisting of aligned nano-tube/wires [5] are relevant examples. These “nano-structured” targets enable a concentration of the electromagnetic field at the target edges and excite plasmons around the structure, resulting in an efficient energy transfer from the laser to the material.

Special attention has also been devoted to the study of optical properties of nanometer-sized particles dispersed in glass matrices, specially when noble metal particle are considered[6,7]. These optically active glasses offer a broad range of applications, also because their functionality can be
modified by appropriate doping and post synthesis thermal processing [8]. In particular, borate glasses are good candidates as optically active glasses. They in fact are robust, non flexible and inexpensive. More importantly, doping the borate glasses with silver oxide and performing subsequent heat treatment causes the reduction of the doped silver ions leading to the formation of metallic silver nanoparticles. Ultraviolet-visible absorption spectroscopy shows a plasmon-related absorption band between 400 and 500 nm indicating the formation of silver nanoparticles [9,10].

Owing to their structural characteristics and optical properties, doped borate glasses appear to be promising systems to be used as solid target to increase effects of resonant absorption in laser-generated plasmas. Furthermore they can be obtained as thin film (thickness lower than 50μm) to be employed at high laser intensity to generate forward directed plasmas.

Here we present a preliminary spectroscopy study on a series of silver borate glasses doped with silver iodide. In these systems the insertion of iodide ions expands the network, resulting in opened up porous structure and formation of AgI aggregates [10,11]. Both characteristics make these systems promising solid targets, able to increase the effects of laser resonant absorption following the interaction with laser light.

2. Experimental details

Three ternary borate glasses belonging to the family \((\text{AgI})_x(\text{Ag}_2\text{O} \cdot \text{B}_2\text{O}_3)_{1-x}\) with an AgI molar fraction, \(x\), of 0.2, 0.4 and 0.6 and pure boron oxide, \(\text{B}_2\text{O}_3\), were investigated. These glasses were prepared by the melt quenching technique, heating at about 1100-1200 K weighted amounts of silver iodide, silver oxide and boron oxide and pouring the melts in stainless steel molds kept at room temperature [12]. No evidence of crystalline structures was found by X-ray diffraction analysis.

The absorption spectra of borate glasses were recorded by using a Perkin Elmer Lambda25 UV-Vis-NIR spectrophotometer (scan speed 120 nm/sec, step 2 nm, range 450 nm - 1100 nm) and applying the diffuse reflectance technique and using an integrating sphere. Diffuse reflectance spectroscopy has proven to be a fast and sensitive technique for qualitative information. However, according to different theories, quantitative data can be derived. The best known Kubelka–Munk theory [13] states that for thick layers, a correlation is obtained between the absolute reflectance \(R_\infty\) and the absorption coefficient \(k\) of the layer at a given wavelength, according to the following Kubelka–Munk function \(F(R_\infty)\):

\[
F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{k}{S} = \frac{\alpha c}{S}
\]

(1)

where \(S\) stands for the scattering coefficient (depending on the size and form of the particles), \(\alpha\) for the molar extinction coefficient of the analyte and \(c\) for its molar concentration. The Kubelka–Munk transformation thus converts a reflectance spectrum into a spectrum similar to a conventional absorbance spectrum for solution samples. In particular, the data reported in this paper have been obtained converting the \(F(R_\infty)\) function into transmission spectra by means of the UV KinLab software.

3. Results and discussion

In figure 1 the transmittance curves as a function of wavelength in the visible and near-infrared regions for pure \(\text{B}_2\text{O}_3\) and for silver borate doped with three different silver iodine content glasses are reported. The investigated samples show transmittance values between 15% and 50% up to 1000 nm whereas at higher wavelengths a strong slope towards enhanced values is observed. This trend clearly indicates a strong absorption ability of these borate glasses in nearly the whole analyzed \(\lambda\) range. It’s worth to note that, a marked transmittance decrease for the doped samples is revealed at wavelength below 650 nm where the pure borate glass shows a rather constant \(T\) value. This occurrence suggests the existence of absorption mechanisms which are activated only in the ternary silver borate glasses.
but not in the pure glassy boron oxide. Otherwise, at 913 nm a transmittance dip is observed for the investigated systems as shown in the inset of figure 1. This finding indicates the presence of an absorption band whose origin should be inquired in the electronic states of the B-O network of the borate matrix since present in all these glasses.

With the aim to exalt such experimental results, focusing the attention on doped silver borate glasses, the electronic absorption spectra of these samples are shown in figure 2 (a).

As expected from the observed $T$ behaviour, the absorbance of these three glasses decreases with increasing $\lambda$ value in nearly all the investigated wavelength range showing two bumps in the visible and near infrared regions. According to literature data [8,9], the marked band at lower wavelength can be ascribed to the surface plasmon resonance from silver nanoparticles present in the studied systems.

In figure 2 (b) the three acquired absorption spectra normalized to the absorbance value at the highest investigated wavelength, where all samples show the lowest absorption, are plotted. This graphic representation allows the comparison of the relative absorbance intensity among all the investigated systems. An increased absorbance with augmented AgI concentration is observed in the whole analyzed spectral range. Most importantly the enhanced intensity of the lower wavelength band with silver iodine content suggests that just the Ag particles belonging to this binary compound give rise to an increased plasmon surface resonance with a consequent higher absorption.
Figure 2. Absorbance spectra (a) and normalized absorbance spectra (b) of silver borate glasses doped with different AgI molar concentrations $x$: $x=0.2$ (dashed line); $x=0.4$ (dotted line) and $x=0.5$ (dash-dotted line). In the inset the $\lambda$ position of the visible absorption peak as a function of AgI molar content is shown.

It is widely accepted that for mean particle radius less than 10 nm, no significant shift in the surface plasmon resonance peak is observed [14,15] while for larger nanoparticle size this band is significantly red-shifted [8,16,17]. A previous study has evidenced that for silver particles having a radius of 10 nm the low wavelength band is located at 409 nm [17]. As a consequence, the marked red-shift of the samples investigated in this paper would suggest a silver particle size greater than 10 nm. In this regard, a future scanning electron microscopy analysis on these system has been planned which would give more information on this issue.

Currently no decisive attribution can be put forward for the absorption band revealed at 913 nm since literature data are defective. For this reason, further detailed analysis will be performed on ternary borate glasses. The next steps will be to investigate the size distribution of the silver nanoparticles as well as the distribution of the nanoparticles in the glass itself as a function of annealing time and temperature and to test the employment of these glasses as solid target for generating resonant absorption of laser light by plasmas.

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