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बोरॉन सिरेमिक में कुल बी की अविनाशी परिमाणन और इसकी समस्थानिक संरचना के लिए पीआईजीई विधियों का विकास एवं अनुप्रयोग

Development and Applications of PIGE Methods for Non-Destructive Quantification of Total B and its Isotopic Composition in Boron Ceramics

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Chemical characterization of materials is the most important step in chemical quality control (CQC) exercises and it involves the determination of elemental and/or isotopic contents at major, minor and trace levels with adequate accuracy and precision for ensuring the quality of the material's finished product as per the specified compositions. Routinely used analytical methods are mostly wet chemical and atomic and mass spectroscopic techniques, which are destructive in nature. When the materials of interest are of complex matrix samples like glass, ceramics, alloys, carbides, oxides and high purity materials, there is a need of simpler non-destructive methods for CQC. Among these samples, boron based ceramic/refractory compounds such as B_4C, transition metal di-borides, and rare earth hexa-borides are key functional materials in nuclear power technology due to higher neutron absorption cross section over a wide range of energy due to the presence of ^{10}B isotope (thermal neutron absorption cross section, 3837 barn). These materials are widely used in control rod, shutoff rod, neutron shielding and neutron sensor applications. As a part of CQC, it is necessary to quantify total B as well as its isotopic composition ($^{10}B/^{11}B$ atom ratio) by suitable analytical technique(s), to know whether the material is natural or enriched with respect to ^{10}B and the total B contents are within specified limits or not. Routinely used techniques for isotopic composition of B is Mass Spectrometry techniques like TIMS and ICP-MS, whereas for total B is determined by techniques like titrimetry, IC, ICP-OES & ID-MS. These techniques yield high sensitive results with very good precision but are destructive in nature. There was a need/scope to analyze these ceramics/refractory samples by non-destructive techniques like Nuclear Analytical Techniques (NATs). Prompt Gamma-ray Neutron Activation Analysis (PGNAA) using n-beam and Particle Induced Gamma-ray Emission (PIGE) using p-beam are two such methods capable of isotopic and total concentration determination. PGNAA using thermal n-beam is a very sensitive method to determine ^{10}B isotope and total B utilizing 478 keV from $^{10}B(n,\alpha)^{7*}Li$, but it is not sensitive for ^{11}B and also it suffers from neutron self-shielding effect at high concentration level. On the other hand, PIGE using low energy proton beam (3-5 MeV) is capable of determining low Z elements (like Li, B, F, Si, Al etc) including IC of B from low to high concentration level [1-3]. It involves measurement of prompt gamma-rays of 429, 718 and 2125 keV from $^{10}B(p,\alpha\gamma)^{7}Be$, $^{10}B(p,p'\gamma)^{10}B$ and $^{11}B(p,p'\gamma)^{11}B$ reactions, respectively.

Development of PIGE Facilities at FOTIA, BARC for Low Z Elements & Isotopic Composition of B

At FOlded Tandem Ion Accelerator (FOTIA), IADD, BARC, vacuum chamber PIGE facility (4 MeV proton beam, with 10-25 nA current) with *in situ* current normalization method utilizing F or Li was developed for low Z elements including B via pellet method using cellulose matrix [1-3]. In order to have rapid analysis of "as received powder" and direct glass/ceramic/alloy samples, an external PIGE facility was setup at FOTIA by extracting the proton beam using a thin 25 μm Ta window, which is a First Of A Kind facility [4]. Samples are wrapped in thin Mylar film and analyzed using external current normalizer either Ta (135 and 165 keV of $^{181}Ta(p,p'\gamma)^{181}Ta$) or N from air (2313 keV of $^{14}N(p,p'\gamma)^{14}N$) for total B in natural and enriched B_4C and other ceramics like di & hexa borides. PIGE facilities and typical prompt gamma-ray spectra are given in Figures 1a-1d. All calculations are done by relative method taking natural B

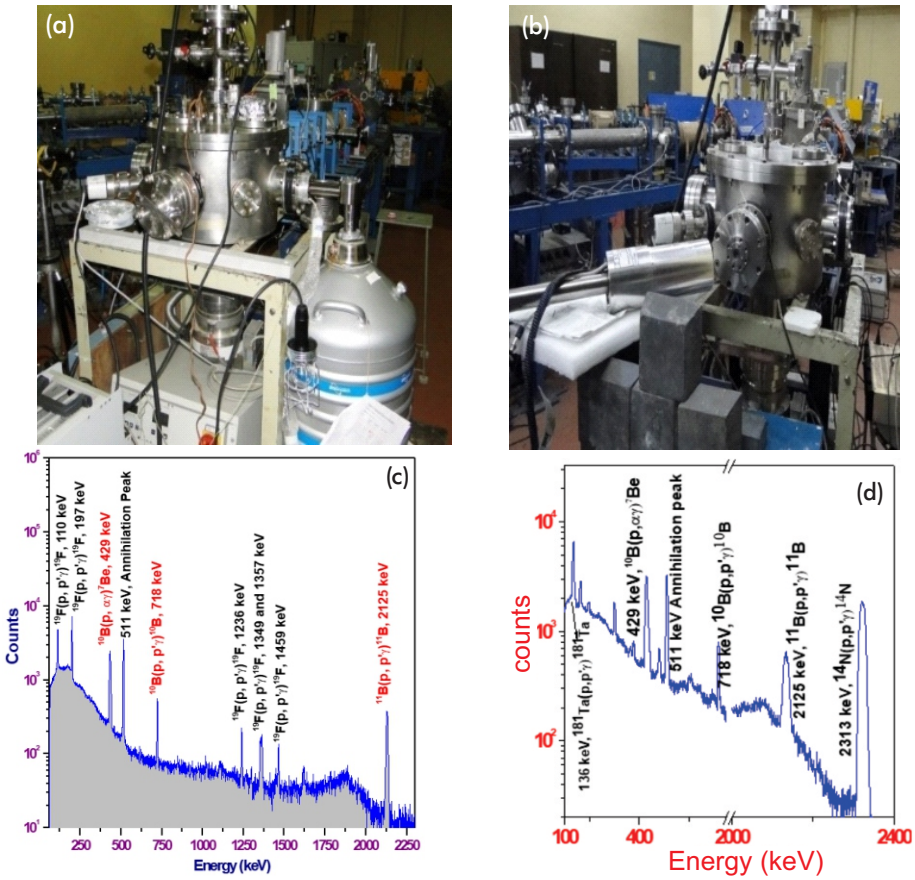

Fig.1: FOTIA PIGE Facilities: (a) Vacuum Chamber, (b) External (in air) with Ta window; vPIGE spectra of B_4C, (c) Conv. PIGE with in situ current normalizer F & (d) Ext-PIGE with Ta & N γ-peaks.

compound. Advantage of PIGE method is that determination of IC of B and 10B isotope content does not need current and mass of sample as input. All these R&D & applied works have been carried out in collaboration with MPD, Materials Group of BARC.

Lab to Industry Applications of Conventional and External PIGE Methods for IC of B and Its Total Content in Boron Based Ceramics

An in situ current normalized vacuum chamber PIGE method using a 4 MeV proton beam to determine total B and its IC in boron-based ceramic and refractory neutron absorbers/ shielding materials (natural and enriched B4C and borides of Ti, Zr, La, Ce etc) using sample pellets in cellulose matrix [1,2]. Results were compared with TIMS and PGNAA for IC or B-10 and with titrimetry and ICP-OES for total B. For Ti & Ti-Cr based ceramics PIGE is found to be suitable method for IC compared TIMS [2]. External (in air) PIGE using 3.5 MeV proton beam on target was utilized for rapid analysis of "as received" samples of B_4C & other ceramic samples for IC determination [4]. This innovative method is very simple, rapid and non-destructive in nature and sample can be returned back after assay as there is no radioactivity. By utilizing this PIGE method, simultaneous quantification of mass fractions of Fe and B in the ferroboron alloys was carried out non-destructively [5]. External PIGE method was employed to prepare in-house reference materials (IRMs) for five isotopic compositions of B from IC of 0.247 (natural, 19.8 atom% ^{10}B) to 2.03 (enriched, 67 atom% of ^{10}B) in B_4C matrices using direct powder and pellets samples. In August 2023, external PIGE method at FOTIA was utilized for commercial application, for the first time, for ^{10}B isotope content certification in industrial natural B_4C samples relevant for Indian power reactors [6]. Results were report with QA/QC of PIGE methods. For single sample analysis, the % uncertainty on obtained results of IC of B is about 1%, whereas for replicate samples (N=5 of higher) both IC of B and total B, the %RSD is about 0.5% or lower. Developed external PIGE method is very suitable for quantifying low Z elements including IC of B as well as total B contents in a simpler and faster way by analyzing "as received" samples compared to conventional vacuum chamber PIGE method.

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