Nanomaterials induced plasma spectroscopy

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Nanomaterials induced plasma spectroscopy

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Abstract. LIBS of nanosecond pulsed Nd: YAG laser (1064 nm) produced plasma from a set of nanomaterial and bulk targets (ZnO, Fe_3O_4, Ag_2O, TiO_2, SiO_2 and Al_2O_3) is investigated at laser fluencies in the range 86 J/cm^2 to 2.5 J/cm^2. The optical emission spectra is recorded at the gate and time delay of 1 μs after the onset of the plasma in air having a constant spot size of 0.9 mm. Nanoparticle targets revealed salient enhanced spectral emission compared to their bulky counterparts. Atomic spectral lines average and integral radiance tend to decrease exponentially with laser fluence. Yet, plasma parameters measurements indicated unnoticeable variation of relative electron density and temperature. Therefore, self-absorption corrected enhanced spectral emission was plausibly attributed solely to variation in the inherent nanoparticle relative concentrations. Viable explanations were elaborated based on changes in the intrinsic physical properties of the nanomaterial under high power laser irradiation.

1. Introduction

LIBS and LIPS acronyms stand for respectively "laser induced breakdown spectroscopy" and "laser-induced plasma spectroscopy" [1, 2], and indicate a technique that has been successfully applied to a wide range of applications, mainly in the field of spectrochemical analysis [3-10]. Although this technique has several advantages, e.g., fast outcomes, freedom from sample preparation and very wide dynamic range, it still suffers from several physical problems that should be carefully addressed, for instance, effects of self-absorption of the strongly emitted spectral lines [11] and the limited sensitivity of the technique [12, 13]. Several schemes were proposed to promote the limit of detection LOD values including the use of double pulse technique [14], femtosecond lasers [15] or even a mixed hyper technique [16].

In contrast, nanomaterials exhibited unique physical properties [17] which proved to be promising to improve signal to noise ratio pertinent to optical signals from trace elements with minute concentrations [18-21].

The first Nanoparticle-Enhanced LIBS (NELIBS) of plant leaf surface coated with thin layer of silver nanomaterials was reported by Ohta *et al.* [18]. Localized surface plasmon resonance (LSPR) was invoked to justify the experimental findings. However, a systematic study of the temporal behavior of the spectral lines emission from ZnO nanomaterial plasma [19] indicated the production of large concentrations (removed mass) to be responsible for the enhanced signals. Nonetheless, the relative plasma parameters (electron density and temperature) tend to bear little impact on observed signal enhancement [18-21].

Significant NELIBS of plasma spectral line emissions from noble-metal colloidal solution [20] were rather correlated with the increase in the mass ejected from nanomaterial suspensions as well as the decrease in the threshold of plasma ignition.

Very recently, De Giacomo *et al.* [21] argued that the basic mechanism of Nanoparticles-Enhanced LIBS (NELIBS) is associated with the laser ablation evolution process.

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In general, it was shown that the physical properties (e.g., the thermal, electrical and optical properties**)** of the nanomaterials are changed upon the decrease of the nanoparticle size [17]. This decrease was attributed to nanoparticle fragmentation into smaller ones via different mechanisms during irradiation of nanomaterials by short laser pulses [22-28].

In this work, we present the results of systematic spectroscopic study of spectral line emission enhancement from different nanomaterials-based plasmas in comparison with bulky ones at different laser fluencies and the possible phenomenological explanation in terms of concomitant changes in the physical properties of the nanomaterials during laser irradiation.

2. Experimental arrangement

The experimental setup is shown in Figure 1 and described in details elsewhere [18]. It comprises A Nd:YAG laser working at the fundamental wavelength of 1064 nm that delivers an energy of ~ 650 mJ with pulse duration of 5 ns. The laser beam was focused with a 10 cm quartz convex lens to a circular focal spot of diameter 0.9 ± 0.1 mm, hence a maximum fluence of ~ 86J/cm^2. The laser fluence at the target surface was tuned by changing the incident laser pulse energy (at fixed laser spot size) using a set of glass absorber sheets. The emitted light from plasma was collected at the entrance hole of the SE200 Echelle-type spectrograph via a quartz optical fiber of diameter of 25 μm, positioned at 5 mm from the laser-plasma axis. The gate and delay times of the camera were kept fixed at constant value of 1 μs.

The nanomaterials (ZnO, Fe_3O_4, TiO_2, SiO_2 and Al_2O_3) are purchased from $MK_{nano}^{®}$ in a powder form as obtained without heat or chemical treatments. The silver nanomaterial (Ag_2O) was purchased from Sigma Aldrish$^{®}$ on the form of a suspension in a buffer liquid and put on the form of drops on a substrate and left until the puffer solution is evaporated.
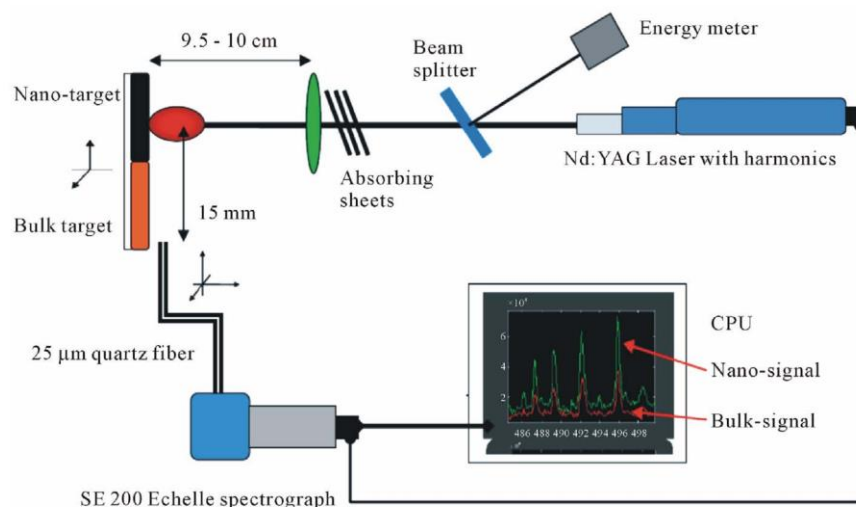
Figure1. Experimental setup.

Both targets (nano & bulk targets) were fixed on a xyφ holder at the same level. Each recorded spectrum was taken under a fresh target condition for three times, which enable us to estimate the error margins. The ratio of nanomaterial to bulk spectral line signal radiance peaks is averaged over different pertinent spectral lines. This procedure is repeated over three shots and the standard deviation about the mean value was taken as the standard error.

3. Optical opacity of plasma to spectral lines

In order to eliminate the effect of plasma opacity to the emitted lines, emitted spectral lines self-absorption should be corrected [11, 18]. This turns out to be crucial [11, 18, 32] to any reliable measurements of the plasma electron temperature as well as relative population density of the ground states (relative concentration). This is usually implemented by using an SA factor [11],

$$SA_{line} = \left(n_{e-line} / n_{e-H_\alpha} \right)^{-1.7858}$$ with values between zero (complete opacity) to one (perfectly optically thin spectral line devoid of any self-absorption). The corrected spectral intensity can be evaluated using the simple relation $I_o(\lambda_o) = \left(I_{\exp}(\lambda_o) / SA_{line} \right)$ where $I_{\exp}(\lambda_o)$ is the experimentally measured peak of spectral radiance at the line center of wavelength (λ_o) [32]. The plasma densities n_{e-H_α} and n_{e-line} are measured using the Stark broadening of the usually observed H_α-line while for the spectral lines other than hydrogen one can use the relation $n_{e-line} \approx \left(\Delta\lambda_{s-line} / 2\omega_{s-line} \right) N_{ref}$ [30], where, $\Delta\lambda_{s-line}$ is the experimentally measured FWHM of Lorentzian line width and ω_{s-line} is the Stark broadening parameter tabulated at certain reference electron densities N_{ref} [cf.31].

4. Results and discussion

Optical emission spectra recorded for different nanomaterial (blue colored) and bulk targets (red colored) at a variety of experimental conditions are displayed in Figures 2a to 2f. The maximum enhancement factor about 37 can be clearly related to nanomaterial silver oxide. The nanomaterial plasma emission atomic spectral lines are favorably enhanced in a descending order as Si I, Zn I, Ti I, Fe I, Ag I and Al I respectively.
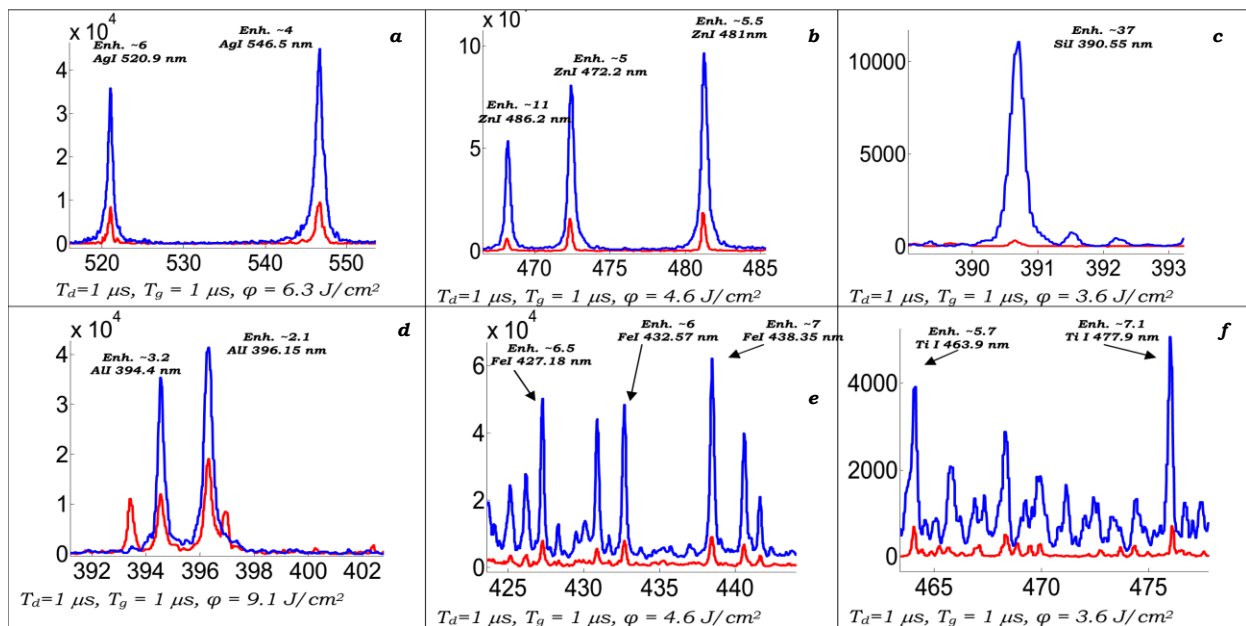

Figure 2. Demonstration of the enhancement factors (as shown) exhibited by the nanomaterial (blue colored) and bulk (red colored) plasma emission spectral lines at different experimental conditions. (a) Ag_2O, (b) ZnO, (c) SiO, (d) Al_2O_3, (e) Fe_3O_4 and (f) TiO_2.

To investigate the effect of laser fluence on the enhancement factor, ZnO nanomaterial and bulk targets plasma emission at 468.2, 472.2 and 481 nm wavelengths were recorded at different laser fluencies as shown in Figure 3. Average peak and integral spectral radiance enhancement factors apparently tend to exponentially decrease as the laser fluence increases Figures 4a, b. The observed signals were not actually corrected against self-absorption effects. It is worth noting that the spectral lines are not equally enhanced which may be related to their different inherent oscillator strengths or to selectively favorable surface plasmon resonance [21].
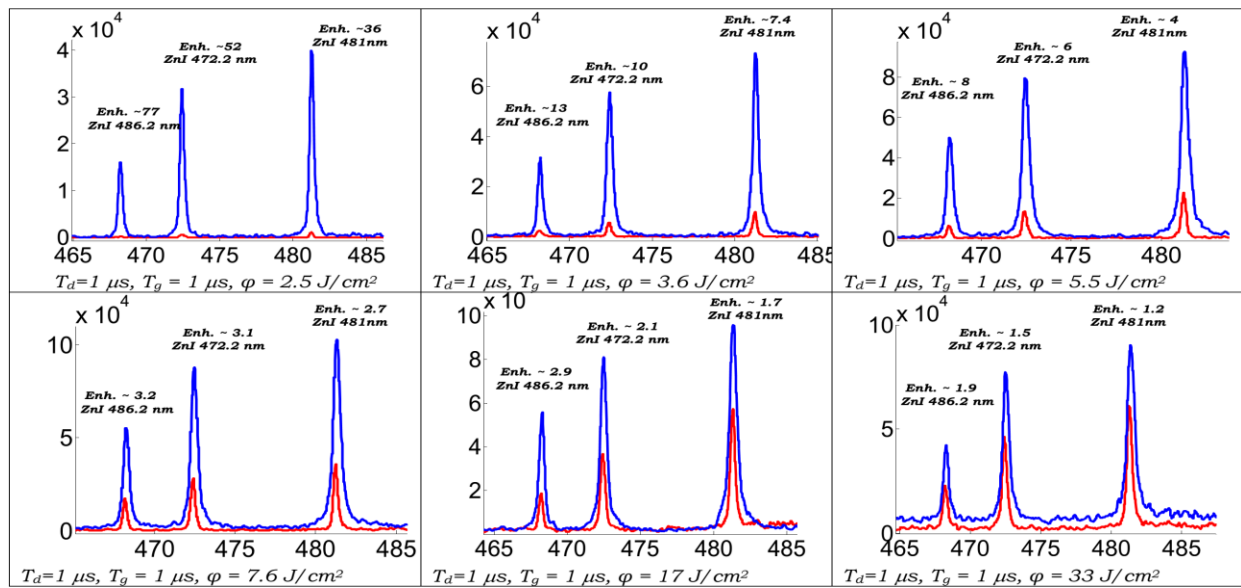
Figure 3. Enhancement factors at different laser fluencies associated with Zn I-lines.

Observed enhancement in spectral line radiance was pursued through the variation of the peak spectral radiance itself as a function of laser fluence. Plasma evolution seems to be influenced slightly differently by nanomaterial and bulk targets. It can be seen from Figure 4c that plasma emerged from the nanomaterial targets tend to decay relatively more slowly than that of the bulk-based plasma.
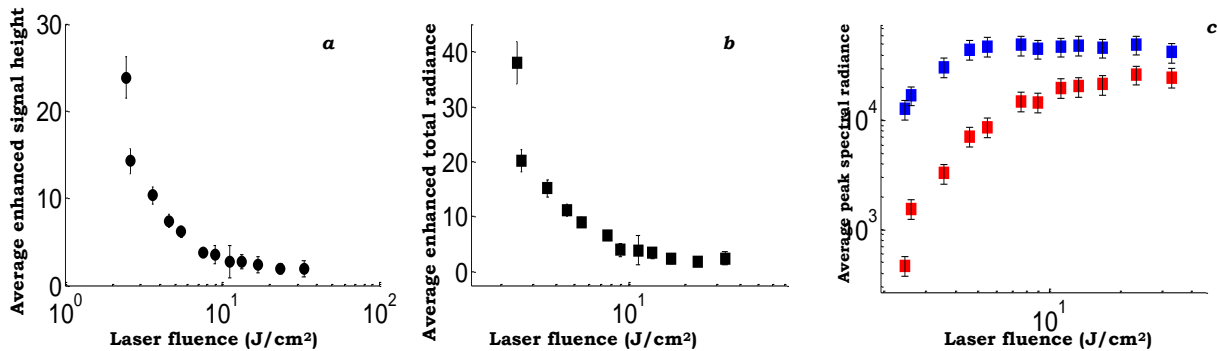
Figure 4. (a) The variation of the average enhancement in peak spectral radiance (signal height) with laser fluence. (b) The variation of the integrated radiance (area under curve). (c) The variation of the peak spectral radiance from nano-based plasma ((blue upper squares) and bulk-based plasma (lower red squares) with laser fluence.

The role played by plasma characteristics, plasma electron density, temperature and stoichiometric concentrations was assessed via optical emission spectroscopy (OES) [18]. Boltzmann plots were performed on peak spectral radiance of the Zn I-lines at 328.23, 330.3, 334.5, 468, 472.2, 480 and 636.23 nm after correction against the effect of self-absorption using available atomic data [33], while the Stark broadening parameters of the different Zn I-lines were taken from Ref. [31].

Figure 5b indicates the quality of the previously suggested method of correction process of spectral radiance against the effect of self-absorption which results in a straight line Boltzmann plot [29].
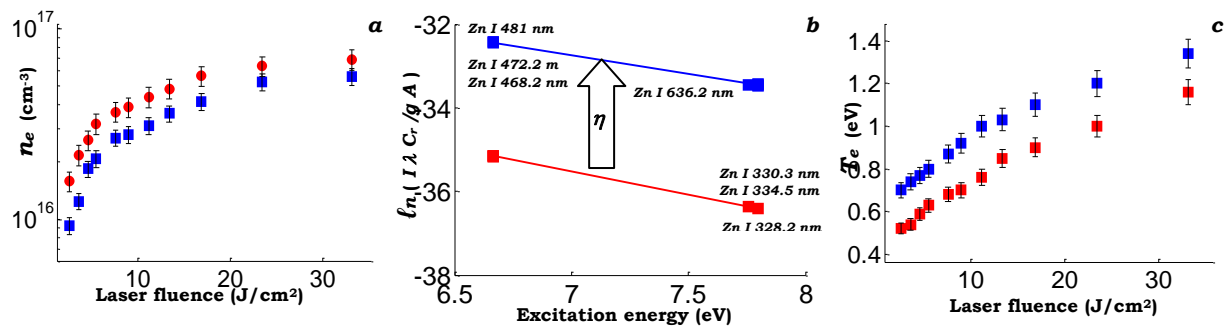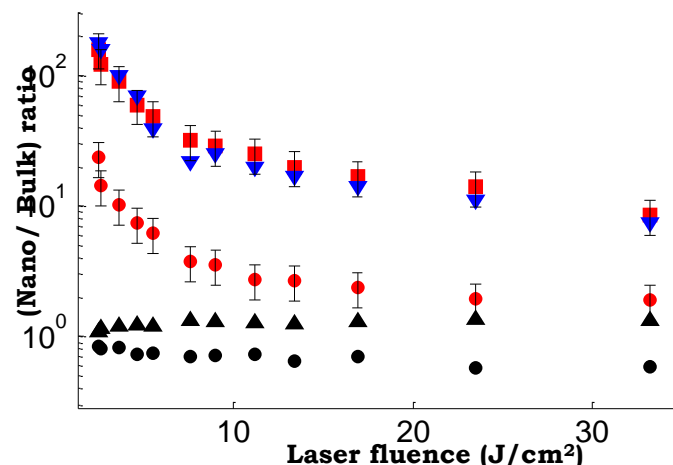
Figure 5. (a) The variation of the electron density with laser fluence for nano-based plasma (lower blue squares) and bulk-based plasma (upper red solid circles). (b) Multi-elemental Boltzmann plot of Zn I lines associated with nano-based (upper blue line) and bulk-based (lower red line) targets at laser fluence of 17 J/cm^2. (c) The variation of the plasma electron temperature for nano-based (upper blue squares) and bulk-based (lower red squares) plasmas.

Notwithstanding the similar trend exhibited by both hotter nanomaterial and denser bulk targets plasma temperature and density in Figures 5a, c [19-21], Boltzmann elemental analysis reveals higher levels of ground state atomic population in favor of nanomaterial targets, see Figure 5b.

The experimental findings indicate that plasma characteristics in terms of plasma density and temperature have little impact on the observed enhancement phenomena in fair agreement with previous reports [18-21]. The relative nanomaterial to bulk plasma stoichiometric concentrations is evaluated in terms of the relative concentration factor $R_c = \exp(\eta) = \left(N_{oN}/N_{oB} \right)$ [19].

A comprehensive relative nanomaterial to bulk data was elaborated as shown in Figure 6 and Figure 7 for ZnO and other nanomaterials respectively. Close examination of Figure 6 reveals a close correlation between the estimated relative concentration and enhancement factor whereby suggesting that the relative concentration enhancement might be the main reason behind the plasma emission spectral line enhancement [19-21].

Figure 6. The variation of ZnO relative electron density (black solid circles), the relative electron temperature (black triangles), enhancement factors with self-absorption (red solid circles), self-absorption free (red squares) and relative concentration (blue inverted triangles).

As clearly seen from Figure 7, a noticeable relative spectral radiance enhancement is set on at threshold laser fluence about ~ 10 J/cm^2 followed by significant increase reminiscent of internal transformation in connection with laser pulse irradiation.
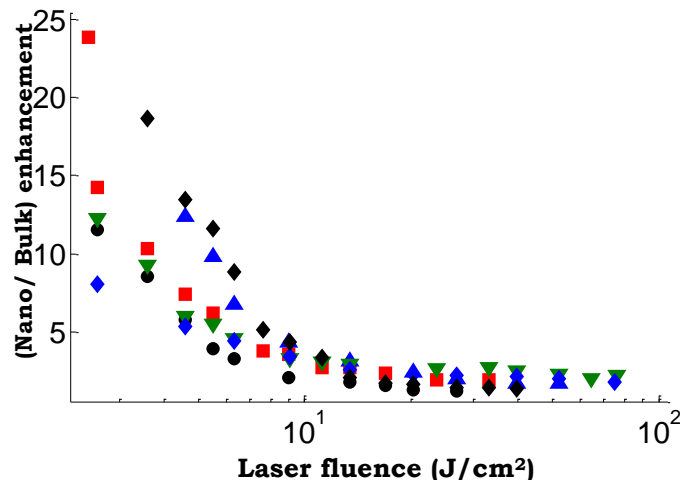
Figure 7. Shown is the variation of the enhanced peak spectral radiance with laser fluence; ZnO (red squares), Fe_3O_4 (black disks), TiO_2 (blue triangles), Al_2O_3 (Inverted green triangles), Ag_2O (blue hex) and SiO_2 (black hex).

Recent experimental findings using transient absorption spectroscopy [22-28] have shown that nanoparticle size is diminished on par with the incident laser fluence due to fragmentation into smaller particles during laser irradiation. Moreover, the time required for this transient size modulation was measured for the gold nanoparticles and amounts to ~ 0.1 ns [26-27] and in the range of femtosecond regime for TiO_2 nanoparticles [28].
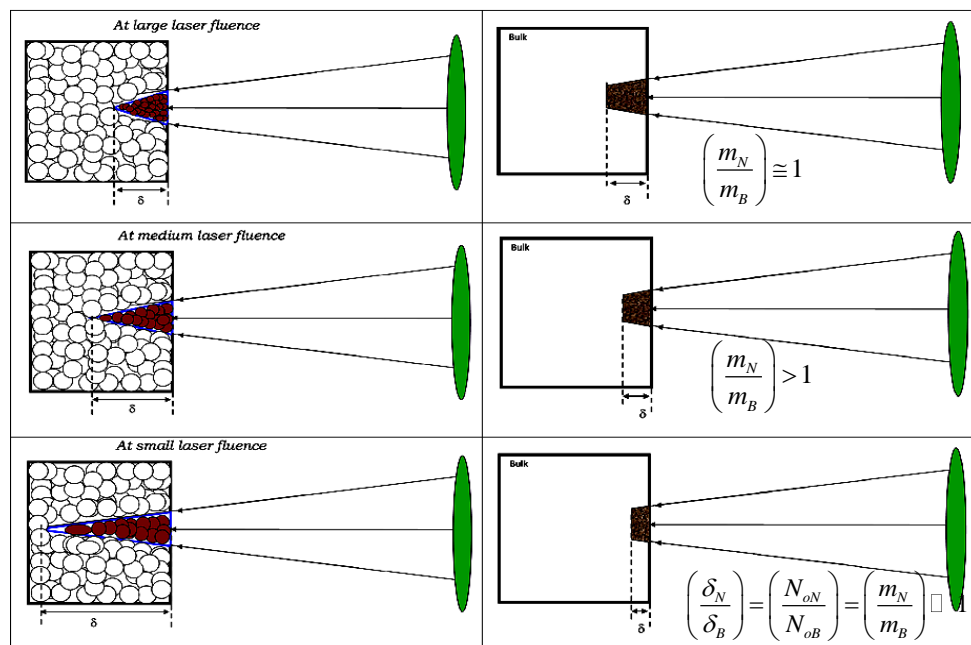
Figure 8. An illustration to possible mechanisms of the interaction of the laser light pulses with nano-based target in comparison with bulk-based target at different laser fluencies.

In accordance with these experimental findings, nanoparticles fragmentation at high laser fluencies may account for the decline in the observed spectral line radiances. Apparent is the decrease in laser fluence due to the larger surface area of fragmented nanoparticles [22-28] accompanied by a sudden

increase in optical conductivity of the nanoparticles [17, 34-35] with less laser light penetration. Figure 8 would justify this decrease. Moreover, inefficient mass ejection is influenced by spatial confinement of laser beam as the refractive index increases [17, 22] assisted by even higher specific heat values [17] at high laser fluencies.

A more theoretical and experimental investigation is needed in particular the use of electron microscopy to monitor relative mass ejected from nanomaterial and bulk targets.

5. Conclusion

The enhanced emission from the ZnO and various nanomaterials as Fe_3O_4, Ag_2O, TiO_2, SiO_2 and Al_2O_3 was examined experimentally with the help of optical emission spectroscopy (OES). High laser fluencies are paradoxically quenching the attainment of high spectral radiance enhancement. Besides, the observed enhanced emission was found to be independent of variations in plasma parameters (electron density and temperature). Higher ground state population density in nanomaterial targets proved to be paramount in spectral line radiance enhancement. The interaction of the high peak power lasers with nanomaterials strongly influence the intrinsic physical properties of irradiated targets which require further investigation.

Acknowledgement

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