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$^{10}B/^{11}B$ isotopic ratio and atomic composition of boron carbide: Determination by proton induced γ-ray emission and proton elastic backscattering spectrometry

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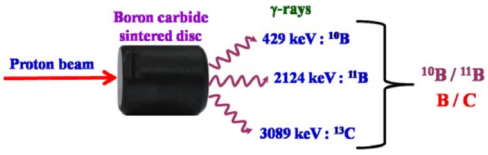
HIGHLIGHTS

- $^{10}B/^{11}B$ and B/C ratios in boron carbide ceramics are determined non-destructively.
- The methods are particle induced γ-ray emission and elastic backscattering spectrometry with protons.
- Powder and also sintered ceramics are analyzed.
- Accurate and precise results are obtained.
- Relative qualitative density of sintered ceramics can be obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

The $^{10}B/^{11}B$ isotopic ratio and the atomic composition of boron carbide, an important non-metallic ceramic, have been determined non-destructively by the particle induced γ-ray emission (PIGE) and elastic backscattering spectrometry (EBS) techniques with proton beams. The analysis has been performed on powder as well as sintered ceramics containing boron in natural or ^{10}B enriched composition. The PIGE technique, performed at a 4.0–4.2 MeV proton energy, utilizes the $^{10}B(p,\alpha\gamma)^{7}Be$, $^{10}B(p,p'\gamma)^{10}B$ and $^{11}B(p, p'\gamma)^{11}B$ nuclear reactions for (a) the isotopic analysis of boron and (b) the determination of total boron, and the $^{13}C(p,p'\gamma)^{13}C$ nuclear reaction for the determination of carbon. The irradiation conditions were optimized by determining the thick targets yields of prompt γ-rays, characteristic of these reactions, in the 3.0–4.2 MeV proton energy range. The quantitative analysis was performed by comparison with standards taking into account the attenuation of γ-rays in the specimens. The uncertainty in the determination of the $^{10}B/^{11}B$ isotopic ratio and the B/C atomic ratio is about 2% and about 5% respectively. The analysis by EBS, on the other hand, involves the $^{10}B(p,p)^{10}B$, $^{11}B(p,p)^{11}B$ and $^{12}C(p,p)^{12}C$ elastic scatterings at the 2.0 MeV proton energy. This method too yields satisfactory results. Between the two, PIGE is the method of choice for bulk analysis while EBS is useful in discerning compositional variations in surface regions.

1. Introduction

Boron carbide, a non-metallic material, is characterized by several unique physical and chemical properties such as high hardness (~30 GPa), low density (~2.52 g cm^{-3}), excellent chemical and thermal stability, and high neutron absorption capability, attributable to the ^{10}B (n, α)^{7}Li nuclear reaction (Thevenot, 1990; Domnich et al., 2011). High hardness and low density make it a premier material for armor and

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ballistic applications while the pronounced thermal and chemical stability render it eminently suitable for refractory applications (Savio et al., 2011; Qian et al., 2015). Its widespread usage in abrasive powders and coatings results from its excellent abrasion resistance (Thevenot, 1990). It is a p-type semiconductor characterized by a band gap of ~ 2.09 eV and displays good thermoelectrical properties as well (Werheit, 2006; Roszeitis et al., 2014). Due to the high cross section of the $^{10}B(n,\alpha)^{7}Li$ nuclear reaction, ~3800 barns for thermal neutrons, boron carbide enriched in ^{10}B isotope is used in control rods in nuclear reactors (Steinbruck, 2014). The rods are manufactured using sintered cylindrical pellets which, in turn, are prepared by hot pressing boron carbide powders at temperatures ≥ 2000 K and pressures ≥ 20 MPa.

Boron carbide is a non-stoichiometric compound. It exists over a large homogeneity range extending from about B_4C, or according to some researchers, $B_{4.3}C$ at the carbon-rich to $B_{12}C$ at the boron-rich limit (Bouchacourt and Thevenot, 1981; Werheit and Kuhlmann, 2012; Gosset et al., 2016). Remarkably, the material maintains phase singularity throughout this compositional range but experiences a change in properties with composition. It is reported that most of the mechanical properties are best realized for carbon-rich compositions (Thevenot, 1990). However, at carbon concentrations in excess of 20 at%, these properties undergo a sharp decline due to the precipitation of the carbon phase from the B_4C solid solution (Niihara et al., 1984). Similar to mechanical properties, Seebeck coefficient and electrical conductivity, the two thermoelectric properties, are also influenced by the carbon content of the ceramic with the former registering an increase and the latter, a decrease with increase in carbon concentration (Thevenot, 1990). Therefore, a determination of the B/C ratio of the ceramic is required for the optimization of the synthetic conditions for preparing ceramics with tailor-made properties. Apart from the B/C ratio, the determination of free carbon and the isotopic analysis of boron are the two other important analytical requisites for a comprehensive evaluation of the properties and performance of the material. Free carbon has a pronounced influence on the densification kinetics of the carbide and affects its properties in multiple ways (Grabchuk and Kislyj, 1975; Schwetz and Grellner, 1981). The isotopic analysis of boron in the powder or sintered product, on the other hand, is important from the point of view of ascertaining its efficacy as a neutron absorber.

Due to its high thermal and chemical stability and low Z non-metallic constituents, boron carbide is an analytically intractable material. The difficulties in analysis are more pronounced in sintered products. The determination of boron (total) is usually accomplished by wet-chemical methods which entail carbonate fusion of the powders (obtained by crushing/grinding in the case of sintered pellets) followed by titrimetry or spectroscopic measurements of the resulting solutions (Gosset and Colin, 1991). Similarly, the isotopic analysis is performed by inductively coupled mass spectrometry measurements of the solutions of the materials. The determination of carbon, on the other hand, involves the combustion of the ceramic in oxygen and the detection of the evolved carbon-dioxide gas with an infra-red detector (Gosset and Colin, 1991). Apparently, the determination of B/C and $^{10}B/^{11}B$ ratios by the chemical method is tedious and time consuming. So far as non-destructive methods of analysis are concerned, X-ray based techniques such as X-ray fluorescence (XRF) and particle induced X-ray emission (PIXE) are not suitable due to the difficulty in the detection of very low energy B K_α (183 eV) and C K_α (277 eV) X-rays. Neutron activation analysis too is not applicable in view of the rather unfavorable nuclear properties of the isotopes of B and C for activation with thermal neutrons.

The difficulties described above warrant the development of a simple methodology for the analysis of boron carbide. In this context we have examined the applicability of particle induced γ-ray emission technique (PIGE), a prominent ion beam analysis (IBA) method, with particular emphasis on the analysis of sintered specimens. It is a non-destructive technique and is widely used for the determination of light elements through the measurement of prompt γ-rays emitted from nuclear reactions (Savidou et al., 1999; Sunitha et al., 2016; Chiari et al., 2016). Presently, the $^{10}B(p,\alpha\gamma)^{7}Be$, $^{10}B(p,p'\gamma)^{10}B$ and $^{11}B(p,p'\gamma)^{11}B$ nuclear reactions that emit 429, 718 and 2124 keV γ-rays respectively are used for the determination of B and the $^{13}C(p,p'\gamma)^{13}C$ nuclear reaction (E_γ = 3089 keV), for the determination of carbon (Lagoyannis et al., 2016; Prekets-Sigalas et al., 2016; Ajzenberg-Selove, 1991; Kiss et al., 1985). The reactions are induced simultaneously in the material at the 3.8–4.2 MeV proton energy range. The method, therefore, not only provides the B/C ratio but facilitates the isotopic analysis of boron as well, addressing in the process two of the three analytical requisites necessary for the development of this important engineering material. In addition to PIGE, the efficacy of elastic backscattering spectrometry (EBS) with protons, yet another important IBA technique, in analyzing the two compositional aspects of boron carbide has been probed.

2. Experimental details

The PIGE and the EBS experiments were performed using the 3 MV Tandetron (High Voltage Engineering Europa, The Netherlands) at NCCCM, Hyderabad. The materials examined included powders of elemental boron (99.0%) and graphite (99.5%), homogenized powders consisting of elemental boron and graphite in 80/20, 70/30 and 50/50 wt proportions, and powders and sintered cylindrical discs of boron carbide. The powders of boron and carbon were used for the determination of thick target yields of the characteristic γ-rays of the elements. These were also used as standards for the quantitative analysis of powder and sintered specimens of boron carbide which are referred to as BC-P and BC-S respectively for the sake of brevity. The mixtures of boron and graphite served as synthetic standards representing 'boron carbide' of different chemical compositions and are referred to as BC-20, BC-30 and BC-50 respectively. Incidentally, the powders of boron and graphite were of natural isotopic abundance.

The powders of the respective materials were pressed into about 1 mm thick and 20 mm diameter discs to serve as targets. The sintered specimens were identical in shape and size, and measured 16.5 mm in length and 17.4 mm in diameter. The PIGE and the EBS experiments were conducted in two different scattering chambers equipped with the requisite experimental gadgets. The specimens were fixed on a sample manipulator inside the scattering chambers for measurements. A −900 V electron suppressor gadget was placed around the sample manipulator for proton current measurements and charge integration. The vacuum in the scattering chambers, pumped by turbomolecular pumps, was about 5×10^{-6} Torr during the course of the experiments.

2.1. PIGE measurements

The PIGE experiments were conducted for two different kinds of measurements. The first involved the determination of thick target yields of the 429, 718 and 2124 keV γ-rays emanating from the $^{10}B(p,\alpha\gamma)^{7}Be$, $^{10}B(p,p'\gamma)^{10}B$ and $^{11}B(p,p'\gamma)^{11}B$ nuclear reactions respectively and the 3089 keV γ-rays produced from the $^{13}C(p,p'\gamma)^{13}C$ nuclear reaction in the 3.0–4.2 MeV proton energy range. The measurements were conducted to determine the optimum conditions of irradiation for the second set of measurements that involved the analysis of the boron carbide specimens. In both kinds of measurements, the beam was incident normally on the targets and the prompt γ-rays were detected by a high purity germanium detector (HPGe) (Bruker Baltic, efficiency: 36%, energy resolution: 1.78 keV at 1332 keV of ^{60}Co) placed in the direction of the beam. The detector subtended a solid angle of 0.46 sr for thick target yield measurements while, 0.12 sr during the analysis of boron carbide specimens. The analysis was performed at the 4.2 MeV proton energy at a beam current of 2–3 nA. The dead time was below 8% during the course of the measurements. Since some of the boron carbide samples were significantly enriched in ^{10}B which, as described in the subsequent sections, has a high thick target yield, their analysis was