Journal of Solid State Chemistry 233 (2016) 1–7

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Crystal growth and anisotropy of high temperature thermoelectric properties of yttrium borosilicide single crystals

M. Anwar Hossain [a,b], Isao Tanaka [b], Takaho Tanaka [a], A. Ullah Khan [a], Takao Mori [a,c,*]

[a] International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan
[b] Center for Crystal Science and Technology, University of Yamanashi, Miyamae 7-32, Kofu, Yamanashi 400-8511, Japan
[c] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8671, Japan

ARTICLE INFO

Article history:
Received 18 July 2015
Received in revised form
30 September 2015
Accepted 3 October 2015
Available online 8 October 2015

Keywords:
Inorganic compound
Crystal growth
Borides
Electrical anisotropy
Thermoelectric materials

ABSTRACT

We studied thermoelectric properties of $YB_{41}Si_{1.3}$ single crystals grown by the floating zone method. The composition of the grown crystal was confirmed by electron probe micro-analysis. We have determined the growth direction for the first time for these borosilicides, and discovered relatively large anisotropy in electrical properties. We measured the electrical resistivity and Seebeck coefficient along [510] (the growth direction) and [052] directions and we found that this crystal exhibits strong electrical anisotropy with a maximum of more than 8 times. An interesting layered structural feature is revealed along [510] with dense boron cluster layers and yttrium layers, with conductivity enhanced along this direction. We obtained 3.6 times higher power factor along [510] compared to that along [052]. Although the ZT of the present system is low, anisotropy in the thermoelectric properties of a boride was reported for the first time, and can be a clue in developing other boride systems also.

1. Introduction

The direct conversion of waste heat to electricity is a large incentive to find viable thermoelectric (TE) materials [1]. Many efforts are being made to find routes to enhance thermoelectric properties. One very recent interesting development was reported in *Nature* on crystals of tin selenide which showed the best thermoelectric properties ever reported, in one direction of the crystal [2]. Boron cluster compounds are attractive candidates as high temperature thermoelectric materials for their stability and generally large Seebeck coefficients [3,5]. Furthermore, they typically exhibit low thermal conductivity [6–9], which is an inherent advantage for thermoelectrics, despite being strongly covalently bonded solids with high sound velocity. Several mechanisms have been proposed to be the origin of this intrinsic low thermal conductivity [5,9,10]. Many of the boron cluster compounds take the variable range hopping transport (VRH) mechanism in which both electrical conductivity and Seebeck coefficient increase with temperature, which is an advantage for thermoelectric performance [4,5,11]. Another attractive feature of boron cluster compounds in general is that the network structures and physical properties have been found to be controllable to some degree through incorporation of metal atoms in the voids of clusters, and also addition of third elements like C, N, Si which can act as bridging sites of the cluster framework [12,13]. Although many borides are being developed as thermoelectric materials [4,14–24], to our knowledge there has been no report regarding the anisotropy of thermoelectric properties of borides. In this work we investigate the thermoelectric anisotropy of a rare earth borosilicide single crystal for the first time.

It has previously been reported that two new phases exist between the previously known phases of YB_{12} and YB_{66} [25] with composition of about [B]/[Y]=25 and 50, respectively. Tanaka et al. has reported that crystal growth of the YB_{50} phase become possible by adding Si in the floating zone method and growing $YB_{41}Si_{1.2}$ crystals [26]. The crystal structure of $YB_{41}Si_{1.2}$ belongs to the orthorhombic system (space group *Pbam*) and is composed of B_{12} icosahedra and $B_{12}Si_3$ polyhedral units. After the successful growth of $YB_{41}Si_{1.2}$ crystals, a lot of research has been carried out on rare earth borosilicides, $REB_{44}Si_2$, to study physical properties [4,8,9,27–37]. The $REB_{44}Si_2$ (*RE* =Tb, Er, Yb) compounds are p-type like boron carbide and have been found to exhibit Seebeck coefficients in excess of 200 $\mu V\,K^{-1}$ at high temperatures above 1000 K and also possess a low thermal conductivity of $\sim 0.02\,W\,cm^{-1}\,K^{-1}$ [8,29]. A beneficial zinc doping effect was discovered for arc-melted yttrium borosilicides, $YB_{44}Si_2$ [4]. Tanaka et al. investigated electrical resistivity and Seebeck coefficient of $YB_{41}Si_{1.2}$ crystal from 77 K to room temperature and they also estimated the figure of merit

* Corresponding author at: International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan.
E-mail address: MORI.Takao@nims.go.jp (T. Mori).

http://dx.doi.org/10.1016/j.jssc.2015.10.006
0022-4596/

using thermal conductivity of YB_{66} at room temperature and obtained very poor values [28]. There is no literature available on high temperature thermoelectric properties of $YB_{44}Si_2$ single crystals. Regarding anisotropy, Mori has found magnetic anisotropy to be indicated in $Tb^{11}B_{44}Si_2$ and $YbB_{45.6}Si_{1.0}$ single crystals but with no information obtainable on crystal orientations [32,36]. In this paper, we report high temperature thermoelectric properties of $YB_{41}Si_{1.3}$ single crystals grown by the floating zone method. For the first time, we have determined crystallographic orientations of a borosilicide crystal and discovered the relatively large anisotropy in electrical properties along the determined directions.

2. Experimental details

Floating zone (FZ) crystal growth was employed to grow yttrium borosilicide $YB_{41}Si_{1.3}$ single crystals using a four-mirror-type infrared image furnace (Crystal System Inc., FZ-T-10000-H-III-VPR) equipped with four 2.5 kW xenon lamps as heat source. The preparation process of the polycrystalline feed rods for FZ crystal growth is as follows: we mixed YB_4 (New Metals Co. 99%), B (SB Boron 99.9%),and Si (Wako 99.9%) powders to obtain a desired final composition, then, pressed it into a rod at a hydrostatic pressure of 300 MPa. Rods having nominal composition $YB_{44}Si_2$ were prepared for both the feed rod and the seed rod to grow crystals by the FZ method. The pressed rod was reacted in a boron nitride (BN) crucible fixed inside a graphite susceptor that was further covered with graphite wool for induction heating. The synthesis was carried out in an RF inductive furnace at 1400 °C for 8 h in vacuum. To obtain high density feed rods, the synthesized rods were grinded and formed again into rods and sintered at the same condition. FZ crystal growth was carried out by driving downward both feed and seed rods at 10 and 8 mm/h, respectively, with counter-rotating at 16 rpm under Ar atmosphere (2.5 L/min).

The grown crystals were characterized by high-resolution powder X-ray diffraction (XRD) and electron probe microanalysis (EPMA). Powder XRD measurements with CuKα radiations (Rigaku Ultima-3) were performed to confirm the required phase formation in the grown crystals, where parts of the crystals were crushed using a stainless steel mortar and then the obtained powder was washed with HCl solution and rinsed with water to remove stainless steel contamination. Rietveld refinement was performed using FullProf Suite software (2.05). Peak shape was refined with the modified Lorentzian function and 6 coefficients polynomial function was used for background refinement. EPMA was carried out in wavelength-dispersive mode using JEOL JXA-8200 instrument. Standard sample used for Y and B were $Y_3Al_{15}O_{12}$ and LaB_6, respectively.

The crystallographic orientation of the $YB_{41}Si_{1.3}$ grown crystals were characterized by pole figure measurements using an X-ray 2D-detector (Bruker Corp., model D8 DISCOVER VANTEC-500). We took two cross-sections, one was approximately perpendicular to growth direction and another one was parallel to growth direction of the grown crystal, for pole figure measurement. We cut the crystal using a diamond wire cutter and then polished the pieces with a diamond solution. The crystallographic orientations were determined from the obtained pole figure data by Multex 3 software.

For high temperature thermoelectric materials the stability at high temperature is essential. Therefore, to check the stability of the grown crystals at high temperature, we also carried out thermogravimetric analysis (TGA, Rigaku, model Thermo plus TG 8120) from 300 K to 1080 K in Ar flow as well as in air flow. Resistivity and Seebeck coefficient were measured with an ULVAC ZEM-2 in the temperature range of 330–1000 K in He atmosphere. To determine the thermal conductivity values, first of all, the room temperature specific heat was measured by using PPMS (Quantum Design, physical property measurement system). Then, the relative specific heat and thermal diffusivity coefficient were measured by laser flash method (ULVAC TC-7000) from 300 K to 1080 K. The thermal conductivity is determined as the product of the density, specific heat, and thermal diffusivity coefficient.

3. Results and discussions

3.1. Crystal growth and characterizations

The boron-rich boride compound YB_{50} which has an orthorhombic crystal structure starts to decompose above 2100 K into phases like YB_{12} and YB_{66} without melting [38]. Tanaka et al. first demonstrated that the melt growth method is applicable to grow an yttrium borosilicide crystal, $YB_{44}Si_{1.0}$ that is iso-structural to YB_{50} by adding a small amount of silicon [26,27]. Another interesting Si addition effect was the enlargement of the lattice parameters which enabled synthesis of $GdB_{44}Si_2$, although GdB_{50} does not form due to the relatively large size of Gd [39]. A view of the crystal structure of $REB_{44}Si_2$ is shown in Fig. 1. The structure is orthorhombic with space group *Pbam*. Fig. 2 shows the picture of a grown crystal. To grow high quality crystals, we used the zone pass technique. The first zone pass was made to obtain uniform composition and the second zone pass was made to grow the crystal.

EPMA results revealed the atomic concentration of Y, B and Si to be 2.3 ± 0.2 at%, 94.4 ± 0.4 at% and 3.1 ± 0.2 at%, respectively. The composition of the grown crystal was determined to be $YB_{41}Si_{1.3}$. Fig. 3 shows powder X-ray diffraction pattern with Rietveld refinement of the grown crystal.

Rietveld refinement for the $YB_{41}Si_{1.3}$ crystal data confirmed $YB_{44}Si_2$ structure type with $R_F = 0.019$ and $R_B = 0.031$, and a very little amount of YB_6 phase was found (2nd row of black Bragg-

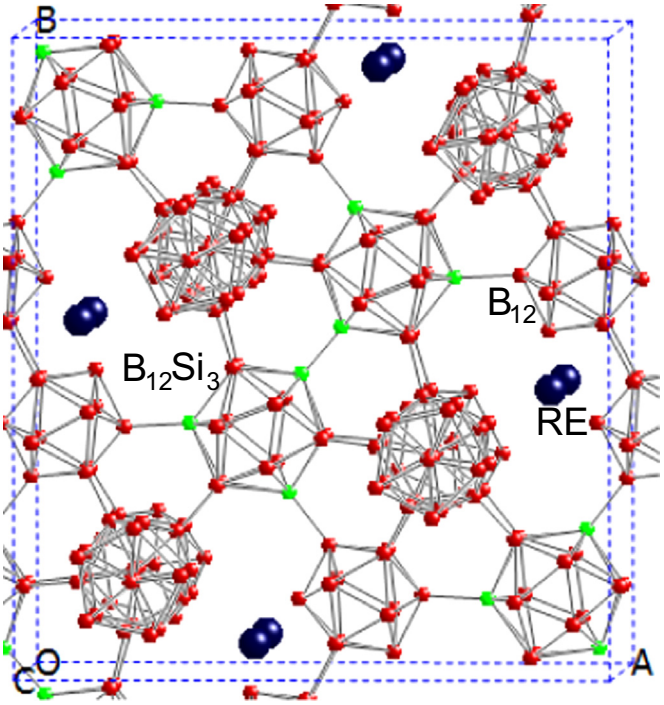

Fig. 1. View of the crystal structure of $REB_{44}Si_2$ from a direction slightly tilted along [001] as indicated by the labels, two kinds of polyhedra are shown: B_{12} icosahedra and $B_{12}Si_3$ polyhedra. Only two of the five structurally independent B_{12} icosahedra are drawn for clarity. The circles indicate rare-earth (in this case, yttrium) atoms which are aligned along [001] in a ladder-like configuration.