Research Article

Studies on the ns-IR-Laser-Induced Plasma Parameters in the Vanadium Oxide

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We report spectroscopic studies of laser-induced plasma (LIP) produced by ns-IR-Nd:YAG laser light pulses of different energies onto four different oxides of vanadium (VO, V_2O_3 , VO_2 , and V_2O_5) in air under atmospheric pressure. For each oxide with a different oxidation state of vanadium, both electron density and plasma temperature were calculated for different time delays and laser pulse energies. The plasma temperature was determined from Boltzmann plot method, whereas the electron number density was estimated from the Saha equation. The decay rates for plasma temperature as well as electron density were observed to follow power law and were independent of the nature of vanadium oxide. These investigations provide an insight to optimize various parameters during LIBS analysis of vanadium-based matrices.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an elemental analysis technique based on the excitation of atoms present on the sample surface, by focusing a pulsed laser beam. Material amounts ranging from ng to μg are ablated in this process producing a microplasma which can be characterized by several of parameters. After the creation of the plasma, electromagnetic radiation is emitted as a consequence of several processes, namely, bremsstrahlung, recombination and de-excitation of atoms and ions occurring inside the plume [1]. De-excitation of atoms and ions leads to emission of light of characteristic frequency which can be used for both qualitative and quantitative determinations. LIBS has several attractive features like the ability to analyze nonconducting and conducting material in any phase (solids, gases, and liquids) as well as refractory materials which are difficult to digest or dissolve (ceramics, superconductors, etc.). The rapidness of analysis and multielemental analyzing capability make LIBS a highly useful technique for trace elemental determination.

Several experimental parameters are reported to affect the LIBS analysis. These include the effect of laser wavelength [2], pulse energy [3], pulse duration and shape [4, 5], and the acquisition time delay. Cabalin and Laserna studied the effect

of thermal property of material on threshold laser fluence variation [6]. The different phases of iron oxide were found to have different plasma characteristics [7]. To the best of our knowledge, the effect of different oxidation states of an element present in the sample on the plasma characteristics has not been reported.

Theoretically, the information regarding laser-induced plasma (LIP) can be obtained by solving a complex system of equations describing all the reactions, for example, ionization, dissociation, recombination, elastic and inelastic collisions, radiative emission, photon reabsorption, bremsstrahlung that occur in the plasma, and the respective reactions' rates. The solution for such an equation is computationally tedious, and many times, all the relevant data needed for such computation cannot be obtained during experiments. Therefore, thermodynamical approach is usually preferred. The principle for characterization of LIP by this approach was described by Adrain and Watson [8] and is based on quantification of main physical parameters like the plasma temperature (T_e), the electron density (N_e), and the number densities of the ionic and the atomic species present in the plasma. These measurements allow improving the various applications of these parameters (namely, optimizing the experimental parameters) and are also useful for a better

understanding of the complex ablation mechanism. Analyses of the spectral lines can give information about the physical state of the emitting species without, in any way, interfering with the plasma. The use of laser-based optical techniques in recent years has replaced spectroscopy as a diagnostic tool to some extent. Nevertheless, spectroscopy still plays a major role in studying the physical processes occurring in the plasma.

N_e can be measured using optical emission plasma spectroscopy [9], Langmuir probe [10, 11], microwave and laser interferometry [12], and Thomson scattering [13]. Thomson scattering is the most direct method for such measurement, while the optical emission spectroscopy (using either Stark broadening of spectral lines or the Saha-Boltzmann equation) is the simplest as far as the instrumentation is concerned.

The T_e is a key plasma parameter when local thermodynamic equilibrium (LTE) condition is satisfied by the plasma. T_e determines the distribution of the species at different excitation levels satisfying the Boltzmann equation and the ionization equilibrium satisfying the Saha equation under the existence of the LTE. For the LTE to exist in the plasma, collisions with electrons have to dominate over the radiative processes, and this requires a sufficiently large electron density. For LTE to exist, a criterion was proposed by McWhirter [14] based on a critical electron density, which required the collision rate to be at least ten times of the radiative rate. For an energy gap difference of ΔE (eV) between the two neighboring states with an allowed transition and T_e in Kelvin unit, the criterion for LTE is

$$N_e \geq 1.6 \times 10^{18} T_e^{1/2} (\Delta E)^3 m^{-3}. \quad (1)$$

The most widely used method for determination of plasma temperature in LTE plasma is based on the fact that the number densities in various excited states follow Boltzmann distribution, and hence, the plasma temperature of the line emissions can be measured from a single species. The Boltzmann plot method provides a single value of the plasma temperature of the plasma.

The aim of the present work was to study the LIP parameters of vanadium in four different vanadium oxides (VOs). The VOs plasma were generated by the fundamental (1064 nm) wavelength of a Q-switched Nd:YAG laser. The plasma temperature and the electron density were determined from the Boltzmann plot and the Saha-Boltzmann equation, respectively. The variation of LIP parameters with acquisition time delay was also estimated using the temporal analysis of the emission lines. In addition, the effect of laser energy on the LIP parameters of vanadium monoxide (VO) and vanadium trioxide (V_2O_3) was also studied. The studies reported in this work will help to optimize different experimental parameters, for example, laser energy, acquisition delay, and so forth, for LIBS analysis of high purity vanadium based materials like crystals, glasses, or nanocomposites, and so forth.

FIGURE 1: Schematic diagram of the LIBS setup.

2. Experimental

2.1. Instrumentation. Spectrolaser 1000 M, from Laser Analysis Technologies (now known as XRF scientific), Victoria, Australia, was used. A schematic diagram of the experimental setup was shown in Figure 1. The LIBS instrument was an integrated analysis system comprising an excitation laser, optical fibers, optical spectrograph, and charge-coupled-device (CCD) array camera and is fully software controlled through a PC. The laser beam from a Q-switched Nd:YAG laser of 7 ns pulse width was capable of delivering maximum laser energy of 200 mJ at 1064 nm wavelength at a repetition rate of 10 Hz. For the present study, laser pulses at a repetition rate of 1 Hz were used for the ablation of the target. The laser was focused on to the sample by a plano-convex lens of 5 cm focal length. The laser spot area is estimated to be $8 \times 10^{-9} \text{ m}^2$. The sample was located on a fast XY-translational stage, which moves the sample between two successive laser pulses, exposing a new and fresh region of the sample for each laser pulse. The emission is focused to an end of a fiber optic fiber (core diameter 200 μm) having a collimating lens (0–45° field of view) placed at an angle of 45° to the direction of the plasma expansion and was transmitted to the entrance slit of spectrographs in Czerny-Turner (C-T) configuration. Four separate optical cables connected to four spectrographs were present which are individually calibrated for specific wavelength range, giving a total spectral range of 180–850 nm at a spectral resolution of 0.6 nm at 300 nm. Each spectrograph was equipped with 2048 element linear CCD array detector. The output from each of the four CCDs was digitized by an analog to digital convertor (ADC) circuit. The plasma light in the entire spectral range is thus recorded simultaneously for each laser pulse. The acquisition of the spectrum can be done at any fixed time delay between plasma ignition and recording of the emission spectrum. The average spectra resulting from the accumulation of 30 laser shots were used for analysis in the present work.

2.2. Sample Preparation and Analysis. Four vanadium oxide samples, namely, VO, V_2O_3 , VO_2 , and V_2O_5 (99.9% pure) were procured from Alfa Aesar, India. The oxide samples were homogeneously mixed with high purity of 99.5% boric

TABLE 1: Composition of the vanadium oxide samples used.

Sample	Oxide taken	Amount taken (gm)		Total amount (gm)	% of V
		Oxide	H ₃ BO ₃		
1	VO	0.6543	1.0065	1.661	49.79
2	V ₂ O ₃	0.7356	0.9995	1.735	50.00
3	VO ₂	0.8134	1.0037	1.817	49.96
4	V ₂ O ₅	0.8913	1.0027	1.894	49.93

FIGURE 2: Typical LIBS spectra of VO at a laser energy 70 mJ and acquisition time delay of 500 ns (solid), 5 μ s (dash).

acid powder (S.D. Fine-Chem. Ltd., India) used as a binder, for 15 min by blending and grinding thoroughly to obtain homogeneous mixture. Mixed powder samples were then pelletized to 3 cm diameter pellets by applying a pressure of 2×10^9 Pa for 3 min. The amount of oxide in each sample was adjusted in such a way that the amount of elemental vanadium remained constant ($\pm 0.15\%$) in each sample pellet. Table 1 gives the compositional data of the samples prepared and used in this work.

3. Results and Discussion

3.1. The Intensity Profile. Emission spectra of the different VO's were recorded at different acquisition delay times (0–8 μ s) and different laser energies (50, 70, and 95 mJ). Typical emission spectra at delay times of 500 ns and 5 μ s at a laser energy of 70 mJ are shown in Figure 2. It is seen that at the early stages of the plasma evolution; that is, at short acquisition delay times, the continuum emission is high, due to mechanisms involving free-free transition of electrons and radiative recombination, and therefore, the spectral information about atomic and ionic species will be inaccurate at short delay times.

Figure 3 shows the temporal emission behavior, that is, the normalized intensity monitored against acquisition delay observed for different vanadium oxides at V(I) 318.54 nm

(a)

(b)

FIGURE 3: The temporal profile of V(I) 318.54 nm and V(II) 292.464 nm LIP normalized emission intensity for different VO's at 70 mJ. Normalization was done w.r.t. total integrated intensity of spectrograph.

and V(II) 292.464 nm at 70 mJ. Normalization was done with respect to the total integrated intensity of the particular spectrograph used to monitor that particular emission line. For example, V(I) 318.54 nm and V(II) 292.464 nm emission lines were normalized with the total integrated intensity of the spectrograph-I, since this was used for monitoring of emission lines from 180–330 nm. The existence of a number of humps is attributed to the possible different effects of the various physical processes governing the plasma behavior. It is seen that for V₂O₃, VO₂, and V₂O₅, the atomic line

TABLE 2: Chosen emission lines for V and their spectroscopic data [15].

Species	Wavelength (nm)	Transition coefficient (A_{ij}) (10^8 s^{-1})	Energy level		g_j	g_i
			Lower (E_j)(cm^{-1})	Upper (E_i)(cm^{-1})		
V(II)	292.464	1.2	2968.22	37150.51	9	9
V(I)	305.633	1.3	0	32738.13	4	4
V(I)	306.638	2.1	552.96	33155.30	10	10
V(I)	318.540	2.7	552.96	31937.27	10	12
V(II)	366.940	0.13	20363.23	47607.79	13	13
V(I)	370.358	0.92	2424.78	29418.07	10	8
V(I)	384.075	0.55	323.46	26352.65	8	6
V(II)	395.197	0.11	11908.27	37204.98	5	7
V(I)	440.764	0.44	2311.36	24992.88	8	8

((V(I) 318.54 nm) shows a sharp decrease of emission intensity after the gate delay of 4-5 μs , in sharp contrast of $\sim 1.5 \mu\text{s}$ for VO. Ionic line shows more or less similar decay patterns of intensities from different oxides with faster decay than that of atomic line due to the recombination processes of electrons and ions. The analysis carried out at 50 and 95 mJ also exhibited the similar temporal profile except for differences in intensities magnitude which showed the order 95 mJ > 70 mJ > 50 mJ. In case of ionic line, there was no difference in the line intensity at the different laser energies for delay times >5 μs in view of their faster decay.

Nasrazadani and Namduri [7] reported that Fe present in a different matrix having similar composition but different phase will show different temporal decay pattern. The four VOs selected for this study also have different phases, that is, cubic for VO, rhombohedral for V_2O_3 , tetrahedral for VO_2 , and orthorhombic for V_2O_5 . The different patterns observed in the emission lines in different VOs used in the present study also indicate the effect of phase difference among the samples. The ionic and atomic temporal decay profiles were also found to be different for different VOs. In addition, the photo-induced nonlinear optical effects [16], which are particularly sensitive to the oxides, could also be responsible for these differences.

3.2. Plasma Temperature. The T_e was determined via the well-known Boltzmann plot method from the relative emission line intensities, provided that their transition probabilities (A_{ij}) from a given excitation state are known. Under the LTE conditions in a plasma, the population of the energy levels for a particular species at a given position within the plasma is given by the Boltzmann equation [17]. The number of species N_i in the i th excited state is given by

$$N_i^z = N^z \frac{g_i^z}{U^z(T_e)} \exp\left(-\frac{E_i^z}{k_B T_e}\right). \quad (2)$$

Here, ionization state of the species is referred by the superscript z , whereas the neutral and singly ionized atomic species are represented by $z = 0$ and $z = 1$, respectively. N_i^z , N^z , E_i^z , and g_i^z denote the population density at i th level (m^{-3}), total population density or number density (m^{-3}), energy of upper energy level (J), and degeneracy or statistical weight factor (dimensionless) of the upper level of the species

with ionization z , respectively. k_B is the Boltzmann's constant (JK^{-1}), T_e is the plasma temperature (K), and $U^z(T_e)$ is the partition function of the species z at plasma temperature T_e . Assuming that the plasma is optically thin, the intensity of emitted radiation (I_{ij}^z) of wavelength λ_{ij} of the species z in plasma can be written as

$$I_{ij}^z = N_i^z A_{ij}^z \frac{hc}{4\pi\lambda_{ij}}, \quad (3)$$

where h is the Planck's constant (Js^{-1}), c is the speed of light (ms^{-1}) in vacuum, and A_{ij}^z is the Einstein's coefficient of transition probability for spontaneous transition from upper level i into lower level j of the species z . Substituting (2) in (3) gives

$$I_{ij}^z = N^z A_{ij}^z \frac{hc}{4\pi\lambda_{ij}} \frac{g_i^z}{U^z(T_e)} \exp\left(-\frac{E_i^z}{k_B T_e}\right). \quad (4)$$

Equation (4) can be transformed

$$\ln\left(\frac{I_{ij}^z \lambda_{ij}}{A_{ij}^z g_i^z}\right) = \ln\left(\frac{hcN^z}{4\pi U^z(T_e)}\right) - \frac{E_i^z}{k_B T_e}. \quad (5)$$

By plotting the left side of (5) against the upper level energy E_i^z (Boltzmann plot), a straight line is expected, whose slope yields the T_e . For high accuracy, the range of upper level energies of the so-called Boltzmann plot should be as large as possible [17]. The emission intensities of nine emission lines of vanadium from VOs LIP were used for constructing the Boltzmann plot. Table 2 lists the spectral lines used and their respective spectroscopic constants. The plasma temperatures are estimated within 10% uncertainty mainly due to uncertainties in the transition probabilities for the lines and the measurement of the integrated line intensities used.

Figure 4 shows the temporal profile of T_e for all the four VOs at a laser energy of 70 mJ. The plasma temperature was found to decrease as the acquisition delay (t_d) was increased. The plasma temperature as a function of t_d is fitted with the power law [18–20]. At a laser energy of 70 mJ, the fitted curves for VO ($T_e \sim t_d^{-0.120 \pm 0.007}$), V_2O_3 ($T_e \sim t_d^{-0.120 \pm 0.007}$), VO_2 ($T_e \sim t_d^{-0.127 \pm 0.008}$), and V_2O_5 ($T_e \sim t_d^{-0.129 \pm 0.004}$) are shown in Figure 4. No drastic

FIGURE 4: The plasma temperature (T_e) as a function of acquisition time delay (d) at 70 mJ for the different VOs.

FIGURE 5: The plasma temperature (T_e) of VO as a function of acquisition time delay (t_d) at laser energies of 50 mJ, 70 mJ, and 95 mJ.

plasma temperature difference was observed at any particular delay among the different VOs. The plasma temperature at the acquisition time delay of 500 ns was in the region of 7000 K which decreases to 5000 K at 8 μ s. Similar temporal profile was observed for other laser energies of 50 mJ and 95 mJ, except for differences in the magnitude of T_e . Figure 5 shows the temporal profile of plasma temperature for VO at different laser energies which was found to increase with laser energy. Based on Figures 4 and 5, the main features of plasma can be summarized as follows.

- There is no significant difference in T_e values obtained for different VOs at constant t_d within the uncertainty of the calculation methodology.
- For all the four VOs, the rate of decay in plasma temperature (i.e., dT_e/dt_d) is almost constant and hence can be assumed to be independent of matrix.
- At a particular delay, with the increase of laser energy, T_e increases. This is due to the fact that kinetic energy gained by the electrons increases as the deposited laser energy increases.
- The temporal profile of T_e also shows faster decay with increasing laser energy. This is expected, as higher T_e means faster expansion of plasma leading to faster decrease of plasma temperature.

It may be noted that the space uniformity of the laser beam is not very crucial parameter in the present studies, since these plasma profiles (decay of T_e and N_e) of different vanadium oxides have been recorded under the identical conditions.

3.3. Electron Density. The N_e can be determined by determining Stark broadening of a well-isolated line in the plasma emission or by using combination of the Saha and Boltzmann equations. Under the present instrumental condition, due to poor resolving power, the application of Stark broadening method was not possible; hence, the latter method was used. Saha equation relates the densities of the subsequent ionization species for a plasma temperature T_e [21]

$$N_e = \frac{N^z}{N^{z+1}} \frac{2U^{z+1}(T_e)}{U^z(T_e)} \left(\frac{2\pi m k_B T_e}{h^2} \right)^{\frac{3}{2}} \exp\left(-\frac{E_\infty^z}{k_B T_e}\right). \quad (6)$$

Here, N_e is the electron number density, E_∞^z is the ionization energy of species z for an isolated system, m is mass of electron (kg).

From (4), the emitted intensity ratio of two emission lines from two species of two different states of ionization can be written as [21]

$$\frac{I_{ij}^{z+1}}{I_{ij}^z} = \frac{N^{z+1}}{N^z} \frac{A_{ij}^{z+1} g_i^{z+1}}{A_{ij}^z g_i^z} \frac{\lambda_{ij}^z U^z(T_e)}{\lambda_{ij}^{z+1} U^{z+1}(T_e)} \exp\left(\frac{E_i^z - E_i^{z+1}}{k_B T_e}\right). \quad (7)$$

Equation (7) can be rearranged as

$$\frac{N^z}{N^{z+1}} = \frac{I_{ij}^z}{I_{ij}^{z+1}} \frac{A_{ij}^{z+1} g_i^{z+1}}{A_{ij}^z g_i^z} \frac{\lambda_{ij}^z U^z(T_e)}{\lambda_{ij}^{z+1} U^{z+1}(T_e)} \exp\left(\frac{E_i^z - E_i^{z+1}}{k_B T_e}\right). \quad (8)$$

Incorporating (8) in (6), the expression of N_e can be written as:

$$N_e = \frac{2I_{ij}^z}{I_{ij}^{z+1}} \frac{A_{ij}^{z+1} g_i^{z+1}}{A_{ij}^z g_i^z} \frac{\lambda_{ij}^z}{\lambda_{ij}^{z+1}} \left(\frac{2\pi m k_B T_e}{h^2} \right)^{3/2} \exp\left(\frac{E_i^{z+1} - E_i^z - E_\infty^z}{k_B T_e}\right). \quad (9)$$

All the right-hand side parameters in (9) can either be measured or obtained from compilation of atomic properties. The electron densities were estimated within 10% uncertainty similar to T_e .

FIGURE 6: The electron density (N_e) as a function of acquisition time delay (t_d) at 70 mJ for the different VOs.

FIGURE 7: The electron density (N_e) of V₂O₃ as a function of acquisition time delay at laser energies of 50 mJ, 70 mJ, and 95 mJ.

The N_e as a function of t_d was found to have the same trend of temporal profile in all the VOs, that is, N_e decreasing with the increase of t_d following a power law. Figure 6 shows a typical temporal profile of N_e with t_d at 70 mJ for all the VOs. N_e decreases fast in the early stage of plasma formation, but after $\sim 3 \mu\text{s}$, there is no appreciable decrease. N_e for V₂O₃ decreased from $\sim 1 \times 10^{23} \text{ m}^{-3}$ to $\sim 6 \times 10^{21} \text{ m}^{-3}$ during of 0.5 to $3 \mu\text{s}$, and this value further reduced to $\sim 1 \times 10^{21} \text{ m}^{-3}$ at $8 \mu\text{s}$. There is no noticeable difference in the N_e among the samples. Similar temporal profiles were also obtained at 50 mJ and 95 mJ laser energies except for

different magnitudes of N_e . N_e as a function of t_d was fitted with the power law similar to that for T_e . The power law fittings for a laser energy of 70 mJ for VO ($N_e \sim t_d^{-1.28 \pm 0.09}$), V₂O₃ ($N_e \sim t_d^{-1.35 \pm 0.07}$), VO₂ ($N_e \sim t_d^{-1.25 \pm 0.09}$), and V₂O₅ ($N_e \sim t_d^{-1.31 \pm 0.07}$) are also shown in Figure 6. It can be seen that similar to T_e , at a particular t_d , the rate of decay of N_e is independent of type of oxide similar to the T_e temporal followup. The dependency of rate of decay with laser energy was examined for V₂O₃ and was found to be faster with reduction in laser energy incident (Figure 7). This is the reverse of that observed for T_e . With increase of laser energy, the amount of material ablated increases. The N_e can be sustained for a longer time; hence, the rate of decay of N_e decreases with increasing ablation. It is interesting to note that the rate of decay of N_e is much faster than that of T_e for all the vanadium oxides. This clearly emphasizes the fact that initially, the N_e is very high, and radiative emission will be a dominating emitting source. Therefore, to obtain good elemental signal, suitable acquisition delay must be employed in LIBS.

4. Conclusion

Using fundamental Nd:YAG laser, LIPs of four different vanadium oxides were investigated. The temporal profiles of ionic or atomic lines have different patterns for different oxides but main LIP parameters, that is, T_e and N_e , do not show any appreciable differences in their temporal profiles. T_e and N_e were measured at different acquisition time delays for all the four VOs. It was found that in all VOs, the rate of decay of both T_e and N_e follows a power law and is constant at a particular plasma temperature. The rate of decay of N_e is much faster than that of T_e in the initial period, that is, 0–3 μs region. With the increase of laser energy, rate of decay of T_e increases for all the VOs, but for N_e , the reverse trend is observed. The studies reported in this work are useful to optimize different parameters, for example, laser energy, acquisition delay, and so forth, for LIBS analysis of high-purity vanadium-based materials.

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