Eximia journal

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Vol. 14/2025

PLUS COMMUNICATION

International Communication & PR

Eximia Journal
Vol. 14, 579-587, May, 2025
ISSN: 2784-0735
www.eximiajournal.com

Annealing Temperature Effect on Phase Transition and Thermoelectric Properties of Doped Zinc-Antimony

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Abstract. The intermetallic compound ZnSb is a (II-V) narrow gap semiconductor with interesting thermoelectric properties. Electrical resistivity, Hall coefficient and thermal conductivity were measured from 300 up to 600 K on Cu once and Ag-doped samples with a concentration of 0.5%, which were the annealed powder was sinterable at 50 MPa in a uniaxial hot press. The work confirms a significant improvement of the thermoelectric Figure-of-merit, *ZT*, 61% for Ag doping and 143% for Cu doping. The optimum doping level is near 0.5 at.% Cu and results in ZT values around 0.916 at 600 K. A significantly lower resistivity, which is linked to a higher concentration of hole charge carriers, is the cause of the improvement. The intrinsic impurity band of ZnSb is said to be enhanced by Cu replacing trace amounts of Zn (around 0.2 at.%) in the crystal structure. It was discovered that excess Cu was segregated at grain borders.

Keywords. Zinc antimony; annealing; crystal structure; thermoelectric; carrier concentration

1. Introduction

The potential of Zn-Sb alloys as thermoelectric materials makes them an attractive option for applications using renewable energy. In reality, attaining greater efficiency is often shown by the figure of merit (ZT)—while maintaining affordable manufacturing costs is a crucial component of their actual implementation. Zn-Sb alloys are unique in that they combine strong thermoelectric capabilities with comparatively inexpensive material prices [1,2]. They can perform much better and become more competitive in energy management systems if their ZT is improved by doping with elements like Cu and Ag. These materials might be crucial in turning waste heat into electrical energy that can be used, which would support sustainable energy solutions, provided they are optimized for increased efficiency [3]. Addressing the intrinsic constraints of Zn-Sb alloys is a crucial part of developing them for thermoelectric applications[4]. Despite its potential, ZnSb's poor figure of merit (ZT) and thermal instability over around 470 K make it unsuitable for use in real-world applications. For it to be a practical alternative to thermoelectric devices, several enhancements are therefore required [5,6]. A well-known method for improving thermoelectric characteristics is doping, which reduces lattice thermal conductivity and alters carrier concentration. Certain dopants, including Cd, In, Mg,

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Vol. 14, 579-587, May, 2025
ISSN: 2784-0735
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Al, Hg, Cu, Nb, Te, and Se, do not yield appreciable performance gains. However, elements like Te, Nb, Cu, Hg, and Al have performed better [7,8]. Ag has fewer valence electrons than Zn, which makes it an intriguing dopant that can raise the concentration of holes. Ag may increase the concentration of p-type carriers in ZnSb, which is required to increase the power factor and, in turn, the overall performance of the thermoelectric system. To overcome some of the difficulties that ZnSb faces in practical applications, it may be possible to increase ZT by assessing the effects of Ag replacement in ZnSb, particularly at low temperatures[9,10]. ZnSb doping can alter the bulk material's Zn/Sb ratio as well as the delicate balance between Zn disorder and Zn shortage in ZnSb. As a result, carrier dynamics and concentration are modulated proportionately [11]. The precise procedure and underlying standards, however, remain intriguing and unclear. Dopants can be added to ZnSb in several ways, including by replacing interstitial Zn atoms or Zn and Sb from conventional framework sites. Consequently, it becomes essential to investigate the structural characteristics of the metal-doped ZnSb system by combining theoretical computations with actual observations [12,13,14]. In the current work, we concentrated on the doping-content dependences of thermoelectric characteristics after the doping of Ag and Cu in ZnSb, building on our initial study of the low-temperature thermoelectric capabilities of doped ZnSb. We attempted to extract some crucial information that would aid in our understanding of Ag and Cu doping and their influence on the thermoelectric characteristics of ZnSb by combining experimental observations with first principles.

2. Experimental Procedure

The specimens were prepared by melting in evacuated silica glass ampoules. For Zn, Sb, Cu and Ag, the corresponding purities were 99.99% and 99.999%. In a stainless steel vial, the material was ball milled for 20 minutes in an argon environment after being quenched, crushed into powder, and annealed for 4 days at 373 k^0 in a vacuum. The resulting powder was sinterable at 50 MPa in a uniaxial hot press. By keeping the temperature close to the melting point, high-density samples were produced. ZnSb sample and Cu and Ag doping of 0.5% wt were prepared. The Seebeck coefficient and the resistivity were measured in a custom-built system between 300 and 600 k^0. The Hall carrier concentration and mobility were measured by a Lake Shore Hall setup. The thermal conductivity was measured using a Netzsch Laser Flash (LFA 457). The samples were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM).

3. Results and Discussion

3.1 XRD Diffraction

XRD patterns show that the dominant phase is ZnSb in the annealed samples (Fig. 1a). The refined lattice parameters based on synchrotron radiation diffraction have orthorhombic structure with P 2 2 2 space group, the lattice parameters: a = 10.09173 A^0, b = 10.09173 A^0, c = 10.09013A˚.

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Vol. 14, 579-587, May, 2025
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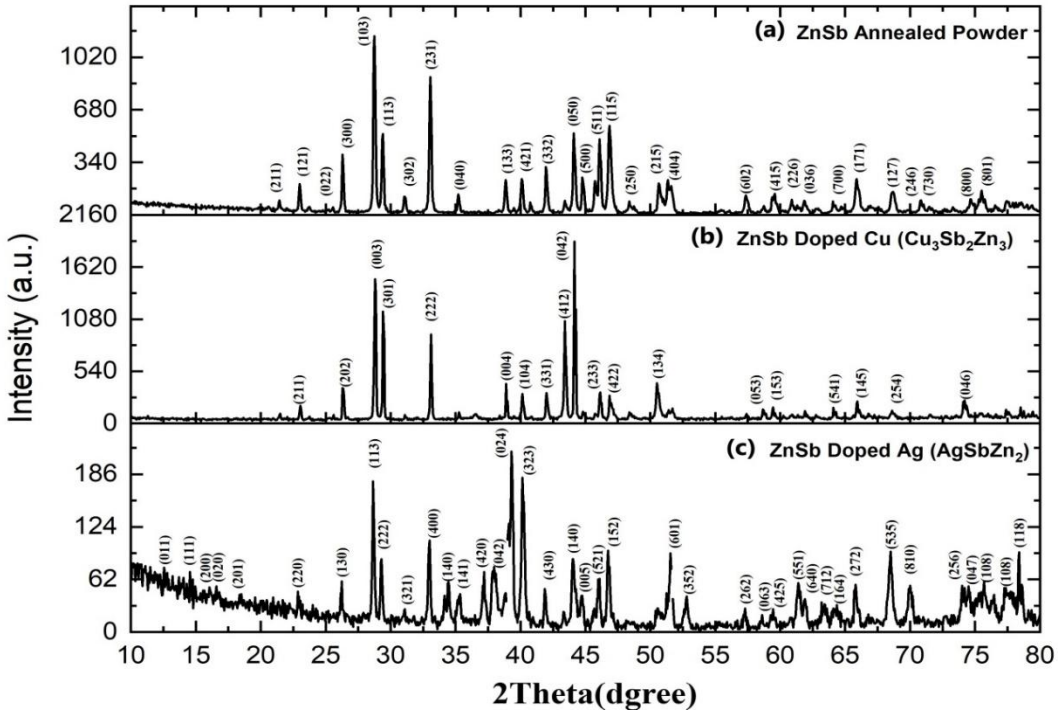

Fig.1. (a) XRD patterns for annealed ZnSb, (b) for ZnSb doped by 0.05% Cu, and (c) for ZnSb doped by 0.05% Ag.

With its orthorhombic structure and P 2 2 2 symmetry, ZnSb would affect its thermoelectric capabilities by influencing its particular band structure, phonon dispersion, and scattering processes. P 2 2 2 space group crystals may exhibit decreased phonon scattering in specific directions, perhaps resulting in increased heat conductivity along those lines [15,16]. Alternatively, phonon scattering could work better in other directions, which could result in reduced thermal conductivity [16]. Low thermal conductivity is frequently required to sustain a high-temperature gradient for efficient thermoelectric performance, hence adjusting the structure to promote phonon scattering in particular directions may be beneficial. Samples of zinc antimony doped with copper With a cubic crystal structure, cell length of 9.83400 A°, and subgroup $F\bar{4}3c$, with cubic symmetry, Fig. 1b has the chemical formula $Cu_3Sb_2Zn_3$ [17]. Because the crystal is isotropic, it frequently offers balanced carrier mobility in all directions, which can be useful for thermoelectric applications because higher symmetry can result in uniform electrical conductivity, which is necessary for stable thermoelectric performance. Seebeck coefficient minimizes heat conductivity and maintains a moderate level of electrical conductivity. To create effective thermoelectric devices, the cubic symmetry provides a solid foundation for isotropic transport characteristics[18,19].

As shown in Figure 1c, the XRD clearly shows peaks corresponding to the impurity $AgSbZn_2$, which have an orthorhombic crystal structure with P 2 2 2 space group and lattice parameters a = 10.83547 A^0, b = 10.74577A^0, and c = 10.09706A^0. The strong symmetry of cubic systems is absent from orthorhombic crystal structures with P 2 2 2 space groups, which may result in anisotropic electrical characteristics along various crystallographic orientations [20]. While maintaining advantageous thermoelectric qualities in other directions, this anisotropy could

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Vol. 14, 579-587, May, 2025
ISSN: 2784-0735
www.eximiajournal.com

enable electrical conductivity optimisation in one axis. Thermoelectric materials frequently exhibit this anisotropic conductivity, where performance can be improved by directed tuning. High Seebeck coefficients can be obtained by varying the charge carrier concentration or band structure because the Seebeck coefficient in orthorhombic materials is sensitive to the effective mass and density of states close to the Fermi level. Additionally, P 2 2 2 symmetry may support bands with directional dependency [21,22].

3.2 Thermoelectric properties

The temperature variation of thermoelectric sample properties was studied from room temperature up to 600 K and shown in Fig. 2. And Table.1 The Seeback and figure of merit are temperature dependency and the type of doping, the figure of merit tends to increase as ZnSb doping by Cu and Ag respectively [23]. Changes in carrier concentration, scattering processes, and band structure can cause changes in the Seebeck coefficient and electrical conductivity as the temperature rises. At high temperatures, phonon-phonon scattering increases, which can favour greater ZT and cause the thermal conductivity (lattice and electronic components) to decrease [24].

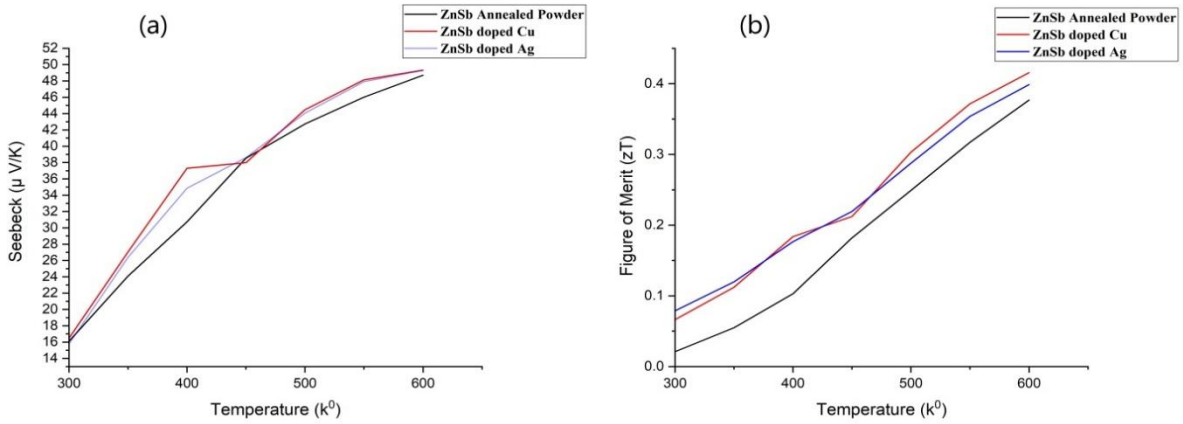

Fig.2 Seeback and the figure of merit for undoped and doped ZnSb samples.

Table 1. Seeback and figure of merit for undoped and doped ZnSb samples.

	ZnSb Annealed Powder		ZnSb doped Cu		ZnSb doped Ag	
Temperature	Seebeck (μ V/K)	Figure of merit (zT)	Seebeck (μ V/K)	Figure of merit (zT)	Seebeck (μ V/K)	Figure of merit (zT)
300 (k^0)	16.1	0.021	19.56	0.062	18.7	0.040
350 (k^0)	24.08	0.055	30.4	0.174	29.03	0.113
400 (k^0)	30.72	0.103	40.92	0.349	37.3	0.214
450 (k^0)	38.53	0.182	41.62	0.419	40.95	0.290

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Vol. 14, 579-587, May, 2025
ISSN: 2784-0735
www.eximiajournal.com

500 (k^0)	42.72	0.249	48.28	0.641	46.26	0.411
550 (k^0)	46.01	0.317	52.03	0.808	50.02	0.529
600 (k^0)	48.7	0.377	53.26	0.916	51.38	0.609

By increasing the concentration of hole carriers, copper doping ZnSb can improve electrical conductivity (σ) and somewhat reduce the Seebeck coefficient due to the greater carrier density. In addition to changing the band structure and carrier concentration, silver may have a different effect than copper on the balance between electrical conductivity and the Seebeck coefficient [25,26]. Ag may enhance phonon scattering and hence reduce lattice thermal conductivity.
To get the figure of merit ZT, low thermal conductivity and a high power factor (Seebeck coefficient squared times electrical conductivity) must be achieved [27]. With these lattice parameters and an orthorhombic structure in space group P222, materials might provide beneficial anisotropic thermoelectric characteristics. Such an orthorhombic structure with space group P222 may exhibit interesting thermoelectric behaviour if doped or alloyed to decrease heat conductivity while adjusting carrier concentration to enhance the Seebeck coefficient and electrical conductivity [28]. This structure is a promising choice for thermoelectric applications if well-tuned due to its low lattice thermal conductivity, adjustable electrical conductivity, and perhaps high Seebeck coefficient [29].

Table 2. Resistance, Hall coefficient and carrier concentration for undoped and doped ZnSb.

Sample	**ZnSb Annealed Powder**	**ZnSb doped Cu**	**ZnSb doped Ag**
Hall coefficient (m^3/coulomb)	$+97\times10^3$	$+7\times 10^3$	$+12\times10^3$
Carrier concentration (m^{-3})	0.64×10^{14}	8.04×10^{14}	5.11×10^{14}

Table. 2 shows the p-type ZnSb sample's hole carrier concentration with the carrier concentration, The Hall coefficient drops when ZnSb is doped with Ag or Cu. The ZnSb matrix gains extra charge carriers (holes) as a result of doping with Cu or Ag. The concentration of hole carriers rises as a result. Copper doping contributes additional holes to the ZnSb structure by acting as an acceptor dopant [30,31]. As a result, the concentration of hole carriers rises dramatically, lowering the Hall coefficient. Although silver adds holes as well, its effect on the carrier concentration may be somewhat different from copper doping because of variations in solubility, bonding, or defect states [32,33].

3.3 SEM

Figure 3 displays the surface topography of the doped and undoped samples. It is difficult to obtain the clear surface amorphous of the annealed ZnSb sample, but the grains are sparse and irregular, which may be identified as clusters rather than grains, and they show a wide grain

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Vol. 14, 579-587, May, 2025
ISSN: 2784-0735
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size distribution ranging from 43 to 53 nanometres with wrinkled surfaces, revealing a three-dimensional surface[34,35]. These SEM results were in good agreement with the XRD results.

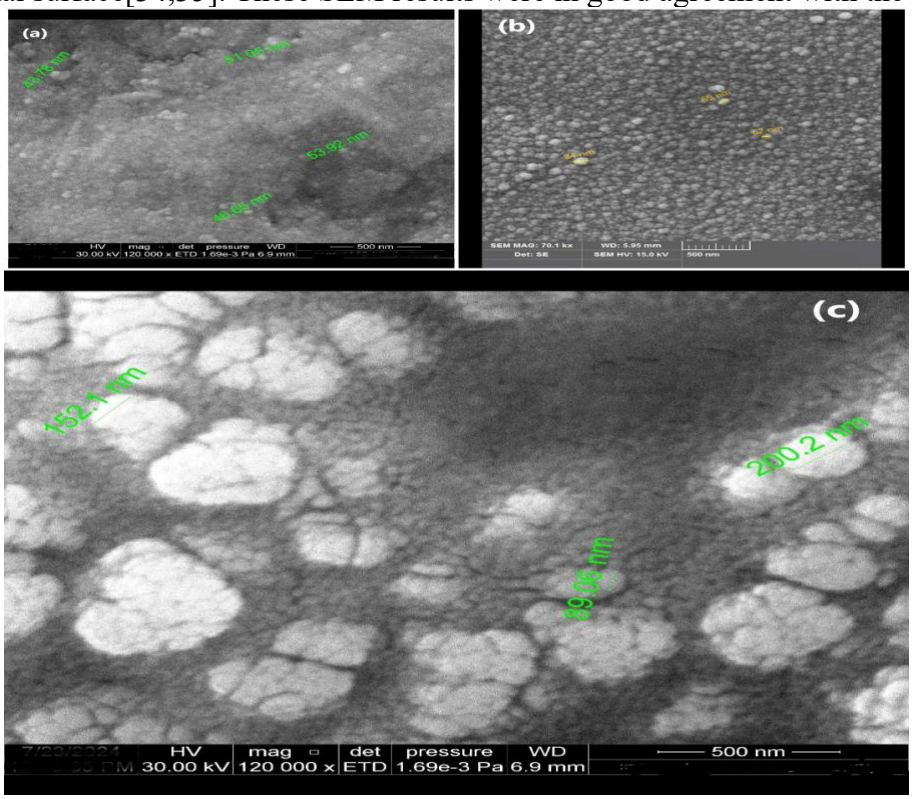

Fig.3 SEM backscattered electron images for a) undoped ZnSb, b) ZnSb-0.5%Cu, and (c) ZnSb-0.5%Ag.

After Cu is doped, the grains are distinctly observed and distributed evenly, together with the nano-particle structure that the average grain size is less than 50 nm. The HRTEM analyses of S2 affirmatives that the thin film is polycrystalline and numerous grain boundaries can be found in the polycrystalline ZnSb thin film. The grain size is about ~ 13 nm which is coincident with the calculation result from XRD, indicating that the thin film has nano-sizes crystallite. Generally, the well-crystallization leads to better electrical transport and nano-structure causes the enhancement of the Seebeck coefficient [36].

The crystalline grain of Ag-doped ZnSb samples was a little fuzzy. The rough surface and almost invisible crystalline grain revealed poor crystallization. It can be seen that the grains were very sparse and irregular. The grain becomes more and more serried and the grain size is between 89 to 200 nm. However, in Ag-doped ZnSb samples, the grain size increases related to undoped ZnS which leads to poor thermoelectric performance. However, the surface morphology and grain size were not as well as expected. At ZnSb samples doped with Ag. $AgSbZn_2$ is the result of doping. Nonetheless, there is evidence of nano-sized Ag-rich particles trapped inside the ZnSb bulk grains in addition to the obvious segregation of silver particles into grain boundaries [37].

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Vol. 14, 579-587, May, 2025
ISSN: 2784-0735
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4. Conclusion

It appears that Cu doping enhances the impurity band of ZnSb, 5% concentration of monovalent Cu changes the chemical structure and the crystal space group, as in a solid solution of $Cu_3Sb_2Zn_3$. For Ag doping, $AgSbZn_2$, which has an orthorhombic crystal structure with P 2 2 2 space group which takes place already for 0.5% Ag. The electrical conductivity of the undoped and doped samples increases rapidly when the temperature is at 600k due to the lower dislocation density and defects. Hence, the Cu doped can optimize the thermoelectric property of the ZnSb bulk sample.

5. Acknowledgment

My thanks and appreciation to the professors of the Physics Department at Al-Qadisiyah University, College of Education, and the Iraqi Ministry of Science and Technology, and thanks to the personnel who work in this institutions.

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