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RESEARCH PAPER

Detection of Trace Elements in Active Luminescent Glass Using Laser-induced Breakdown Spectroscopy Combined with Laser-induced Fluorescence

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Abstract: In the preparation of active luminescent glass, trace elements are generally co-doped to improve the properties. To overcome the poor sensitivity of laser-induced breakdown spectroscopy (LIBS) on detecting trace elements in glass, LIBS combined with laser-induced fluorescence was utilized to detect trace Yb, Al and P. A wavelength-tunable laser was used to excited Yb ions, Al atoms, and P atoms. The transition process in laser-induced fluorescence was described. The results showed that the spectral intensities of Yb, Al and P were enhanced by 23, 50 and 8 times, respectively. LIBS sensitivity was demonstrated to be greatly improved by combining laser-induced fluorescence.

Key Words: Laser-induced breakdown spectroscopy; Laser-induced fluorescence; Glass

1 Introduction

Active luminescent glass is a kind of active light media, which is doped with rare-earth element ions to amplify light. Due to its advantages such as high monochromaticity and electro-optics conversion efficiency, active luminescent glass has attracted much attention[1–4] and has been widely used in active fibers, lasers, and amplifiers. Generally, trace elements are co-doped in the glass[5] to improve its properties. For example, ytterbium (Yb) can change the absorption band and improve absorption efficiency, aluminum (Al) can reduce ionic agglomeration, phosphorus (P) can improve refractive index performance. These auxiliary elements play important roles in improving properties of active luminescent glass though with very low concentration. Therefore, it is necessary to realize rapid detection of these trace elements in the glass manufactories.

Conventional methods for glass analysis include inductively coupled plasma optical emission spectrometry (ICP-OES)[6], inductively coupled plasma mass spectrometry (ICP-MS)[7], atomic absorption spectrometry[8,9], and so on. These methods need to dissolve samples with hydrofluoric acid because glass contains high concentration of silica. Then much toxic gas of silicon tetrafluoride is generated and harms the operators' health and the environment. Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)[10,11] and electron microprobe analysis (EPMA)[12] methods developed in recent years require vacuum chamber and complex facilities. Overall, because the lengthy processing times and complex operation, most of the methods mentioned above are only applied in laboratories, not suitable for industries.

Laser-induced breakdown spectroscopy (LIBS) is a new analytical technique[13–15]. In LIBS, plasma is generated by laser pulse, then the spectra emitting from the plasma are

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analyzed to deduce elemental information[16]. Because of such advantages as non-contact, in-situ analysis, rapid detection, no sample preparation, and no need for vacuum, LIBS showed great potentials in metallurgy[17], space exploration[18], steel detection[19], environmental protection[20], polymer classification[21], and nuclear reaction monitoring[22]. Generally, increasing laser energy can improve analytical sensitivity because higher laser energy results in more ablation volume and higher spectral intensity. However, high energy ablation on glass leads to surface cracking. Therefore, increasing laser energy in glass analysis is not recommended.

LIBS combined with laser-induced fluorescence (LIBS-LIF) is an enhancement technique in LIBS. A laser beam with a specific wavelength was used to resonantly excite specific atoms/ions to emit fluorescence[23]. LIBS-LIF was tentatively applied in trace elements detection of soil[24,25], metal[23,26–28], and aqueous solution[29,30] for its high enhancement factor and high selectivity. However, few studies were reported about trace elements detection in glass using LIBS-LIF. In present work, we take active terbium (Tb) glass as example. A wavelength-tunable laser was used to radiate plasmas to enhance the spectra of trace Yb, Al and P. The mechanisms of laser-induced fluorescence were discussed.

2 Experimental

2.1 Experimental setup

The schematic diagram of the LIBS-LIF setup used in this work is shown in Fig.1. Ablation laser beam was output from a Q-switched Nd:YAG laser (Quantel, Brilliant series, 6 ns, 532 nm, 10 Hz, flattened Gaussian beam), reflected by a dichroic mirror, and focused by a UV-grade quartz lens (f = 100 mm) to generate plasmas. The ablation energy was 3 mJ. The craters on the glass surface were about 0.1 mm in diameter. An optical parametric oscillator (OPO) wavelength-tunable laser (Opotek, Vibrant HE 355 LD, 225–2400 nm, 10 ns) was used to radiate the plasma. The power density of OPO laser at the plasma was about 4.25 MW cm^{-2}. The emission light from the plasma was collected by a light collector (Ocean Optics, 84-UV-25, 200–2000 nm) and coupled in to a C-T spectrometer (Princeton Instruments, SCT320, grating of 1200i, resolution of 0.09 nm). An intensified charge-coupled device (ICCD) was used to record the spectra and transmit data to a computer. The two laser devices and the ICCD were trigged by a digital generator (Stanford Instruments, DG535). Because the fluorescence signal and the OPO laser pulse were almost synchronous, the ICCD gate and OPO laser Q-switch simultaneously switched. The gate width was 10 ns. The interpulse delay between the two lasers was 2 μs.

2.2 Preparation of samples

The glass sample used in present work was shown in Fig.2. It was prepared by leaching the borate phase out from phase-separated alkali borosilicate glass in hot acid solutions. The doping concentrations of the auxiliary elements were 80, 150 and 96 μg g^{-1} in Yb, Al and P, respectively. The size was about 9 mm × 9 mm × 1 mm.

3 Results and discussion

3.1 Ionic spectra of Ytterbium

Yb element exists in the glass as Yb^{3+} ions. Pump energy is transferred by Yb^{3+} ions to realize upconversion luminescence. To our knowledge, no study was reported on the detection of Yb element using LIBS-LIF. Due to low second ionization energy (12.176 eV) of Yb atom, the major emission from Yb element in laser-induced plasma was Yb^{+} ionic spectrum. The Yb^{1+} ions in ground-state (0 cm^{-1}) were chosen as targets for resonant excitation. The maximum of stimulated absorption transition probabilities of these Yb^{1+} ions was 6.92 × 10^{20} s^{-1} with 328.97 nm excitation. As shown in Fig.3a, 328.97 nm laser beam provided by the OPO laser was absorbed by Yb^{+} ions. These Yb^{+} ions in 0 cm^{-1} state transited up to 30392 cm^{-1} by the stimulated absorption process, and then transited down to 27061 cm^{-1} by collision process. A large sum of Yb^{1+} ions in 27061 cm^{-1} spontaneously transited to 0 cm^{-1} and emitted 369.42 nm fluorescence. The observed spectra were shown in Fig.3b. Yb II 369.42 nm was weak without OPO laser radiation. The spectral intensity was enhanced by about 23 times when the plasma was radiated by 328.97 nm laser beam.

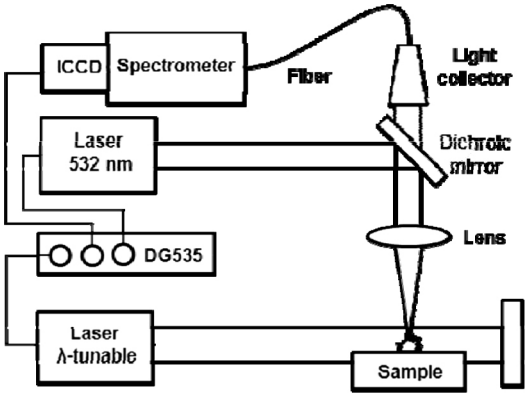

Fig.1 Schematic diagram of LIBS-LIF setup

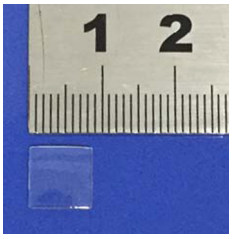

Fig.2 Glass sample with trace Yb, Al and P