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BORON ISOTOPIC RATIO (δ^{11}B) MEASUREMENTS IN BORON CARBIDE (B_4C): BENCHMARKING BETWEEN SF-ICP-MS AND PIGE TECHNIQUES[†]

Dmytro Kutnii*, Stanislav Vanzha, Dmytro Burdeynyi, Volodymyr Levenets, O. Omelnik, A. Shchur

National Science Center "Kharkiv Institute of Physics and Technology" of NAS of Ukraine
**Corresponding Author: d_kutniy@kipt.kharkov.ua*
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The results of comparing the analytical capabilities of Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS) and Particle Induced Gamma-ray Emission (PIGE) methods for determining the $^{11}B/^{10}B$ isotope ratio in boron carbide samples (B_4C) are presented. The following nuclear reactions excited by protons on the stable boron isotopes are considered: ^{10}B(p,αγ)^{7}Be, ^{10}B(p,pγ)^{7}Be and ^{11}B(p,γ)^{12}C. The optimum proton energy range was determined to be within 550 to 600 keV, while the energies of the induced gamma-radiation that can be used for quantitative estimation of the boron isotopes were 429 keV and 4439 keV for the isotopes ^{10}B and ^{11}B, respectively. Considering the uncertainties of measurements, the data for the $^{11}B/^{10}B$ isotope ratios, measured by the SF-ICP-MS and PIGE methods, are found to correlate with each other; yet they are characterized by a systematic bias. The uncertainty of measurements by the PIGE method was somewhat higher in comparison with SF-ICP-MS, and ranged from ± 4.1 % to ± 4.3 %, and from ± 1.1 % to ± 3.5 %, respectively.
Keywords: ICP-MS, PIGE, boron carbide, isotopic ratio, nuclear application, benchmarking
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Boron has two naturally occurring isotopes ^{10}B (19.9 %) and ^{11}B (80.1 %). Due to a relatively large mass difference (10 %) between the two isotopes and high volatility, the boron isotopic ratio ranges from − 70 to + 60 % in natural materials (rocks, natural waters and sediments), and is used as a tracer for studying continental weathering, plate subduction processes, pH variability in the oceans and anthropogenic pollution [1]. Boron isotopic ratios are conventionally expressed in delta notation ($\delta^{11}B$), which denotes the deviation of measured $^{11}B/^{10}B$ ratios from the standard (in parts per thousand), using the equation below [2]:

$$\delta^{11}B(\%) = \left[\frac{(^{11}B/^{10}B)_{meas.}}{(^{11}B/^{10}B)_{NIST\,951}} - 1\right]\cdot 10^3 ,$$

where $(^{11}B/^{10}B)_{NIST\,951} = 4.04362 \pm 0.00137$ is the abundance ratio from the accepted international reference material NIST SRM 951 (boric acid).

The accurate knowledge of the boron isotope ratio is of particular importance for neutron-absorbing materials in nuclear reactors. In a boiling water reactor (BWR) and a fast breeder reactor (FBR), boron carbide (B_4C) serves as a neutron-absorbing material for the control rods. Furthermore, in a pressurized water reactor (PWR), a solution of boric acid (H_3BO_3) is added to the primary cooling water to adjust the reactivity of the reactor core [3]. The boron isotopic ratio is one of the most important parameters that qualifies the applicability of B_4C in the nuclear reactor, considering due to the fact that the isotope ^{10}B has a significantly higher thermal neutron absorption cross-section compared to ^{11}B, namely 3840 barn vs. about 0.005 barn [4].

The isotope composition control is also of importance for predicting the material behavior under irradiation conditions, when even a minor variation in the isotopic abundance ratio may cause a substantial change in material properties.

The traditional method for determining the isotopic composition of boron ($\delta^{11}B$) most accurately (RSD of ± 0.3 %) is the thermal ionization mass-spectrometry (TIMS). Other mass-spectrometric methods with ionization in inductively coupled plasma (ICP-MS) are also widely used for measuring various isotopic ratios. In the boron analysis case, the MC-ICP-MS multicollector systems can provide measurement uncertainty ± 0.2 %. For double focusing sector field mass-spectrometers SF-ICP-MS, the typical value of uncertainty is ± 2 %, and for quadrupole-based mass-spectrometers Q-ICP-MS it makes $\delta^{11}B$ ± 15 % [5-8].

Furthermore, for isotopic analysis, nuclear physics methods are also used, which involve the Rutherford ion backscattering spectrometry, and also, the nuclear reactions excited by charged particles and neutrons on different isotopes of one and the same chemical element [9-11].

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This paper presents the results of benchmarking between the SF-ICP-MS and PIGE methods at determining the $^{11}B/^{10}B$ isotope ratio in boron carbide samples (B_4C). The traditional mass-spectrometric methods for determining isotopic composition provide high precision, but, on the other hand, often require labor-intensive sample preparation, such as chemical purification of the analyte, and expensive auxiliary equipment. In this context, the PIGE is considered as an alternative nondestructive express-method for measuring the ^{10}B and ^{11}B isotopic abundance in the field of nuclear applications.

MATERIALS AND METHODS

The samples used in the measurements were B_4C powders with different particle sizes varying from 50 to 70 μm. For purposes of the studies, pellets-targets were prepared from boron of natural isotopic composition and ^{10}B enriched. The pellets of diameter 9 mm were made by pressing the B_4C powder under pressure of 25 kg/cm^2 for 3 minutes.

Amorphous boron powder enriched to 96.2 % at. in the ^{10}B isotope (produced by the National High Technology Centre of Georgia) was used as a reference material to assure the accuracy of boron isotope measurements and to correct the isotopic ratios in the samples for mass bias. No additional drying or homogenization was carried out on the reference material.

The boron isotope measurements were performed using a double-focusing magnetic sector inductively coupled plasma mass spectrometer equipped with a single electron multiplier SF-ICP-MS ELEMENT 2 (Thermo Fisher Scientific GmbH, Germany); its technical characteristics are given in Table 1. All measurements were carried out in the low mass resolution mode ($m/\Delta m = 300$).

Table 1. Technical characteristics of SF-ICP-MS ELEMENT 2

Mass range	from 2 to 264 a.m.u.
Sensitivity	~ 10^6 cps for 1 ppb ^{115}In
Detection limit	1 ppq for non-interfering elements
Dark noise	< 0.2 cps
Dynamic range	> 10^9
Mass resolution	low (300), middle (4000), high (10000) at 10 % peak height
Signal stability	better than 1 % for 10 min.

Thermo Tuning Solution A, containing the elements ^{7}Li, ^{9}Be, ^{59}Co, ^{115}In, ^{138}Ba, ^{140}Ce, ^{206}Pb and ^{238}U at 10 μg L^{-1}, was used for tuning.

The samples were introduced into the SF-ICP-MS through a Nd:YAG deep UV (213 nm) laser ablation system NWR-213 (New Wave Research, Inc., USA). The generated plume was transported from the laser ablation cell to the SF-ICP-MS plasma by means of a laminar flow of Ar gas. Further details on the optimized instrumental settings as well as on the applied data acquisition parameters are reported elsewhere [12].

The nuclear physical analytical complex SOKOL (NSC Kharkiv Institute of Physics and Technology, Ukraine) was used to determine the boron isotopic ratio by the PIGE method [13].

The targets were placed into the multi-position cassette located in the irradiation chamber, which was evacuated to a pressure lower than 10^{-6}MPa, and were alternately exposed with a proton beam under identical conditions. The current integrator was used to measure the proton beam current, while the chamber itself, being out of contact with the ion guide, the vacuum and adjusting systems served as a Faraday cup.

The accelerator energy calibration was performed against the resonances of 991.2 keV protons and 1779 keV gamma-quanta from the ^{27}Al(p,γ)^{28}Si reaction.

The protons were incident on the target along the normal to its surface. The beam projection on the target represented a circle 3 mm in diameter.

The gamma-quanta were registered by a Ge(Li) detector located outside the chamber, at a distance of 1.5 cm from the target and at a 0° angle to the proton beam direction. The energy resolution (FWHM) of the detector at the 661 keV line was 1.5 keV.

The characteristic X-ray excited in the samples was registered by a Si-pin detector with the crystal measuring 3 mm × 500 μm. The detector, having the 165 keV energy resolution at 6.4 keV line, was located outside the chamber, at a distance of 4.5 cm from the target and at a 135° angle to the proton beam direction. The characteristic X-ray was extracted from the chamber and was guided to the detector through the window made from a 25μm thick Be-foil. A polyethylene absorber 150 μm thick was used to suppress low-energy radiation. To eliminate the edge effects during the X-ray registration by the detector, a 5 mm thick aluminum collimator, having a hole with diameter of 1.5 mm, was arranged between the detector and the target.

The optimum measuring conditions have been established and a series of measurements of gamma-ray spectra from both natural and ^{10}B-enriched samples was performed. In the experiments, the proton energy was 600 keV, the beam current – 500 nA, the proton charge on the target varied from 200 to 500 μC. Five replicate measurements were performed for each of the samples.

The prepared sample pellets were placed into the laser ablation chamber. The raw data obtained by the SF-ICP-MS analysis were first corrected for the gas blank. The boron isotopic ratios were calculated subsequently as the ratios of the background-corrected signals after ablation. All the results reported here are based on five replicate measurements of each sample. All indicated uncertainties are the combined standard uncertainties and include a coverage factor of 2.

The mass bias correction was calculated using a boron powder enriched in the ^{10}B isotope to 96.2 % at. The signal intensity ratio of each sample was corrected by multiplying the mass bias coefficient thus obtained from the signal intensity ratio of boron powder enriched in the isotope ^{10}B .

For many years now the nuclear physics methods have been used for the analysis of elemental and isotopic composition of substances, as well as for studies of spatial distribution of matrix and impurity elements, including the depth distribution gradients, i.e., the concentration profiles [14].

Table 2 lists the data for proton-excited nuclear reactions on stable boron isotopes, which can be used to determine the isotopic composition.

Table 2. Data for proton-excited nuclear reactions on stable boron isotopes

Reaction	Gamma energy, keV	Resonance energy, keV	Resonance width, keV	Resonance cross-section, barn	Reference
$^{10}B(p,\alpha\gamma)^{7}Be$	429	None	-	-	[15]
$^{10}B(p,p\gamma)^{7}Be$	718	None	-	-	[15]
$^{11}B(p,\gamma)^{12}C$	4439, 11680, 16110	163	7	0.157	[16]

As is evident from Table 2, for determination of the ^{10}B isotope, gamma-quanta of energies 429 keV and 718 keV can be used. In the process, as the experimental data demonstrate, the 429 keV radiation appears much more intense. For the ^{11}B isotope analysis, it is advantageous to use 4439 keV gamma-quanta, because the registration efficiency of 11680 keV and 16110 keV quanta is appreciably lower. In the proton energy range up to 600 keV, the contribution of 4439 keV gamma-quanta to the peak is mainly due to the resonance at a proton energy of 163 keV, and hence, the radiation intensity in this energy range remains essentially the same. Yet, at proton energies above 600 keV, the emission of 429 keV gamma-quanta from the $^{10}B(p,\alpha\gamma)^{7}Be$ reaction substantially increases, and this complicates the operation of the spectrometer. Then, for determination of the boron isotopic composition, it is expedient to measure the gamma-ray spectra at proton energies ranging from 550 to 600 keV.

RESULTS AND DISCUSSIONS

Figures 1a, 1b show the gamma-ray spectra, measured under the above-described conditions, with the use of samples from boron of natural composition and boron enriched in the ^{10}B isotope.

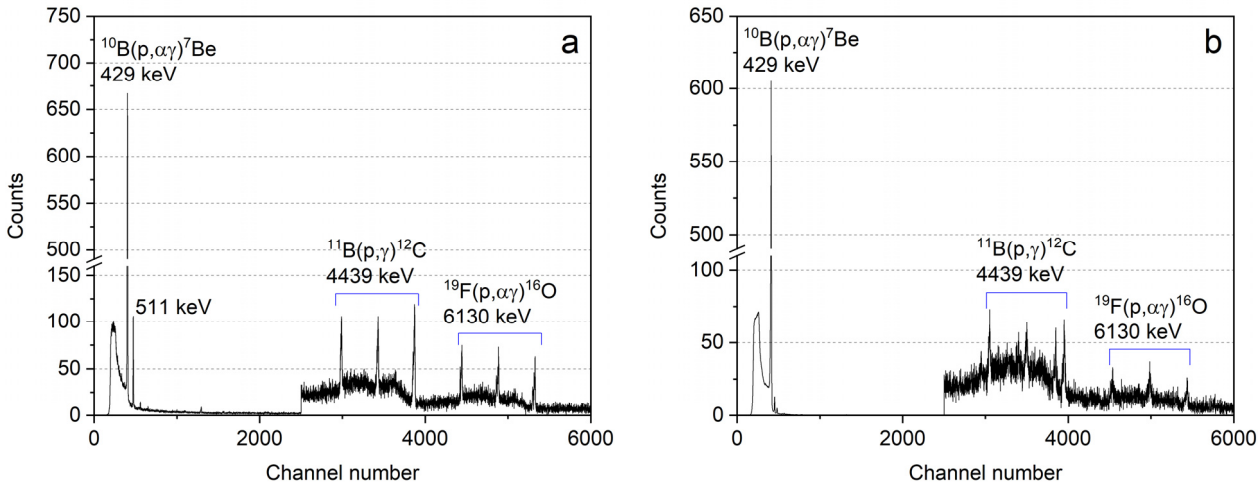

Figure 1. Spectra of gamma radiation induced by proton irradiation of boron samples: a – sample of natural isotopic composition; b – sample enriched with ^{10}B

As is obvious from the spectra, in the proton energy range under consideration, the gamma-radiation intensity resulting from the reaction on the ^{10}B nuclei is considerably higher than that from the reaction on the ^{11}B nuclei. With increase in the proton energy, the intensity of the 429 keV gamma radiation from the $^{10}B(p,\alpha\gamma)^{7}Be$ reaction strongly increases, thereby complicating the operation of the spectrometer, in particular, for registration of a substantially less intense 4439 keV gamma-rays from the $^{11}B(p,\gamma)^{12}C$ reaction.

Figure 2 shows the SF-ICP-MS and PIGE measurement data on the $^{11}B/^{10}B$ isotopic ratios for four B_4C samples in comparison with the reference $(^{11}B/^{10}B)_{NIST951}$ values.

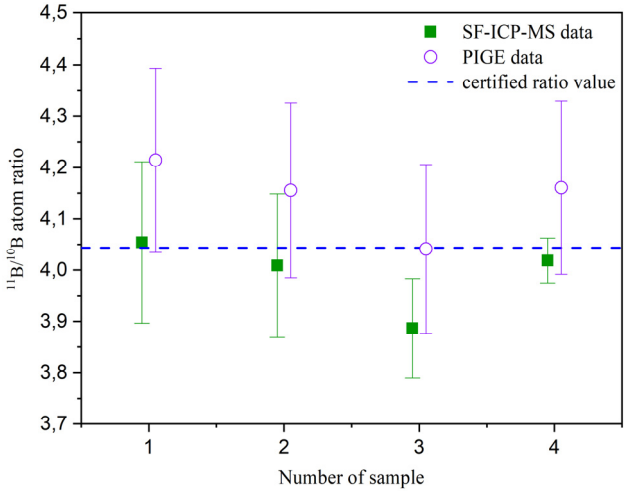

Figure 2. $^{11}B/^{10}B$ isotopic ratios in four samples of boron carbide measured by SF-ICP-MS and PIGE methods vs accepted international reference value 4.04362 ± 0.00137

With allowance made for the uncertainties of measurements, the data are seen to correlate between themselves, but at the same time, they are characterized by a systematic bias. The use of the SF-ICP-MS technique allows one to assume that the isotopic composition of one of the B_4C samples under analysis is probably not natural, whereas the PIGE data show no difference in the said samples. On the whole, the uncertainty of the PIGE data appears somewhat higher compared to the SF-ICP-MS measurement results, ranging from ± 4.1 % to ± 4.3 % versus ± 1.1 % to ± 3.5 %, respectively.

Figures 3 and 4 show the estimates of statistical correlation and agreement of the SF-ICP-MS and PIGE measurement data, as determined by the regression analysis and the Bland-Altman comparison, respectively.

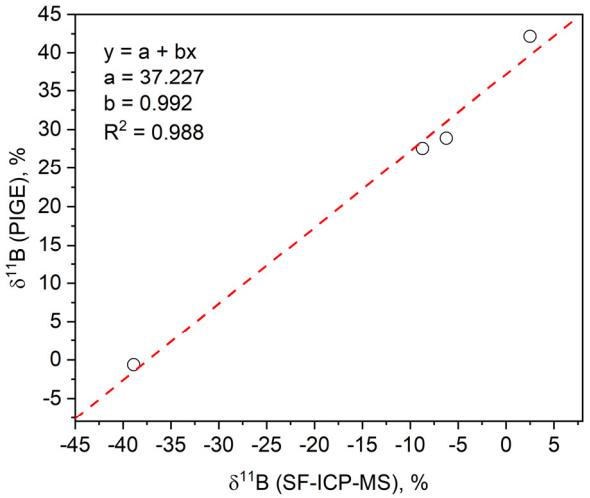

Figure 3. Relation between $\delta^{11}B$ determined by both SF-ICP-MS and PIGE for all B_4C samples and their linear approximation

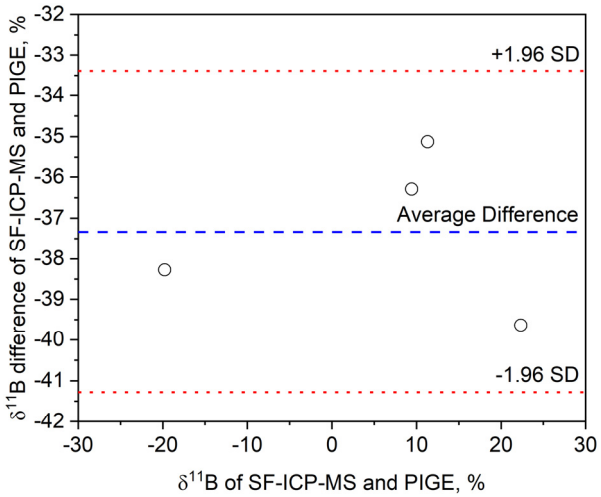

Figure 4. Bland-Altman comparison of the SF-ICP-MS and PIGE $\delta^{11}B$ determinations of B_4C samples

As can be seen from the scatter diagram in Fig. 3, there is strong correlation between the two methods. The calculated linear regression equation is given by: $y = 37.227 + 0.992 \cdot x$ with the coefficient of determination (R-Square) being close to 1. But, it is important to note that the correlation is not the same as the agreement. In some cases, the regression analysis may lead to improper conclusions. This just relates to the problems of comparing two measuring techniques, when the choice of independent variable is ambiguous.

In order to more readily see the difference between the two measurement techniques, it is useful to plot the means of each pair of measurements versus the difference between the measurements. Such a plot is known as the Bland-Altman Plot, which is shown in Fig. 4. The average difference in $\delta^{11}B$ values measured by SF-ICP-MS and PIGE is – 37.3 and there is no tendency for the difference to vary with variation of isotopic ratios. The limits of agreement within 95 % of the differences expected were calculated according to the Bland-Altman approach as to be – 41.3 and – 33.4. The

agreement of the SF-ICP-MS and PIGE methods is confirmed by the fact that the values in Fig. 4 are clustered around the mean of the differences, and certainly within two standard deviations of the mean.

CONCLUSIONS

Benchmarking assessment of the boron isotopic ratio values measured in boron carbide by both the SF-ICP-MS and PIGE techniques has been performed. As nuclear reactions excited by protons on stable boron isotopes, consideration has been given to the $^{10}B(p,\alpha\gamma)^{7}Be$, $^{10}B(p,p\gamma)^{7}Be$ and $^{11}B(p,\gamma)^{12}C$ reactions. The optimum proton energy range has been determined to be between 550 and 600 keV. The induced gamma-radiation energies, which may be used for quantitative estimation of boron isotopes, have been found to be 429 keV and 4439 keV for the isotopes ^{10}B and ^{11}B, respectively. It has been demonstrated that with allowance for measurement uncertainties, the isotopic ratio $^{11}B/^{10}B$ values measured by the SF-ICP-MS and PIGE methods correlate with each other, yet at the same time, are characterized by a systematic bias. The uncertainty in the PIGE data is somewhat greater compared to the SF-ICP-MS data, namely, it varies from ± 4.1 % to ± 4.3 % and from ± 1.1 % to ± 3.5 %, respectively. The agreement of the SF-ICP-MS and PIGE methods has been confirmed by the Bland-Altman comparison.

ORCID IDs

Kutnii Dmytro, https://orcid.org/0000-0001-9591-4013; **Vanzha Stanislav**, https://orcid.org/0000-0003-0949-947X
Burdejnyi Dmytro, https://orcid.org/0000-0003-4431-7264; **Volodymyr Levenets,** https://orcid.org/0000-0002-6439-0576

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ВИМІРЮВАННЯ ІЗОТОПНОГО СПІВВІДНОШЕННЯ БОРУ ($\delta^{11}B$) У КАРБІДІ БОРУ (B_4C): ПОРІВНЯННЯ МЕТОДІВ SF-ICP-MS ТА PIGE

Д.В. Кутній, С.О. Ванжа, Д.Д. Бурдейний, В.В. Левенець, О.П. Омельник, А.О. Щур
Національний науковий центр «Харківський фізико-технічний інститут» НАН України

У роботі представлені результати порівняння аналітичних можливостей методів магнітосекторної мас-спектрометрії з індуктивно-зв'язаною плазмою (SF-ICP-MS) та спектрометрії гамма-випромінювання із ядерних реакцій, що індуковані важкими частинками (PIGE) при визначенні ізотопного відношення $^{11}B/^{10}B$ в карбіді бору (B_4C). Розглянуто такі ядерні реакції, що збуджуються протонами на стабільних ізотопах бору: $^{10}B(p,\alpha\gamma)^{7}Be$, $^{10}B(p,p\gamma)^{7}Be$ и $^{11}B(p,\gamma)^{12}C$. Визначено оптимальний діапазон енергій протонів в інтервалі від 550 до 600 кеВ, для індукування гамма-випромінювання з енергіями 429 та 4439 кеВ, які можуть бути використані для кількісної оцінки ізотопів ^{10}B і ^{11}B, відповідно. Показано, що з урахуванням невизначеності вимірювань величини ізотопних відношень $^{11}B/^{10}B$, що виміряні методами SF-ICP-MS і PIGE узгоджуються між собою, проте всі результати характеризуються систематичним відхиленням. Невизначеність вимірювань PIGE методу дещо вище порівняно з SF-ICP-MS, і варіюється від ± 4,1 % до ± 4,3 %, і від ± 1,1 % до ± 3,5 %, відповідно.

Ключові слова: ICP-MS, PIGE, карбід бору, ізотопне відношення, ядерне застосування, порівняння результатів