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# Design and fabrication of full-Heusler compound with positive Seebeck coefficient as a potential thermoelectric material

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ABSTRACT

To explore full-Heusler compounds with positive Seebeck coefficient, we calculated thermoelectric (TE) properties of several Co- and Mn-based full-Heusler compounds. Relatively high Seebeck coefficients were obtained in the calculation, indicating a potential of full-Heusler compounds as TE materials. As a candidate, we prepared a $Mn_2VAl$ sample and measured its TE properties. As predicted in the calculation, the $Mn_2VAl$ sample exhibited a positive Seebeck coefficient from 315 K to 1020 K. The maximum power factor was $2.7 \times 10^{-4}$ $Wm^{-1}$ $K^{-2}$ at 717 K. This study embodies great significance for future study on design and fabrication of full-Heusler compounds with high TE properties.



Thermoelectric (TE) materials, which can directly convert thermal energy into electricity or vice versa [1–4], have attracted much attention due to their possibilities of application to power generation and refrigeration devices [5,6]. The efficiency of a TE material is evaluated by the dimensionless figure of merit, $zT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. The power factor, $PF = S^2\sigma$, is also used as a measure of electric power obtained by using the TE material.

Full-Heusler compounds have been extensively studied experimentally and theoretically as potential TE materials [7–16]. Quite recently, our group found that $Co_2MnSi$, one of the half-metallic full-Heusler compounds, exhibited a high PF of $2.9 \times 10^{-3}Wm^{-1}$ $K^{-2}$ at 550 K [16], which is comparable to that of $Bi_2Te_3$ [17] ($4.5 \times 10^{-3}$ $Wm^{-1}$ $K^{-2}$ at 298 K). $Co_2MnSi$ shows a negative Seebeck coefficient, indicating that it can be used as a promising n-type TE material. Although the absolute value of Seebeck coefficient is at most several tens of microvolts per Kelvin, it is relatively high compared with typical metals whose Seebeck coefficient is several microvolts per Kelvin. In addition, $Co_2MnSi$ has a high electrical conductivity, resulting in the high PF.

To realize a power generation device using full-Heusler compounds, a p-type full-Heusler compound with a high PF should be developed. In this work, we calculated TE properties of several Co-based and Mn-based full-Heusler compounds. Among the full-Heusler compounds, we prepared a $Mn_2VAl$ polycrystalline sample as a candidate of the p-type full-Heusler compound. We also evaluated its PF and $zT$ by measuring the Seebeck coefficient, electrical conductivity, and thermal conductivity.

Co-based full-Heusler compounds, $Co_2YZ$ ($Y$ = Ti, V, Cr, Mn, Fe; $Z$ = Al, Si, Ga, Ge), and Mn-based full-Heusler compounds, $Mn_2YZ$ ($Y$ = Ti, V, Cr; $Z$ = Al, Si, Ga, Ge), were selected for the calculation. Based on the first-principles density functional theory, their ground states, electronic band structures, and electronic density of states (DOS) were calculated using the WIEN2k code [18]. A fully-ordered $L2_1$ phase was used for the crystal structure. The total number of $k$-points in the irreducible Brillouin zone was 3107. Using the electronic band structures, TE properties (the Seebeck coefficient, $S$, and electrical conductivity over relaxation time, $\sigma/\tau$) were calculated using the BoltzTraP code [19] on the basis of the Boltzmann's transport equations.

A mixture of stoichiometric amounts of Mn grains (99.9%), V powder (99.5%) and Al grains (99.99%) were arc-melted for five times under Ar atmosphere to obtain a homogeneous $Mn_2VAl$ ingot (GMAC-1100, G.E. S). The ingot was pulverized and then densified by spark plasma sintering (SPS) at 1173 K for 15 min under an applying pressure of 50 MPa (SPS-520S, Fuji Electronic Industrial). A relative density of the SPSed $Mn_2VAl$ sample was over 90%.

The crystal structure of the SPSed $Mn_2VAl$ sample was analyzed by powder X-ray diffraction (XRD) with a Cu Kα radiation (Bruker, D8 ADVANCE). The Seebeck coefficient and electrical conductivity were measured simultaneously in a He atmosphere from 315 K to 1020 K using a Seebeck coefficient/electrical conductivity measurement system (ZEM-3, Advance-Riko). The thermal conductivity was measured by the laser flash method using a thermal parameter measurement system (TC-7000, Advance-Riko) using an equation of $\kappa = D\rho C_p$, where $D$, $\rho$,

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and $C_p$ are the thermal diffusivity, density, and specific heat, respectively.

First we confirmed a ground state of Co-based and Mn-based full-Heusler compounds. For $Mn_2VSi$, $Mn_2VGe$, $Mn_2CrSi$, and $Mn_2CrGe$, a total energy of the nonmagnetic state was equal to or slightly lower than that of the ferromagnetic state, consistent with previous studies [20,21]. On the other hand, the ground state of the other Co-based and Mn-based full-Heusler compounds was ferromagnetic and ferrimagnetic metals, respectively, as reported previously [9,11,20–29]. Some Co-based full-Heusler compounds ($Co_2TiAl$, $Co_2TiSi$, $Co_2TiGe$, $Co_2VGa$, $Co_2VGe$, $Co_2CrAl$, $Co_2CrSi$, $Co_2CrGe$, $Co_2MnSi$, $Co_2MnGe$) and a Mn-based full-Heusler compound ($Mn_2VAl$) had an energy gap at the Fermi level in the minority and majority bands, respectively, indicating a half-metallic characteristic of these compounds.

Next we calculated the Seebeck coefficient, $S$, and electrical conductivity over relaxation time, $\sigma/\tau$, at 300 K and 1000 K of Co-based and Mn-based full-Heusler compounds in the ground state. Fig. 1 shows their Seebeck coefficients at 300 K as a function of valence electron counts (VEC). One can see that both negative and positive Seebeck coefficients were obtained for the full-Heusler compounds studied. Some full-Heusler compounds exhibited a high absolute value of Seebeck coefficient (several tens of microvolts per Kelvin), indicating their potential as TE materials. In Fig. 2, the Seebeck coefficient, $S$, vs electrical conductivity over relaxation time, $\sigma/\tau$, is plotted. The gray curves indicate contours of power factor over relaxation time, PF/$\tau$. It was found that $Co_2MnSi$ exhibited the highest PF/$\tau$ at 300 K and 1000 K among the n-type materials with a negative Seebeck coefficient. As for the p-type materials with a positive Seebeck coefficient, a high PF was expected for $Mn_2VGa$, $Mn_2TiGe$, $Mn_2VSi$, $Co_2VGe$, $Co_2TiGa$, $Co_2VSi$, $Mn_2CrSi$, $Mn_2CrGe$, $Mn_2VAl$, and $Co_2CrSi$ at 300 K. At 1000 K, $Mn_2VSi$, $Mn_2VGe$, $Mn_2CrSi$, $Mn_2CrGe$, $Mn_2VGa$, $Co_2TiGa$, $Co_2VGe$, $Co_2VSi$, and $Mn_2VAl$ were expected to show a high PF. Although $Mn_2VAl$ did not show the highest PF/$\tau$, we prepared $Mn_2VAl$ as a candidate of p-type full-Heusler compounds due to the ease of its preparation.

Fig. 3 shows the XRD pattern of a SPSed $Mn_2VAl$ sample. A simulated XRD pattern of $Mn_2VAl$ in the fully-ordered $L2_1$ structure using a lattice constant of $a = 5.897$ Å reported in Ref. [30] is shown for comparison. The measured XRD peaks were well indexed with the full-Heusler phase with a lattice constant of $a = 5.9133(2)$ Å evaluated by the Le Bail method. Atomic ordering in a full-Heusler compound can be observed by XRD; the presence of the 111 peak in a XRD pattern reflected a formation of the $L2_1$ structure, while the absence of this peak corresponds to atomic disorder with the B2 and/or A2 structures [25]. Since the 111 peak intensity in the measured XRD pattern shown in Fig. 3 was lower than that in the simulated one, the $Mn_2VAl$ sample was found to crystalize in a $L2_1 + B2$ structure.

In general, the sign of the Seebeck coefficient of metals is determined by the energy derivative of DOS at the Fermi level. According to a previously study [31] and our calculation (although not shown here), DOS for minority states of $Mn_2VAl$ decreases with increasing energy across the Fermi level, making the Seebeck coefficient positive in the calculation. Fig. 4(a) shows the temperature dependence of measured Seebeck coefficient of the $Mn_2VAl$ sample. As expected in the calculation, the $Mn_2VAl$ sample exhibited positive Seebeck coefficients from 315 K to 1020 K, i.e., it was a p-type full-Heusler compound. The measured Seebeck coefficient at 315 K was higher than that of the calculation shown in Fig. 1. Such deviation between measured and calculated Seebeck coefficient is also reported in the cases of Co-based full-Heusler alloys [16]. One possible reason is the crystal structure; the measured Co-based full-Heusler alloys contain a disordered B2 phase, while a fully ordered $L2_1$ structure is used for the calculation. It is suggested that the B2 phase shows a higher Seebeck coefficient than the $L2_1$ phase due to a lower carrier density, based on an example that the DOS of $Co_2CrAl$ in the B2 structure near the Fermi level is lower than that in the $L2_1$ structure [32]. The measured $Mn_2VAl$ sample crystallized in the $L2_1 + B2$ structure; the B2 phase may possess a higher Seebeck coefficient than the calculation using the $L2_1$ structure. With increasing temperature, the Seebeck coefficient of the $Mn_2VAl$ sample increased and then decreased above 717 K approaching nearly 0 $\mu VK^{-1}$. The decrease in the Seebeck coefficient above 717 K may relate to a ferrimagnetic-paramagnetic phase transition. In fact, it is reported that the Curie temperature of $Mn_2VAl$ is 760 K [33], which agrees well with the temperature where the Seebeck coefficient began decreasing. The highest Seebeck coefficient of the $Mn_2VAl$ sample was 26.4 $\mu VK^{-1}$ at 717 K, being lower than the absolute value of the n-type $Co_2MnSi$ full-Heusler compound ($-40\ \mu VK^{-1}$ at 960 K [16]), but higher than those of typical metals (several microvolts per Kelvin).

Fig. 4(b) shows the temperature dependent electrical conductivity of the $Mn_2VAl$ sample. The electrical conductivity decreased as the temperature increased from 315 K to 717 K, being a typical behavior of metals. Similar to the Seebeck coefficient, the temperature dependence of the electrical conductivity also changed above 717 K; the electrical

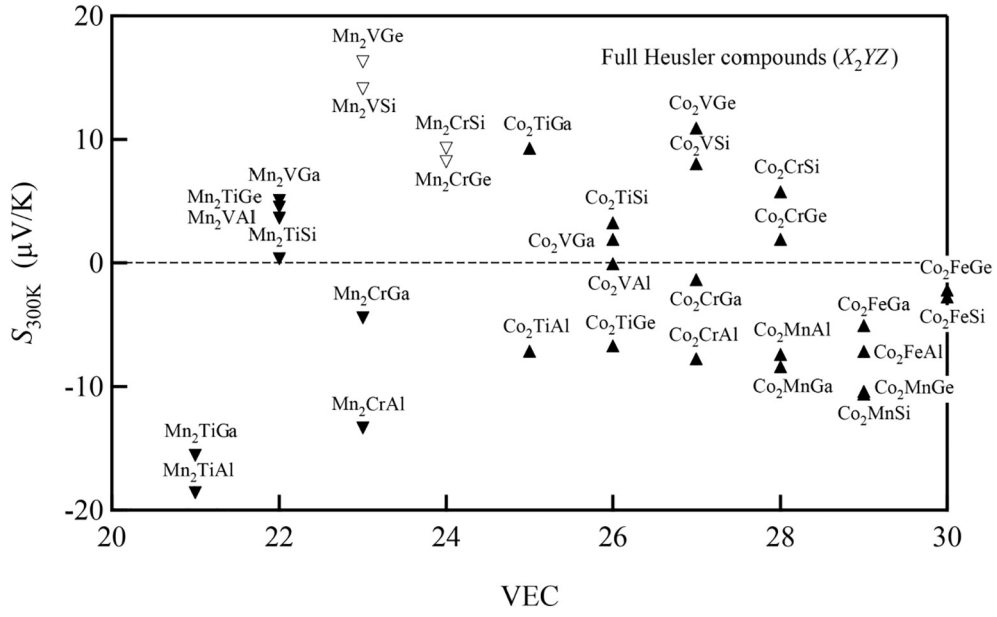


**Fig. 1.** Calculated Seebeck coefficients at 300 K, $S_{300K}$, of Co-based and Mn-based full-Heusler compounds.