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Research Report

Goniopolar materials for transverse thermoelectric device

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Thermoelectric generators are solid-state devices capable of directly converting heat to electricity. The performance of these modules is limited by the tendency of the metal–semiconductor contacts at the hot-side to degrade due to chemical reactions and/or elemental diffusion. Transverse thermoelectric modules can be employed to address these issues because the temperature gradient and electricity are orthogonal to one another. Consequently, the exposure of metal–semiconductor contacts to high-temperature environments can be avoided, thereby improving the long-term thermal stability of the device. One approach to designing transverse thermoelectric devices is to use materials having goniopolarity, which simultaneously exhibit p- and n-type conduction along different crystallographic directions. Here, we report the goniopolarity of Mg_3Sb_2 and Mg_3Bi_2 due to their band anisotropy.

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1. Introduction

A large amount of energy from different devices is discharged as heat, and society needs a technology that can effectively utilize this unused heat (waste heat). Thermoelectric modules that directly convert temperature differences into electricity are solid-state devices that do not require working fluids and are maintenance-free in principle, and thus research is being actively conducted on these modules as an environmental power generation technology that utilizes waste heat. The dimensionless figure of merit, ZT, of thermoelectric materials is expressed as $ZT = S^2T/\rho\kappa$, where T is the absolute temperature, S is the Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity. As can be seen from this expression, society is demanding the development of materials that have seemingly incompatible properties, such as low electrical resistivity and thermal conductivity. The most famous example of a practical material is the Bi_2Te_3-based material (ZT is approximately 1 at room temperature). A worldwide search has been conducted for materials that surpass Bi_2Te_3 in terms of performance and cost, and promising materials have been reported one after the other in the past 20 years. However, thermoelectric modules using these new materials are still in the basic research stage and have yet to be implemented in practical applications. The lack of a high-performance thermoelectric module that can operate in a high-temperature range is thought to be hindering the progress of using waste heat by thermoelectric power generation.

Conventional thermoelectric modules have a so-called "π-type" structure, in which p- and n-type semiconductors are assembled using electrodes (Fig. 1). Due to the use of the Seebeck effect, in which a thermoelectromotive force is generated by a temperature difference, the temperature difference and power generation are inevitably in the same direction (here called a "longitudinal" structure). Although we wrote "maintenance-free in principle" at the beginning of this text, the reality is that bringing the thermoelectric module into contact with a high-temperature heat source to create a temperature difference results in the deterioration of the module due to the chemical reactions, element diffusion, and cracks in the interface of thermoelectric material and electrodes. Diffusion prevention layers and coating technologies for suppressing interface reactions are being examined to improve durability.

A "transverse" thermoelectric module, in which the directions of the temperature difference and power generation are perpendicular to each other, is expected to fundamentally solve the problems of conventional longitudinal thermoelectric modules (Fig. 1). In this case, a highly durable thermoelectric module is thought to be realized by the spatial separation of the electrode interface, which is the cause of deterioration in the conventional module, from the high-temperature heat source. Building a transverse thermoelectric module requires obtaining an electromotive force that is perpendicular to the temperature difference, and although some devices use a magnetic field or a composite material [1,2], in this paper, we will introduce the use of the off-diagonal terms of the Seebeck tensor using goniopolar materials [3].

The proportionality coefficient of the thermoelectromotive force, ΔV, generated by the temperature difference, ΔT, is the Seebeck coefficient ($\Delta V = -S\Delta T$). The Seebeck coefficient in normal materials is given as a function of the effective mass and carrier density, and is an isotropic value that does not change with direction. However, when the Seebeck coefficient changes with direction (indicating anisotropy), it becomes a tensor that is expressed by a matrix and generates an electromotive force in the x direction, which is perpendicular to the temperature difference in the y direction (S_{xy} has a finite value). For example, in a material with a layered structure, if we set the Seebeck coefficients in the in-plane and cross-plane directions of conduction as S_{IP} and S_{CP}, respectively, and the angle between the temperature difference direction and cross-plane direction as θ, then $S_{xy} = (S_{CP} - S_{IP})\sin(\theta)\cos(\theta)$ (Fig. 1) [4]. As can be seen from this equation, the use of goniopolar materials that have the extremely unique property of the carrier polarity changing based on the direction is effective in increasing S_{xy} (*gonio* refers to "rotation" or "angle" in Greek). The signs of the Seebeck coefficients of the p- and n-type materials are positive and negative, respectively, and thus S_{xy} is expected to have a large value as a result. Of the massive number of inorganic materials reported, only approximately 10 types have been experimentally observed to have

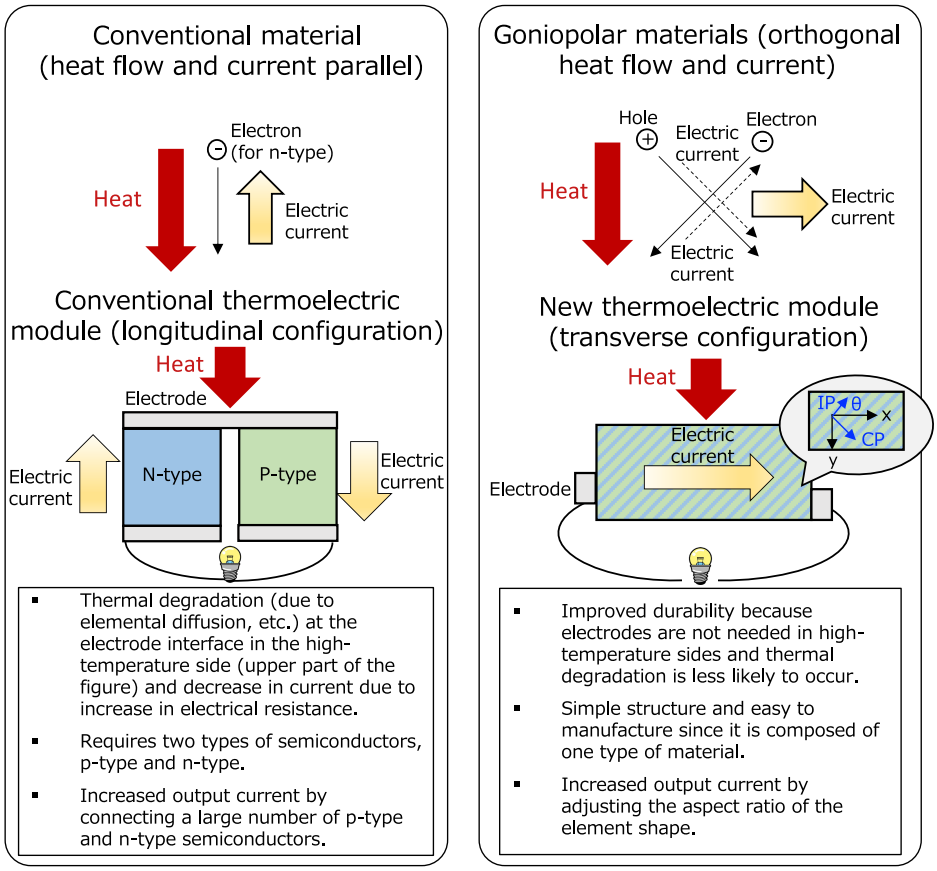

Fig. 1. Schematic representations of the conventional longitudinal and novel transverse thermoelectric module. One approach to designing transverse thermoelectrics is to use materials having goniopolarity, which simultaneously exhibit p- and n-type conduction along different crystallographic directions.

goniopolarity, until a few years ago. However, a study in 2021 reported a transverse figure of merit $Z_{xy}T = S_{xy}T^2/\rho_x\kappa_y = 0.7$ at 980 K for Re_4Si_7 [4], and momentum has been building for the development of new materials (note that the goniopolarity of Re_4Si_7 itself was reported in 2002 [5,6]).

We have recently discovered that Mg_3Sb_2 and Mg_3Bi_2 are goniopolar materials [7]. These compounds are the so-called "122-type Zintl phase" compounds, which are layered materials with a crystal structure in which bonded Mg–Sb/Bi anion networks and ionically bonded Mg cations are alternately stacked (Fig. 2). This compound can undergo n-type doping, which is a rare property among the Zintl phase thermoelectric materials. The compound also exhibits a high value of longitudinal ZT that exceeds 1, and does not contain rare elements such as Te, which has led to research worldwide on this compound as a promising candidate for surpassing the practical material Bi_2Te_3 [8]. In this paper, we first present the experimental results of goniopolarity and then use first-principles computations to show that band anisotropy is the origin of goniopolarity. Finally, given the existence of many similar compounds, we show that the 122-type Zintl phase is a candidate for a new goniopolar material and discuss future developments.

2. Goniopolarity of Mg_3Sb_2 and Mg_3Bi_2

We prepared Mg_3Sb_2 single crystals using the Sb flux method. Figure 3(a) shows the Seebeck coefficient of a representative sample. The sign of the Seebeck coefficient is negative in the in-plane direction of conduction, indicating that electrons are the main carriers. Conversely, the Seebeck coefficient is

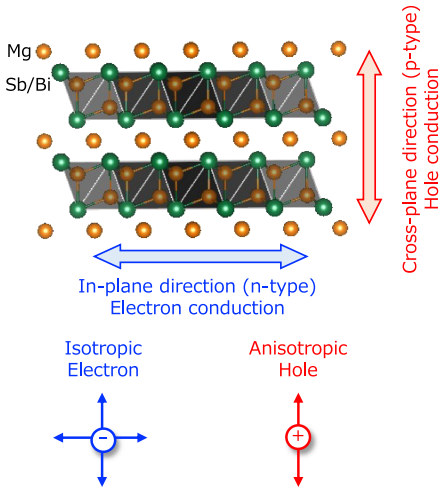

Fig. 2. Crystal structure of $Mg_3(Sb,Bi)_2$. Goniopolarity is induced because of the combination of the isotropic electron and anisotropic hole conduction.

positive in the cross-plane direction, indicating that holes are the main carriers. In other words, we determined that this was a goniopolar material, in which the p- and n-type changed in the same sample depending on the direction. The values at 300 K were relatively large, at $S_{IP} = -222\,\mu V/K$ and $S_{CP} = +227\,\mu V/K$, respectively. As shown in Fig. 3(b), the electrical resistivity had high values in the in-plane as well as cross-plane directions, with a semiconductor-like temperature change being exhibited. This was due to the low carrier den-

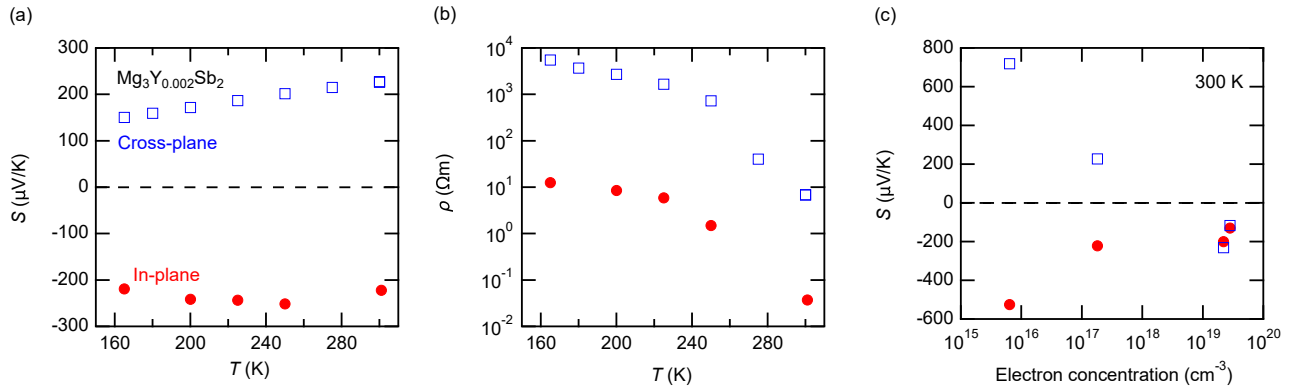

Fig. 3. Temperature dependence of (a) the Seebeck coefficients and (b) the electrical resistivity of Mg_3Sb_2 single crystal for a 300 K electron concentration of 1.8×10^{17} cm^{-3}. (c) Seebeck coefficients as functions of electron concentration at 300 K [7].

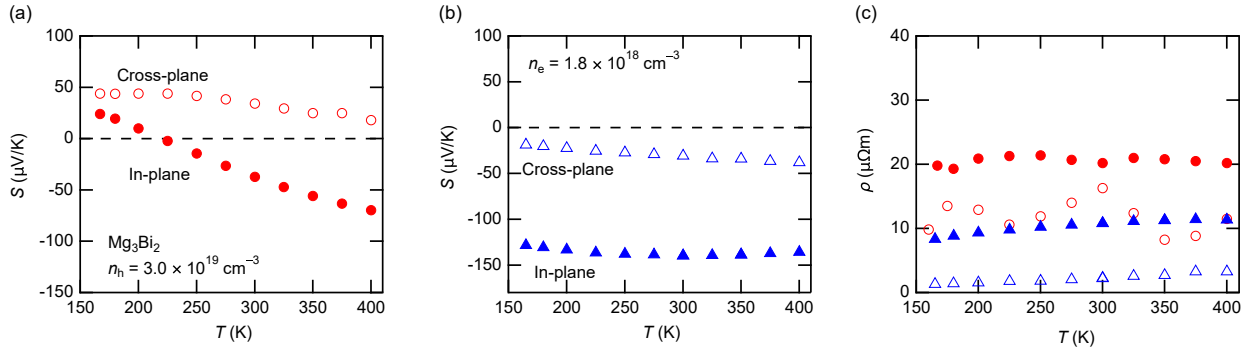

Fig. 4. Temperature dependence of (a, b) Seebeck coefficients and (c) electrical resistivity of Mg_3Bi_2 crystals. Hole and electron concentrations (n_h or n_e) are indicated [7].

sity of the sample, with a value of 1.8×10^{17} cm^{-3} (assuming carrier scattering due to lattice vibration in a single parabolic band, the Seebeck coefficient, S, has the relationship $S \propto m^* \cdot n^{-2/3}$ between the effective mass, m^*, and carrier density, n). Figure 3(c) shows the variation of the Seebeck coefficient at 300 K with respect to the carrier density. Samples with different carrier densities were obtained by varying the amount of Y, an electron dopant, and the annealing temperature in the Mg atmosphere after synthesis. Goniopolarity was observed to appear in the region at or below 10^{18} cm^{-3}. Qualitatively, this indicates that electron doping is conducted on Mg_3Sb_2, which is a semiconductor with a band gap, in the low carrier region at or below 10^{18} cm^{-3}, but holes, which are the minority carriers, behave as the main carriers only in the cross-plane direction. Samples doped with electrons at a high concentration of 10^{19} cm^{-3} or more have a Fermi level close to the bottom of the conduction band, and thus holes, which are minority carriers, cannot contribute to conduction. This results in the disappearance of goniopolarity and the appearance of isotropic properties. A detailed discussion of the electronic structure based on first-principles computations will be given later.

We also examined the goniopolarity of Mg_3Bi_2, in which Sb was replaced by Bi, a homologous element. As shown in Fig. 4(a), Mg_3Bi_2 was also found to be a goniopolar material, with the sign of the Seebeck coefficient changing based on the measurement direction. The Seebeck coefficients at 400 K were $S_{IP} = -70\,\mu V/K$ and $S_{CP} = +18\,\mu V/K$. The carrier density was 3.0×10^{19} cm^{-3} and goniopolarity was observed even in a higher carrier density region than Mg_3Sb_2. In fact, the electrical resistivity was low at 20 μΩ m or less in both directions (Fig. 4(c)). This was due to the fact that Mg_3Bi_2 has a semimetallic electronic structure in which the electron as well as hole bands contributed to the electrical conduction of Mg_3Bi_2. Mg_3Bi_2 is the first example of a semimetal that exhibits goniopolarity and this is thought to be an important finding in the search for materials that exhibit high thermoelectric performance while maintaining goniopolarity. Figure 4(b) shows the Seebeck coefficients of Mg_3Bi_2 with different carrier densities. The in-plane and cross-plane directions were both n-type, but anisotropy was large, with values at 400 K being $S_{IP} = -136\,\mu V/K$ and $S_{CP} = -38\,\mu V/K$, respectively. A large anisotropy is effective for improving S_{xy}, and when combined with the measured results of electrical resistivity and thermal conductivity, the transverse figure of merit at 300 K was estimated to be $Z_{xy}T = 0.06$. Here, we used the measurement results of the thermal conductivity in the in-plane direction due to the difficulty of the measurements of the thermal conductivity in the cross-plane direction. In reality, the thermal conductivity in the cross-plane direction was thought to be lower, so this estimate emphasizes that at least the figure of merit is not overestimated.

3. Elucidating the origin of goniopolarity by first-principles computations

First-principles computations were conducted in order to elucidate the origin of goniopolarity observed in Mg_3Sb_2 and Mg_3Bi_2. Figure 5(a) shows the band structure of Mg_3Sb_2. The valence band maximum (VBM) is at the Γ point and the

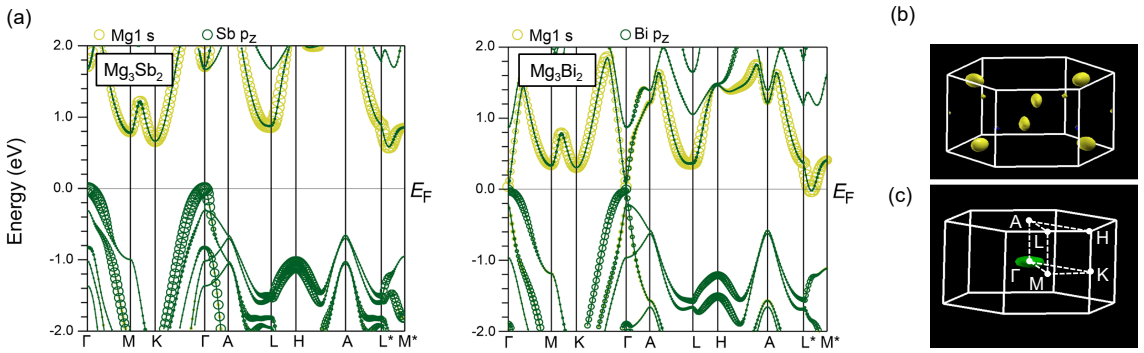

Fig. 5. (a) Band structures calculated for Mg_3Sb_2 and Mg_3Bi_2. In these diagrams, the Fermi energy (E_F) is set to 0 eV. Yellow and green circles show the components associated with Mg1 s and Sb/Bi p_z Wannier orbitals, respectively. (b) Fermi surface of the bottom of the electron pocket along the L*–M* line for Mg_3Sb_2, showing the Mg1 3s region. (c) Fermi surface of the top of the hole pocket at the Γ point for Mg_3Sb_2, showing the Sb $5p_z$ region [7].

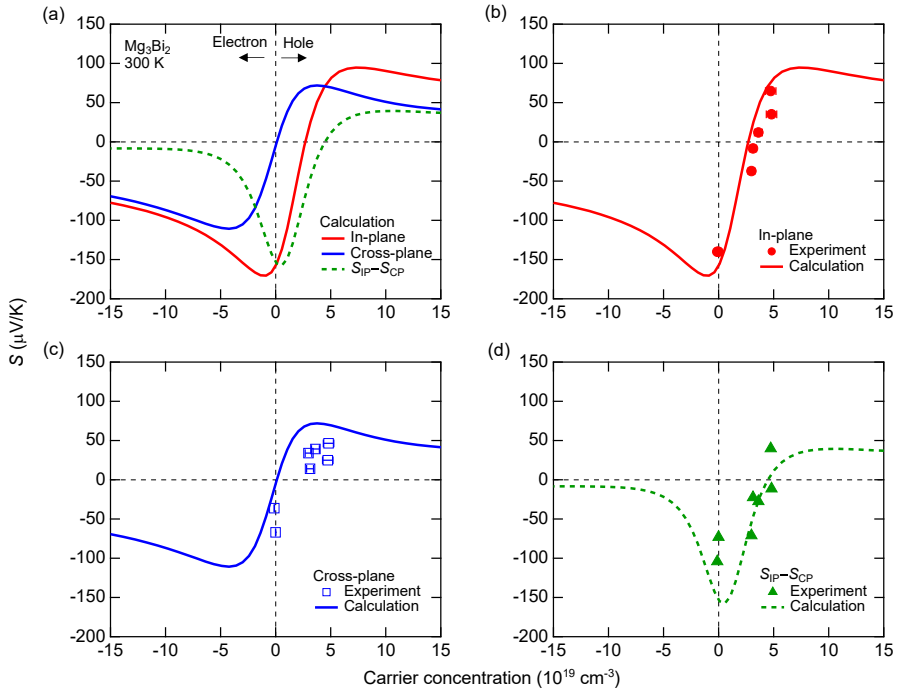

Fig. 6. (a) Calculated Seebeck coefficient tensors for Mg_3Bi_2 at 300 K as functions of carrier concentration. Positive and negative carrier concentration values indicate hole and electron concentrations, respectively. The difference between the Seebeck coefficients in the in-plane and cross-plane directions ($S_{IP} - S_{CP}$) is also shown. (b, c, d) Experimentally determined and calculated in-plane Seebeck coefficients, cross-plane Seebeck coefficients and ($S_{IP} - S_{CP}$) values for Mg_3Bi_2 at 300 K as functions of carrier concentration [7].

conduction band maximum (CBM) is near the L*–M* line ($L^* = (0, 0.417, 0.5), M^* = (0, 0.417, 0)$). A notable feature is that the valence band has a large dispersion in the Γ–A direction. This is because the VBM is mainly composed of Sb p_z orbitals, which results in the holes having a small effective mass in the cross-plane direction, regardless of Mg_3Sb_2 having a layered structure. This band anisotropy can also be seen from the pillow-shaped oblate Fermi surface shown in Fig. 5(c). In contrast, the electron pocket near the L*–M* line is mainly composed of s orbitals of Mg and has an isotropic Fermi surface. Therefore, the combination of anisotropic VBM and isotropic CBM enables goniopolarity.

Mg_3Sb_2 has a semiconducting band structure, whereas Mg_3Bi_2 has a semimetallic band structure in which the electron as well as hole bands contribute to the Fermi surface. However, the abovementioned band anisotropy is maintained in Mg_3Bi_2. Furthermore, an important aspect for quantitative discussion is that the semimetallic band structure enables the computation of transport coefficients assuming Boltzmann distribution. Figure 6(a) shows the results of computing the Seebeck coefficient using the Boltzmann transport properties (BoltzTraP) algorithm, which solves the Boltzmann transport equation under the constant relaxation time approximation. From the results, it was observed that the anisotropy of the Seebeck coefficient became significant in the region where the carrier density was lower than 3.0×10^{19} cm^{-3}. An interesting aspect with regard to the carrier amount was that even in the hole-doped side, a region existed where the in-plane Seebeck coefficient exhibited a negative value (electronic band behaves as the main carrier), which is due to the abovementioned band anisotropy. First-principles computations showed the anisotropy of the Seebeck coefficient ($S_{IP} - S_{CP}$) was predicted to reach $-150\,\mu V/K$ when the carrier density was 5×10^{18} cm^{-3}. A comparison of the experimental results with the

first-principles computations showed that the two values agreed within a reasonable range. However, the experimentally obtained ($S_{IP} - S_{CP}$) was $-100\,\mu V/K$ at maximum, which was smaller than the prediction of the first-principles computations. Single crystal growth with precise control of the carrier density is required for further performance improvement.

4. Conclusion

We fabricated Mg_3Sb_2 and Mg_3Bi_2 single crystals and demonstrated experimentally and theoretically that these crystals are goniopolar materials. A 2016 study reported that $Mg_3(Sb,Bi)_2$ exhibited high thermoelectric performance, and since then, this material has attracted a considerable amount of attention in thermoelectric research. Nevertheless, our report is the first measuring the goniopolarity of this material. Previous research has mainly been, for example, an attempt to improve the figure of merit through the creation of a solid solution of $Mg_3(Sb,Bi)_2$, which degenerates multiple electron bands in the conduction band in terms of energy, which is referred to as "band convergence" [9]. In contrast, an important concept in terms of goniopolarity is band anisotropy, i.e., a combination of an isotropic electron band and an anisotropic hole band. In particular, despite having a layered structure, the valence band is composed of the p_z orbital of Sb/Bi, which results in the distinctive feature of holes being conducted in the cross-plane direction. This enables the combination of 122-type Zintl phase compounds, including $Mg_3(Sb,Bi)_2$, with a variety of elements, and many compounds have similar band anisotropy. Single crystal growth has been reported for some of these compounds. An effective method in module construction is to grow not only large single crystals but also oriented polycrystals [10]. In the future, material exploration in terms of band anisotropy is expected to lead to the discovery of new goniopolar materials and the realization of high-performance horizontal thermoelectric modules.

Acknowledgements

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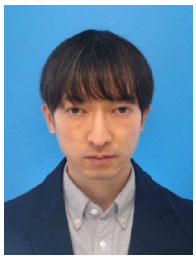
Technical term

122-type Zintl phase compound
Compound consisting of covalently-bonded anion network and cations ionically bonded to it. This term is used when the ratio of the constituent elements is 1:2:2. In the case of Mg_3Sb_2 and Mg_3Bi_2, Mg occupies two cation sites, so these are classified as 122-type Zintl phase compounds.

Profile



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