Synthesis and Thermal Stability of B20-Type TMGe (TM = Mn, Fe and Co) Intermetallic Compounds Prepared by Mechanical Milling

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We propose a new synthesis method of transition-metal monogermanides (TMGe, TM = Mn, Fe, and Co) with a B20-type chiral structure. Arc-melting followed by mechanical milling can be used to produce ~70–110 Å-sized B20-type structures. Differential scanning calorimetry and heat-treatment tests indicated that the B20-phases are stable below 673 K, 873 K and 773 K for MnGe, FeGe and CoGe, respectively. We also demonstrated that sintering tests are able to yield dense compacts from the FeGe and CoGe B20-phase powders.

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1. Introduction

Transition-metal monogermanides (TMGe, TM = Cr, Mn, Fe, Co, and Ru) with a B20-type chiral structure (Fig. 1(a)) exhibit various physical properties, from semiconducting RuGe¹⁾ to metallic helical magnetic FeGe.²⁾ B20-type intermetallic compounds are of recent interest for two reasons, namely, for the formation of magnetic skyrmions^{3–8)} and in thermoelectric material applications.¹¹⁾

Magnetic skyrmions, which are defined as topologically protected vortex-like spin objects, appear as non-centrosymmetric chiral magnets, such as MnSi,^{3,4)} (Fe_{1–x}Co_x)Si,^{5,6)} FeGe,⁷⁾ (Mn_{1–x}Fe_x)Ge,⁸⁾ and recently discovered Co–Zn–Mn compounds.⁹⁾ The former monosilicides and monogermanides belong to the same non-centrosymmetric space group of *P*2₁3, and are a B20-type structure, whereas the latter Co–Zn–Mn compounds have a *P*4₁32 or *P*4₃32, which depends on their handedness, and their crystal structure is isostructural to the β -Mn structure. The spatial inversion symmetry breaking is an essentially important in the formation of skyrmions, and most studies on magnetic skyrmions in metallic system have focused on the B20-type compounds.¹⁰⁾ The FeGe B20-phase has the highest transition temperature of $T_c \sim 278$ K (almost near room temperature) among the B20-type chiral magnets,⁷⁾ which may indicate that it is a good candidate for application in skyrmions for next-generation magnetic memory devices.

With regards the transport properties of the TMGe B20 compounds, a larger negative thermoelectric power of $-82 \mu\text{V/K}$ (at room temperature) is reported because of an asymmetric band with a pseudo-gap electronic structure in CoGe, and a resultant higher dimensionless figure of merit ($ZT \sim 0.11$) among the other B20-type compounds.¹¹⁾ ZT is defined as:

$$ZT = \frac{S^2 \sigma}{\kappa} T,$$

where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Although this ZT value is low for commercial use ($ZT \sim 1$), the power factor ($S^2 \sigma = \sim 3 \text{ mW/mK}^2$) is as comparably high as commercially used Bi–Te-based thermoelectric materials (5.5 mW/mK^2 for the p-type and $3.3\text{--}4.3 \text{ mW/mK}^2$ for the n-type) at ~ 300 K.¹²⁾ The main reason for a suppressed ZT value in CoGe results from the relatively large thermal conductivity component ($\sim 8.9 \text{ W/mK}$ at 300 K). Therefore, if a reduction in lattice thermal conductivity by nanostructuring is achieved, the ZT values should be enhanced further. Theoreticians predict a new mechanism for the enhancement of thermoelectric power (or Nernst effect) in the presence of magnetic skyrmions.¹³⁾ In other words, a series of TMGe compounds has significant potential application in advanced magnetic and/or thermoelectric materials.

Tiny single crystals (~ 1 mm) have been prepared *via* the vapor transport method,¹⁴⁾ and polycrystalline TMGe B20-type compounds have typically been obtained by high-pressure and high-temperature (HPHT) synthesis at $\sim 4\text{--}5$ GPa and ~ 1000 K.¹⁵⁾ The limited sample volume of the high-pressure apparatus is unsuitable for the large-scale production of B20-type compounds. Thus, an easy large-scale synthesis of the B20-type TMGe compound series is required. In previous reports, the B20-type FeGe phase has been produced by mechanical-milling from raw-material powder.^{16,17)} The formation and/or thermal stability of other binary TMGe B20-phases has not been reported.

We synthesized a series of TMGe (TM = Mn, Fe, and Co) B20-type powders by mechanical milling, and discuss and characterize the thermal stability of the obtained powders. We also prepared sintered compacts by using the spark plasma sintering (SPS) method. Our method is a convenient alternative to HPHT synthesis for preparing B20-type TMGe compounds and may be useful for investigations of magnetic skyrmions and thermoelectric materials.

2. Experimental Method

Stoichiometric amounts of high-purity (>99.9 mass%

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Fig. 1 (a) The crystal structure of the TMGe (TM = Mn, Fe and Co) B20-phase was constructed by using the VESTA 3 program package.²⁵⁾ (b)–(d) Powder XRD patterns of investigated TMGe (TM = Mn, Fe, and Co) compounds. The lower vertical bars in each figure represents the calculated intensity distribution of the TMGe B20-phase. The upper part shows the as-milled and annealed powder sample at appropriate temperatures for 72 h. For comparison, samples after arc-melting are shown in the top part. The notation Ge, $\text{Mn}_{11}\text{Ge}_8$, H_{Fe} , T, Fe, H, and C represents the identified phases. H_{Fe} , H, C, and H_{Co} are the Fe-rich hexagonal- $\text{Fe}_{13}\text{Ge}_8$, high-temperature hexagonal FeGe (or CoGe) and C-centered-monoclinic-CoGe, and Co-rich hexagonal Co_5Ge_3 respectively. Asterisks are unidentified phases. (e) The annealing temperature dependence of the crystallite sizes of the B20-phases is estimated by the Scherrer method. Solid lines are guides for the eye.

purity) elemental Mn, Fe, Co, and Ge were weighed as TM:Ge = 1:1 and melted by an arc-melting method on a water-cooled Cu hearth (NEV-AD-03 or NEV-ACD-05; Nissin-Giken Co., Ltd., Saitama, Japan). Mother ingots were reduced to small pieces, and fine powders were obtained by using a tilted planetary ball-mill (Planet Min; Nagao system Inc., Kanagawa, Japan) with a zirconia jar and balls (5-mm diameter) at a rotor speed of 600 rpm for 1 h. The milling conditions are provided in Ref. 18). The mass ratio of sample

and balls was set as 3 g:80 g. The sample phase characterization was performed by X-ray diffractometry (XRD) using $\text{CuK}\alpha$ radiation with an operating voltage and current of 40 kV and 30 mA, respectively (SmartLab; Rigaku Co., Ltd., Tokyo, Japan). The thermal stability of the as-milled powders was determined by differential scanning calorimetry (DSC, DSC7020; Hitachi High-Technologies Co., Ltd., Tokyo, Japan) and by heat treatment at various temperatures for 72 h in an Ar atmosphere. The ramp-up rate for the DSC measurement was chosen as 10 K/min. The maximum temperature of the DSC measurement was 873 K.

Based on the thermal stability experiments, the sintering test for FeGe and CoGe was performed by SPS to form a bulk sample. In the SPS process, we chose the sintering pressure and temperature as 600 MPa and 773 K, respectively, to obtain a high-density sample. The holding time at 773 K was set to 10 min. Sintered compacts were annealed at 873 K for FeGe or at 773 K for CoGe for 72 h in Ar. Bulk sample densities were measured by the Archimedes method using water. The microstructures were studied by scanning electron microscopy (SEM) with an operating voltage of 20 kV (JSM-6010LA, JEOL Co., Ltd., Tokyo, Japan).

3. Results and Discussion

Figures 1(b), (c), and (d) show powder XRD patterns for (b) MnGe, (c) FeGe, and (d) CoGe for the as-milled and annealed samples at several temperatures for 72 h. All main peaks of the as-milled samples, except for small broad peaks notated by asterisks, can be indexed as a cubic lattice with $a = 4.796(5)$ (MnGe), $4.696(3)$ (FeGe), and $4.646(4)$ Å (CoGe), which is consistent with the reported B20-type compounds of $a = 4.7925$ (MnGe),¹⁵⁾ $4.6995(2)$ Å (FeGe),¹⁹⁾ and $4.637(3)$ Å (CoGe),²⁰⁾ respectively. The intensity distributions are also similar to those of the calculated distributions^{15,19,20)} (as shown by the vertical bars). Thus, we conclude the successful synthesis of the series of TMGe with a B20-structure by ball-milling within 1 h. The salient broadness of the Bragg peaks of the as-milled samples can be explained by the crystallite size effect as addressed later. No B20-phases formed after the arc-melted sample (see each upper figure), i.e., $\text{Mn}_{11}\text{Ge}_8 + \text{Ge}$, H_{Fe} (Hexagonal Fe-rich $\text{Fe}_{13}\text{Ge}_8$) + T (Tetragonal FeGe_2), and C (C-centered-monoclinic CoGe) + H_{Co} (Hexagonal Co-rich Co_5Ge_3) phases exist for MnGe, FeGe, and CoGe mother ingots, respectively. As a result, the mechanical-milling process is critically important for the formation of B20-type phases. We do not discuss the detailed formation mechanism of the B20-phases during mechanical milling; however, a local melting mechanism is proposed in the FeGe case.¹⁵⁾ Here, asterisks in Fig. 1(c) and (d) is should be assigned as the intermediate phase toward B20-phase and/or nano-sized H_{Fe} , H_{Co} and C phase.

To discuss the thermal stability of the synthesized B20-phases, we measured the DSC curve up to 873 K for each sample as shown in Fig. 2. An endothermic peak was only observed at approximately 755 K for MnGe, whereas, exothermic peaks were observed at approximately 560 K and 620 K for MnGe, 640 K for FeGe, and 640 K for CoGe. Based on the DSC measurement and the later thermal-

Fig. 2 DSC curves for MnGe, FeGe, and CoGe. The ramp-up rate is set to 10 K/min. Inverted filled triangles and open triangles represent the exothermic and endothermic peaks, respectively. Vertical bars show the heat-treatment temperatures that we tested for 72 h (see also Fig. 1).

treatment test (Figs. 1(b)–(d)), the endothermic peak corresponds to a decomposition of the B20-phase. No significant difference in phases was observed between the exothermic peaks, which may result from the sintering or grain growth effect to reduce the surface energy of the nanosized particle.

We used heat-treatment tests combined with DSC data to study the temperature stability of the B20-phases. As shown in Figs. 1(b)–(d), upon heating, the Bragg peaks become increasingly sharper and finally, the B20-phase decomposes to $\text{Mn}_{11}\text{Ge}_4 + \text{Ge}$, FeGe (hexagonal phase) + bcc-Fe, and CoGe (C-centered-monoclinic phase) for MnGe, FeGe, and CoGe, respectively.

Figure 1(e) shows the crystallite size for each temperature process, as estimated from the integral breadth of the Bragg peak, β , by using the conventional Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta},$$

where D , λ , and θ are the crystallite size, the X-ray wavelength, and the Bragg angle, respectively. K is the shape factor (Scherrer constant) and we chose $K = 1$ in this study. Each mean crystallite size D is estimated from some Bragg peaks. The peak-broadening from the lattice-strain effect during ball milling is negligible because no significant evidence of lattice strain exists in the Williamson–Hall plot²¹⁾ compared with the Si standard (NIST 640d). The crystallite sizes for the as-milled MnGe, FeGe, and CoGe powders were estimated as 110 ± 20 , 80 ± 20 , and 70 ± 20 Å, respectively. Upon heating, before the decomposition of the B20-phase, the crystallite grows to 350 ± 40 , 700 ± 50 , and 250 ± 50 Å for MnGe, FeGe, and CoGe, respectively. Note that the measurable crystallite size is estimated to be less than 1000 Å under our experimental conditions.

The crystallite size of the FeGe increases significantly with an increase in annealing temperature. Such increases are not observed clearly for the MnGe and CoGe powders under our heat-treatment conditions. The difference may result from their thermal stability; according to the TMGe binary phase diagrams,^{22,23)} only the FeGe B20-phase is thermodynamically stable up to 903 K, i.e., stable MnGe and CoGe

B20-phases are not reported at ambient pressure. Therefore, our method can produce *metastable* B20-phases at ambient pressure without a HPHT synthesis. Note that our method is also efficient to prepare the B20-type solid-solutions, such as the $(\text{Fe}_{1-x}, \text{Mn}_x)\text{Ge}$ compounds,²⁶⁾ which have thus far been synthesized only by a HPHT technique.⁸⁾

The estimated crystallite size for FeGe is comparable with or smaller than the reported magnetic skyrmion size of ~ 700 Å.⁷⁾ Thus, the formation of the magnetic skyrmions in our samples may be important and our approach may provide insight into the formation of magnetic skyrmions over that obtained from epitaxial thin-film studies.²⁴⁾

It may be necessary to apply TMGe compounds in bulk, so we performed sintering experiments to obtain a FeGe and CoGe bulk sample. We also attempted the SPS method on MnGe powder; however, we failed to obtain sintering compacts because of the relatively low decomposition temperature (< 773 K) of the MnGe B20-phase (see Fig. 1(a)). Figure 3(a) and (b) show SEM images of sintered FeGe and CoGe, respectively. Besides the small pore size ($< \sim 50$ μm) in the CoGe sample, no significant cracks were observed. The measured bulk densities are 7.92 and 8.13 g/cm³, and the relative density from a structural model of the B20-phase is 96.3% and 92.4% for FeGe and CoGe, respectively. Figure 2(c) shows the XRD patterns of sintered compacts of FeGe and CoGe. Except for small amounts of impurities denoted by asterisks in CoGe, all peaks can be assigned as a B20-phase. Thus, the sintering method is able to yield dense compacts from our powder. The thermal conductivity for sintered compacts of CoGe is 6.3 W/mK at 377 K, which is much lower than the literature value (8.9 W/mK at 300 K¹¹⁾). Thus, our method is efficient for about 30% reduction of the thermal conductivity. The main reason for that is from an increase in the phonon scattering effect by the nanocrystalline structure. Whereas, the obtained ZT value is low as 0.053 at 373 K, which is about half of literature ($ZT \sim 0.11$ at 300 K).¹¹⁾ The suppressed ZT value is understood by the relatively small Seebeck coefficient (-45 μV/K at 373 K; -82 μV/K at 300 K in literature¹¹⁾) in our sample, possibly due to the influence of secondly phases. Further improvement of ZT in the transition-metal monogermanide B20-phases should be achieved by optimizing the synthesis conditions.

4. Conclusions

We propose a new convenient synthesis method to prepare TMGe (TM = Mn, Fe, and Co) with a B20-type chiral structure. B20-type TMGe compounds with the crystallite size of 70–110 Å were synthesized by mechanical milling within 1 h after arc-melting. The crystallite size of B20-phases increased by heat treatment, and which finally decomposed into other crystalline phases over 673 K, 873 K, and 773 K for MnGe, FeGe, and CoGe, respectively. We also performed sintering experiments on the FeGe and CoGe B20-phases by SPS method, and successfully obtained a high-density bulk form. The thermal conductivity for sintered compacts of CoGe efficiently decreased by 30% compared with that for CoGe synthesized by a HPHT process. Our method is suitable for large-scale synthesis

Fig. 3 Backscattered electron microscope image of (a) FeGe and (b) CoGe. The measured sample bulk density is also shown. Besides the sub-100- μm pores as shown in (b), no apparent cracks are shown in both samples. (c) XRD patterns of sintered FeGe and CoGe. Besides the small amounts of impurity phases denoted as H_{Co} and C (same notation as Fig. 1) in CoGe, all peaks can be assigned as a B20-phase.

of B20-type transition-metal monogermanides aiming to the applied research of magnetic skyrmions and/or highly efficient thermoelectric materials.

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