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(54) **THERMOELECTRIC MATERIAL AND  
METHOD FOR PRODUCING SAME**

(76) Inventors: **Takashi Harada**, Hyogo (JP); **Naohiro  
Toda**, Hyogo (JP); **Hitoshi Sumiya**,  
Hyogo (JP)

Correspondence Address:  
**MCDERMOTT WILL & EMERY LLP**  
**600 13TH STREET, N.W.**  
**WASHINGTON, DC 20005-3096 (US)**

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(57) **ABSTRACT**

A thermoelectric material has an average crystal particle size of at most 50 nm and has a relative density of at least 85%. A method of manufacturing a thermoelectric material includes the steps of preparing a fine powder and sintering or compacting the fine powder under a pressure of at least 1.0 GPa and at most 10 GPa.

## THERMOELECTRIC MATERIAL AND METHOD FOR PRODUCING SAME

### TECHNICAL FIELD

[0001] The present invention relates to a thermoelectric material that is a constituent of a thermoelectric element used for thermoelectric power generation utilizing the Seebeck effect and for direct cooling/heating utilizing the Peltier effect. The thermoelectric material used for the thermoelectric element includes such known materials as  $\text{Bi}_2\text{Te}_3$ -based material,  $\text{CoSb}_3$ -based intermetallic compound with the Skutterudite structure,  $\text{ZrNiSn}$  for example with the half-Heusler structure ( $\text{MgAgAs}$ ),  $\text{FeSi}_2$ , and  $\text{MnSi}_{1.73}$ .

### BACKGROUND ART

[0002] The thermoelectric technology including the thermoelectric power generation utilizing the Seebeck effect and the direct cooling/heating utilizing the Peltier effect has the following characteristics as compared with the conventional compressor-based technology:

[0003] 1. system structure is simple and can be reduced in size;

[0004] 2. such refrigerants as chlorofluorocarbons are not used; and

[0005] 3. no moving part, which provides excellent durability, reliability and low noise.

[0006] The thermoelectric technology is thus potentially and considerably excellent. Actually, however, the energy conversion efficiency of a thermoelectric element is lower than that of the conventional system using a compressor. Therefore, the thermoelectric element is only used for cooling a high performance CPU and an LD used for long-haul optical communication or used as a Peltier element of a portable refrigerator, for example. In order to expand the applications of the thermoelectric technology, it is indispensable to improve the conversion efficiency. For this purpose, thermoelectric characteristics of the thermoelectric material have to be improved.

[0007] The performance of the thermoelectric material is represented by the thermoelectric figure of merit determined by the following expression:

$$Z=S^2/(\rho\cdot\kappa)$$

where  $S$  is Seebeck coefficient (V/K),  $\rho$  is electrical resistivity ( $\Omega\text{m}$ ) and  $\kappa$  is thermal conductivity (W/mK). It is thus seen that an increase of the Seebeck coefficient and decreases of the electrical resistivity and thermal conductivity are effective in improving the performance of the thermoelectric material.

[0008] Since the Seebeck coefficient depends on the electronic structure of a substance, the Seebeck coefficient is substantially determined by the material and composition thereof. Thus, for increasing the Seebeck coefficient, it is important to search through materials and optimize doping agents and amount, for example. In contrast, the electrical resistivity is affected not only by the electronic structure but also by such factors as lattice vibration and impurities. Further, regarding the thermal conductivity, lattice vibration generally contributes to more than a half of factors that determine the magnitude of the thermal conductivity of a high performance thermoelectric material. Therefore, in

order to decrease the electrical resistivity and thermal conductivity, structural control for example in terms of materials engineering would be important.

[0009] Studies on improvements in performance of the thermoelectric material have been conducted with the purpose of decreasing the thermal conductivity. Specifically, miniaturization of crystal size of the structure or impurity doping has been performed in order to increase phonon scattering. For example, Japanese Patent Laying-Open No. 56-136635 discloses a method according to which two types of ultrafine powder and powder that is larger in particle size than the ultrafine powder are mixed together and sintered to produce a highly dense sintered body without pores. As a method of producing an ultrafine powder to be used as a raw material, Japanese Patent Laying-Open No. 2-27779 for example discloses a technique using the arc plasma sputtering.

[0010] Japanese Patent Laying-Open No. 2000-252526 discloses a method of producing a thermoelectric material by synthesizing a fine powder to be used as a raw material through the solution processing for example and sintering the powder. Japanese Patent Laying-Open No. 2000-349354 discloses a method of producing a thermoelectric material by preparing a fine powder using the mechanical alloying method and plasma-sintering the powder.

[0011] Further, Japanese Patent Laying-Open No. 10-209508 discloses a method of improving the performance by providing a particle size of at least 50 nm and at most a carrier diffusion length and discloses that a particle size of less than 50 nm causes an empirical deterioration in performance. Although no reason for the performance deterioration is mentioned, it is considered that the smaller particle size causes an increase of impurities and a decrease of the relative density. Japanese Patent Laying-Open No. 2002-76452 discloses a thermoelectric conversion material having crystals with a particle size of at least 0.5 nm and at most 100 nm that are deposited or dispersed therein. This thermoelectric conversion material, however, has a problem of a low relative density resulting in a deterioration in performance due to the deposition or dispersion of the crystals that are components of the thermoelectric conversion material.

[0012] It has been confirmed that, an improvement in thermoelectric figure of merit of the thermoelectric material, in terms of the decrease of the thermal conductivity, is achieved to some degree by, for example, using the above-described ultrafine powder as a raw material and thereby making the structure finer or by impurity doping. Specifically, by providing a fine crystal structure, the phonon scattering is increased to lower the thermal conductivity. Actually, however, the improvement in performance is limited within a certain range, since there are limits to the technique of producing ultrafine powders and the sintering technique and thus it has been impossible to produce a sintered body having a fine crystal structure. Moreover, since a finer crystal is usually accompanied by a higher electrical resistivity, the thermoelectric figure of merit as a whole is not increased in some cases.

### DISCLOSURE OF THE INVENTION

[0013] An object of the present invention is to provide a thermoelectric material of high performance by solving the



above-described problems of the conventional art and lowering the thermal conductivity of the thermoelectric material with a minimum increase in electrical resistivity.

**[0014]** The present invention is a thermoelectric material having an average crystal particle size of at most 50 nm and having a relative density of at least 85%.

**[0015]** Preferably, according to the present invention, an EDS analysis of a grain boundary portion of the thermoelectric material shows that impurity elements have a detected intensity of at most one-fifth of a maximum detected intensity of an element among constituent elements of the thermoelectric material.

**[0016]** Preferably, according to the present invention, the thermoelectric material has an electrical resistivity of at most  $1 \times 10^{-3} \Omega\text{m}$ .

**[0017]** Preferably, according to the present invention, the thermoelectric material has a thermal conductivity of at most 5 W/mK.

**[0018]** Preferably, according to the present invention, the thermoelectric material has a thermal conductivity of at most 1 W/mK.

**[0019]** Further, the present invention is a method of manufacturing a thermoelectric material including the steps of preparing a fine powder and sintering or compacting the fine powder under a pressure of at least 1.0 GPa and at most 10 GPa.

**[0020]** Preferably, according to the present invention, the method of manufacturing a thermoelectric material further includes the step of annealing polycrystalline body resultant from said sintering or compacting step.

#### BEST MODES FOR CARRYING OUT THE INVENTION

**[0021]** The inventors of the present invention have conducted studies with the purpose of solving the aforementioned problems to find that an average particle size of at most 50 nm of crystals constituting a thermoelectric material provides a remarkable decrease in thermal conductivity and accordingly a small increase in electrical resistivity, and further find that it is effective for lowering the electrical resistivity to reduce unavoidable impurities that are present at grain boundaries. The inventors further find a manufacturing method controlling impurities to minimize the impurities being present at grain boundaries and thereby obtain a fine crystal structure. The inventors accordingly finish the present invention based on these findings.

**[0022]** Specifically, a thermoelectric material of the present invention has a feature that an average crystal particle size is at most 50 nm. The average crystal particle size is controlled so that the size is at most 50 nm, and accordingly, phonon scattering in a sintered body can be enhanced to lower the thermal conductivity and thereby improve the performance of the thermoelectric material. Although the relation between the average crystal particle size and the thermal conductivity of the thermoelectric material differs between materials, the average crystal particle size that is at most 50 nm provides a greater effect of lowering the thermal conductivity. It is presumed the reason therefor is that the average crystal particle size is sufficiently small relative to a mean free path of phonons to increase

phonon scattering and lower the thermal conductivity of the thermoelectric material. In terms of the decrease in thermal conductivity of the thermoelectric material, a smaller average crystal particle size is more preferable. The minimum average crystal particle size, however, is approximately  $0.001 \mu\text{m}$  that is practically a production limit. The average crystal particle size of the thermoelectric material herein refers to an average size of a plurality of crystallites (fine crystals that can be regarded as single crystals) constituting one crystal grain of the thermoelectric material that can be identified by an observation using a transmission electron microscope. Specifically, the average crystal particle size is determined in the following way. On an arbitrary area of an image of a transmission electron microscope (hereinafter abbreviated as TEM), a straight line is drawn that passes through 50 crystallites. Then, the sum of respective lengths of sections of the straight line that pass through respective crystals is divided by 50, which is the number of the crystallites, and the numerical value determined by the division is used as the average crystal particle size of the thermoelectric material.

**[0023]** Preferably, the thermoelectric material of the present invention has a relative density of at least 85% which is more preferably at least 90%. A relative density of the thermoelectric material that is less than 85% slightly lowers the thermal conductivity of the thermoelectric material. However, less contacts between crystals that are necessary for electron transmission cause the sudden decrease of the electrical conductivity resulting in considerable deterioration in performance. Here, the relative density refers to the ratio of the volume of the thermoelectric material except for pores to the volume of the whole thermoelectric material.

**[0024]** Further, regarding the thermoelectric material of the present invention, when an EDS analysis of a crystal grain boundary portion of the thermoelectric material is conducted, the detected intensity of impurity elements is preferably at most one-fifth of the maximum one of detected intensities of respective constituent elements of the thermoelectric material. By keeping the low level of the impurities at crystal grain boundaries, the electrical resistivity of the thermoelectric material can be kept low to further improve the performance of the thermoelectric material. Impurities present at crystal grain boundaries contribute to phonon scattering and thus are effective in lowering the thermal conductivity of the thermoelectric material. Therefore, it is preferable that a small amount of impurities are present. However, the impurities have an adverse effect of considerably hindering electrical conduction between particles that form the crystal grain boundaries. For this reason, preferably the amount of impurities is fairly small. The fact that the detected intensity of impurity elements is at most one-fifth of the maximum detected intensity of an element among the constituent elements of the thermoelectric material may involve the fact that an EDS analysis of grain boundaries does not detect the intensity since the amount of impurity elements is smaller than the detection limit of the machine. Here, the EDS analysis refers to an analysis by means of an X-ray energy dispersion spectrometer.

**[0025]** Furthermore, according to the present invention, preferably the thermoelectric material has an electrical resistivity of at most  $1 \times 10^{-3} \Omega\text{m}$ . This is for the reason that a lowered electrical resistivity of the thermoelectric material can increase the above-described thermoelectric figure of



merit. At the same time, since a lower thermal conductivity of the thermoelectric material can also improve the thermoelectric figure of merit, preferably the thermoelectric material of the present invention has a thermal conductivity of at most 5 W/mK. Moreover, a thermal conductivity of the thermoelectric material of the present invention that is at most 1 W/mK is further preferable since it can further improve the thermoelectric figure of merit of the thermoelectric material. Although the thermal conductivity of the thermoelectric material varies depending on for example the type of the thermoelectric material, the amount of impurities and the crystal structure, a manufacturing method of the present invention can adjust the thermal conductivity within the above-described range (at most 5 W/mK or at most 1 W/mK).

**[0026]** The thermoelectric material of the present invention is manufactured by a method including the-steps of preparing a fine powder and sintering or compacting the fine powder under a pressure of at least 0.5 GPa and at most 10 GPa, which is preferably at least 1.0 GPa and at most 10 GPa.

**[0027]** The fine powder used for the present invention may be particles for example having an average particle size of at most 50 nm, since the particles with the average particle size of 50 nm or less can be used to produce a thermoelectric material having an average crystal particle size of at most 50 nm.

**[0028]** Preferably, the fine powder includes secondary particles with the particle size of 0.1  $\mu\text{m}$  to 100  $\mu\text{m}$  composed of crystallites with an average particle size of at most 50 nm that are coupled and adhered to each other. This is for the following reason. When such a fine crystal structure as that of the thermoelectric material of the present invention is to be obtained, required particles should have a considerably small particle size and thus the particles are highly active. Accordingly, the surfaces of the particles are likely to be contaminated by impurities.

**[0029]** Further, preferably the fine powder includes particles containing dislocations. This is for the following reason. When particles contain dislocations or defects, recrystallization occurs from any dislocation or defect in a sintering or compacting process or an annealing process preceding or following the sintering or compacting process and accordingly the thermoelectric material of the present invention can have a fine crystal structure. Here, particles containing dislocations refer to particles containing dislocations or defects and having a crystallinity of at most 70% that is measured by X-ray diffraction.

**[0030]** The total scattering intensity of X-rays, more accurately the intensity of coherent scattering except Compton scattering, is always constant regardless of the ratio between respective amounts of an amorphous portion and a crystalline portion. Therefore, the crystallinity measured by the X-ray diffraction can be determined by a value (%) that is the ratio (%) of the X-ray scattering intensity of a crystalline portion of particles containing dislocations to the X-ray scattering intensity of particles with 100% crystallinity, or is calculated by subtracting from 100 the ratio (%) of the X-ray scattering intensity of an amorphous portion of particles containing dislocations to the X-ray scattering intensity of 100% amorphous particles.

**[0031]** The fine powder used for the present invention may be prepared by such a mechanical milling method as ball

milling, gas atomization in a vacuum or inactive atmosphere, or through a process of preparing a fine powder by means of thermal plasma. The mechanical milling method refers to a method of milling particles by shear force exerted between balls and a pot of the ball milling for example. With this method, particles that are reduced in particle size can form secondary particles having crystals that are coupled and adhered to each other by pressure from the balls and pot, or dislocations or defects can be caused in particles constituting the fine powder. The gas atomization can reduce the amount of impurities to a greater degree as compared with such a mechanical milling as ball milling. Since the gas atomization method blows gas to particles in a melted state so that the particles become droplets and quenched, fine particles containing many defects can be produced. The process for preparing a fine powder by thermal plasma is a method that the raw material of the fine powder vaporized by high-temperature plasma is quenched and condensed thereby fine particles containing many defects are produced.

**[0032]** The dislocations and defects generated by these methods serve as origins from which recrystallization occurs to constitute a fine structure and further serve as an origin of phonon scattering in a sintered body to provide the effect of lowering the thermal conductivity of the thermoelectric material.

**[0033]** The fine powder prepared through any of the methods described above is sintered or compacted under a pressure of at least 0.5 GPa and at most 10 GPa that is preferably at least 1.0 GPa and at most 10 GPa. This process is performed for sintering or compacting the fine powder and thereby making it highly dense without causing an excessive growth of particles. In order to obtain a highly dense thermoelectric material without causing particle growth, a fracture process by pressurization, a process of allowing particles to slide over each other and a densification process through such a process as plastic flow are necessary. When the fine powder is sintered or compacted under a pressure of less than 0.5 GPa, the process of allowing particles to slide over each other is not promoted so that a highly dense thermoelectric material is hard to be produced. When the fine powder is sintered or compacted under a pressure of less than 1.0 GPa, particles that constitute the fine powder do not sufficiently fracture and consequently a highly dense thermoelectric material is tend to be difficult to be produced, while this result depends on shear strength of particles constituting the fine powder. In contrast, while sintering or compacting of the fine powder at a pressure higher than 10 GPa can produce a highly dense thermoelectric material without causing particle growth, the cost of sintering or compacting is considerably higher and the volume of the resultant thermoelectric material is smaller. Here, according to the present invention, sintering refers to a phenomenon of causing two or more particles to be coupled to each other through heating. Further, according to the present invention, compacting refers to a phenomenon of causing two or more particles to be coupled to each other by any process other than the sintering.

**[0034]** Preferably, the process of sintering or compacting the fine powder is carried out at a temperature of at least 25% and at most 60% of the lowest melting point  $T_1$  (K) on the absolute-temperature-basis of any of constituent materials of the fine powder. When the sintering or compacting process of the fine powder is carried out at a temperature lower than



25% of T1, there is a tendency that the fine powder is not sufficiently sintered or compacted. When the temperature is higher than 60% of T1, there is a tendency that a sudden particle growth occurs.

[0035] Preferably, the method of manufacturing a thermoelectric material of the present invention includes the step of annealing polycrystalline body after the sintering or compacting step. The inventors of the present invention have found that a process of heating (annealing) the polycrystalline body at a predetermined temperature after the sintering or compacting provides an improvement in performance of the thermoelectric material while suppressing particle growth. The annealing is effective in removing distortions for example of grain boundaries in the polycrystalline body after the sintering or compacting. Further, this annealing is also effective, as different from normal annealing, in that the former causes almost no particle growth in the polycrystalline body after the sintering or compacting.

[0036] Preferably, the annealing is performed at a temperature of at least 45% and at most 65% of a lowest melting point T2 (K) of any of constituent materials of the polycrystalline body after the sintering or compacting. Annealing at a temperature lower than 45% of melting point T2 (K) tends to make it difficult to achieve the effect of removing distortions for example of grain boundaries. Annealing at a temperature higher than 65% of melting point T2 (K) tends to deteriorate the performance of the thermoelectric material due to a sudden particle growth that results in a considerable increase in thermal conductivity of the thermoelectric material.

[0037] Still preferably, regarding the method of manufacturing a thermoelectric material of the present invention, the step of preparing a fine powder and the step of sintering or compacting the fine powder are performed in an inactive gas atmosphere or vacuum atmosphere, for preventing impurities from contaminating the thermoelectric material.

[0038] A specific embodiment of the present invention is hereinafter described in connection with examples.

#### EXAMPLE 1

[0039] As a thermoelectric material, FeSi<sub>2</sub> whose material is cheap and easy to be obtained was selected to verify effects of the present invention. A commercially available FeSi<sub>2</sub> powder (particle size: 10 to 20  $\mu\text{m}$ ) was enclosed in an iron pot together with iron balls, and the atmosphere therein was an inactive gas atmosphere generated by Ar substitution. Then, by planetary ball milling, the powder was ground for 10 hours. After the grinding, it was confirmed through an SEM observation that the particle size of secondary particles of the FeSi<sub>2</sub> powder was 0.5 to 2  $\mu\text{m}$ . The size of crystallite was determined based on the integral breadth obtained from XRD measurement of the FeSi<sub>2</sub> powder (Hall method), and it was found that the crystal size was 5 to 10 nm (average crystal particle size: 8 nm). In an Ar globe box, the FeSi<sub>2</sub> powder was enclosed in a capsule made of Ni to fill the capsule and sintered under a pressure of 3 GPa at 700° C. for 30 minutes. From XRD measurement after the sintering, it was confirmed that the sintered body was FeSi<sub>2</sub> single phase. From a TEM observation of the structure of the sintered body, it was found that crystals constituting the sintered body have an average particle size of 15 nm. The relative density of the sintered body was 93%.

[0040] From this sintered body, a disk-shaped sample with a diameter of 10 mm and a thickness of 1 mm was produced

and its thermal conductivity was measured by the laser flash method. The measured thermal conductivity was 0.98 W/mK.

#### COMPARATIVE EXAMPLE 1

[0041] In Comparative Example 1, the powder was used as it was and the powder was sintered under 200 MPa at 1150° C. for one hour. Then, annealing was performed at 800° C. for 10 hours for causing a high-temperature phase resultant from transformation by the sintering to return to a low-temperature phase. It was confirmed through XRD measurement that this sintered body was also FeSi<sub>2</sub> single phase. A sample which was also in the shape of a disk was produced from the sintered body. The thermal conductivity of the sample was 10 W/mK.

#### EXAMPLE 2

[0042] A sintered body was produced through the same process as that of Example 1 except that the time for grinding by ball milling was five hours, and the average particle size of crystals constituting the sintered body and thermal conductivity were measured. The results are shown in Table 1 below. In Table 1, No. 4 shows the results of Example 2 and No. 5 shows the results of Example 1. The average crystal particle size after ball milling was 35 nm. From the results shown in Table 1, it is found that the thermal conductivity considerably lowers when the particle size of crystals of the sintered body structure is 0.05  $\mu\text{m}$  or less.

#### COMPARATIVE EXAMPLE 2

[0043] A sintered body was produced through the same process as that of Example 1 except that the time for grinding by ball milling was zero hour, one hour and two hours, and the average particle size of crystals constituting the sintered body and thermal conductivity were measured. The results are shown in Table 1 below. In Table 1, No. 1 corresponds to the milling time of zero hour, No. 2 corresponds to the milling time of one hour and No. 3 corresponds to the milling time of two hours. Respective average crystal particle sizes after ball milling were at least 5  $\mu\text{m}$  (No. 1), 0.9  $\mu\text{m}$  (No. 2) and 85 nm (No. 3) respectively.

TABLE 1

Results of Examples 1 and 2 and Comparative Example 2			
No.	ball mill time (hr)	average particle size of sintered body ( $\mu\text{m}$ )	thermal conductivity (W/mK)
1	0	20	10
2	1	1	6.4
3	2	0.1	3.9
4	5	0.05	2.0
5	10	0.015	0.98

#### EXAMPLE 3

[0044] From the sintered body of Example 1 (No. 5 in Table 1), a sample of 1 mm×1 mm×15 mm in size was cut, and the electrical resistivity was measured by the four-terminal method. Further, through an EDS analysis of a grain boundary portion of the sintered body, constituent elements were identified. In addition, under the same conditions as those of No. 5, two types of sintered bodies were produced by ball milling in air with no Ar substitution (No. 6) and by enclosing in atmosphere the powder in the Ni



capsule before sintering (No. 7). For these sintered bodies, the electrical resistivity was measured and the EDS analysis was conducted in the manner as described above. The results are shown in Table 2.

[0045] From the results, it was found that impurities (oxide in this case) of grain boundaries have a great influence on the electrical resistivity, and the reduction of the impurities could make the electrical resistivity lower even the crystal structure was a fine crystal structure.

TABLE 2

Results of Example 3			
No.	ball mill time (hr)	electrical resistivity ( $\Omega\text{m}$ )	O-peak intensity by EDS*
5	10	$9 \times 10^{-4}$	0.15
6	10	$5 \times 10^{-3}$	0.30
7	10	$1.5 \times 10^{-3}$	0.25

\*relative intensity with respect to intensity 1 of  $\text{K}\alpha$  of Si that is main peak

## EXAMPLE 4

[0046] An Fe powder and an Si powder were mixed and melted to undergo the process of gas atomizing in a vacuum and thereby produce a fine powder. For the atomizing, He gas of high cooling ability was used and a gas pressure was  $100 \text{ kgf/cm}^2$ . This powder was observed through the SEM to find that the particle size was 5 to  $20 \mu\text{m}$ . Through the XRD measurement, the size of crystallites was determined that was 2 to 10 nm (average particle size: 7 nm).

[0047] This powder was enclosed and sintered as done in Example 1. The resultant sintered body was TEM-observed to find that the sintered body had a crystal particle size of 5 to 20 nm (average particle size: 15 nm). Further, the thermal conductivity of the sintered body was measured as done in Example 1 to find that the thermal conductivity was  $0.94 \text{ W/mK}$ . It is thus seen that the gas atomizing method is also appropriate for manufacturing a sintered body having a fine crystal structure.

## COMPARATIVE EXAMPLE 3

[0048] A sintered body was produced as Example 1 except that sintering was performed under  $0.2 \text{ GPa}$  at  $700^\circ \text{C}$ . for 30 minutes. The resultant sintered body was brittle and had a lower relative density of 70%. Then, the sintering temperature was changed to  $1000^\circ \text{C}$ . A sintered body thus produced had a relative density of 90% with a certain degree of strength. This sintered body, however, had a crystal particle size of 0.1 to  $2 \mu\text{m}$ , which means that a fine crystal structure could not be obtained. The measurement of the thermal

conductivity of this sintered body was  $5.9 \text{ W/mK}$  and the electrical resistivity thereof was  $8 \times 10^{-4} \Omega\text{m}$ . Thus, under any sintering conditions that are out of the sintering conditions of the present invention, no thermoelectric material having a fine crystal structure like the desired one of the present invention could be obtained.

## EXAMPLE 5

[0049] The sintered bodies produced in Example 1 and Example 2 were annealed at respective temperatures of 670 K (45% of melting point  $T_2$ ), 800 K (54% of melting point  $T_2$ ) and 960 K (65% of melting point  $T_2$ ) for one hour in an Ar atmosphere. As a result, sintered bodies annealed at respective temperatures of 670 K and 800 K had the thermal conductivity that was unchanged while they had improved electrical conductivity that was 1.3 times and 1.5 times respectively as high as the original one. Through electron microscope observations, it was confirmed that the crystal particle size of the sintered bodies before annealing and that after annealing were identical. The sintered body annealed at 960 K had the electrical resistivity and the thermal conductivity that were respectively twice and 1.5 times as high as original ones.

[0050] The sintered bodies produced in Example 1 and Example 2 were annealed in an Ar atmosphere at respective temperatures of 600 K (41% of melting point  $T_2$ ) and 1030 K (70% of melting point  $T_2$ ) for one hour. The sintered body annealed at 600 K had its thermal conductivity and electrical conductivity that were unchanged and had no change in structure found through electron microscope observations. Any sintered bodies annealed at 1030 K had the electrical conductivity that was twice as high as the original one while the thermal conductivity thereof was increased to approximately  $6 \text{ W/mK}$  that was in the range from three times (relative to that of Example 2) to six times (relative to that of Example 1) as high as the original one, leading to a decrease in thermoelectric figure of merit.

## EXAMPLE 6

[0051] Thermoelectric materials except for  $\text{FeSi}_2$  were examined as done for Examples 1 to 4. The results are shown in Table 3 (No. 8-No. 19) below. The Seebeck coefficient had almost no dependency on the particle size. Therefore, Table 3 shows nothing about this. It was found that, under the sintering conditions of the present invention, a thermoelectric material having a fine crystal structure that was a desired one of the present invention could be produced. It was also found that a thermoelectric material of the present invention having an average crystal particle size of at most 50 nm and a relative density of at least 85% had a tendency to have a relatively lower electrical resistivity and a relatively lower thermal conductivity at a room temperature ( $25^\circ \text{C}$ ).

TABLE 3

Results of Examination of Example 6									
No.	material system	ball mill time (hr)	sintering temperature ( $^\circ \text{C}$ .)	sintering pressure (GPa)	average particle size of sintered body ( $\mu\text{m}$ )	relative density (%)	impurity oxygen intensity relative to peak intensity by EDS	comparison to relative electrical resistivity (comparison to HP: times)	thermal conductivity at room temperature ( $\text{W/mK}$ )
8	ZnO	4	900	1	0.05	89	—	1.00	10
9	ZnO	4	900	3	0.035	93	—	0.98	8

TABLE 3-continued

Results of Examination of Example 6									
No.	material system	ball mill time (hr)	sintering temperature (° C.)	sintering pressure (GPa)	average particle size of sintered body (μm)	relative density (%)	impurity oxygen intensity relative to peak intensity by EDS	comparison to relative electrical resistivity (comparison to HP: times)	thermal conductivity at room temperature (W/mK)
10	ZnO	4	820	5	0.023	96	—	1.03	4.8
11	CoSb <sub>3</sub>	10	600	1	0.050	85	0.03	0.98	4
12	CoSb <sub>3</sub>	10	600	3	0.030	90	0.03	0.95	3.5
13	CoSb <sub>3</sub>	10	500	10	0.025	98	0.04	0.87	3.1
14	Zn <sub>4</sub> Sb <sub>3</sub>	8	250	2	0.010	100	0.01	1.00	0.36
15	Zn <sub>4</sub> Sb <sub>3</sub>	8	250	5	0.010	100	0.01	1.02	0.35
16	Mg <sub>2</sub> Si	4	400	3	0.020	100	0.08	0.95	1.4
17	MnSi <sub>1.75</sub>	4	400	3	0.020	100	0.05	0.97	1.6
18	ZrNiSn	10	700	5	0.027	100	0.03	0.98	4.7
19	ZrNiSn	10	700	10	0.010	100	0.03	1.05	3.8

## COMPARATIVE EXAMPLE 6

[0052] Using thermoelectric materials except for FeSi<sub>2</sub>, sintered bodies were produced under conditions as shown in Table 4 below that were different from those of Example 6 to conduct examinations as done for Examples 1 to 4. The results are shown in Table 4 (No. 20-No. 37). As shown in Table 4, in Comparative Example 4 in which sintered bodies were produced under conditions different from those of Example 6, no sintered body had an average crystal particle size of at most 50 nm nor a relative density of at least 85%. Further, the sintered bodies (No. 20-No. 37) of Comparative Example 4 had a tendency, as compared with the sintered bodies (No. 8-No. 19) of Example 6, that those sintered bodies of Comparative Example 4 superior in both of electrical resistivity and thermal conductivity are smaller in number.

[0053] In Table 3 and Table 4, “material system” refers to the composition of a constituent material of a thermoelectric material. Zn of ZnO in Table 3 and Table 4 (No. 8-No. 10, No. 20-No. 26) refers to Zn doped with 2 atomic % of Al.

[0054] Further, “impurity oxygen intensity relative to peak intensity by EDS” refers to the ratio of the intensity of oxygen impurities to the maximum intensity detected through an EDS analysis. Since oxygen is not impurities for the material of the composition ZnO (No. 8-No. 10, No. 20-No. 26), the impurity oxygen intensity relative to peak intensity by EDS is indicated as “—”.

[0055] Furthermore, the value of the relative electrical resistivity is represented as a ratio to the value obtained when hot press (HP) sintering is performed under a pressure

TABLE 4

Results of Examination of Comparative Example 4									
No.	material system	ball mill time (hr)	sintering temperature (° C.)	sintering pressure (GPa)	average particle size of sintered body (μm)	relative density (%)	impurity oxygen intensity relative to peak intensity by EDS	comparison to relative electrical resistivity (comparison to HP: times)	thermal conductivity at room temperature (W/mK)
20	ZnO	4	1400	0.1	5	82	—	1.00	42
21	ZnO	4	1300	0.8	1.5	84	—	1.00	30
22	ZnO	4	750	0.5	—	n.s.*2	—	—	—
23	ZnO	4	850	0.5	0.02	73	—	32.00	18
24	ZnO	4	850	0.1	0.04	66	—	126.00	7
25	ZnO	4	1050	0.5	0.07	80	—	15.00	20
26	ZnO	4	1100	0.8	0.09	86	—	5.70	25
27	CoSb <sub>3</sub>	10	800	a.p.*1	—	n.s.*2	0.03	—	—
28	CoSb <sub>3</sub>	10	800	0.1	1.4	90	0.03	1.00	7.5
29	CoSb <sub>3</sub>	10	800	0.3	1.2	92	0.04	0.91	7
30	CoSb <sub>3</sub>	10	650	0.9	0.075	85	0.04	3.20	7
31	CoSb <sub>3</sub>	10	600	0.9	0.045	77	0.03	10.30	4.5
32	CoSb <sub>3</sub>	10	600	0.8	0.05	78	0.04	14.50	5.5
33	Zn <sub>4</sub> Sb <sub>3</sub>	8	500	0.1	1	97	<0.01	1.00	0.7
34	Mg <sub>2</sub> Si	4	600	0.1	1	98	0.08	1.00	2.3
35	MnSi <sub>1.75</sub>	4	600	0.1	1	97	0.05	1.00	3.2
36	ZrNiSn	10	850	0.1	1.2	97	0.03	1.00	10
37	ZrNiSn	10	850	0.5	0.9	98	0.03	1.02	9

\*1atmospheric pressure

\*2non-sintered



of 0.1 GPa. The value of 1.0 or less of the relative electrical resistivity indicates that the electrical resistivity decreases.

#### Industrial Applicability

**[0056]** As heretofore described, the thermoelectric material of the present invention as well as the method of manufacturing a thermoelectric material of the present invention can minimize an increase in electrical resistivity to lower the thermal conductivity and thereby improve the thermoelectric performance.

**[0057]** Moreover, the present invention is applicable to any material other than those used in Examples, contributing to improvements in performance of existing thermoelectric materials.

1. A thermoelectric material having an average crystal particle size of at most 50 nm and having a relative density of at least 85%.

2. The thermoelectric material according to claim 1, wherein an EDS analysis of a grain boundary portion of said thermoelectric material shows that impurity elements have a detected intensity of at most one-fifth of a maximum

detected intensity of an element among constituent elements of said thermoelectric material.

3. The thermoelectric material according to claim 1, wherein said thermoelectric material has an electrical resistivity of at most  $1 \times 10^{-3} \Omega\text{m}$ .

4. The thermoelectric material according to claim 1, wherein said thermoelectric material has a thermal conductivity of at most 5 W/mK.

5. The thermoelectric material according to claim 1, wherein said thermoelectric material has a thermal conductivity of at most 1 W/mK.

6. A method of manufacturing a thermoelectric material comprising the steps of:

preparing a fine powder; and

sintering or compacting said fine powder under a pressure of at least 1.0 GPa and at most 10 GPa.

7. The method of manufacturing a thermoelectric material according to claim 6, further comprising the step of annealing polycrystalline body resultant from said sintering or compacting step.

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