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In Situ Preparation and Thermoelectric Properties of B_4C_{1-x}–TiB_2 Composites

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B_4C_{1-x}–TiB_2 composites were prepared by *in situ* reactive spark plasma sintering of B_4C with addition of nano-TiO_2 powder. The effect of TiO_2 addition on the sinterability of boron carbide was studied. The composition and the microstructure of the dense composites are characterized by means of x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive x-ray spectroscopy (EDX). The studies show that the composites contain boron carbide and TiB_2 phases with a homogeneous structure. In addition, the correlation between the composition and the thermoelectric properties was investigated. The electrical conductivity of the composite increased with increasing addition of TiO_2, and the Seebeck coefficient decreased with TiO_2 addition. The percolation threshold $\o_c$ for TiB_2 in the B_4C_{1-x}–TiB_2 system was found to be in the range of 0.139 to 0.189. The thermal conductivity was reduced in the whole measuring temperature range from 50°C to 800°C below $\o_c$. Accordingly, a significant enhancement in the dimensionless figure of merit ZT of the composites was achieved compared with that of boron carbide without TiO_2 addition, with ZT achieving its maximum value at 10 wt.% TiO_2.

Key words: Boron carbide, titanium dioxide, titanium diboride, composite, thermoelectric properties

INTRODUCTION

Thermoelectric (TE) materials, which can directly convert heat into electrical energy, are receiving increased attention due to their applications for waste heat recovery. The efficiency of a TE material is characterized by the dimensionless figure of merit $ZT = (S^2\sigma/\kappa)T$, where S, σ, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Boron carbide ceramics are known as candidate materials for high-temperature thermoelectric energy conversion; in particular, boron-rich carbides (B_4C_{1-x}) have shown promising TE properties such as large Seebeck coefficient, moderate electrical conductivity, and relatively low thermal conductivity.[1] The outstanding thermoelectric properties of boron carbides are considered to be related to their unique crystal structure.[2,3] As a single phase, boron carbides exhibit a wide homogeneity range from 8.8 at.% C ($B_{10.4}C$) to 20 at.% C (B_4C) and have rhombohedral elementary cells composed of 12-atom icosahedra and 3-atom chains.[4,5] The substitution of carbon atoms by boron atoms in the chains or within icosahedra induces a high concentration of defects accompanied with structural disorder throughout the entire homogeneity range.[6] Such intrinsic defects in boron carbides generate split-off valance states in the bandgap and play an essential role in their transport properties.[2] The correlation between the thermoelectric properties and stoichiometry of boron carbide was investigated by Bouchacourt and Thevenot;[7] the highest ZT was found in $B_{6.5}C$ at 13.3 at.% C. However, in order to prepare boron-rich carbides, use of high-purity boron is required, and the relatively high

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