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Synthesis and thermoelectric performance of titanium diboride and its composites with lead selenide and carbon

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ABSTRACT

The exploration of new thermoelectric material is the current area of research in energy conversion and storage technologies, in that nanocomposite approach is a promising root to get desirable thermoelectric properties. The present study demonstrates a composite containing highly conductive titanium diboride (TiB_2), polyvinyl alcohol (PVA) as binder and lead selenide (PbSe) as semiconductor. The synthesis and transport physics are studied with an intention to increase the power factor and figure of merit (ZT) of TiB_2 by reducing thermal conductivity through creating inhomogeneity in microstructures. Sol gel method and carbothermal reduction reaction have been used to synthesize TiB_2. More than 95% of thermal conductivity is reduced due to the phonon scattering, which is desirable to achieve a high power factor and ZT. TiB_2/PVA composite possesses a very low Seebeck coefficient and exhibits three order of magnitude reduction in electrical conductivity, which hinders in achieving a good power factor and ZT. Power factor of 25.3 μW/mK^2, Seebeck coefficient of 36.3 μV/K at 550 K and electrical conductivity of 2.5×10^4 S/m at ~300 K and ZT of 0.064 at 550 K are worth to report in this study. Finally, the synthesized TiB_2 is incorporated into PbSe to evaluate thermoelectric properties. Maximum ZT of 0.12 at 495 K, Seebeck coefficient of −342 μV/K at 550 K, electrical conductivity of 2.8×10^3 S/m at 400 K, thermal conductivity of 1.03 W/mK at 550 K and highest power factor of 280.2 μW/mK^2 at 495 K have been achieved in this composite.

1. Introduction

Thermoelectric energy conversion is a promising technology for the conversion of waste heat into electricity. It has a potential to address the current energy crisis. However, the low efficiency hinders its vast commercial usage. Currently there are few examples of its use in military and space applications. Researchers around the globe are working for the betterment of performance of thermoelectric devices. The required properties of materials for thermoelectric energy conversion are impossible to achieve in conventional materials [1,2]. Therefore, the main focus of the present research is to develop a thermoelectric material with high power factor and figure of merit (ZT) in a particular range of temperature. Thermoelectric performance of materials is expressed by power factor and a dimensionless parameter ZT [2], which are proportional to electrical conductivity as well as Seebeck coefficient and inversely proportional to thermal conductivity of materials [3–7]. These are represented as

$$PF = \sigma S^2 \tag{1}$$

$$ZT = \frac{\sigma S^2}{K} T \tag{2}$$

Where, PF is the power factor, σ is the electrical conductivity, S is the Seebeck coefficient, K is the total thermal conductivity and T is the absolute temperature.

Two strategies are used to increase the ZT of thermoelectric material: decreasing the thermal conductivity through increasing phonon scattering via atomic level defects to grain boundaries [2,8,9], and increasing the power factor [σS^2] through enhancement of electrical conductivity and/or Seebeck coefficient via band engineering or band modification [2,10,11].

The nanocomposite approach has been recently studied in the thermoelectric society [2,3]. However, in depth analysis of the materials having distinct properties, nature and scope are rarely studied. Hence, composite approach could be more beneficial to understand the physics behind the materials having dissimilar thermoelectric properties, in such cases forming a composite of metallic and semiconductor can result something interesting. In this context, titanium diboride (TiB_2) is one of the hardest refractory materials having very low

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electrical resistivity (10^{-6} Ω m) and high thermal conductivity (25–77 W/mK) [12]. TiB_2 also resists oxidation till 1000 °C, and mostly inert in all corrosive environment [13]. In addition, the thermoelectric studies of pristine TiB_2 are not widely explored till date. The past report suggests that the Seebeck coefficient of ~ −5 to −10 μV/K is achieved in dense TiB_2 having a high thermal conductivity of ~ 90 W/m K and low ZT of ~ 0.004 at 500 K, which suppresses all possibility to use it as thermoelectric material [14]. However, it is obvious that the high electrical conductivity of TiB_2 will be helpful to increase ZT as well as power factor, which is directly proportional to electrical conductivity. But on the other hand the voltage generating ability is reduced dramatically. TiB_2 has been incorporated in few other materials to make composites for improved thermoelectric performance. Like, TiB_2 with ZnO composite has been synthesized via sol-gel method to improve thermoelectric properties [15]. Though there are positive effects on conductivities but at the same time Seebeck coefficient is as low as −75 μV/K, which decreases the power factor and ZT of composite to 1.8×10^{-4} W/m K^2 and 0.02 at 800 K, respectively. Thermoelectric performance of B_4C/TiB_2 composite has also been reported. Ball milling and hot pressing techniques are used to incorporate 25 vol% of TiB_2 in B_4C [16]. Both electrical and thermal conductivities increase and as expected Seebeck coefficient decreases manifold. These further decrease the ZT, although the values of ZT and power factor in the composite are higher as compared to the base material till 700 K. TiB_2 has also been used with β-$FeSi_2$ to improve its thermoelectric properties [17]. Seebeck coefficient decreases as the amount of TiB_2 in the composite increases with reduced ZT, which is lower than the base material. Spark plasma sintering is also used to synthesize highly dense TiB_2/B_4C composite. Improved thermoelectric properties have been reported, where ZT is improved by 9 times [18]. The high thermal as well as electrical conductivity of TiB_2 as mentioned in the aforementioned studies are the major constraints to get fruitful thermoelectric properties. In order to eliminate these constraints the addition of porosity/secondary phase particles could restrict the phonon transport rate more than electrical transport. Therefore, along with porosity, the selective incorporation of binder as secondary phase has been chosen, which would suppress the phonon transport of bulk TiB_2 by acting as a barrier.

Traditionally high-performance inorganic materials such as telluride-based materials (e.g., PbTe, Bi_2Te_3, GeTe, etc.) [19–22], skutterudites [23,24], half-heusler (HH) alloys [25], $MgSi_2/FeSi_2$ [26,27], SnSe [28], $CuSe_2$ [29], etc. are widely studied as thermoelectric material. The aforementioned materials have ZT of 1.5–2 in the temperature range of 700–1000 K.

State of the art thermoelectric material PbSe has a wide range of application in photovoltaic, thermoelectric, optoelectronic devices, etc [9]. PbSe is a promising material in the field of thermoelectric due to low cost as compared to tellurium based materials. It has a stable rock salt structure with a band gap of 0.28 eV. Seebeck coefficient for pristine PbSe is 200 μV/K at 300 K. PbSe has been doped with various materials in order to improve its thermoelectric properties. Doping has improved the electrical conductivity of PbSe significantly while its Seebeck coefficient has been degraded after doping due to increased number of charge carriers. Doping has also increased the room temperature thermal conductivity of PbSe, which decreases with an increase in temperature due to phonon-phonon scattering [9]. Furthermore, PbSe having high Seebeck coefficient, electrical conductivity, power factor and ZT could explore the understanding of typical behavior of TiB_2 on electrical/thermal transport mechanism and will improve thermoelectric performance.

In the present work, PbSe has been incorporated with as synthesized TiB_2 to study its effects on the thermoelectric properties of PbSe. TiB_2 will provide a high electrical conductivity path and introduce a phonon blocking through extra phonon-disorder scattering via PVA, which is used as binder and hence a decreased thermal conductivity can be obtained. Again, the synthesis of nano-sized particles of TiB_2 provides an easy route than conventional melting.

TiB_2 can be synthesized by different methods like carbothermic reduction of TiO_2 and B_2O_3 mixture [30], direct reaction of Ti, its oxide and hydrides with boron [31], chemical vapor deposition [32], solvothermal route [33], reaction of $NaBH_4$ and $TiCl_4$ [34], and ball-milling or self-propagating high-temperature synthesis (SHS) [35]. Sol-gel and carbothermal reduction methods are used in the present work to prepare less agglomerated TiB_2 nanoparticles at comparatively low temperature. A binder, PVA is incorporated in TiB_2 to increase the compactness of the TiB_2 nanoparticles, reduce the thermal conductivity and to make pallets for thermoelectric characterization. Finally, TiB_2 is used to enhance electrical transport of PbSe.

2. Experimental

2.1. Materials

$Ti(OC_3H_7)_4$ (titanium tetra isopropoxide, TTIP) (99.9% purity) and boron carbide (B_4C) (99% purity) were purchased from Sigma Aldrich.

2.2. Synthesis of TiB_2, PbSe and its composites

TiB_2 was synthesized via sol-gel method using various compositions of precursors and chelating agents. The two main precursors used to synthesize TiB_2 were B_4C and TTIP and their ratios were varied from 1.3 to 2.5. The reaction was performed under inert atmosphere to cope with the hygroscopic nature of TTIP.

2-propanol (C_3H_8O) was used as a solvent for this synthesis due to good solubility and compatibility of TTIP and citric acid (used as chelating agent). Initially TTIP was added with a stoichiometric amount of 2-propanol in an inert atmosphere (inside the glove box) at a rate of 1 ml/min for 1.3–2.5 precursor ratio. After the addition of TTIP, chelating agent (citric acid, 1 M solution) was added drop wise with various compositions for different precursor ratios. The solution was stirred further at 300 rpm for 0.5 h. After the preparation of homogeneous solution, B_4C was added very slowly and stirred at 650 rpm for another 12 h for homogenization. DI (deionized) water was added drop wise to obtain a gel and then subjected to ageing at room temperature.

After the formation of gel, the carbothetmal reduction was performed by heating the material up to 1400 °C. To observe the effect of binder, different wt% of PVA (3, 5, 9 and 10 wt%) were used to prepare composites with TiB_2. A low wt% of PVA (say 1 and 2 wt%) provides insufficient binding strength and these compositions have been excluded for the formation of the composites. 10 mm diameter pellets were prepared by pressing with hydraulic press under a load of 5 t and subjected to various characterizations. PVA was used as a binder and therefore, the material was annealed at 650 °C to convert it into carbon (above 250 °C).

PbSe was prepared by solid state reaction by mixing the elemental Pb and Se at stoichiometric ratios. The mixture was sealed into vacuum sealed ampules and heated up to 1200 °C for 12 h and hold at this temperature for 24 h. The sample was cooled down to room temperature naturally. Crystalline ingots were grinded to fine powder. The pallet samples of PbSe were prepared with 5 and 10 wt% of TiB_2 to evaluate various thermoelectric properties.

2.3. Characterization

Structural analysis was done by X-ray diffraction in Xpert Pro PANalytical XRD (λ ~ 1.5418 Å). The surface morphology was examined by SEM (SEM Zeiss EVO MA-15). XPS (XPS; PHI 5000, Versa Prob II, FEI Inc. spectrometer) and EDS (JEOL JSM-6010LA) analyses were performed to know the chemical state of elements and compositional analysis. The thermoelectric characterizations were performed comprising electrical conductivity and Seebeck coefficient using LSR-3 (Linseis, Germany) under helium environment and thermal conductivity using LFA-1000 (Linseis, Germany).