Journal of Quantitative Spectroscopy & Radiative Transfer 111 (2010) 689–695

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Laser-induced breakdown spectroscopic studies of marbles

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ARTICLE INFO

Article history:
Received 24 July 2009
Received in revised form
6 November 2009
Accepted 11 November 2009

Keywords:
Laser-induced breakdown spectroscopy (LIBS)
Marbles

ABSTRACT

We present laser-induced breakdown spectroscopic studies of variety of marbles extracted from Quetta region of Boluchistan, Pakistan using a Nd:YAG laser (532 nm) in conjunction with LIBS 2000 detection system. The emission spectra of Onyx (white spot) and Quetta Green Marble samples have been recorded as a function of laser irradiance. The elemental composition and their relative abundance in each sample are fond to be quite different. In Onyx (white spot), calcium dominates while in the Quetta Green marble magnesium is the dominant element. In addition the effect of the laser irradiance on the emission intensity, width and shift of the transition lines have been studied.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a technique that has been extensively used in different fields of science for the last couple of decades. It is an analytical technique for the quantitative and qualitatively elemental analysis of materials. In this technique, a high power laser light is focused on a target sample which generates luminous micro plasma. The luminescence is basically due to de-excitation of atoms and molecular species present in the plasma plume. The observed transitions reveal the identity of different constituent elements and the intensity of the spectral lines relates to the relative concentration of the emitting species of the target material.

The laser-induced break down spectroscopy (LIBS) has been used for the study of marbles [1,2], pigments [3–5], multi-layered ceramics and metals [6,7]. Gornushkin et al. [8] studied the line broadening mechanism of the spectral profiles of Ca and Rb using LIBS. The plasma of $CaCo_3$ matrix doped with Rb was generated using a Nd-YAG laser (1064 nm). Lazic et al. [2] using third harmonic (355 nm) of a Nd-YAG Laser, performed LIBS studies of different clean and dirty surfaces of marble fragments collected from ancient quarries in Greece, Turkey and Italy. Lazic et al. [9] reported the presence of iron, copper-based alloys, precious alloys, marble and wood in sea-water using single and dual pulse LIBS techniques. LIBS also have been used to investigate the geological material and minerals and their elemental composition [10–12]. Giakoumaki et al. [13] discussed the applications and prospects of LIBS technique in archeological science. They analyzed and characterized the composition of a broad variety of objects of cultural heritage including painted art works, icons, polychromes, pottery, sculpture, metal glass and stone artifacts.

The motivation for the work presented in this paper was to get detailed information about the elemental composition and the relative abundance of different varieties of marbles extracted from different parts of Pakistan. Using LIBS we have investigated the effect of the laser irradiance on the emission intensity and width of the transition lines.

2. Emission spectra of Onyx white marbles

In the first experiment we have recorded the emission spectra of the clean surface of Onyx (white spot) marble

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0022-4073/$ - see front matter
doi:10.1016/j.jqsrt.2009.11.012

in air. The experimental arrangement consists of a Nd: YAG laser and a LIBS 2000 detection system. The Nd-YAG Laser (Quanttal Brillent) having pulse duration of 5 ns and repetition rate 10 Hz was operated in the Q-switch mode and capable of delivering 400 mJ at fundamental (1064 nm), 200 mJ at SHG (532 nm) and 90 mJ at THG (355 nm). The laser beam was focused through a 20 cm focal length quartz lens perpendicular to the target sample. The laser energy was varied through the flash lamp Q-switch delay. The LIBS 2000 detection system consists of five spectrometers, each equipped with 2400 line/mm holographic gratings of 5 μm slit width and covering the range between 200–700 nm. Each spectrometer has 2048 element linear charge coupled devices (CCD) array and the spectral resolution of ≈ 0.05 nm has been determined using a narrow band width dye laser. The integration time is about 2 ms and the delay time in acquiring the data is about 3.5 μs. The system has been calibrated in wavelength by recording the well-known lines of neon, argon and mercury, the uncertainty in the measured wavelength is ≈ 0.02 nm [14].

The emission spectrum presented in the Fig. 1 was recorded using the SHG 532 nm of Nd-YAG Laser, at 4×10^{10} W/cm^2 laser irradiance. The spectra were obtained by averaging 10 data of single laser shot under identical experimental conditions. The emission spectrum consists of neutral and singly ionized spectral lines of calcium, magnesium, strontium and some transitions of neutral iron and sodium. Some of the observed transitions for neutral calcium are identified as 4s4p $^3P_1\rightarrow 5s^2\ ^1S_0$, 3d4s $^3D_{1,2,3}\rightarrow$4s4p $^3P_{0,1,2}$, 4s5s $^3S_1\rightarrow$ 4s4p $^3P_{0,1,2}$, 3d4p $^3D_{1,2,3}\rightarrow$3d4s $^3D_{1,2,3}$, 4s4f $^3F_2\rightarrow$3d4s $^3D_{1,2,3}$, 4s4d $^3D_{1,2,3}\rightarrow$4s4p $^3P_{0,1,2}$, 3p^{6}4p^2 $^3P_{0,1,2}\rightarrow$4s4p $^3P_{0,1,2}$ and 3s5d $^3D_{1,2,3}\rightarrow$4s4p $^3P_{0,1,2}$. The well-known sodium D lines 3p $^2P_{1/2,\ 3/2}\rightarrow$3s $^2S_{1/2}$ at 589.6 and 589.0 nm have also been observed. The calcium line at 445.71 nm corresponding to the 4s4d $^3D1\rightarrow$4s4p$^3P^2$ transition remains prominent among the neutral lines of all the elements, because of their high transition probability. The level assignments have been made using the NBS (NIST) database [15]. The wavelengths of all the observed spectral lines along with their relevant spectroscopic data are presented in Tables 1–3.

3. Quality analysis of Onyx (white spot) marbles

The LIBS spectra of the Onyx White Marbles collected from Quetta region of Boluchistan Province of Pakistan were recorded while the laser was focused on its white spot. The analysis reveals that the main composition of the sample is based on calcium, magnesium and strontium. Some traces of iron and sodium are also detected. We selected the strongest lines of these elements and determined the integrated line intensities of the transitions 4s4d $^3D_1\rightarrow$4s4p $^3P_2$ at 445.71 nm for Ca, 3s4s $^3S_1\rightarrow$ 3s3p $^3P_2$ at 518.36 for Mg, 3d^{7}4s $^5G_5\rightarrow$3d^{7}4s $^3F_4$, 438.46 nm for Fe and 3p $^2P_{3/2}\rightarrow$3s $^2S_{1/2}$ 589.0 nm for Na, respectively. The integrated intensities of the strongest lines of each element are considered as their abundance. A plot of the relative abundance versus the pertinent elements is shown in Fig. 2. The relative abundance of these elements present in this sample is calcium (56.9%), followed by magnesium (17.2%), strontium (13.4%) and iron (11%). Evidently the relative abundance of calcium is more than any other element. The spectra presented in Fig. 1 shows a number of well-known transitions of magnesium and strontium in the Onyx White Marbles that is an evidence of the presence of magnesium and strontium in the marble samples located in Quetta region. Lazic et al. [2] presented a similar study on the marble samples collected from different quarries of Italy, Turkey and Greece and reported that the main composition of

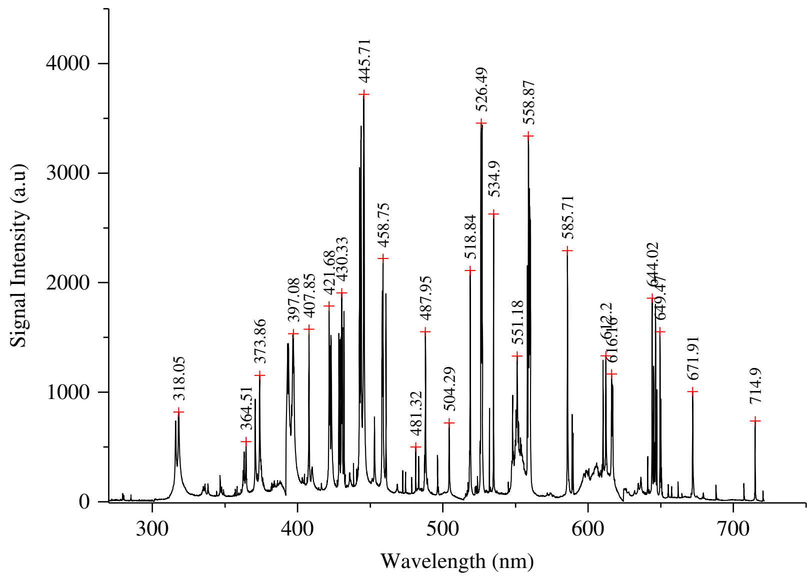

Fig. 1. Emission spectrum of Onyx (white spot) Marble, recorded in the spectral region from 200 to 720 nm in air using SHG of a Nd-YAG Laser.