10th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy

EMSLIBS 2019

Brno | Czech Republic
8th – 13th September

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A non-calorimetric study of hygrothermal aging of pyrotechnic material by using Laser-Induced Breakdown Spectroscopy

EMSLIBS 2019

Ji-Hoon Ryu, Jun-Ho Yang, and Jack J. Yoh

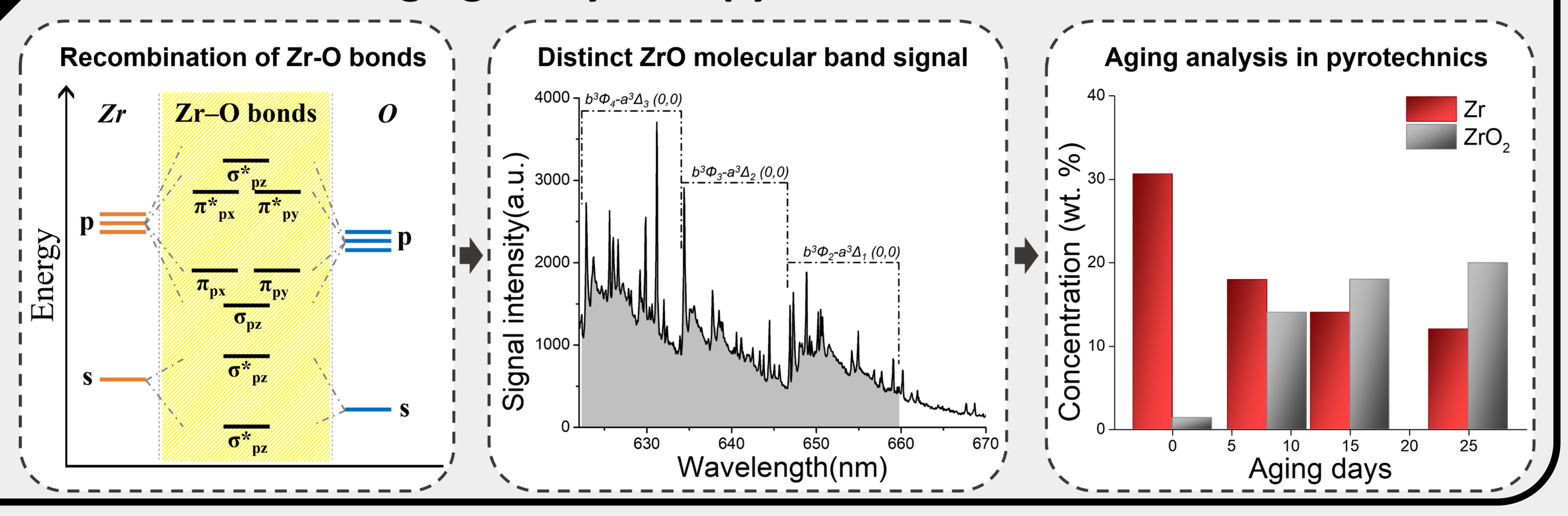
Department of Mechanical and Aerospace Engineering, Seoul National University, Seoul, 08826, South Korea

Ji-Hoon Ryu
(jhr7101@snu.ac.kr)

Highlights

- Estimate the aging level of pyrotechnics using LIBS
- Determine a composition changes of pyrotechnics with aging based on spectral results
- Novel spectroscopic study for predicting a thermal property

Direct aging analysis of pyrotechnics based on LIBS



Introduction

Pyrotechnics

The substances that emit high energy through combustion in a short time

Aging pyrotechnics

In long-term storage, aging is of critical concern
Aging in pyrotechnics is highly related to defense and economic issues

Thermal property ➡ **Performance** ➡ **Cost**

- Thermal property
  - Change of heat of reaction & burning rate
  - Decrease of reaction rate and exothermic heat
- Performance
  - Instability of ignition
  - Incomplete combustion
  - Deviation from intended performance
- Cost
  - Shortened life span
  - Increase in budget

Objective of research

What **Quantitative estimation of pyrotechnic delay according to aging level**
- Compositional changes
- Thermal performance (Heat of reaction)

How **2 spectroscopic methods & 1 calorimetric method**
- Laser-induced breakdown spectroscopy (LIBS)
- X-ray photoelectron spectroscopy (XPS)
- Differential scanning calorimetry (DSC)

Methods

Layout of Experiment

Spectroscopy
- **LIBS** – Laser induced breakdown spectroscopy: Determination of **pre-oxidation level of Zr fuel**
- **XPS** – X-ray photoelectron spectroscopy: **Chemical change of each oxidant**

Calorimetry
- **DSC** – Differential scanning calorimetry: **Energy release** of pyrotechnic delay

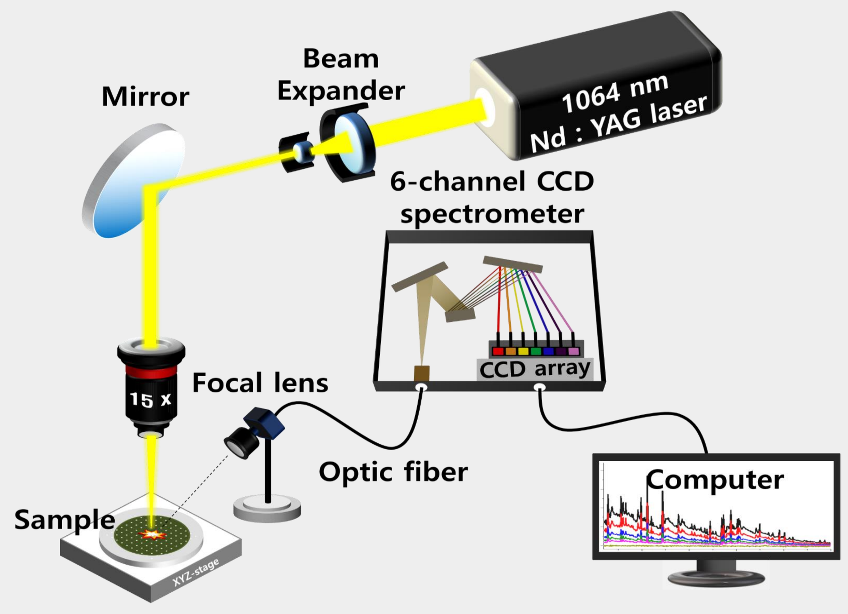
(NASA CEA code) **(AKTS program)**

Thermal performance (ΔH)

LIBS setup

Q-switched Nd:YAG laser (RT-250Ec)
- 1064 nm, 10 mJ (Energy), 5 ns (Duration)

ICCD camera
- Gate delay (0.5 μs), Gate width (1.05 ms)



Sample preparation

Pyrotechnic delay
- Fuel : Zr (32%)
  Oxidizer : $BaCrO_4$ (53%)
  $KClO_4$ (14%)
  Binder : Rareox#14 (1%)


Pyrotechnic delay

	Standard sample	Aging sample	
Zr	32 x	32	**<Aging conditions>** 71°C & RH 70%
ZrO_2	32 (1-x)	0	
$BaCrO_4$	53	53	**<Aging levels>** 0, 8, 15 and 25 days
$KClO_4$	14	14	
Binder	1	1	

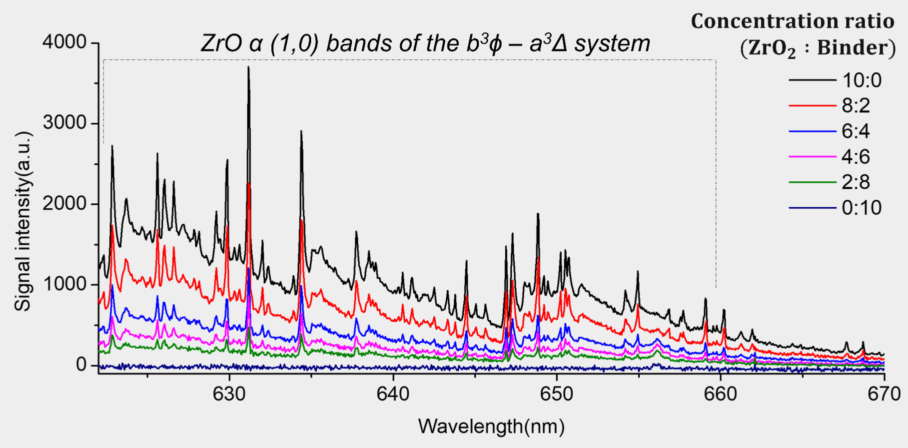
Note: x indicates $Zr/(Zr+ZrO_2)$ ratio ($0 < x < 1.0$)

Results

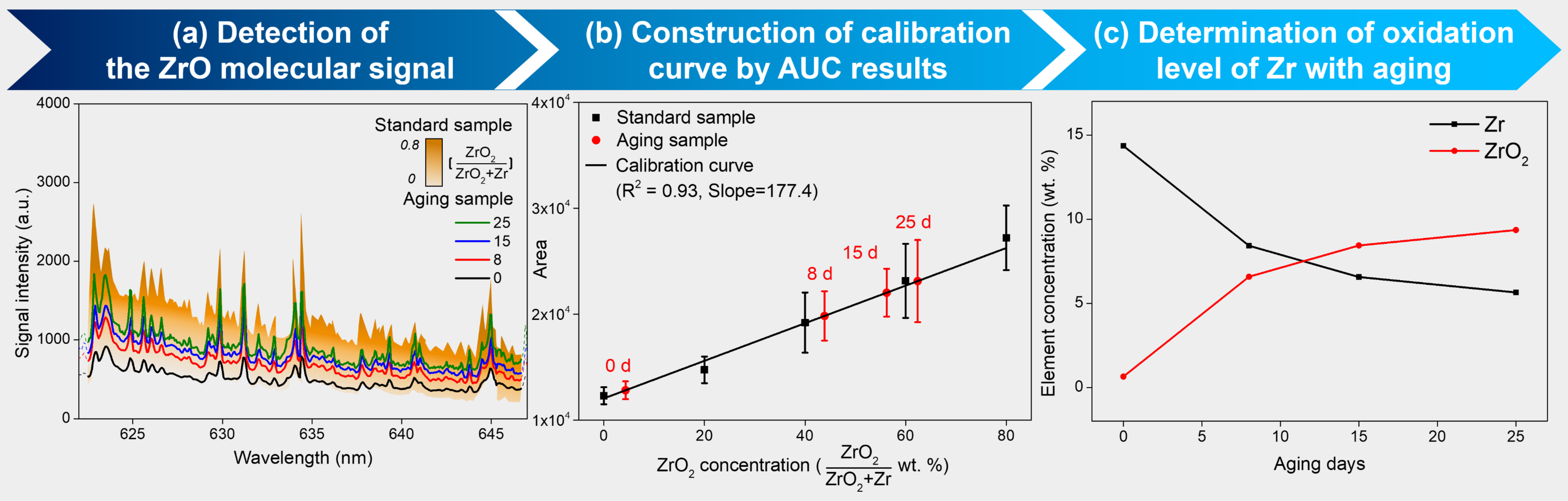
1. Validation for ZrO band signal

3 distinct ZrO transitions

Intensity of ZrO
- ZrO signal is highly related to Zr & ZrO_2
- ZrO signal increases as Zr turns to ZrO_2
- Binder is inactive to LIBS



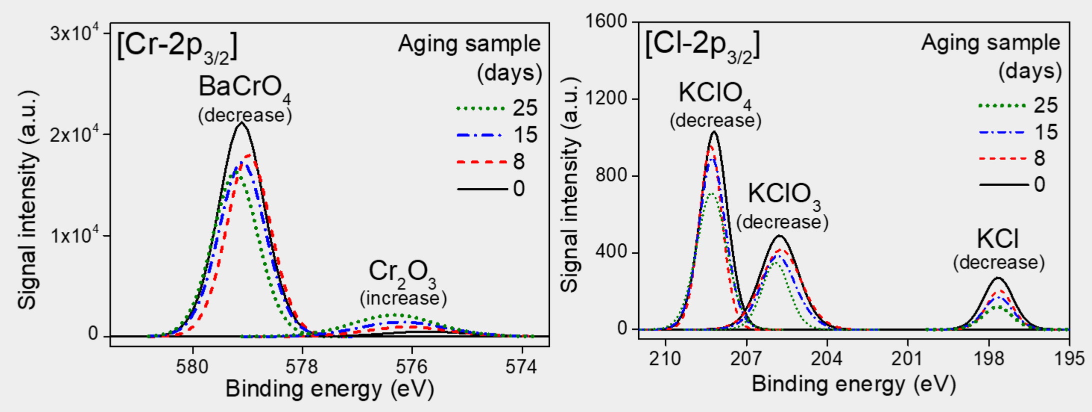
2. LIBS analysis (for fuel)



3. XPS analysis (for oxidizers)

$BaCrO_4$
- $BaCrO_4$ turns to Cr_2O_3

$KClO_4$
- $KClO_4$ turns to $KClO_3$, KCl
- The content of $KClO_x$ ($0<x\leq4$) gradually decreased



4. Compositional changes (for each element)

Integrate each spectral signal value

Fuel (by LIBS)
Oxidizer (by XPS)
Binder (Ignorable)

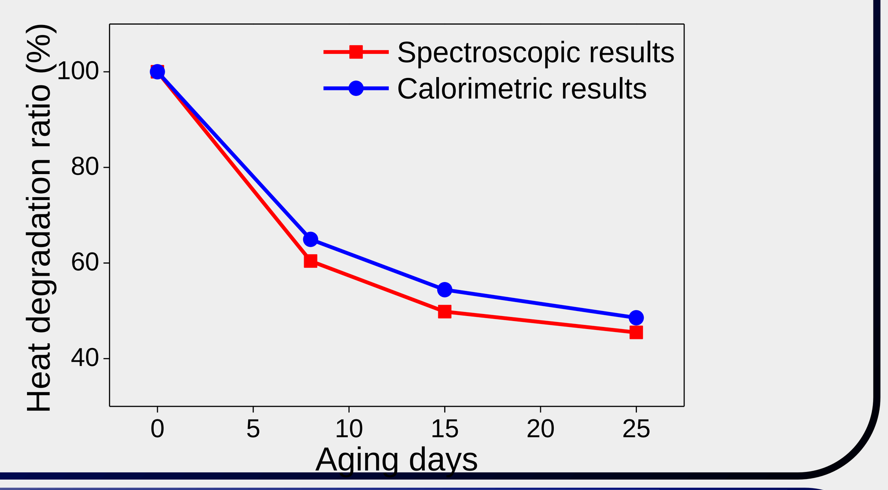
Aging days		0	8	15	25
Fuel	Zr	30.62	17.96	14.02	12.03
	ZrO_2	1.38	14.04	17.98	19.97
Oxidizer	$BaCrO_4$	52.27	50.34	48.92	46.84
	Cr_2O_3	0.72	2.66	4.08	6.16
	$KClO_4$	7.78	7.14	6.56	5.07
	$KClO_3$	3.68	2.92	2.50	2.11
	KCl	2.55	2.20	1.85	1.50

5. Thermal performance

Heat of reaction
- Spectroscopic > Calorimetric
- Limitation of DSC operating temperature

Aging days	Spectroscopic results (NASA CEA)		Calorimetric results (AKTS)	
	Heat of reaction [J/g]	Heat degradation ratio (%)	Heat of reaction [J/g]	Heat degradation ratio (%)
0	1,998.1	100.0	684.7	100.00
8	1,207.1	60.4	445.4	65.0
15	995.3	49.8	373.8	54.6
25	908.7	45.5	340.3	49.7

Heat degradation ratio
- The change in thermal performance is similar in both methods



Conclusion

- **We approached the pyrotechnics aging through the unique ZrO signal in LIBS.**
- **Through LIBS and XPS analysis, we were able to spectroscopically predict the thermal property of pyrotechnics, which was only performed by calorimetric.**

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A non-calorimetric study of hygrothermal aging of pyrotechnic material by using laser-induced breakdown spectroscopy

Ji-Hoon Ryu[1] Jun-Ho Yang[1] Jack J. Yoh*[1]

Email: jjyoh@snu.ac.kr

1. Department of Mechanical and Aerospace Engineering, Seoul National University

The degradation of thermal properties such as burning rate and exothermic heat of reaction due to aging is a serious issue associated with a long-term storage of a pyrotechnic material. This study investigates the effect of the excessive exposure to moisture for the aging pyrotechnic delays, composed of metal fuel (Zr) and oxidizers ($BaCrO_4$, $KClO_4$). The laser-induced breakdown spectroscopy (LIBS) was used to effectively obtain both molecular and atomic signals by detecting the zirconi-um-oxygen (Zr-O) bonds. The rising trend of a distinctive molecular signal provides meaningful interpretation of the oxida-tion level for metal fuel. The additional complementary spectroscopic techniques such as x-ray photoelectron spectroscopy and scanning electron microscopy were used to investigate the chemical changes in oxidizers and the physical changes in the fuel, respectively. As a result, one enriches the understanding of aging mechanism from the calorimetric assessment together with the spectroscopic analyses for the underlying cause of aging.

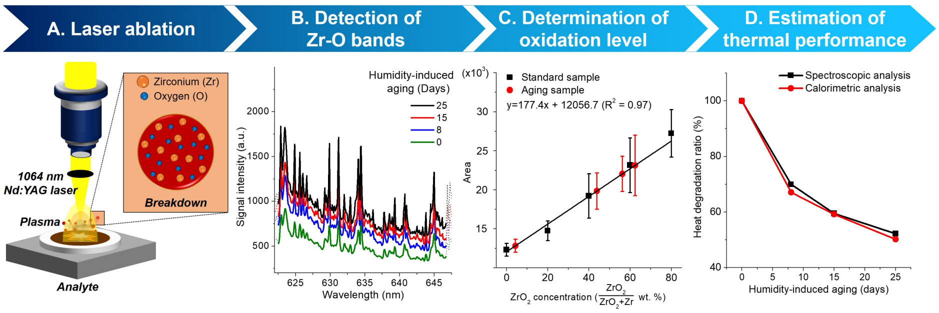

Fig1.: The experimental procedure utilizing LIBS for studying the aging mechanism.

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