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RELATIVE INTENSITY MEASUREMENTS OF LIBS EMISSION SPECTRA OF ALKALI HALIDES AND THEIR APPLICATION TO ELEMENTAL ANALYSIS OF MINERALOGICAL SAMPLES

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LIBS spectra were obtained for 20 alkali halides using a hand-held instrument. The intensities of the strongest emission lines were determined for Li, Na, K, Rb, Cs, F, Cl, Br, and I, and their corresponding electronic transitions assigned. Halogen peak intensities are observed to be at least two orders of magnitude smaller than those of the alkali metals. Thus, halogens are difficult to detect and identify with certainty. Relative intensity ratios of halogen/alkali metal aid in identification of those non-metals, particularly in mineralogical samples.

Keywords: *laser induced breakdown spectroscopy, electronic transitions, mineralogical samples.*

ИЗМЕРЕНИЯ ОТНОСИТЕЛЬНОЙ ИНТЕНСИВНОСТИ СПЕКТРОВ ИЗЛУЧЕНИЯ ГАЛОГЕНИДОВ ЩЕЛОЧНЫХ МЕТАЛЛОВ И ИХ ПРИМЕНЕНИЕ В ЭЛЕМЕНТНОМ АНАЛИЗЕ МИНЕРАЛОВ

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Зарегистрированы LIBS-спектры 20 щелочных галогенидов. Определены интенсивности наиболее сильных линий излучения Li, Na, K, Rb, Cs, F, Cl, Br, I и соотнесены с электронными переходами. Показано, что максимальные интенсивности линий галогенов по меньшей мере на два порядка меньше, чем у щелочных металлов, т. е. галогены трудно обнаружить и идентифицировать. Относительные соотношения интенсивностей излучения галогена и щелочного металла помогают идентифицировать указанные неметаллы, особенно в минералогических образцах.

Ключевые слова: *лазерно-искровая эмиссионная спектроскопия, электронный переход, минерал.*

Introduction. For decades, the Handbook of Chemistry and Physics was the source of spectroscopic emission data for nearly all the elements, based on flame, “arc,” and “spark” techniques [1]. The current online NIST tables [2] are more extensive, usually listing thousands of emission lines for a given element, and include information about specific electronic transitions and *J* transitions for most of the emission lines listed.

Laser induced breakdown spectroscopy (LIBS) is one technique replacing arc and spark methodology for elemental identification in samples. The online Army Research Laboratories website [3] lists some critical wavelengths for identification of many elements by LIBS, with journal article references, but at least 14 elements have no data on that website. The recently developed hand-held LIBS instruments are mobile, easy to use, less expensive, and known for rapid results. A built-in computer and spectral library conveniently provide a tentative analysis of the sample but sometimes fail to detect some elements present, particularly the rare earths, non-metals such as the halogens, or trace components. The important emission wavelengths for those elements with a LIBS instrument needed verification.

The initial goal was to create a large spectral library of elements, compounds, and mineralogical samples using a LIBS hand-held instrument, as well as to determine the strongest emission peaks for every available element. We have so far created a library of LIBS spectra of 77 elements and a large number of mineralogical samples.

Methodology and results. The SciAps LIBZ 300 GEO hand-held LIBS instrument used in this study provides essentially instantaneous emission data points every 0.033 nm over the wavelength range 188–950 nm using a pulsed 1064 nm Nd:YAG laser with an average pulse energy of 5.5 mJ and a pulse width of 2 ns. The sample is simply held directly in front of the instrument opening, the sample viewed through a magnified screen on the instrument, and the trigger pressed. Usually 12 laser shots strike the sample, for which the beam spot is about 100 μm. Three spectrometers are incorporated into the optical system. For the spectral region 188–365 nm, the first spectrometer has a spectral resolution of 0.18 nm full width at half maximum (FWHM). For the spectral region 365–620 nm, the second has a spectral resolution of 0.24 FWHM, and for the spectral region 620–950 nm, the third has a spectral resolution of 0.24 nm FWHM. Detector details are proprietary. The optical system is described in a US Patent [4].

The full printed spectrum of over 23,000 data points was initially visually examined for each sample to note the dominant emission peaks. Then the large numerical data base was examined in detail to determine the maximum intensity and wavelength of each of those peaks to five significant figures. Comparison to published data [1–3] confirmed the elemental identities.

The strongest peaks for metallic elements (as cations or atoms in solids) are generally rather high in intensity, the highest peaks for metals ranging from 4,000 up to 30,000 arbitrary units. In contrast, the strongest peaks for non-metal elements (as anions or atoms in solids) exhibit significantly lower peak intensities, often less than 1/100th those of the cations. Thus, detection and identification of non-metals is more challenging.

To establish the crucial emission wavelengths for the halogens using our LIBS instrument, we obtained the full LIBS spectra of twenty alkali halides (Li, Na, K, Rb, and Cs with F, Cl, Br, and I). Analyzing five different compounds for each halogen was intended to provide comparison and verification. Crystals at least 3 mm in diameter generally worked well, but powders or soft chunks could not be used, as the powders scattered, occasionally entering the "nose" chamber of the instrument. Deliquescent salts very quickly would absorb water, some literally within seconds. Methods we tried for challenging samples included using a small, hand-held pellet press, melting powders in a 6 cm diameter platinum dish using a Bunsen burner and allowing the solid to form quickly upon cooling, gluing tiny non-deliquescent crystals onto stiff card stock, or pressing them into a sliced paraffin candle.

Results and calculations are listed in Table 1. The wavelength of the most intense observed LIBS emission line for the cation and the anion in each compound and the measured intensities (arbitrary units) are listed, together with the calculated anion/cation ratios and uncertainties. The electronic transitions for the most intense cation peaks are for np^1–ns^1 (ground state) electronic transitions for Li, Na, K, and Rb, specifically, from $2p^1$–$2s^1$ for Li to $5p^1$–$5s^1$ for Rb. We have data for cesium for the $6p^1$–$6s^1$ transition, but it was not the most intense LIBS peak, so data are given for the $7p^1$–$6s^1$ cesium transition instead. The J transitions are all 3/2 to 1/2 for those cations.

The ground states for the anions end in np^5. The strongest peak for iodine is, indeed, for the expected transition from $6s^1$–$5p^5$, the ground state of iodine. The J transition for this iodine peak is from 3/2 to 1/2. Analogous transitions for the other halogens, $(n+1)s^1$ to np^5, are not detectable with our LIBS method, since the energies lie too far into the ultraviolet range (wavelengths less than 188 nm). According to NIST data [2], the expected wavelengths for the $(n+1)s^1$–np^5 transitions for F, Cl, and Br are at about 81, 119, and 132 nm, respectively. The most intense peaks for F, Cl, and Br we observed are for the $(n+1)p^1$–$(n+1)s^1$ transitions, specifically, $3p^1$–$3s^1$ for fluorine, $4p^1$–$4s^1$ for chlorine and $5p^1$–$5s^1$ for bromine. The J transitions for those three halogens are 7/2 to 5/2.

Finally, we determined the ratios of anion peak intensity/cation peak intensities for all 20 alkali halides, together with the estimated uncertainties in those measurements. Those ratios are all much lower than 1. These observations and results substantiate the fact that the halogens are more difficult to identify and confirm than metal atoms, even if they exist in a 1:1 atom ratio in the compound.

Mineralogical applications. Halogens are relatively uncommon in mineral samples, except for halite, NaCl, one of the most important and commonly found minerals on earth [5]. Even if the atom ratio of metal to halogen is 1:1 or 1:2, as in fluorite, CaF_2, it may be difficult to prove the identity of the halogen because the predicted ratio of peak intensities of the halogen to those of the metal in the sample is quite small. Most mineralogical samples that contain a halogen have a formula that indicates far fewer atoms of the halogen compared to atoms of other elements, further complicating the challenge of elemental identification or verification.

TABLE 1. Wavelength, Intensities, and Intensity Ratios for LIBS Analysis of Alkali Halides

Alkali halide	λ_{cation}, nm	I	λ_{anion}, nm	I	$I_{\text{anion}}/I_{\text{cation}}$	Uncertainty
LiF	670.71	12770	685.6	48.6	0.00381	0.0002
NaF	589.0	13357	685.6	79.9	0.00598	0.0001
KF	766.5	3885	685.6	12.6	0.00324	0.0004
RbF	780.17	2800	685.6	17.0	0.00668	0.0009
CsF	455.66	3990	685.6	47.5	0.01190	0.0008
LiCl	670.71	5283	837.6	55.1	0.0104	0.0001
NaCl	589.0	26700	837.6	485	0.0182	0.0002
KCl	766.5	3260	837.6	72.6	0.0223	0.0015
RbCl	780.17	9455	837.6	430	0.0455	0.0012
CsCl	455.66	3343	837.6	91.4	0.0273	0.0010
LiBr	670.71	4553	827.27	44.4	0.0098	0.0003
NaBr	589.0	15360	827.27	481.0	0.0346	0.0006
KBr	766.5	9296	827.27	537.6	0.0578	0.0021
RbBr	780.17	5884	827.27	577	0.0981	0.0045
CsBr	455.66	1901	827.27	360.9	0.1898	0.0034
LiI	670.71	3943	206.17	455	0.1154	0.0005
NaI	589.0	10140	206.17	342	0.0337	0.0005
KI	766.5	2873	206.17	405	0.1410	0.0063
RbI	780.17	3124	206.17	405	0.1296	0.0034
CsI	455.66	2102	206.17	297	0.1413	0.0034

For an unknown mineralogical sample or to verify the elemental composition of a mineral known to contain a halogen, the appropriate intensity ratio from Table 1 could be multiplied by the intensity of the dominant alkali metal peak in the sample's spectrum to determine the expected intensity of a possible F, Cl, Br, or I in the sample. This approach may help distinguish some peaks from noise.

For example, a small, white, fairly translucent crystalline sample is supposedly cryolite, Na_3AlF_6. Its LIBS spectrum was obtained (Fig. 1a). The sodium line at 589.0 nm has an intensity of 5349, which is quite low compared to the intensity of the sodium line in most samples, probably due to the translucency of the sample. Using the F/Na ratio of 0.00598, the expected intensity of the fluorine emission line at 685.6 nm is calculated to be near 32. Although not visually obvious on the full spectrum, an expansion of the 680 to 700 nm region of the spectrum (Fig. 1b) shows the fluorine line to appear with an intensity of about 42, not much more than base noise, but it is there, along with the additional 690.25 nm fluorine peak. The strongest aluminum lines are clear at 309.27 and 396.12 nm, confirming the identity of the sample.

Sodalite is a deep blue mineral with the formula $Na_4Al_3Si_3O_{12}Cl$. The chlorine component is quite likely to be difficult to confirm with LIBS, due to the fact that only one Cl atom is found for every four Na atoms, plus the Al, Si, and O atoms. The intensity of the sodium line in a sodalite spectrum (Fig. 2a) is 10,972, which, multiplied by the Cl/Na ratio of 0.0182, gives a predicted intensity for Cl of about 200. However, if we divide that value by 4, considering the mineralogical formula, the intensity of the 837.6 nm peak should be about 50. In actuality the intensity of the Cl peak was ~22 (Fig. 2b). The strongest aluminum peak is at 396.13 nm and the strongest silicon peak is at 288.13 nm.

Fluorite, CaF_2, contains no alkali metal, so the calculated ratios in Table 1 cannot be used but simply indicate the likelihood of a low intensity fluorine peak compared to the calcium peaks. The LIBS spectrum of a dark green fluorite sample showed an intensity of about 30,800 (Fig. 3a) for the calcium peak at 393.3 nm, and an intensity of ~205 at 685.6 nm (Fig. 3b) for fluorine, verifying its presence. Note also a second fluorine peak at 690.25 nm. Interestingly, the F/Ca intensity ratio 0.0067 is not drastically different from the F/alkali halide ratios in Table 1.

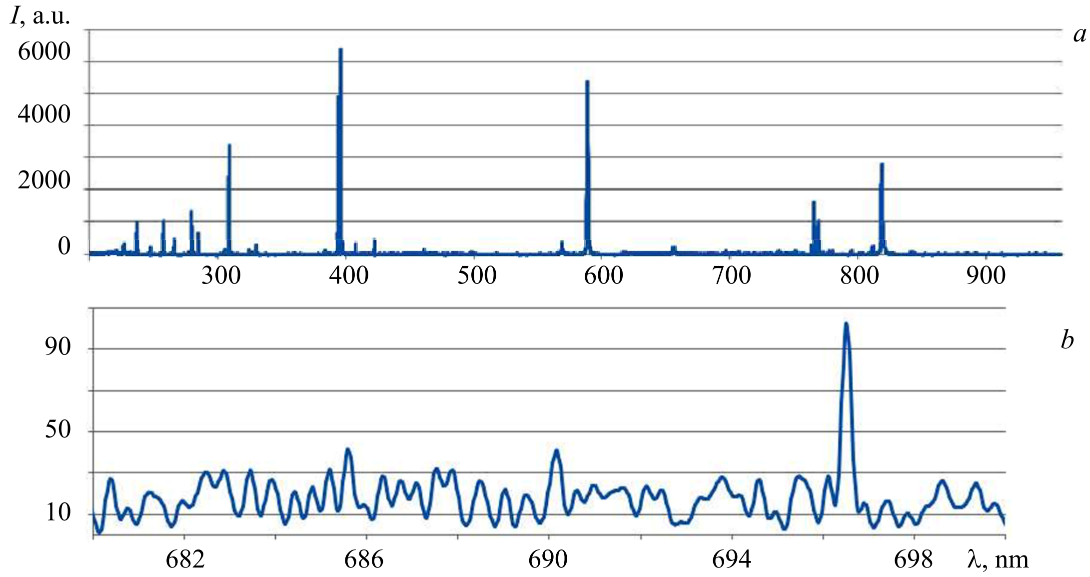


Fig. 1. LIBS spectrum of cryolite, Na_3AlF_4, region (a) 200–960 and (b) 680–700 nm, F peaks at 685.6 and 690.2 nm are visible.

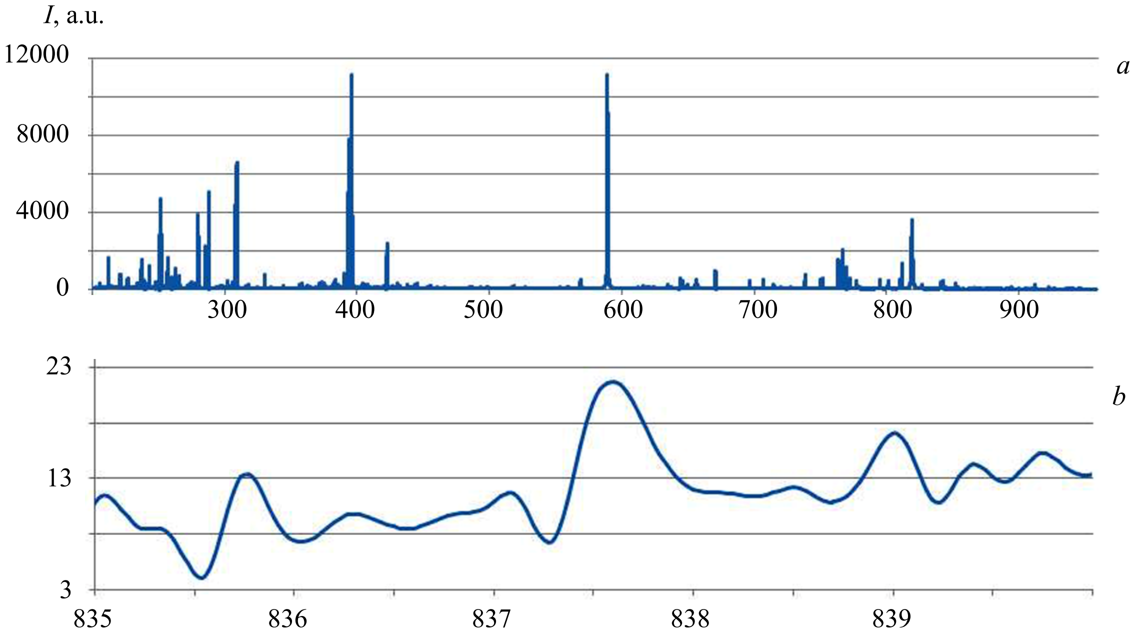


Fig. 2. LIBS spectrum of sodalite, $Na_4Al_3Si_3O_{12}Cl$, region (a) 200–960 and (b) 835–840 nm, Cl peak observed at 837.6 nm.

Topaz has the mineralogical formula $Al_2SiO_4(F,OH)_2$. Does a sample of yellow topaz from Topaz Mountain in Utah contain fluorine or hydroxide (or both) ions? Since no alkali metal was present, intensity ratios in Table 1 could not be used. The LIBS spectrum of the topaz sample showed no conclusive evidence for fluorine peaks above noise, but the small hydrogen peak at 656.3 confirmed OH (Fig. 4a). The LIBS results do not exclude the possibility that trace amounts of fluorine may also be present and might be verified by other methods. As with all the samples in this study, the elemental characterization of the topaz sample was then sought by using SEM-EDS analysis with a Phenom Pro-X instrument (Nanoscience). The SEM-EDS results indicated the presence of Al, Si, O, and F (Fig. 4b). SEM cannot detect the presence of hydrogen. Thus, the topaz sample likely contains both F and OH.

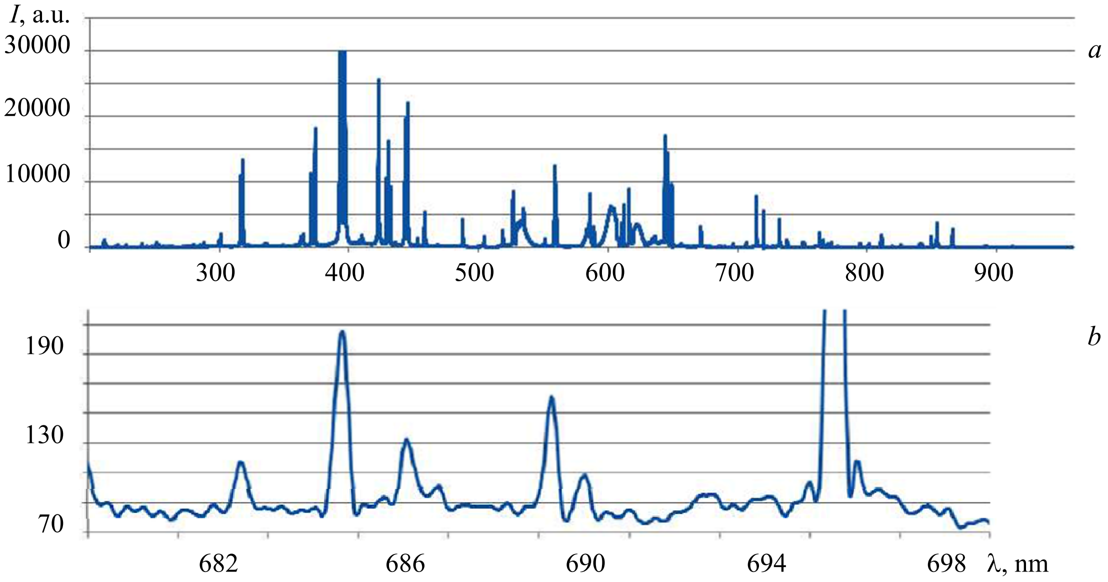
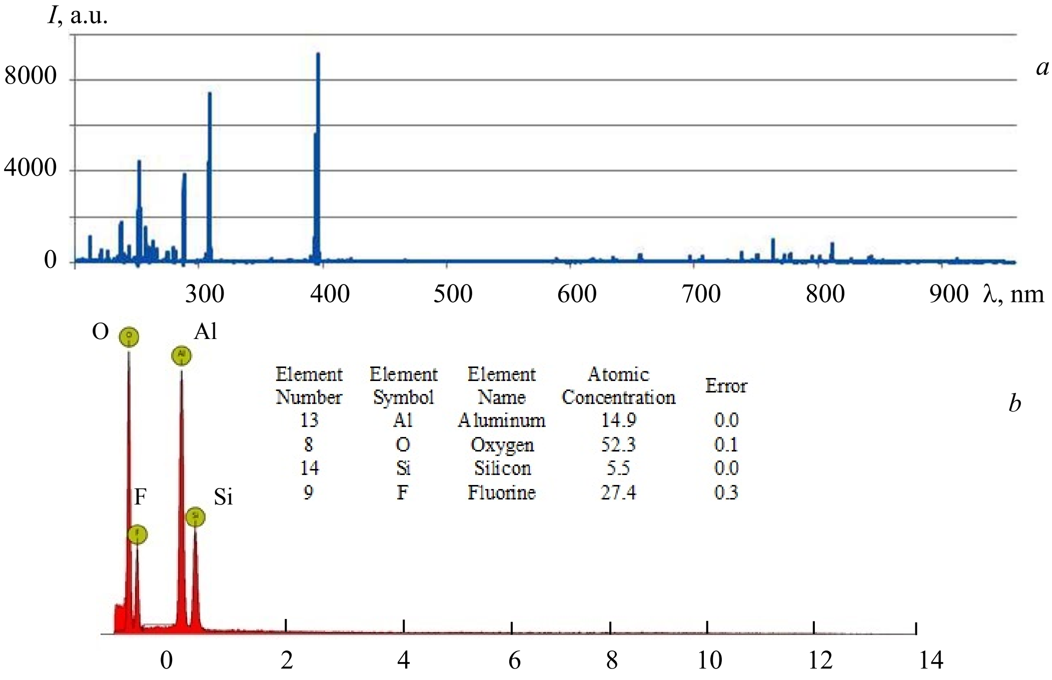


Fig. 3. LIBS spectrum of fluorite (dark), region (a) 200–960 and (b) 680–700 nm, F peaks at 685.6 and 690.3 nm.



Element Number	Element Symbol	Element Name	Atomic Concentration	Error
13	Al	Aluminum	14.9	0.0
8	O	Oxygen	52.3	0.1
14	Si	Silicon	5.5	0.0
9	F	Fluorine	27.4	0.3

Fig. 4. LIBS spectrum (a) and SEM-EDS analysis (b) of topaz, $Al_2SiO_4(F,OH)_2$.

Conclusions. The intensities of LIBS peaks for metals are generally at least two orders of magnitude larger than the intensity of LIBS peaks for halogens, resulting in the halogens being far more difficult to confirm by this method. This is even true if the cation/anion ratio is 1:1 (as in the alkali halides) or even 1:2 (as in fluorite, CaF_2). The ratios of intensities of halogens/alkali metals have been calculated from careful examination of LIBS spectra and used to help confirm the presence of halogens in a variety of salt and mineralogical samples.

One would expect that the LIBS intensities for other non-metals, such as C, N, S, O, and P, would also be quite low compared to intensities of metals. Our LIBS spectra of numerous compounds and mineralogical samples containing those elements show this to be true. Communication with the authors regarding examples of our analyses involving those elements is welcome.

Note that the intensity of the emission peaks using the hand-held LIBS instrument may depend on the absorption of the laser light, the extinction coefficient of the alkali halide, the thermal properties of the materials, the wavelength of the laser, the temperature of the sample, the ground state electron configuration itself, and/or some other factor. Thus, the proposed procedure of verification of the existence of halogens in mineral samples based on measured relative intensity ratios of halogen/alkali metal can be preliminary and should be confirmed by other techniques.

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