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Facile synthesis of earth-abundant and non-toxic p-type $Si_{96}B_4/SiC_p$ nanocomposites with enhanced thermoelectric performance

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ABSTRACT

One of the impediments in the development of thermoelectric devices for power generation is that they mostly contain toxic and expensive elements and/or are synthesized using expensive or time-consuming material processing methodology. We report the synthesis of Silicon–Boron ($Si_{96}B_4$) alloy employing earth abundant constituent element using a facile single-step reactive sintering using spark plasma sintering technique. In order to enhance its mechanical properties, the synthesized $Si_{96}B_4$ alloy was dispersed with SiC nanoparticles and the effect of its addition on the thermoelectric and mechanical properties in the resulting $Si_{96}B_4$/SiC nanocomposite has been investigated. A thermoelectric figure-of-merit ZT ~ 0.27 at 1123 K was realized at an optimized composition of $Si_{96}B_4$/1 wt% SiC nanocomposite. This enhancement in ZT primarily originates from a noticeable reduction in the thermal conductivity on SiC dispersion in $Si_{96}B_4$ alloy, owing to the scattering of heat-carrying phonons by nanoscale SiC particles and mesoscale SiB_3 precipitates, formed in-situ. The synthesized samples were characterized using X-ray diffraction and field emission scanning electron microscopy, based on which the enhancement in their thermoelectric and mechanical properties are discussed. Considering the low-cost and non-toxicity of the constituent elements coupled with facile and up-scalable one-step processing employed in its synthesis, $Si_{96}B_4$/SiC nanocomposites could be a potential p-type thermoelectric material for high-temperature power generation applications.

1. Introduction

Thermoelectric devices play an important role in the generation of electrical energy by utilizing the waste heat from different heat sources, such as, automotive exhaust, industrial furnaces, nuclear reactors, boilers etc. The performance of thermoelectric material is determined by its dimensionless figure-of-merit, $ZT = S^2\sigma T/\kappa$, where S, σ, T and κ are Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively [1]. The thermal conductivity consists of contributions from the lattice thermal conductivity (κ_l) and the electrical thermal conductivity (κ_e) ($\kappa = \kappa_l + \kappa_e$).

Most of the efficient thermoelectric materials (ZT > 1) discovered till date with, such as, Chalcogenides [2], half-Heuslers, Skutterudites and other multi-elemental solid-solutions (LAST, TAGS) contain toxic (Pb) or expensive constituent elements (Ag, Te, Co, rare-earths) and/or are synthesized employing time-consuming and expensive material processing methodology, which together accounts for nearly 2/3rd of the final device cost [3]. Therefore, the focus of research on thermoelectric devices is currently on reducing material and processing costs, which are equally, if not more important than their thermoelectric performance, if these devices have to complete with the other existing sources of renewable energy.

Although there is an abundance of efficient thermoelectric materials reported for low and mid temperature thermoelectric generator applications, but only a few have been explored for high temperatures applications SiGe [4], $Hf_{0.75}Zr_{0.25}NiSn$ [5], $Yb_{14}MnSb_{11}$ [6], $Ba_8Ga_{16}Ge_{30}$ [7] etc and among them $Si_{80}Ge_{20}$ has been widely studied due to their excellent thermal stability and thermoelectric performance [8,9]. However, due to the prohibitive cost of Ge, research is presently focused on alternative thermoelectric materials for high temperature applications.

Polycrystalline Si is materials known to possess properties desirable for a high temperature thermoelectric material, including earth-abundance, non-toxicity and favorable electrical properties. However, bulk Si exhibits high values of thermal conductivity [10] thus limiting its thermoelectric performance in terms of its ZT. Various groups have

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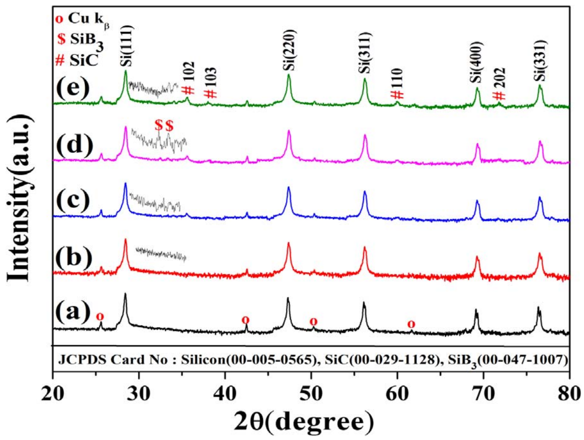

Fig. 1. XRD pattern of (a) Si powder, (b) $Si_{96}B_4$ alloy, (c) $Si_{96}B_4$/1 wt% SiC nanocomposite, (d) $Si_{96}B_4$/2 wt% SiC nanocomposite & (e) $Si_{96}B_4$/4 wt% SiC nanocomposite.

reported enhancement in the thermoelectric properties of Si primarily by reducing its thermal conductivity. Kessler et al. [11] reported a ZT ~ 0.32 at 973 K in nanocrystalline B-doped Si synthesized using decomposition of silanes followed by rapid thermal annealing, which is a multi-step process. Xie et al. [12] have also reported a ZT ~ 0.23 at 1073 K for B-doped Si synthesized employing arc melting and melt spinning followed by spark plasma sintering. Recently a composite approach has also been employed in many thermoelectric materials [13–15], by incorporation of nano-inclusions, which play a significant role in the enhancement of ZT by reducing the thermal conductivity [16–18].

In the current study, we report the synthesis of $Si_{96}B_4$ and its nanocomposite $Si_{96}B_4$/SiC, which consists of earth-abundant and non-toxic constituent elements. A $(ZT)_{max}$ ~ 0.27 at 1123 K has been realized for the optimized nanocomposite composition of $Si_{96}B_4$/1 wt% SiC, which was synthesized in single step reactive sintering process employing spark plasma sintering, which enables complete alloy-formation as well consolidation in a single step and this process is also up-scalable. Pristine SiC could be either p or n-type semiconductor depending on its doping, however, the role of SiC nanoparticles in Si96B4 alloy matrix is primarily to scatter heat-carrying phonons, without significantly affecting the electrical transport properties, with an aim to enhance the ZT and also the mechanical properties. The synthesized nanocomposites have been characterized using X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), based on which the enhancement in their thermoelectric properties has been discussed.

2. Experimental details

High purity powders of Si (Alfa Aesar, 99.999%), B (Alfa Aesar, 99.95%) and SiC nanoparticle powders were weighed in proper proportions and blended in Agate mortar pastel. The blended powders were subjected to spark plasma sintering at optimized parameters of 1423 K in vacuum for 5 min at a pressure of 60 MPa in a high-strength graphite die. The density of all synthesized samples was measured using the Archimedes principle and found to be close to theoretical density for all the samples. XRD analysis was carried out using monochromatic Cu-Kα radiation by X-ray diffractometer (Rigaku; Miniflex-II) and the microstructural characterization was carried out using FESEM (Zeiss, Supra 40VP). A circular disc specimen of 12.7 mm diameter with 2.4 mm thickness was used for thermal diffusivity measurement, which was measured using a Lineis-make Laser Flash Analyser **(**LFA 1000**)** in vacuum. The thermal conductivity was calculated by using $D \times C_p \times d$, where D, C_p and d are the thermal diffusivity, specific heat capacity and density, respectively. The temperature dependent specific heat was measured by differential scanning calorimetry (DSC, Netzsch-F404) in nitrogen atmosphere. The electrical conductivity and Seebeck coefficient were measured by the four probe DC method in helium atmosphere using Ulvac-make apparatus (ZEM-3) on rectangular specimens of dimensions $10 \times 3 \times 3\ mm^3$ cut from the centre of the sintered

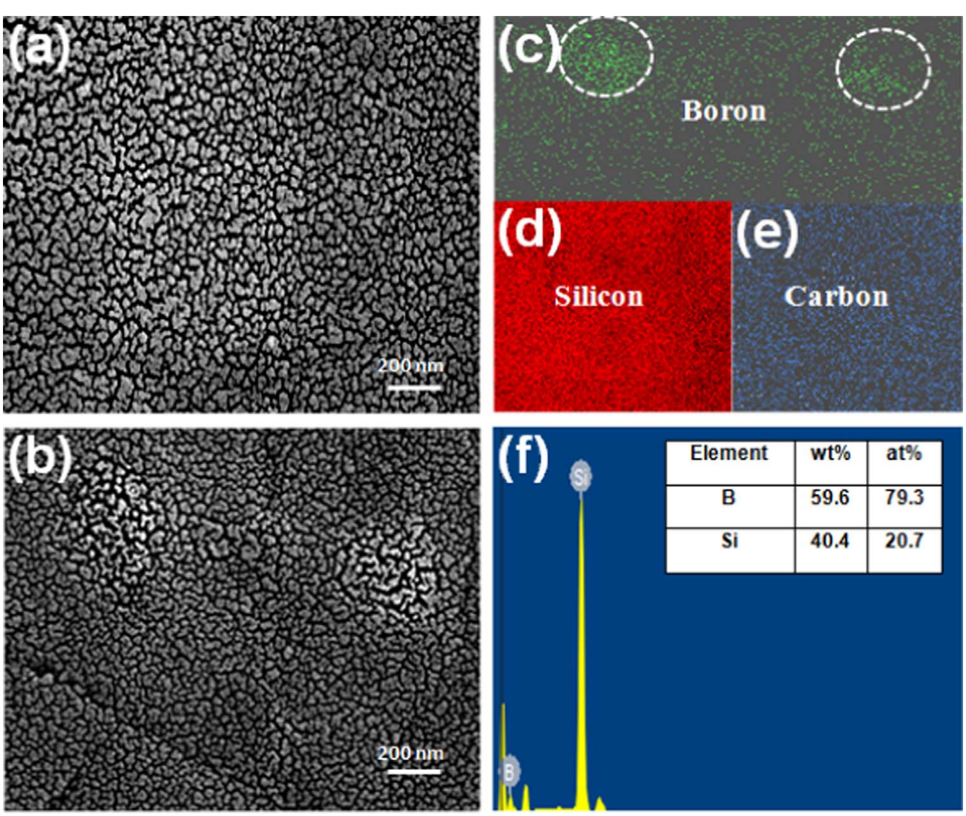

Fig. 2. FE-SEM images (a) $Si_{96}B_4$, (b) $Si_{96}B_4$/1 wt% SiC nanocomposite, (c-e) Elemental mapping of $Si_{96}B_4$/1 wt%SiC nanocomposite (white dotted area indicates B-rich region) and (f) EDS analysis of boron rich region.