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APPLICATION OF LASER INDUCED BREAKDOWN SPECTROSCOPY AS NONDESDUCTRIVE AND SAFE ANALYSIS METHOD FOR COMPOSITE SOLID PROPELLANTS

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Abstract. Nowadays many methods have been proposed for the analysis and evaluation of the energetic materials and their properties. In this work, laser induced breakdown spectroscopy (LIBS) as a new method was introduced as a safe and nondestructive analysis method to study chemical structure of composite solid propellants. Spectral peaks of the carbon, hydrogen, nitrogen, oxygen and aluminum atoms, which belong to the binder polymer structure and metallic fuel, were observed. The presence of emission lines relevant to the chlorine atoms can be used to represent using ammonium perchlorate as oxidizer. Moreover, emission lines relevant to the elements such as calcium, potassium, sodium and iron were confirmed to show the use of suitable additives for increasing performance and processing. In addition, C_2 swan bands and CN violet radiation were observed that are due to reaction of carbon atoms of propellant and nitrogen atoms of air.

Keywords: Laser Induced Breakdown Spectroscopy (LIBS), solid composite propellant, HTPB, safety

Introduction

Energetic materials are widely produced in order to use in civil and military applications (Agrawal, 2010; Keshavarz, 2011). Among different categories of energetic materials, i.e. propellants, explosives and pyrotechnics, chemical propellants in common use deliver specific impulse values up to about 300 seconds, which are widely used in solid and liquid rocket propulsion (Davenas, 1993; Keshavarz, 2006). Chemical structure identification of energetic materials is very impressive in performance improvement. It is very important to access nondestructive methods during construction, particularly in the chemical process. So far many chemical, mechanical and thermal analysis methods were provided and used in energetic materials investigations.

Several laser based techniques have been recently developed to investigate and analysis of the energetic materials (Kim et al., 2011; Leahy-Hoppa et al., 2010; Moros et al., 2011; Skvortsov, 2012; Wallin et al., 2009). Among these methods, Laser Induced Breakdown Spectroscopy (LIBS) has been established as a successful analytical method for elemental analysis (Hahn & Omenetto, 2010; 2012). A high power pulsed laser is focused in LIBS on a sample surface to generate a plume of plasma that is rich in atoms, ions, molecules and free electrons. The emitted radiation of the atoms, ions and molecules in the plasma can be used to characterize the elemental composition of the sample (Wainer et al., 2001). In fact, each wavelength corresponds to the unique transition in an atom or ion that can be used for identification of materials. LIBS technique has superior advantages with respect to the other methods, i.e. non-destructive, simultaneous multi elemental analysis, fast detection, no initial preparation, on-line and in-situ (Hahn & Omenetto, 2010; Lucena et al., 2011; Rusak et al., 1997).

Ammonium perchlorate composite propellant (APCP) is a composite propellant containing both fuel and oxidizer mixed with a rubbery binder. It is most often composed of ammonium perchlorate (AP), an elastomer binder such as hydroxyl-terminated polybutadiene (HTPB) or polybutadiene acrylic acid acrylonitrile prepolymer (PBAN), small amounts of powdered metal, typically aluminum (Al), and various burn rate catalysts as well as curing additives, which induce elastomer binder cross-linking to solidify the propellant before use. The purpose of this work is to use LIBS technique as a novel analysis method for the study of APCP samples. Atomic and molecular structure of matter will be investigated through the identification of spectral lines. As can be seen, all expected elements are detected and identified. Moreover, some of molecular bonds such as CN and C_2 are detected.

Experimental

Instrumentation

A LIBS apparatus (LIBSCAN100, Applied Photonic LTD, United Kingdom) was used in this research. This system is consisting of a laser source, a spectroscopy unit and an ablation chamber. A Q-switched Nd:YAG laser (Quentel, USA) at 1064 nm with the pulse duration of 5-9 ns is employed. The laser pulse energy varies from 10 to 100 mJ and the maximum laser irradiance on the sample is up to 1.4 GW/cm^2. A sample is placed on X, Y, Z translation stage that is controlled by internal software (LIBSoft V9.0.9, Applied Photonic LTD). Internal software enables to precise adjustment of the

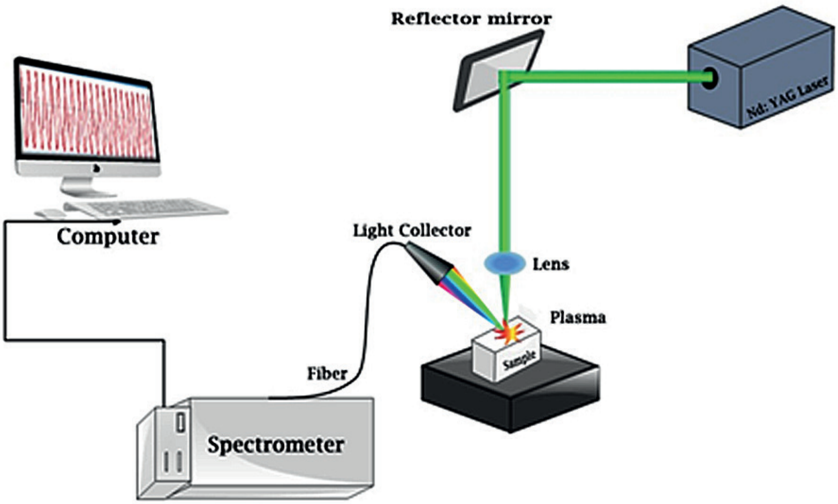

Fig. 1. Schematic diagram of the experimental LIBS set-up

ablation plume with respect to the optical axis of the detection system. An optical system collects emitted light from the sample and transmits it to the detector. The detector consists of eight spectrometer (Avantes-20-01-13-A, Netherland), which can give 0.04 nm resolution for spectral analysis from 182 to 1057nm. The LIBS spectrum is analyzed by Plasus Specline software (Plasus, Germany). The spectroscopic constants that used in analysis derived from the available atomic spectra data. Figure 1 shows the schematic of LIBS set-up.

Materials and methods

Chemical structure of solid composite propellants consists of aluminum (10-15%), AP (70-80%) and HTPB (10-20%) as well as the other usual additives such as burning rate catalyst. The HTPB-based propellant without a precise formulation selected in this study to check the reliability of the new method.

The sample was placed on the stage in experimental setup for testing. Laser pulse with high intensity was focused on the sample. Plasma was also formed by laser ablation above the surface. This unstable plasma was very excited that can emit in each direction. This radiation is collected by lens and transfer to the spectrometer by fiber, which is detected in the spectrometer. Spectrum is also sent to computer for analysis. Thus, one spectrum is obtained that each peak is relevant to one atomic, ionic or molecular transition.

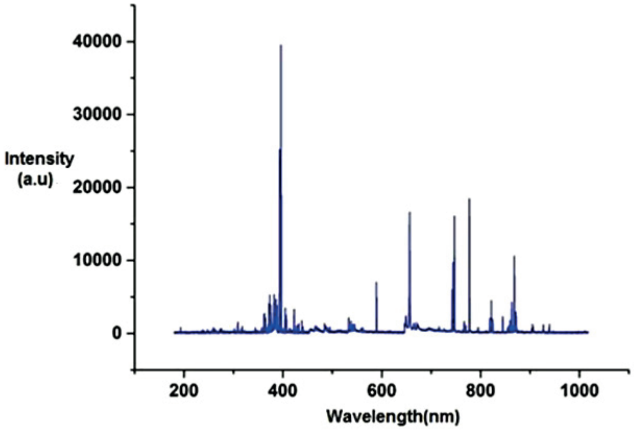

Fig. 2. LIBS spectrum of the propellant

Each of the peaks represents a unique atomic or ionic transition. It should be noted that the spectral peaks are the area where the Signal-to-Noise ratio (SNR) is high. The spectral data for these peaks can be extracted from the database by which each of these peaks is identified.$^{1)}$ For suitable selection of the peaks, the first elements corresponding to each high peaks must be recognized. Each of these elements afterward should be checked over the entire spectrum. If there are any other peaks of element that introduced in the database completely, we can definitively confirm the presence of that element in the chemical structure. In most cases, atomic emission is associated with a single transition that producing a line at a discrete wavelength. Emission of molecules corresponds to vibrational states (known as vibrational emissions), which are derived from electronic transitions of the molecules. Although molecular emission has been widely studied (Lucena et al., 2011), vibrational emission of molecules is not so often investigated in LIBS (Homkohl et al., 2011; Ndaiye & Lago, 2011; Nemes et al., 2005; Parigger, 2013). The response of CN molecular moiety emission to laser ablation has a great potential since CN is presented in every carbon material when ablated in the presence of nitrogen. Furthermore, the SNR of this molecular band is usually the highest in LIBS spectra of solid composite propellants. This emission and its relation to the molecular structure can get useful information for the distinction of organics through LIBS. A deeper understanding of the principal formation routes of CN and the other species exist in laser-induced plasmas.

Table 1. Elements spectral peaks

Elements	Wavelength(nm)	Elements	Wavelength(nm)
Fe	238.20 239.56 259.81 261.18 263.10 271.91 273.95 275.01 275.57 371.99 373.48 373.71 374.55 374.82 374.94 375.82 404.85 406.35 430.79 432.50 438.35	Al	257.51 308.21 309.20 394.41 396.15
		H	486.13 656.20
		N	742.30 744.22 746.83 824.2 856.77 859.41 862.92 865.58 868.31 870.32 871.17 871.8
		K	766.48 769.89 795.53
Ca	393.36 396.84 422.67 445.47 646.25 649.37	O	777.19 844.67
		Na	588.99 589.59 818.32
C	247.85	Cl	821.20 822.17

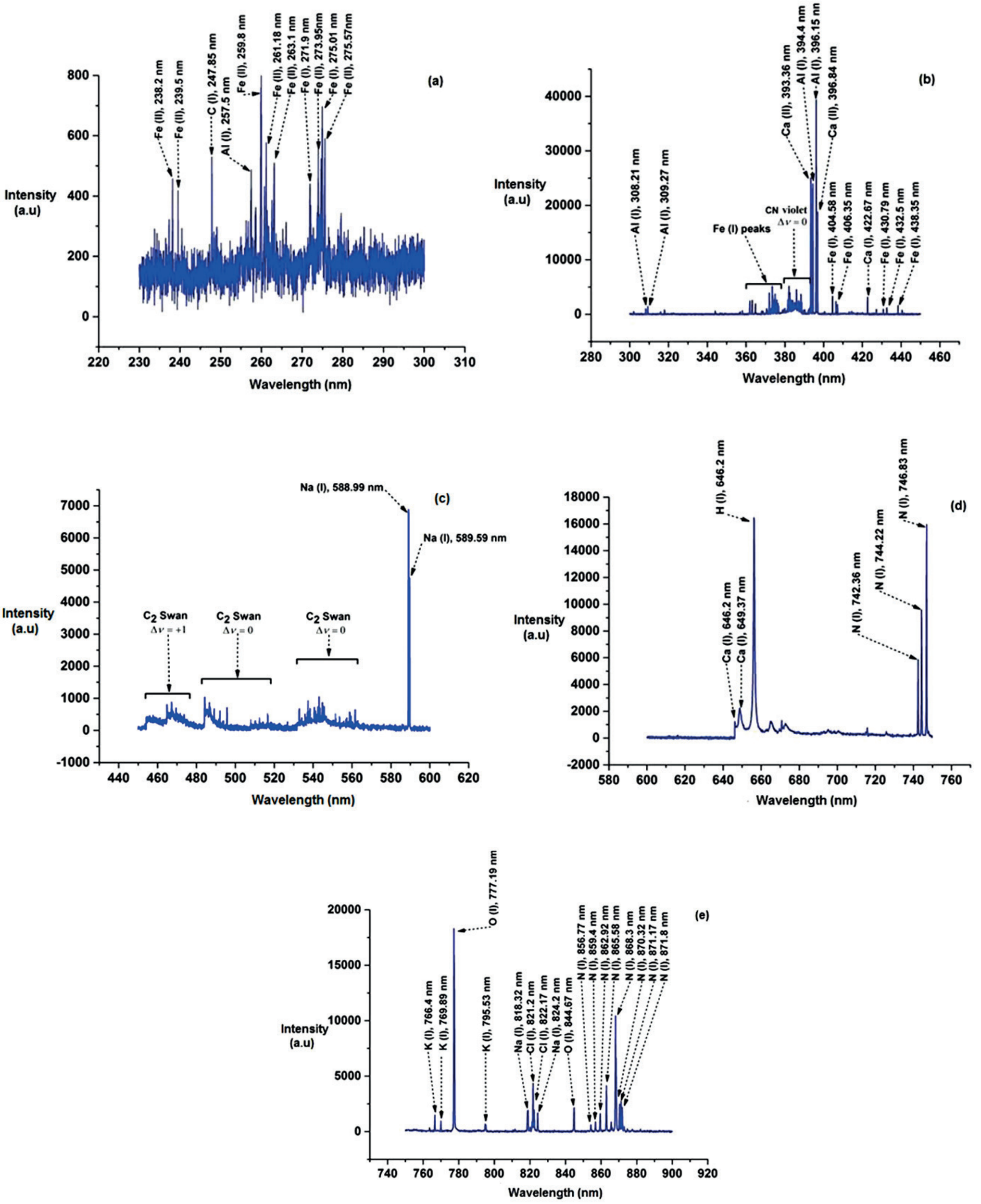

Fig. 3. Spectral peaks identification

Results and discussion

LIBS spectrum of the propellant sample has been showed in Fig. 2. All peaks are normalized to the maximum peak intensity (Al 396.15) in order to reduce the impact of the test parameters especially frequency shift. There are two methods for each spectrum investigation. In the first case, chemical structure and their elements are obvious, which can be confirmed by LIBS.

For precise investigation, this spectrum was divided to five wavelength intervals so that all peaks were identified. Fig. 3 represents these spectrums in which each peak relevant to atoms or ions was identified by using the mentioned methods. Summary of data on the spectral peaks is given in Table 1.

As can be seen from Fig. 3 and Table 1, the number of spectral peaks is different for each element. For confirmation of the presence of each element, one or more main peak should be exist. The main peak for nitrogen atoms is 746.83 nm, which also has several other spectral peaks. Carbon atoms have the main peak in 247.85 nm so that its intensity is very weak because they exist in the structure of polymer. Nitrogen, hydrogen and oxygen atoms, which are jointly in the atmosphere and the propellant, have main spectral peaks 746.83, 656.2 and 777.19 nm, respectively, which are clearly seen in the spectrum. The main spectral peak wavelength of chlorine is 822 nm, which is due to the presence of AP. According to the detailed checking, iron atom has the most peak in the data base for which all peaks of iron atoms in the spectrum were recorded. The existence of the other metal elements including potassium, calcium and sodium will be confirmed in the structure, which their main peaks are in 393.36, 589.59 and 766.48 nm, respectively. It should be noted that the other smaller peaks of radiation caused by the ions of the same elements. In addition to the detected atoms and ions, CN and C_2 bonds are recorded in the spectrum. For more accurate results, the main wavelength and vibration levels involved in these radiations are given in Tables 2 and 3.

Table 2. CN vibrational bond

Vibrational Bonds	Wavelength(nm)
(0-0)	388.30
(1-1)	387.10
(2-2)	386.12
(3-3)	385.44
(4-4)	385.05

The exact location of spectral peaks corresponding to the CN radiation has been shown in Fig. 4. The observed CN bond in the spectrum of the radiation corresponds to the $B^2\Sigma^+ - X^2\Sigma^+$ transition from the $\Delta\nu = 0$ state (Hahn & Omenetto, 2010). The formation of CN bond is due to reaction between the released carbon atoms of sample and nitrogen of air according to the following reactions, which show low intensity spectral peak of carbon (Hahn & Omenetto, 2012; Wainner et al., 2001).

Table 3. C_2 vibrational bond

Vibrational Bonds	Wavelength(nm)	Vibrational Bonds	Wavelength(nm)
(0-0)	516.40	(5-4)	467.8
(1-1)	512.95	(0-1)	563.55
(2-2)	509.71	(1-2)	558.53
(1-0)	473.65	(2-3)	554.04
(2-1)	471.45	(3-4)	550.14
(3-2)	469.7	(4-5)	547.17
(4-3)	468.43	(5-6)	544.73

$$C + N_2 \rightarrow CN + N \tag{1}$$

$$C_2 + N_2 \rightarrow 2CN \tag{2}$$

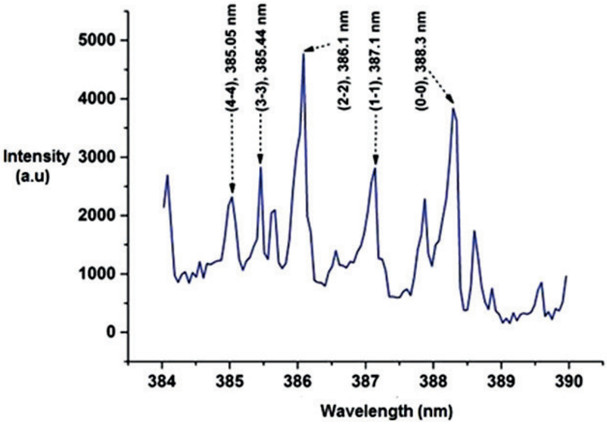

Fig. 4. CN spectral peaks

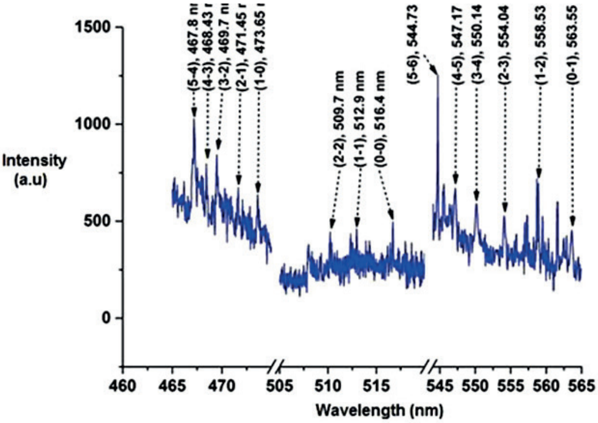

Fig. 5. C_2 spectral peaks

Two complementary processes are also involved in formation of C_2 molecules: (i) electron collisions that caused by decomposition of carbon skeleton in the plasma; and (ii) recombination of the released carbons.

However, due to high plasma ionization, usually C_2 production by carbon skeleton decomposition can be neglected, and the second mechanism is dominant. Radiation of C_2 due to $d^3\Pi_g - a^3\Pi_u$ transition has been happened with $\Delta\nu = 0, \pm 1$ modes (Hahn & Omenetto, 2010). Fig. 5 shows the exact location of spectral peaks for each bond.

Conclusion

Composite solid propellants are widely used in rocket vehicles. It is important to use suitable methods with high accuracy for investigation and identification of chemical structure of propellants. It was shown in this research that it is possible to use the new method of LIBS for identifications of some chemical constituents in composite solid propellants. Four elements of oxygen, nitrogen, hydrogen and carbon, that forming binder polymer structure, with aluminum as the metal fuel were identified. Moreover, it was indicated that the presence of the other elements potassium, calcium, sodium and iron were specified. The presence of chlorine atoms, corresponding to the use of ammonium perchlorate as oxidizer, was confirmed by observation of their spectral peaks. Besides these atoms, the spectral peaks due to the vibrational transitions in the C_2 and CN bond indicate the interaction of carbon and nitrogen atoms.

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NOTES

1. http://Physics.nist.gov/physrrefdata/ASD/lines-frome.html

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