Laser Induced Breakdown Spectroscopy of high energy materials using nanosecond, picosecond, and femtosecond pulses: Challenges and opportunities

S. Venugopal Rao,[*] S. Sreedhar, M. Ashwin Kumar, P. Prem Kiran, Surya P. Tewari, G. Manoj Kumar[a]

Advanced Centre of Research in High Energy Materials (ACRHEM)
University of Hyderabad, Hyderabad 500046, India.
***,a** Authors for correspondence: svrsp@uohyd.ernet.in; manojsp@uohyd.ernet.in

ABSTRACT

We present some of our initial experimental results from laser induced breakdown spectroscopy (LIBS) studies of few high energy materials such as a simple match stick (MS) and $BKNO_3$ (BPN), and ammonium perchlorate (AP) using nanosecond (ns), picosecond (ps), and femtosecond (fs) pulses. The characteristic peaks of each sample in different time domains are analyzed. The merits and de-merits of ultrashort pulses in LIBS experiments for discrimination of high energy materials are highlighted.

Keywords: LIBS, femtosecond, nanosecond, high energy materials, gating

1. INTRODUCTION

LIBS is an attractive and a versatile technique for the detection of hazardous and prohibited substances, including stand-off detection capability, constraint of a very small amount of material, and high detection speed. Several detailed studies in the last few years have resulted in the development of man-portable LIBS and standoff detection up to 100 m distances [1-7]. LIBS has been successfully evaluated for detection of explosive residues [8-11], hazardous chemical and biological materials [12,13] landmines [14-16]. Ultrashort laser pulses have tremendous potential in designing novel and sensitive systems for laser induced breakdown spectroscopy (LIBS) analysis [17]**.** Conventional LIBS uses nanosecond (ns) pulses whereas shorter pulse LIBS uses typically femtosecond (fs) pulses and this has specific advantages [18-20]. Fs LIBS has been used in variety of applications including distinguishing of explosives[21-25], animal tissues studies [26], identification of bacteria [27], in cultural heritage monitoring [28], microanalysis of alloys [29], discrimination of microbiological samples [30], high spatial resolution analysis of biological molecules [31], depth profiling of historical objects [32] etc. to name a few. The usgae of ultrashort pulses (compared to longer ns pulses) in the areas of micromachining has been well established over the last few years [33, 34]. There have been few initial studies with fs pulses in LIBS experiments on explosive related materials and the mandate has been divided over the advantages of ultrahshort pulses. The major challenge in idenifying high energy materials (HEM's) is the presence of common elements (C, N, O, and H) in all these materials. Moreover, identifying HEM's among themselves is also another huge challenge. Herein, we present some of our experimental results from the LIBS measurements of simple high energy materials such as match stick, $BKNO_3$ (Boron potassium nitrate, BPN), and Ammonium Perchlorate (AP). The LIBS spectra were collected using ns, ps, and fs pulses using a simple spectrometer without any gating. The ns LIBS spectra was also collected using a gated ICCD and the various spectra obtained are compared and analyzed.

2. EXPERIMENTAL DETAILS

Ns pulses at 532 nm (10 Hz, 6 ns, ~400 mJ), ps/fs pulses at 800 nm (1 kHz, ~2 ps/~40fs, ~2.5/~2.0 mJ) were used for the experiments (see table 1). The spectra were collected with simple configuration using a high resolution USB spectrometer (MAYA, Ocean Optics). The data collection geometry included either of (i) a single fiber with large core diameter (ii) collection of lenses for guiding the plasma emission to the spectrometer in free space. Nanosecond LIBS studies were also performed using a gated ICCD coupled to Mechelle spectrograph (ANDOR). Figure 1(a) shows the schematic of the experimental set up used for ns LIBS experiment while figure 1(b) shows the fs LIBS experimental set up. Typical energies used were 15-30 mJ for ns case, ~1 mJ for the ps/fs case.

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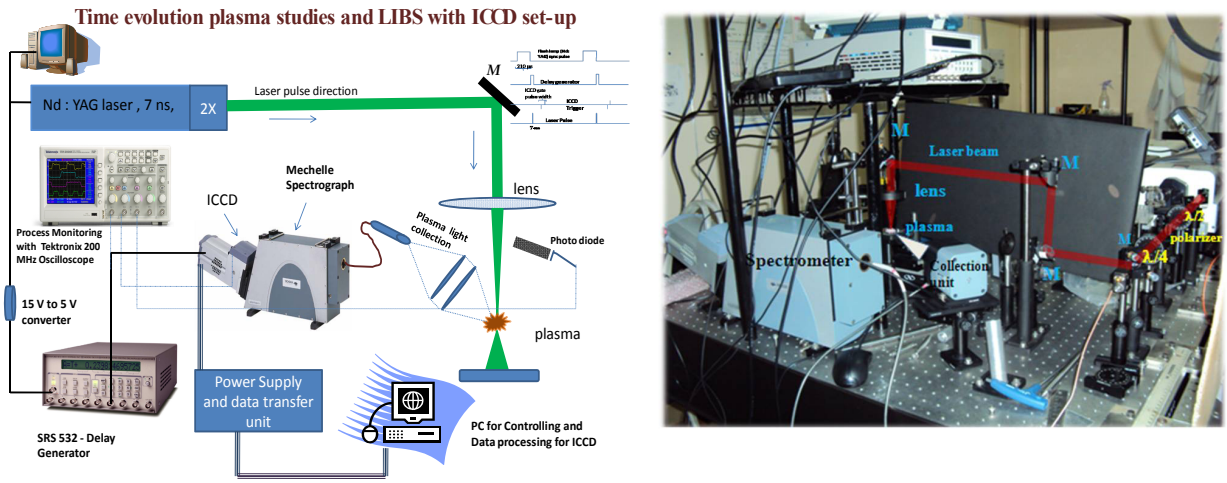
Experimental parameters	Nanosecond pulses	Picosecond pulses	Femtosecond pulses
Pulse width **(τ)**	7 **ns**	~2 **ps**	~40 **fs**
Bandwidth **(Δλ) nm**	< 0.1	1-2	~26
Typical Energy **(mJ)**	20	1.6	1.8
Wavelength **(nm)**	532	800	800
Focusing lens Focal length **(mm)**	80 (Plano convex lens)	75 (achromatic doublet)	75 (achromatic doublet)
Spot size $2\omega_0$ **(μm)**	~25	~25	~25



(a) **(b)**

Figure 1 Experimental setup using (a) ns pulses and (b) fs pulses

3. RESULTS AND DISCUSSION

LIBS spectra were recorded for (a) match stick as is (b) pure $BKNO_3$ and in pellet form (c) Ammounium perchlorate in pellet form. Figures 2(a)-2(c) shows the LIBS spectra obtained with ns, ps, and fs pulses for the sample match stick, respectively. Matchstick is normally made up of sulphides of arsenic or antimony, phosphorus and potassium chlorate. There could be some binders used such as gelatin (sodium also might be mixed). We observed the ionic peaks of S, P, N and O, and line emission of H, N, O, K, Na elements. With ns and ps pulses the presence of ionic peaks was dominant. Compared with the ns LIBS spectra ionic features were less intense in ps LIBS spectra and further decrement in intensity was observed in the fs LIBS spectra. K line intensity in the ns spectra was very strong while it decreased drastically in the ps spectra and was negligible in the fs spectra. Certain peaks were present only in fs spectra [e.g. S^+(534.57) etc.] whereas few peaks were exclusive for the ns domain [e.g. S^{2+} (363.42 nm), (K (691.108, 766.67), P^+(427.85) etc.]. Another important feature observed was the decrease in continuum amount from ns to ps spectra. All the spectra were recorded with USB (Maya, Ocean optics) spectrometer. Manganese peaks were also found at 403.27 nm in all the spectra. Figure 2(d) shows the time evolution of the ns LIBS spectra obtained with an ICCD and Mechelle spectrometer combination. Figure 3 shows the LIBS data of MS acquired using the gate option (500 ns width and 500 ns delay). Some of the peaks were well resolved and some additional peaks were also observed (e.g. Mn (401.81 nm, 408.36), possibly an impurity) which could not be obtained using an ordinary spectrometer. The contiuum has substantially decreased beyond the gate delay of 1 μs. The possibilities and challeneges for identification of such materials include (a) Identification of peaks exclusive to each domain (devoid of gating, gating with various widths and delays) and understanding the reason for their presence/absence (b) evaluating the ratios of specific atomic peaks (c) identifying the emission signatures of atomic and molecular species (d) understanding the time evolution of each of these species. In our case further analysis (including temperature evaluation and temporal intensity decay) is pending.

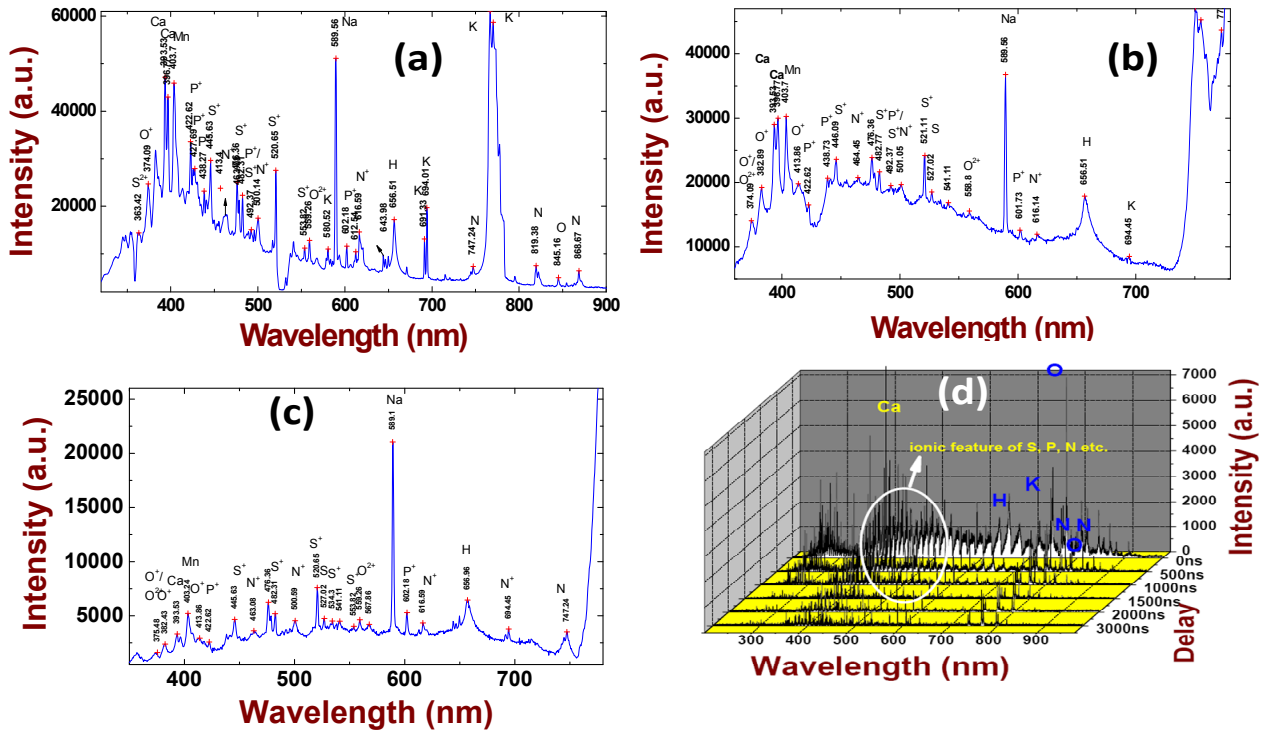


Figure 2 LIBS spectra of a simple match stick obtained with (a) ~6 ns pulses (b) ~2 ps pulses (c) ~40 fs pulses using a non-gated spectrometer (MAYA, Ocean optics). Bottom curve depicts the time-resolved ns LIBS spectrum obtained with an ICCD and Mechelle spectrograph combination. The gate width and gate delay were both set to 500 ns. Certain elemental peaks existed even after 3 μs.

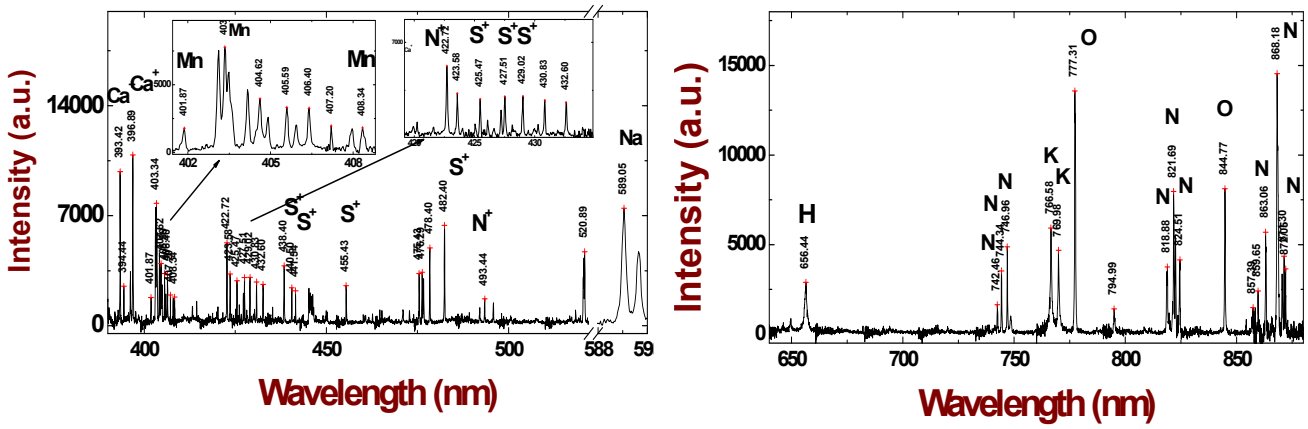


Figure 3 LIBS spectra of match stick with ns pulses using ICCD from 300 – 600 nm range (left) and from 600 – 900 nm (right). ICCD gate delay was 500 ns with a gate width of 500 ns.

Figures 4(a)–3(c) shows the LIBS spectra of the pure sample BPN (a primary explosive) obtained with ns, ps, and fs pulses. K and Na (impurity in $BKNO_3$) lines are fingerprints for this material. K has two major lines, one at 766.67, 770.13 nm (doublet) and another at 691.88, 694.4 nm (doublet). In the ns LIBS spectra the 691 nm line was not observed clearly but 766 nm doublet line was present. In ps LIBS spectra both doublet lines were present and in the fs LIBS spectra only 691 nm doublet lines were present. The other line could have been supressed by the pump because fs pulses possess broad bandwidth (~26 nm FHWM) compared to ns (<0.1 nm FWHM) or ps (1-2 nm) FWHM pulses.

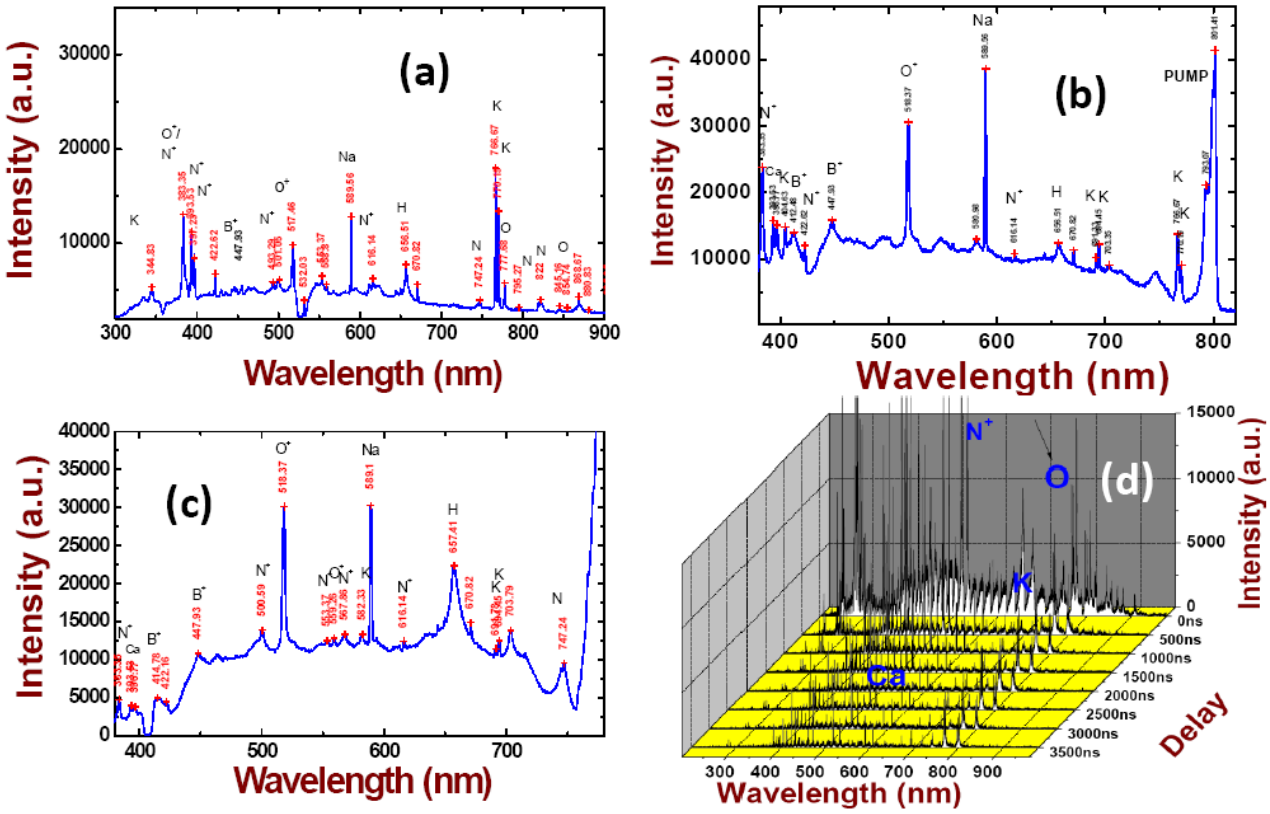


Figure 4 LIBS spectra of $BKNO_3$ pellet obtained with (a) ~6 ns pulses (b) ~2 ps pulses (c) ~40 fs pulses using a non-gated spectrometer (MAYA, Ocean optics). (d) Time-resolved ns LIBS spectrum of $BKNO_3$ pellet obtained with an ICCD and Mechelle spectrograph combination. The gate width and gate delay were both set to 500 ns. Certain elemental peaks existed even after 3.5

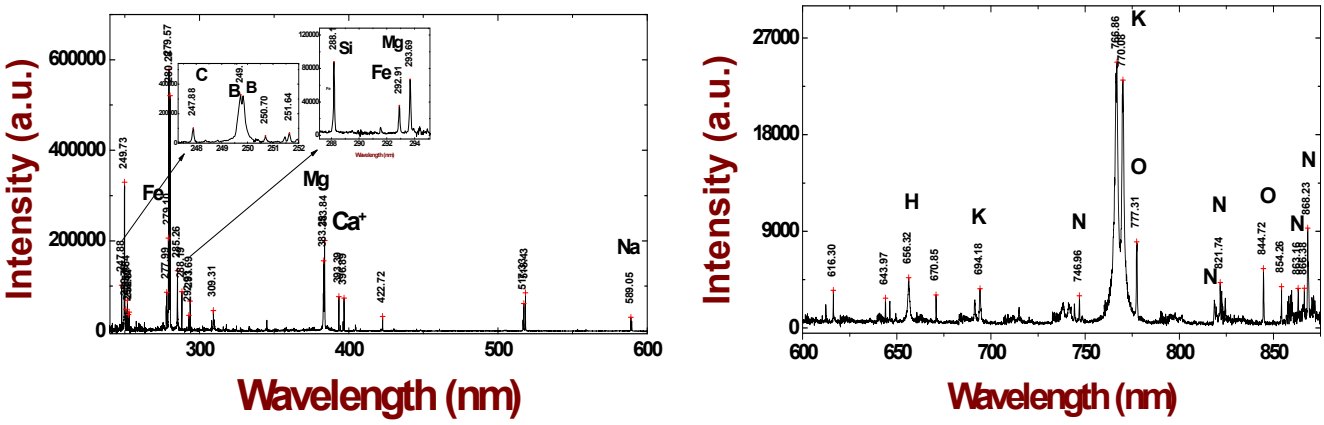


Figure 5 LIBS spectra of $BKNO_3$ between 200 nm to 500 nm (left) and between 500 nm to 900 nm (right). ICCD gate delay was 500 ns with a gate width of 500 ns.

Potassium atomic lines can be seen at 770.05 nm and 766.65 nm in the ns LIBS spectra of BPN. The nitrogen lines are seen at 822.1 nm, 868.61 nm and Oxygen at 777.57 nm and 844.88 nm. As nitrogen and oxygen are also present in the sample as well as the ambient air, we observe a variation of the strengths of these lines when compared to the ambient air alone. B^+ peak apart from N, O, K, peaks has been observed in all the spectra. However, the ratios of atomic peak intensities varied from ns to fs case. Figure 4(d) depicts time evolution of the ns LIBS spectra of $BKNO_3$ in pellet form (especially the evolution of Ca, K, N^+, and O) obtained with an ICCD with gate width and gate delay values of 500 ns. The elemental peak intensities were significant even after 3.5 μs

Figure 5 shows the ICCD LIBS spectra of BPN pellets and it is evident that more peaks were observed using gate delay of 500 nm and a gate width of 500 ns. Boron peak (249.69 nm) was well resolved (B^+ was identified in spectrometer data) along with some impurities such as Ca, Fe, Si, Mg, and C, possibly entering while preparing the pellets, in the spectra (left). Time evolution studies of the K, O peaks (766.86 nm and 770.07 nm for K and 777.31 nm for oxygen, left part) and N peaks (near747 nm, right part) are depicted in figure 6. The K peak was long lived while the O peak near 777 nm, interestingly, was a short lived one (<1 μs). There were no molecular species observed in the ns spectra.

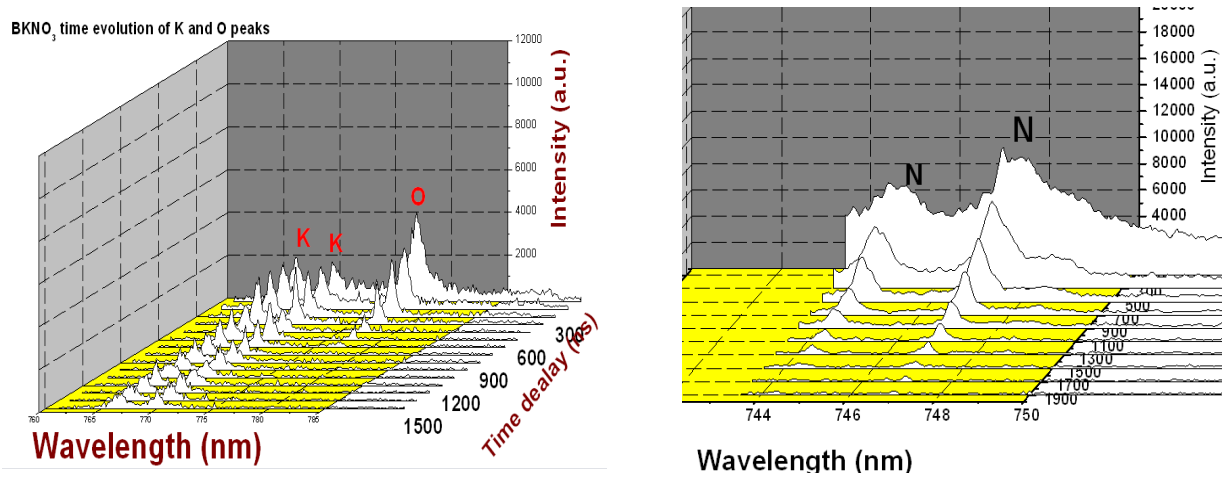


Figure 6 Time evolution of the K, O peaks (766.86 nm and 770.07 nm for K and 777.31 nm for oxygen, left part) and N peaks (near 747 nm, right part). Gate width used 100 ns with a gate delay of 100 ns.

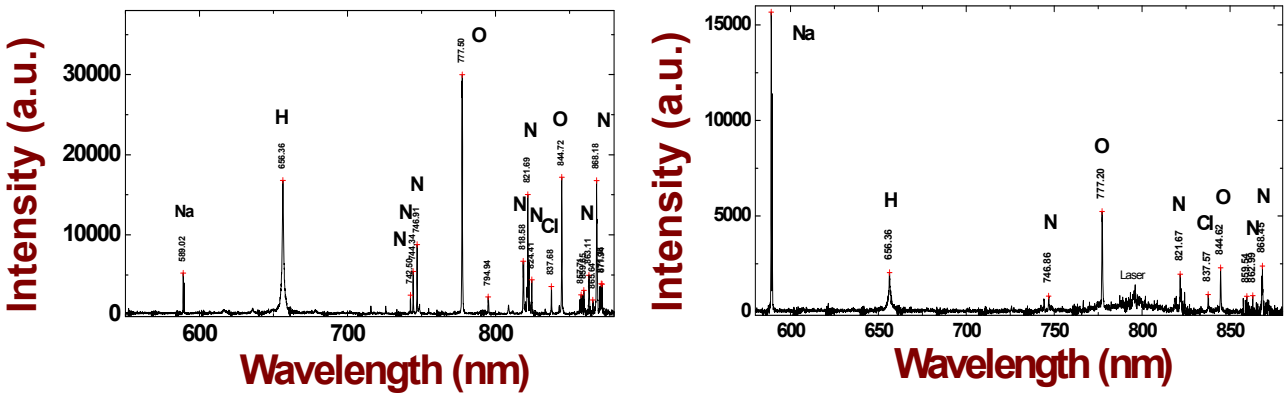


Figure 7 LIBS spectra of AP pellet using ICCD with ns pulses (left) and fs pulses (right). Gate width is 1000 (800) ns and gate delay is 1000 (200) for ns (fs) case. Typical input energies were ~25 mJ and ~1.5 mJ for ns and fs cases, respectively.

When AP is mixed with a fuel (like a powdered aluminum and/or with an elastomeric binder) it can generate self-sustained combustion at far under atmospheric pressure. It is an important oxidizer with a decades-long history of use in solid rocket propellants- space launch, military, amateur, hobby high powered rockets and in some fireworks. Figure 7 shows the gated LIBS spectra of AP with ns pulses (left) and fs pulses (right). Ns spectral lines were more than the fs spectral lines. Nonetheless, there were subtle differences in the peak intensity ratios of N, Cl, H, and O. Further analyses could throw some light on the mechanisms of ionization and the chemistry of recombination processes taking place using ns and fs pulses. Several studies over the last few years have confirmed that ultrashort laser pulses offer several advantages over the ns counterparts. A number of the merits that have been indentified include (a) Low ablation threshold (b) Less thermal damage to the sample (c) Higher efficiency/Higher reliability. The background is in general bereft of lines arising from the ambient air. As the pulse width is shorter there is no interaction or minimal interaction of the generated plasma with the pulse itself. Observation of molecular species in fs LIBS has been highlighted as one of the advantages. Dikmelik et al [22,23] had observed emission from CN and C_2 molecules as the marker for the explosive with fs LIBS. The most significant differences between the ns and fs spectra were the absence of atomic emission in the femtosecond spectrum for species associated with TNT along with the presence of molecular emission that was attributed to CN and C_2 [22,23]. De Lucia et al. [24] studied several explosives and explosive residues with various pulse energies using ns and fs LIBS. In contrast to earlier fs LIBS spectra of explosives, they had observed atomic emission peaks for the constituent elements of explosives – carbon, hydrogen, nitrogen, and oxygen. Their preliminary results indicated that several advantages attributed to femtosecond pulses were not realized at higher laser fluences. The important observation made from their studies was carbon atomic emission intensity relative to the aluminum atomic emission intensity was greater for the femtosecond spectrum.

There are several issues / challenges to be resolved / surmount before ultrashort pulse LIBS could be realized a potential technique for unambiguous identification of explosives and explosive residues from other organic molecules. Some of them are (a) atmospheric air: LIBS spectra in practicality will be recorded in atmospheric conditions and should be able to provide reliable data in atmosphere (b) single pulse/double pulse: Identification/Optimization of single pulse or double pulse (fs pulse followed by ns pulses in collinear/non-collinear geometries etc. [35-37] (c) evaluate the effects of sample temperature and substrates on the LIBS spectra [38-40] (d) dependence of fs pulses shape and bandwidth on the LIBS spectra [41] (e) influence of ns, fs pulse polarization properties [42]. It was shown that the continuum emission produced in the ablation of an Al target with ns pulses was much more strongly polarized than the discrete line emission. This effect can be utilized to improve the resolution of the LIBS spectrum by using a polarizer to filter out the continuum background. (f) energy dependence of the LIBS signal [43] (g) Ratiometric methods for stoichiometric analysis [44] (h) new laser sources and wavelengths [45] might provide additional insights into the understanding of LIBS dynamics along with providing novel, compact laser sources for stand-off detection. Some of the recent reports of fluence dependence indicate that the ratio of atomic-to-molecular emission increased as femtosecond pulse fluence is increased. Further opportunities include pulse shaping with ultrashort pulses for additional information from LIBS spectra. Accurate kinetic modeling of the recorded LIBS spectra in each time domain is essential to understand the effects of atmosphere, presence of particular molecular species etc. and resolve the discrepancies [46-48]. Furthermore, detailed analyses is required for each set of LIBS data for classification and several detailed studies on same molecules are necessary [49]. Identification and understanding of the molecular species in short pulse LIBS spectra could be one of the directions [51]. Ultimately time-resolved data in each time domain could provide the key for identification, classification, and unambiguous detection of hazardous materials.

4. CONCLUSIONS

In conclusion we have recorded the ns, ps, and fs LIBS spectra of match stick, $BKNO_3$, and Ammonium perchlorate using a simple spectrometer without gating and ns/fs spectra for AP using gated ICCD coupled to a Mechelle spectrometer. The differences and similarities observed in the initial LIBS spectra with different pulse widths have been analyzed. Some of the major challenges in detection of high energy materials using ultrashort pulses have been outlined.

5. ACKNOWLEDGMENTS

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Peaks found in LIBS spectra of Matchstick			Assignment using NIST atomic spectral database.
ns	ps	fs	
363.42			S^{2+}(363.197)
374.09	374.09	375.48	O^{+} (374.16),O2+(375.46)
382.43	382.89	382.43	O^{+}(382.15), O(382.34)
393.53	393.53	393.53	Ca^{+} (393.366)
396.77	396.77		Ca^{+} (396.847)
403.7	403.7	403.24	Mn (403.27)
422.62	422.62	422.62	P^{+}(422.21),
427.69			P^{+}(427.85)
438.27	438.73		P^{+}(438.53)
445.63	446.09	445.63	S^{+}(445.63)
463.08	464.45	463.08	N^{+}(463.05), N^{2+} (463.41)
482.31	482.77	482.31	S^{+}(482.40)
492.37	492.37		S^{+}(492.41,492.53),P^{+}(492.72)
500.14	501.05	500.59	N^{+} (500.14, 500.27, 500.51)
520.65	521.11	520.65	S^{+}(520.10,520.13)
	527.02	527.02	S (527.87)
		534.3	S^{+}(534.57)
553.82	553.82	553.82	S^{+}(553.672)
559.26	558.8	559.26	O^{2+}(559.23)
589.56	589.56	589.1	Na (588.9, 589.59)
602.18	601.73	602.18	P^{+}(602.41)
616.59	616.14	616.59	N^{+} (616.77)
656.51	656.51	656.96	H (656.4)
691.33			K (691.108)
694.01	694.45	694.45	K(693.877)
747.24	750.33	747.24	N(742.36, 744.22, 746.83)
766.67			K(766.49)
770.19	772.39		K(769.896)
819.38			N(820.03)
845.16			O(844.67)
868.67			N(868.61)

Peaks Observed in LIBS spectra of $BKNO_3$			Assignment NIST atomic spectral database.
ns	ps	fs	
344.83			K (344.63,344.73)
383.35	383.35	383.35	N^{+} (383.837)/ O^{+} (383.307,383.02)
393.53	393.53	393.53	Ca^{+} (393.366)
397.23	396.77	396.77	Ca^{+} (396.847)
	404.63	404.63	K (404.414, 404.721)
415.24	412.48	414.78	B^{+} (412.193)
422.62	422.62	422.16	N^{+}(422.77)
447.93	447.93	447.93	B^{2+}(448.705),B^{+}(447.28)
464.91		463.08	N^{+}(463.05), N^{2+} (463.41)
501.05	500.14	500.59	N+ (500.14, 500.27, 500.51)
517.46	518.37	518.37	O^{+} (517.589, 519.04)
546.11	547.92	559.26	N+ (549.56)
553.37		553.37	N+ (553.53)
567.86		567.86	N^{+}(567.95, 567.60)
	559.71		O^{+} (558.3232), O^{2+}(559.237)
	580.98	582.33	K(580.17, 581.21)
589.56	589.56	589.1	Na (588.9, 589.59)
594.52		594.07	N+ (594.16)
616.14	616.14	616.14	N^{+} (616.77)
656.51	656.51	657.41	H (656.4)
	691.33	691.78	K (691.108)
	694.45	694.45	K(693.877)
747.24		747.24	N(742.36, 744.22, 746.83)
766.67	766.67		K(766.49)
770.19	770.19		K(769.896)
777.68			O(777.19,777.41,777.53)
822			N (822.31), O (822.18,822.76)
845.16			O (844.62, 844.63, 844.67)
868.67			N(868.02, 868.34, 868.61)

Table 1 Summary of peaks obtained from the LIBS spectra using Maya spectrometer and the assignment using NIST data base for match stick (left) and BPN (right) using ns, ps, and fs pulses

Peak observed in ICCD LIBS spectra of $BKNO_3$	Assignment using NIST atomic spectral database
247.88	C- (247.85)
249.73	B- (249.67,249.77)
250.69	Fe - (250.65)
251.63	Fe - (251.65)
252.42	Fe - (252.42)
277.99	Mg - (277.98)
288.18	Si - (288.15)
292.90	Fe - (292.90)
293.68	Mg - (293.65)
383.24	Mg - (383.23)
383.83	Mg - (383.82)
393.39	Ca^{+}- (393.36)
396.88	Ca^{+}- (396.84)
518.42	Fe - (518.426)
589.05	Na - (588.99, 589.59)
656.32	H- (656.5)
694.18	K - (693.87)
746.95	N (746.83)
766.86	K- (766.48)
770.07	K - (769.89)
777.31	O (777.53)
821.74	N (821.072, 821.63)
844.72	O (844.62, 844.63)
863.16	N - (862.92)
868.22	N (868.02, 868.34,)

Peaks observed in LIBS spectra of AP		Assignment using NIST database
Ns (nm)	fs (nm)	
588.96	588.96	Na (588.9)
589.60	589.60	Na (589.59)
656.36	656.35	H (656.27)
742.50		N (742.36)
744.33	744.33	N (744.22)
746.91	746.85	N (746.83)
777.50	777.20	O (777.19, 777.41.777.53)
818.57	818.57	N (818.48)
821.69	821.67	N (821.63)
824.41	824.41	N (824.23)
837.67	837.56	Cl (837.59)
844.72	844.62	O (844.67)
857.70		
859.64	859.54	N (859.40)
863.11	862.98	N (862.92)
865.64		N (865.58)
868.17	868.45	N (868.02, 868.34, 868.61)
871.35		N (871.17)
871.93		N (871.88)

Table 2 Summary of peak obtained in BPN ns LIBS spectra obtained using ICCD (left) and in AP LIBS spectra using ns and fs pulses using ICCS (top)

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