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論　文　内　容　要　旨

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学位論文題目	Finely Grained PbTe and BiSbTe for Low Thermal Conductivity and High *ZT* values （低熱伝導率と高*ZT*のための微細結晶粒テルル化鉛とテルル化ビスマスアンチモン）		

内容要旨

Thermoelectric materials have the ability to transform thermal energy into electrical energy and vice versa, allowing waste heat to be harvested as useful electrical energy. With no moving parts, thermoelectric generators provide long duration operational reliability. Advances in fabricating materials improve thermoelectric performance in space exploration and vehicles that use renewable energy. Energy conversion in such materials can be determined by the dimensionless thermoelectric figure of merit (*ZT*). Thermoelectric materials have been widely studied and various methods have been used to improve the dimensionless figure of merit *ZT*.

PbTe is among a good performing thermoelectric materials in an intermediate temperature range up to 450-850 K. Undoped PbTe samples were melted at 1123 K, ball milled (BM) at rotation speed from 90 to 180 rpm and there was hot pressing (HP) at 147 MPa and 650 K. Milling at 120 rpm produced minimum phonon thermal conductivity value of 1.29 W m $^{-1}$ K^{-1} and average grain size of 0.80 μm. Phonon thermal conductivity was constant from coarse grain size to fine grain size of 1 μm and decreased at rotation speed up to 120 rpm. Phonon thermal conductivity and average grain size agreed with theoretical calculations up to 120 rpm. The observed critical point of phonon thermal conductivity differed from theoretical calculations by grain boundary scattering. Focusing on grain size, microstrain and phonon thermal conductivity (κ_{phonon}) of undoped bulk PbTe processed by mechanical grinding (MG) and alloying (MA) using milling rotation speed of 90-180 rpm followed by HP. PbTe samples prepared by MG-HP had single-phase, high relative density (more than 99%) and uniform structure. Samples prepared by MA-HP were over theoretical relative density. At 150 rpm milling, minimum κ_{phonon} of MG-HP was 1.03 W m^{-1} K^{-1} and average grain size was 0.47 μm, due to an increase in microstrain. At 120 rpm milling, minimum κ_{phonon} of MA-HP was 1.74 W m^{-1} K^{-1} and average grain size was 0.52 μm, due to a decrease in microstrain. Electrical conductivity and Seebeck coefficient in MA-HP showed behavior like *p*-type doped materials compared with MG-HP. Reducing κ_{phonon} below 1 μm was necessary to produce high microstrain.

Bi_2Te_3-based materials have high *ZT* values, i.e., around 1.0 near room temperature, and are promising for use in energy harvesting power generation and wearable thermoelectric devices.*p*-Type $Bi_{0.3}Sb_{1.7}Te_{3.0}$ thermoelectric materials were prepared by various ball milling speed with yttria-stabilized zirconia ceramics vessel (YSZ) and balls, and then HP. Milled powders prepared at ball-milling speeds greater than or equal to 150 rpm were completely alloyed and single-phase $Bi_{0.3}Sb_{1.7}Te_{3.0}$ was

obtained. The grain size of a disk sintered at 350 ℃ was approximately 1 μm at the fracture surface. Seebeck coefficients of sintered disks obtained by YSZ milling were higher, and electrical conductivity were lower, than those of disks prepared using a stainless-steel vessel and Si_3N_4 balls; this is because YSZ milling suppressed contamination by materials that acted as carrier dopants in the $Bi_{0.3}Sb_{1.7}Te_{3.0}$ bulk materials. Contamination from the YSZ vessel and milling balls did not affect the phonon thermal conductivity of the $Bi_{0.3}Sb_{1.7}Te_{3.0}$ bulk materials. The dimensionless figure of merit ZT values for samples prepared by milling at 150 rpm with a YSZ vessel and balls followed by sintered at 350 ℃ were enhanced approximately 1.7 times than that for the sample prepared by milling with stainless-steel vessel and Si_3N_4 balls. ZT values remained above 1.0 and reached a peak of 1.16 (α : 295 μV K^{-1}, σ : 4.16 ×10^4 S m^{-1}, κ : 0.94 W m^{-1} K^{-1}, T : 300 K) for samples milled at 130 rpm and then hot pressed at 350 ℃. The results show that the thermoelectric properties can be improved by selection of appropriate milling vessels and balls.