

Long Wave-Infrared Laser-Induced Breakdown Spectroscopy Emissions from Potassium Chloride (KCl) and Sodium Chloride (NaCl) Tablets

Olusola O. Oyebola,* Muteeu A. Olopade and Kayode I. Ogungbemi
Department of Physics, University of Lagos, Akoka-Yaba, Lagos, Nigeria
*ooyebola@unilag.edu.ng

Abstract

Laser-Induced Breakdown Spectroscopy (LIBS) as a technique for determining the elemental composition of a chemical substance has been extended into the long wavelength infrared (5–10 μm) region. Pumping with a 1064 nm Nd:YAG pulse laser, long wavelength infrared emissions from LIBS plasma produced from potassium chloride (KCl) and sodium chloride (NaCl) were examined between 5 μm and 10 μm . Atomic emission lines with peaks around 4.9, 6.3, 7.4 and 8.5 microns were observed in the KCl sample while the NaCl sample produced emission lines with peaks around 5.0, 5.4, 7.4 and 9.0 microns. Compared with the National Institute of Standards and Technology (NIST) atomic spectra database, the 6.3 micron emission peaks observed in the KCl sample identifies the presence of potassium in the sample while all the observed lines in the NaCl sample are consistent with the NIST data, suggesting the presence of sodium in the sample. The emissions were studied both in air and under a nitrogen-purged environment in order to remove the possible effect of water (H_2O) and carbon dioxide (CO_2) absorption within that wavelength range. Our preliminary report indicates that the LIBS technique can be extended to the long wavelength infrared (IR) region for the identification of trace elements in materials.

Keywords: breakdown spectroscopy, infrared lasers, trace elements

Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is a technique used for investigating trace elements in materials (Cremers and Radziemski, 2006) and it has been widely investigated in the visible (Gonzaga and Pasquini, 2008) and near infrared (NIR) emission bands (Pasquini *et al.*, 2008). Much LIBS research has not been done beyond the NIR region. In fact, its debut appearance in the mid-infrared (MIR) region is due largely to the work carried out at Hampton University, United States (Yang *et al.*, 2007), where atomic transitions of potassium (K) and sodium (Na) within the 2–5 μm wavelength region were observed, consistent with the National Institute of Standards and Technology (NIST) standard data of atomic transitions (Ralchenko *et al.*, 2008; Yang *et al.*, 2008). In two recent publications, this group has extended the LIBS technique into the long wavelength infrared (4–12 μm) region, where they observed molecular emission signatures from some energetic materials (Yang *et al.*, 2012), and several organic pharmaceuticals (Yang *et al.*, 2014).

The observance of the atomic emission lines of potassium in the MIR region indicates that the LIBS technique can be used to investigate the constituents of a substance under ordinary atmospheric conditions given that the 2–5 μm region is the atmospheric window. However, it is not clear how atmospheric

conditions, particularly water and carbon dioxide (CO_2) absorption would influence the LIBS–infrared spectra in that region.

The goal of this research is to extend the study of the infrared LIBS spectra for KCl and NaCl to the long wavelength infrared (5–10 μm) region, both in air and under a nitrogen-purged environment to see the possible effect of water and CO_2 absorption.

Materials and Methods

The details of the materials preparation and the experimental setup for the LIBS–IR spectroscopy as well as the atomic emission lines corresponding to potassium in KCl and sodium in NaCl in the 2–5 μm spectral range have been described elsewhere (Yang *et al.*, 2007; Yang *et al.*, 2008; Oyebola *et al.*, 2011).

LIBS–IR experiments were performed on KCl and NaCl for the long-wavelength infrared (5–10 μm) region using a liquid nitrogen-cooled Mercury Cadmium Telluride (MCT) detector. Water and carbon dioxide absorption can hardly be ignored within this wavelength range. Hence the experiments were carried out both in air and under a nitrogen-purged environment. The nitrogen-purged environment was created by enclosing the LIBS–IR setup in a closed transparent box as shown in Figure

1. For effective nitrogen-purging, the optics of the LIBS-IR setup was realigned to reduce the entire optical path between the sample and spectrometer. The calcium fluoride (CaF₂) lenses were also

replaced with zinc selenide (ZnSe) lenses because long wavelength radiation is cut off by the former while the latter has an optical window that extends to the long wavelength region.

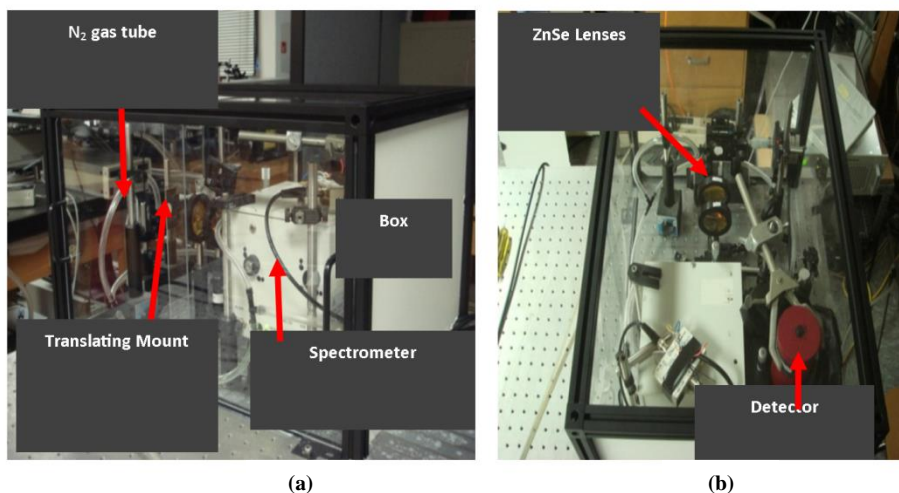


Figure 1: Photograph of the enclosed LIBS-IR setup showing the side view (a) and top view (b)

Results and Discussion

The 5–10 μm LIBS-IR spectra of KCl and NaCl in air and under nitrogen purging, are shown in Figure 2 and the transition assignments are given in Table 1.

In both samples, the nitrogen-purged spectra showed reduced emission intensities. However, the purging appeared to have removed much of the background observed in the spectra under air. In the KCl sample, only the 6.28 μm peak could be matched with the NIST data (Ralchenko *et al.*, 2008). It is interesting to note that the 7.44 μm peak appeared in both KCl and NaCl. A sodium (Na) emission line was clearly identified, as it well matches a distinct sodium emission line in the NIST data as shown in Table 1. However, the presence of the same line in the potassium spectrum would need to be further investigated, as there is no corresponding K match in

the NIST data. The appearance of transitions corresponding to K and Na in the samples investigated lends credence to the suggestion that the LIBS technique, operating in the long wave infrared region can be used for trace element identification.

Since it is a well-known fact that molecules exhibit spectroscopic signatures in the long-wavelength IR region due to vibrational and rotational transitions, the results presented here could also give further molecular information on the samples if they were exposed to further investigations, such as Fourier-transform infrared (FT-IR) spectroscopy. The instrumentation for the FT-IR investigation was not immediately available. These results are therefore preliminary but are quite suggestive of the suitability of long-wavelength infrared LIBS for trace element identification

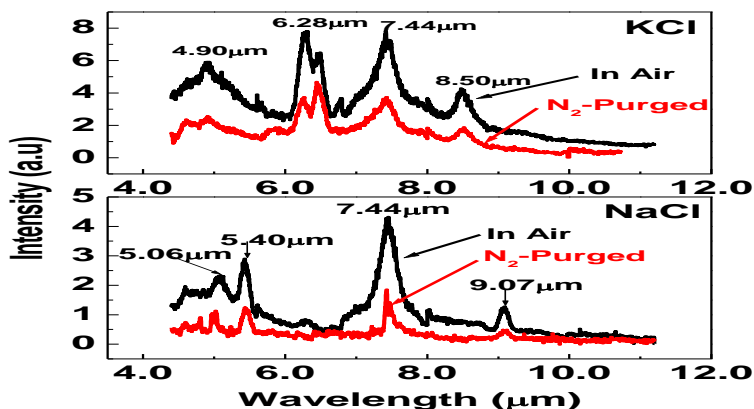


Figure 2: Overview LIBS-IR spectra for KCl and NaCl in the 5–10 μm region

Table 1: Transition Assignments of K and Na Atomic Transitions in the 5–10 μm range

	* λ_{obs} (μm)	** λ_{lit} (μm)	Transition Probability (s^{-1})	Assigned Transition	E_i (cm^{-1})	E_j (cm^{-1})
K	4.90			No NIST Data Available		
	6.26	6.21	7.8×10^5	$6^2\text{P}_{3/2} - 4^2\text{D}_{5/2}$	27397	29007
	7.44			No NIST Data Available		
	8.50			No NIST Data Available		
Na	5.06	5.02	1.69×10^6	$5^2\text{D}_{5/2} - 5^2\text{P}_{3/2}$	35042	37036
	5.40	5.43	1.43×10^6	$5^2\text{P}_{3/2} - 5^2\text{S}_{1/2}$	33200	35042
	7.44	7.43	1.95×10^5	$8^2\text{F}_{7/2} - 6^2\text{D}_{5/2}$	38387	39734
	9.07	9.09	1.43×10^5	$4^2\text{P}_{3/2} - 3^2\text{D}_{5/2}$	29172	30272

* Observed values of λ ** Values of λ obtained from the Literature (Ralchenko *et al.*, 2008; Yang *et al.*, 2008)

Conclusion

The MIR LIBS spectra of potassium chloride (KCl) and sodium chloride (NaCl) were observed showing distinct K and Na atomic transitions within the 5–10 μm wavelength range. The observed emissions and their assigned transitions are consistent with the NIST data of atomic transitions. This extends the application of the LIBS technique to the long IR wavelength region. As the mid-infrared LIBS technique is further developed, improvements in experimental conditions are expected to yield higher sensitivity and improved signal-to-noise ratios of the LIBS spectra.

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