

Article

Experimental Realization of Heavily p-doped Half-Heusler CoVSn Compound

Sadeq Hooshmand Zaferani ^{1,2,*}, Alireza Darebaghi ¹, Soon-Jik Hong ³, Daryoosh Vashae ^{2,4,*} 
and Reza Ghomashchi ^{1,5,6,*}

¹ School of Mechanical Engineering, University of Adelaide, Adelaide, SA 5005, Australia; alireza.darebaghi@adelaide.edu.au

² Department of Electrical and Computer Engineering, North Carolina State University, Raleigh, NC 27606, USA

³ Division of Advanced Materials Engineering, Kongju National University, Chungnam 331-717, Korea; hongsj@kongju.ac.kr

⁴ Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27606, USA

⁵ ARC Research Hub for Graphene Enabled Industry Transformation, University of Adelaide, Adelaide, SA 5005, Australia

⁶ Institute For Photonics And Advanced Sensing, University of Adelaide, Adelaide, SA 5005, Australia

* Correspondence: sadeq.hooshmandzaferani@adelaide.edu.au (S.H.Z.); dvashae@ncsu.edu (D.V.); reza.ghomashchi@adelaide.edu.au (R.G.)

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Abstract: Hypothetical half-Heusler (HH) ternary alloy of CoVSn has already been computationally investigated for possible spintronics and thermoelectric applications. We report the experimental realization of this compound and the characterizations of its thermoelectric properties. The material was synthesized by a solid-state reaction of the stoichiometric amounts of the elements via powder metallurgy (30 h mechanical milling and annealing at 900 °C for 20 h) and spark plasma sintering (SPS). The temperature-dependent ternary thermodynamic phase diagram of Co-V-Sn was further calculated. The phase diagram and detailed analysis of the synthesized material revealed the formation of the non-stoichiometry HH CoVSn, mixed with the binary intermetallic phases of SnV₃, Co₂Sn, and Co₃V. The combination of X-ray diffraction, energy-dispersive X-ray spectroscopy, and thermoelectric transport properties confirmed the formation of a multi-phase compound. The analysis revealed the predicted thermoelectric features ($zT = 0.53$) of the highly doped CoVSn to be compromised by the formation of intermetallic phases ($zT \approx 0.007$) during synthesis. The additional phases changed the properties from p- to overall n-type thermoelectric characteristics.

Keywords: half-Heusler; CoVSn; thermoelectric; heterogeneous structure

1. Introduction

There have been substantial progress in thermoelectric (TE) materials over the last two decades. Thermoelectric technology, which was mainly based on alloys of bismuth telluride [1] for Peltier cooling modules, or silicon-germanium alloys [2] for radioisotope thermoelectric generators used in NASA spacecraft, has expanded to new compounds for power generation and cooling [3]. New materials and material structures have been discovered with considerably enhanced thermoelectric properties [4]. In particular, some materials like half-Heusler (HH) alloys have shown an inherently large thermoelectric power factor, although they have generally higher thermal conductivity than alloys such as Skutterudites [5] and Clathrates [6]. Since the thermal conductivity can be decreased by structural engineering, their potential to provide inherently significant power factors has attracted much attention lately. Recently, a new class of HH compounds was predicted with low thermal

much attention lately. Recently, a new class of HH compounds was predicted with low thermal conductivity [7]. In this regard, the sheer number of HH compounds to investigate is vast, and computationally and in this regard, the sheer number of HH compounds to investigate is vast, and computational progress (first principle calculations [8] and machine learning-based methods [9]) is making quick progress. First principle studies [8] and theoretical calculations [9] have shown that some of the $\text{K}(\text{Fe}(\text{NO}_2)_2)$ impurities in the arrangement of $\text{K}(\text{Fe}(\text{NO}_2)_2)$ have a crystal structure due to their (NO₂)₂ and the anisotropic high temperature $\text{K}(\text{Fe}(\text{NO}_2)_2)$ have a layered structure (Figure 1, Table 1) and their characteristics, high-temperature stability, and doping capabilities (Figure 1, Table 1).

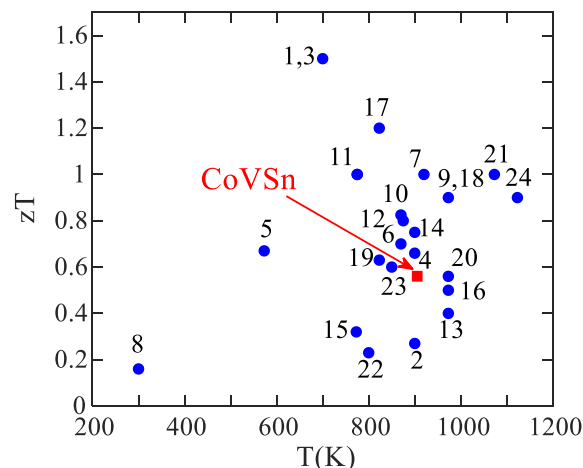


Figure 1. Selected alloys with their corresponding TE properties, which have been studied as half-Heusler (numbers are the items given in Table 1).

Table 1. Compounds cited in Figure 1.

Item	Compound	Ref.	Item	Compound	Ref.
1	$\text{Ti}_{0.5}(\text{Zr}_{0.5}\text{Hf}_{0.5})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[11]	13	$\text{Zr}_{0.5}\text{Nb}_{0.5}\text{CoSb}$	[12]
2	$\text{Ti}_{0.5}(\text{Zr}_{0.5}\text{Hf}_{0.5})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[13]	14	$\text{Zr}_{0.5}\text{Nb}_{0.5}\text{CoSb}$	[14]
3	$(\text{Zr}_{0.5}\text{Hf}_{0.5})\text{Ti}_{0.5}\text{Ni}_{0.998}\text{Sb}_{0.002}$	[15]	15	$\text{Ti}_{0.5}\text{Zr}_{0.5}\text{Ni}_{0.998}\text{Sb}_{0.002}$	[16]
4	$\text{Ti}_{0.5}(\text{Zr}_{0.5}\text{Hf}_{0.5})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[17]	16	VCoSn	[18]
5	$\text{Ti}_{0.5}(\text{Zr}_{0.5}\text{Hf}_{0.5})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[19]	17	$\text{Ti}_{0.5}\text{Zr}_{0.5}\text{Ni}_{0.998}\text{Sb}_{0.002}$	[20]
6	$(\text{Hf}_{0.6}\text{Zr}_{0.4})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[21]	18	$(\text{Hf}_{0.6}\text{Zr}_{0.4})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[22]
7	$(\text{Hf}_{0.7}\text{Zr}_{0.3})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[23]	19	$(\text{Hf}_{0.7}\text{Zr}_{0.3})\text{Ni}_{0.998}\text{Sb}_{0.002}$	[24]
8	$1.5\% \text{Y-Co doped Ti-Ni-Sn}$	[25]	20	$(\text{TiNiSn})_{0.985}(\text{MnNiSb})_{0.015}$	[26]
9	$1.5\% \text{Y-Co doped Ti-Ni-Sn}$	[27]	21	$\text{Zr}_{0.5}\text{Hf}_{0.5}\text{Co}_{0.99}\text{Sb}_{0.01}$	[28]
10	$(\text{Zr}_{0.3}\text{Ti}_{0.65}\text{Ta}_{0.05})\text{NiSn}$	[29]	22	$\text{Zr}_{0.5}\text{Hf}_{0.5}\text{Co}_{0.99}\text{Sb}_{0.01}$	[30]
11	$(\text{Ti}_{0.4}\text{Zr}_{0.5}\text{Hf}_{0.5})\text{Ta}_{0.01}\text{NiSn}$	[31]	23	$\text{Ti}_{0.6}\text{Zr}_{0.4}\text{Pd}_{0.03}\text{Bi}_{0.17}$	[32]
12	$(\text{Ti}_{0.4}\text{Zr}_{0.5}\text{Hf}_{0.5})\text{Ta}_{0.01}\text{NiSn}$	[33]	24	$\text{Ti}_{0.83}\text{Ni}_{0.81}\text{Sb}_{0.17}$	[34]
	ZrNiSn	[33]	25	$\text{Nb}_{0.93}\text{CoSb}$	[35]
Predicted TE factors of CoVSn compound, $\kappa = 4.1 \text{ W/mK}$, $S = 175 \mu\text{V K}^{-1}$, $zT = 0.53$ at 900 K.					

In 1995, Ögüt et al. [36] predicted CoVSn with a MgAgAs (C1b) crystal structure as an intermetallic semiconductor using density functional theory (DFT) band structure calculations. Another study [37] applied the full-potential linear muffin-tin orbital (FP-LMTO) method to evaluate the electronic properties of CoVSn alloy and showed an indirect energy bandgap of 0.75 eV. Shi et al. [38] calculated the electronic structure using the modified Becke-Johnson (MBJ) potential. Also, the transport coefficients were computed employing the Boltzmann theory within the constant scattering time approximation. Moreover, spin-orbit coupling (SOC) was considered in the electronic and transport calculations. Figure 2 shows the calculated electronic band structure and density of states (DOS) of CoVSn alloy [38]. Based on this electronic structure, the alloy was predicted as a p-type semiconductor with a bandgap (W-X) of 0.85 eV.

the presence of three binary intermetallics, namely, SnV_3 , Co_2Sn , and Co_3V , in addition to the non-stoichiometry CoVSn (half-Heusler alloy). Therefore, the synthesized compound was shown to be a multi-phase material. Further, the back-scattered electron (BSE) image and the energy-dispersive spectroscopy (EDS) maps of the material, as shown in Figure 4, illustrated a heterogeneous microstructure, which agrees with the observation from the XRD analysis. The non-uniform dispersion of Co, V, and Sn provide evidence of the presence of a multiphase structure with various micro-clusters.

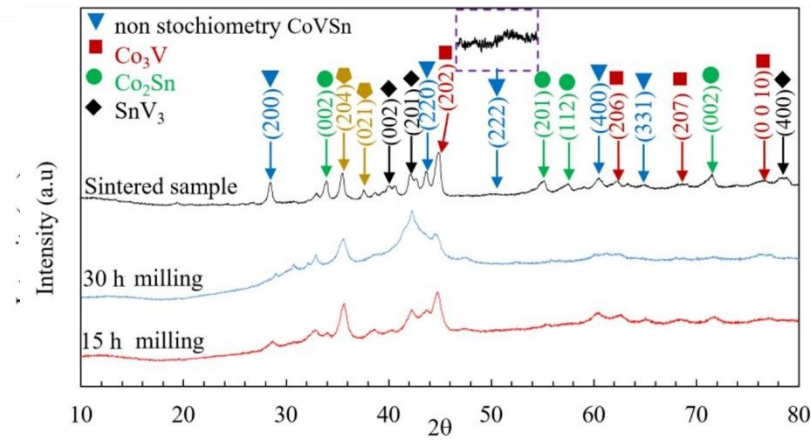


Figure 3. XRD patterns of the synthesized CoVSn compound.

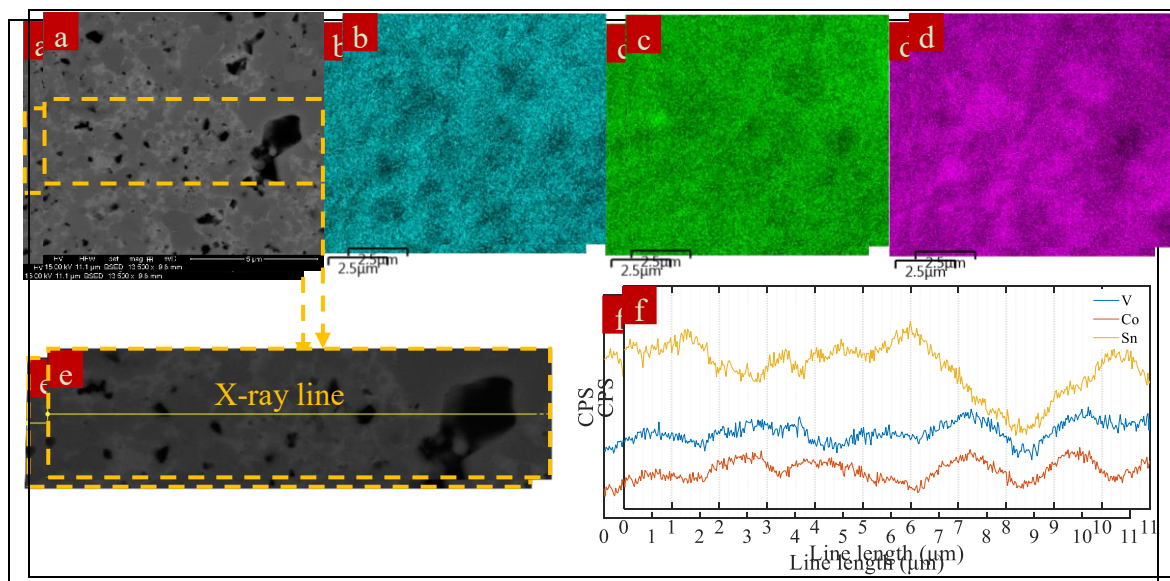


Figure 4. (a) BSE micrograph of the synthesized CoVSn compound and EDS maps of (b) Co, (c) V, and (d) Sn. (e) X-ray line scan and (f) element distribution along with the X-ray line scan.

Figure 5 shows the thermoelectric parameters S , σ , κ (thermal conductivity), and zT of the synthesized compound over a temperature range of 25 to 550 °C. The Seebeck coefficient was negative, indicating an n-type semiconductor. This is in contrast with the theoretical prediction that the CoVSn compound should be a p-type semiconductor [38,39]. The physical properties of the Heusler-based compounds are generally highly related to the crystallographic order [40]. The observed multiphase structure (Figure 5) combining metallic and semiconductor characteristics due to the presence of intermetallics (SnV_3 , Co_2Sn , and Co_3V) and a semiconductor (CoVSn) respectively. Therefore, the carrier type of the composition cannot be assigned to the single phase half-Heusler CoVSn compound.

As illustrated in Figure 4, the multi-phase structure containing various intermetallic compounds with both semiconductor and metallic characteristics provides semiconductor-metal interfaces [42]. The CoVSn compound containing the intermetallic phases has both ionic and covalent bonds. The presence of both ionic and covalent bonds in CoVSn (VS_n: ionic-rock salt; CoSn: covalent-Zinc blend) can influence the stability of the semiconductor-metal interfaces (i.e., interface behavior) [43]. The metal–semiconductor contact lines up the chemical potentials and develops a Schottky barrier at the interface that can lead to distinct chemical and electrical properties different from the bulk compounds [44]. It is instructive to look at the thermodynamics of the ternary phase diagram of CoVSn. Such data are not currently available, being a new alloy. Therefore, we calculated the ternary phase diagram of the Co-V-Sn over the temperatures range of interest, 25 to 1200 °C. The Thermo-Calc 2016a package was used for this calculation. Figure 6 shows the ternary phase diagrams at the selected temperatures of 1100, 900, 600, and 25 °C.

Table 2. Phase compositions of the nominated areas in Figure 6.

Temperature (°C)	Label	Phase (s)
25	a ₂	Co ₃ Sn ₂ _A + HCP_A3 + HCP_ORD
	b ₂	Co ₃ Sn ₂ _A + CoSn + HCP_ORD
	c ₂	CoSn + HCP_ORD + Sn ₃ V ₂
	d ₂	CoSn + CoSn ₂ + Sn ₃ V ₂
	e ₂	BCT_A5 + CoSn ₂ + Sn ₃ V ₂
	f ₂	HCP_ORD + Sn ₃ V ₂ + SnV ₃
	g ₂	CoV ₃ _A15 + HCP_ORD + SnV ₃
	h ₂	BCC_B2 + CoV ₃ _A15 + SnV ₃
	i ₂	BCC_B2 + CoV ₃ _A15
600	a ₆	Co ₃ Sn ₂ _A + FCC_L12
	b ₆	Co ₃ Sn ₂ _B + FCC_L12 + HCP_ORD
	c ₆	Co ₃ Sn ₂ _B + HCP_ORD
	d ₆	Co ₃ Sn ₂ _B + CoSn + HCP_ORD
	e ₆	ALTA_SIGMA (V,Co) + CoSn + HCP_ORD
	f ₆	ALTA_SIGMA (V, Co) + CoSn
	g ₆	ALTA_SIGMA(V, Co) + CoSn + SnV ₃
	h ₆	CoSn + Sn ₃ V ₂ + SnV ₃
	i ₆	LIQUID + CoSn + Sn ₃ V ₂
	j ₆	LIQUID + Sn ₃ V ₂
	k ₆	ALTA_SIGMA(V, Co) + SnV ₃
	l ₆	ALTA_SIGMA(V, Co) + CoV ₃ _A15 + SnV ₃
	h ₂	BCC_B2 + CoV ₃ _A15 + SnV ₃
	i ₂	BCC_B2 + CoV ₃ _A15
	o ₆	BCC_B2
	p ₆	BCC_B2 + SnV ₃

Table 2. Cont.

Temperature (°C)	Label	Phase (s)
900	a ₉	FCC_L12
	b ₉	Co ₃ Sn ₂ _B + FCC_L12
	c ₉	Co ₃ Sn ₂ _B + FCC_L12 + HCP_ORD
	d ₉	Co ₃ Sn ₂ _B + HCP_ORD
	e ₉	ALTA_SIGMA(V, Co) + Co ₃ Sn ₂ _B + HCP_ORD
	f ₉	ALTA_SIGMA(V, Co) + Co ₃ Sn ₂ _B
	g ₉	Co ₃ Sn ₂ _B + BCC_B2 + CoSn
	h ₉	ALTA_SIGMA(V, Co) + Co ₃ Sn ₂ _B + BCC_B2
	i ₉	BCC_B2 + Co ₃ Sn ₂ _B
	j ₉	LIQUID + BCC_B2 + CoSn
	k ₉	ALTA_SIGMA (V, Co) + CoV ₃ _A15 + BCC_B2
	l ₉	BCC_B2 + CoSn
	i ₂	BCC_B2 + CoV ₃ _A15
	o ₆	BCC_B2
	o ₉	LIQUID + SnV ₃
	p ₉	LIQUID + BCC_B2 + SnV ₃
	p ₆	BCC_B2 + SnV ₃
	r ₉	LIQUID + BCC_B2
	s ₉	ALTA_SIGMA(V, Co) + BCC_B2
1100	a ₉	FCC_L12
	b ₉	Co ₃ Sn ₂ _B + FCC_L12
	c ₁₁	LIQUID + Co ₃ Sn ₂ _B + FCC_L12
	d ₁₁	LIQUID + FCC_L12
	e ₁₁	LIQUID + ALTA_SIGMA
	f ₁₁	LIQUID + ALTA_SIGMA (V, Co) + FCC_L12
	g ₁₁	LIQUID
	h ₁₁	LIQUID + ALTA_SIGMA(V, Co) + BCC_B2
	i ₁₁	ALTA_SIGMA (V, Co) + BCC_B2
	o ₆	BCC_B2
	p ₆	BCC_B2 + SnV ₃
	l ₁₁	LIQUID + BCC_B2
	m ₁₁	LIQUID + LIQUID #2 + SnV ₃
	n ₁₁	LIQUID + LIQUID #2 + BCC_B2
	l ₁₁	LIQUID + BCC_B2
	o ₉	LIQUID + SnV ₃
	q ₁₁	LIQUID + LIQUID #2

Figure 5. Temperature dependence thermoelectric parameters of CoVSn compounds. (a) electrical conductivity and Seebeck coefficient, (b) Thermal conductivity and zT.

As illustrated in Figure 4, the multi-phase structure containing various intermetallic compounds with both semiconductor and metallic characteristics provides semiconductor-metal interfaces [42]. The CoVSn compound containing the intermetallic phases has both ionic and covalent bonds. The presence of both ionic and covalent bonds in CoVSn (VS_n: ionic-rock salt; CoSn: covalent-Zinc blend) can influence the stability of the semiconductor-metal interfaces (i.e., interface behavior) [43]. The metal-semiconductor contact lines up the chemical potentials and develops a Schottky barrier at the interface that can lead to distinct chemical and electrical properties different from the bulk compounds [44]. It is instructive to look at the thermodynamics of the ternary phase diagram of CoVSn. Such data are not currently available, being a new alloy. Therefore, we calculated the ternary phase diagram of the Co-V-Sn over the temperatures range of interest, 25 to 1200 °C. The Thermo-Calc 2016a package was used for this calculation. Figure 6 shows the ternary phase diagrams at the selected temperatures. Figure 5 shows the temperature dependence thermoelectric parameters of CoVSn compounds. (a) electrical conductivity and Seebeck coefficient, (b) Thermal conductivity and zT.

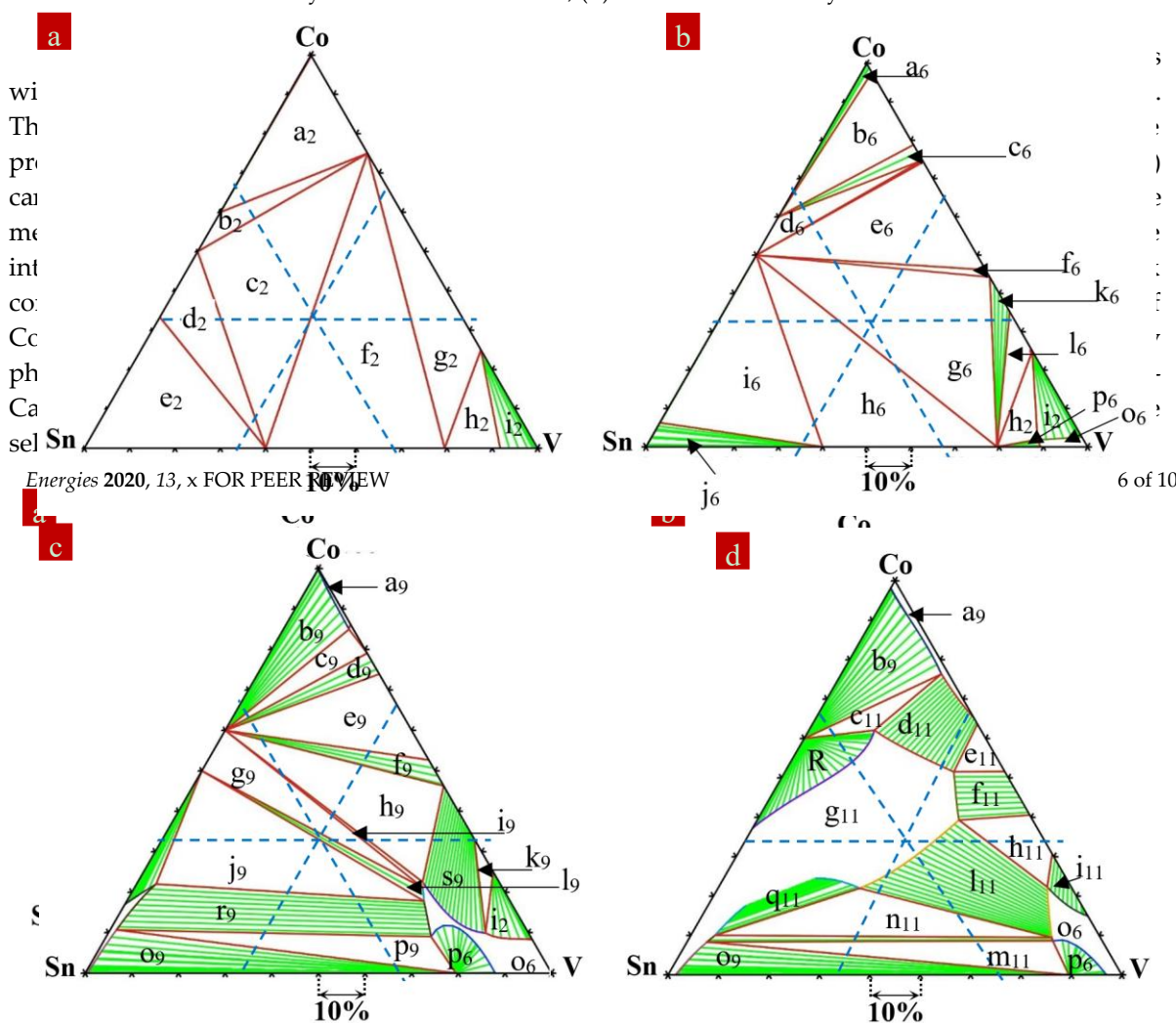


Figure 6. Calculated ternary phase diagrams (atomic ratio) of Co-V-Sn at (a) 25 °C, (b) 600 °C, (c) 900 °C, and (d) 1100 °C. Crossing point showed a composition of 1:1:1 of atomic percent and a weight percent of Co: 26 wt.%, V: 22 wt.%, and Sn: 52 wt.%. Thermo-Calc 2016a package was employed to calculate the ternary phase diagrams under the atmospheric pressure. Table 2 give the phase compositions of the nominated areas in Figure 6.

Table 2. Phase compositions of the nominated areas in Figure 6.

Temperature (°C)	Label	Phase (s)
	a2	Co ₃ Sn ₂ _A + HCP_A3 + HCP_ORD
	b2	Co ₃ Sn ₂ _A + CoSn + HCP_ORD
	c2	CoSn + HCP_ORD + Sn ₃ V ₂

Table 3 lists the different phases at the center of the phase diagram (i.e., the equal atomic concentration of the elements over 100-degree temperature steps from 25 to 1100 °C). These diagrams further confirm that at thermodynamic equilibrium, the material decomposes into multiple phases, as listed in Table 3, which agrees with the observation in the microstructural analysis (Figures 3 and 4).

Table 3. The phase composition of CoVSn compound (1:1:1) at the temperature of 25 to 1100 °C.

T (°C)	Phase/Crystal Structure/Elements
25	CoSn, HCP_ORD (Co, V) and Sn ₃ V ₂
100	SnV ₃ , HCP_ORD (Co, V) and Sn ₃ V ₂
200	SnV ₃ , HCP_ORD (Co, V) and Sn ₃ V ₂
300	CoSn, HCP_ORD (Co, V) and Sn ₃ V ₂
400	CoSn, HCP_ORD (Co, V) and Sn ₃ V ₂
500	CoSn, HCP_ORD (Co, V) and Sn ₃ V ₂
600	CoSn, SnV ₃ , ALTA_SIGMA (V, CO)
700	SnV ₃ , BCC_B2 (Co,V,Sn), ALTA_SIGMA (V, Co)
800	Equilibrium line between two areas of (CoSn, BCC_B2 (Co,V,Sn)) and (ALTA_SIGMA (V, Co), CoSn, BCC_B2 (Co,V,Sn))
900	Equilibrium line between two areas of (CoSn, BCC_B2 (Co,V,Sn)) and (LIQUID, CoSn, BCC_B2 (Co,V,Sn))
1000	LIQUID, BCC_B2 (Co,V,Sn)
1100	LIQUID

As shown in Table 3, there is no single phase of CoVSn, but mainly binary compounds of CoSn, SnV₃, Co₃V, and Sn₂V₃. Our observation of the multiphase structure, containing three binary intermetallics, contradicts previous studies [38,45]. In the theoretical analysis of this composition (1:1:1) [45], the calculated phase diagram showed a specific area for the stable CoVSn compound. However, the presence of this single-phase alloy was not experimentally confirmed.

4. Conclusions

The single-phase half-Heusler CoVSn was predicted theoretically as a stable thermodynamic material with prospective properties for spintronics and thermoelectric applications, although it was never experimentally confirmed. According to the theoretical and experimental data presented here, the CoVSn phase was found to be thermodynamically unstable, and its partial decomposition into metallic phases is unavoidable at the equilibrium state. In this study, the experimental realization of the CoVSn compound with a heterogeneous microstructure was represented. The material analysis showed the presence of the half-Heusler ternary alloy of non-stoichiometry CoVSn as the semiconductor phase, mixed with three binary intermetallics: SnV₃, Co₂Sn, and Co₃V. The combination of X-ray diffraction, energy-dispersive X-ray spectroscopy, and transport properties confirmed the formation of the composite structure. The composite material demonstrated a metallic electronic behavior with a degenerate carrier concentration.

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Conflicts of Interest: There is no conflict to declare.

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