Effect of Ag Doping on Mechanical Properties of Cu₆Sn₅ Intermetallic Compounds

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Abstract: Cu₆Sn₅-xAg alloys (x = 0, 3, 6; %, mass fraction) were synthesized using Ag as a dopant through a high-temperature melting technique. The microstructure of the alloy was analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and other equipment, while the hardness of the alloy was measured to investigate the impact of Ag addition on the structure and microstructure of the Cu₆Sn₅ intermetallic compound. This study explored the influence of varying Ag contents on the properties of Cu₆Sn₅ intermetallic compounds, with calculations based on first principles revealing the mechanical properties and density of states of η'-Cu₆Sn₅ and its Ag-doped systems. The results indicated that Cu₆Sn₅-xAg alloys predominantly existed in three distinct forms, all exhibiting large masses without any impurities or precipitates. First-principle calculations demonstrated that Ag substitution in certain sites suppressed the anisotropy of the Young’s modulus of Cu₆Sn₅, particularly in the Cu₁, Cu₃, Sn₁, and Sn₃ positions, while the effect was less significant at the Cu₂, Cu₄, and Sn₂ sites. The introduction of Ag through doping enhanced the covalent bonding within the η'-Cu₆Sn₅ structure, promoting the formation of a stable (Cu, Ag)₆Sn₅ structure.

Keywords: Ag; intermetallic compounds; first-principle calculations; anisotropic

1. Introduction

The electronics industry is rapidly evolving towards miniaturization and multifunctionality, driving electronic packaging technology to advance in high-density, functionality, and integration aspects [1]. Lead-free solder has emerged as the primary material in electronic packaging due to its excellent electrical conductivity, mechanical properties, and cost-effectiveness [2]. Reflow soldering is predominantly used for connecting electronic components [3]. During the soldering process, a chemical reaction between Sn and the Cu substrate forms an intermetallic compound (IMC) at the solder joint interface. The primary component of the IMC is Cu₆Sn₅, with a melting point of 415 °C and strong thermodynamic and kinetic stability [4,5]. Cu₆Sn₅ exhibits two crystalline structures: a monoclinic crystal structure (η-phase) below 186 °C and a hexagonal crystal system structure (η-phase) above 186 °C [6]. The phase transformation results in a 2.15% volume change, increasing compressive stress within the solder joint, potentially leading to crack formation or propagation and compromising solder joint reliability [7–9].

The mechanical properties of Cu₆Sn₅ alloys have been extensively studied both domestically and internationally. Through nanoindentation experiments, researchers have measured the Young’s modulus (E) and hardness (H) of Cu₆Sn₅, revealing significant anisotropy in both properties when compared to (Cu, Ni)₆Sn₅ [10]. Choudhury [11] et al. further delved into the anisotropic mechanical properties of single-grain Cu₆Sn₅ using nanoindentation and electron backscatter diffraction. However, the experimental methods used to gather information on these anisotropic properties are limited due to challenges in obtaining data from all directions. In microelectronic soldering processes, the
Cu-Sn alloy, a common intermetallic compound, tends to form small interfacial compounds in lead-free solder joint experiments, leading to inaccuracies in measuring its mechanical properties. Doping with trace elements like Ni [12], Co, In [13], Zn, Au, and Pd has been shown to inhibit the phase transition of η-CuSn₆, thereby enhancing its mechanical properties. Studies have demonstrated that the addition of Zn, Au, and In can stabilize the high-temperature η-CuSn₆ phase within a specific temperature range, with these atoms occupying specific Cu or Sn sites to create a more thermodynamically stable phase. It was observed that Au and In increased the cell volume of CuSn₆, while Zn caused a reduction, leading to a balance in strain energy that prevented phase transition [14].

Zhou et al. [15] investigated the impact of Ni element doping on the mechanical and electronic characteristics of high-temperature η-CuSn₆ phases. Their findings revealed that the inclusion of Ni enhanced the mechanical stability, brittleness, modulus, and Debye temperature of high-temperature η-CuSn₆. It is crucial to ensure the physical and thermal stability of the interfacial layer in solder joints, typically dominated by CuSn₆ intermetallic compounds, due to the thermal cycling and shock experienced by electronic devices [16–20]. The crystal structures of CuSn₆ can vary, with η′-CuSn₆ being the predominant phase in solder joint service. This phase significantly influences the mechanical behavior of microscale solder joints. Elastic anisotropy is linked to microcrack formation, underscoring the importance of a systematic analysis of the mechanical properties and elastic anisotropy of η′-CuSn₆ to enhance solder joint reliability.

Numerous studies have been conducted on the impact of Ag addition on solder joint reliability and interfacial reactions. While experimental determination of the crystal structure’s anisotropy is relatively consistent, investigating the effects of Ag substitution on properties of CuSn₆ by simulating the anisotropic distribution of properties like elastic modulus and hardness through mechanical calculations can enhance understanding of the crystal structure’s various mechanical properties. This paper calculates the mechanical properties and density of states of Ag-doped CuSn₆ intermetallic compounds based on first principles and explores the atomic-scale effect of Ag atomic doping on the anisotropy of CuSn₆ intermetallic compounds. The theoretical explanation of the enhancement effect resulting from Ag doping is provided, along with the rationale behind the formation of enhancers. These calculations are crucial for studying the diffusion paths of Cu and Sn atoms in η′-CuSn₆ post-doping, and for designing subsequent polyalloys. The findings of this study are anticipated to be beneficial for the future design and development of Sn-Cu solders.

2. Materials and Methods

Ag powder obtained from Henan Lebleu Metal Materials Technology Co (Henan, Lebleu, China) was utilized as the doping agent. This Ag powder was blended with high-purity Sn powder and Cu powder sourced from Hebei Shengte Metal Materials Co (Hebei, Shengte, China), both with purities exceeding 99.5%. The Cu-Sn alloy phase diagram indicates that when the mass percentage of Sn is 61 wt% and the mass percentage of Cu is 39 wt%, the Cu-Sn alloy is formed upon melting. The alloys with varying Ag contents were labeled as S0, S1, and S2 for clarity, and the compositions of the mixed metal powders can be found in Table 1. To enhance the homogeneity of the mixed powders, ball milling was conducted. A PU-80 high energy ball mill (Cunqiu, Guangzhou, China) was employed with a ball milling duration of 4 h, a rotational speed of 800 r/min, and a mass ratio of large balls, φ10 mm, to small balls, φ6 mm, of 1:4. Subsequently, the mixed powders were filled into custom-made moulds, pressed into φ15 mm × 30 mm press blanks using a WE-30 universal testing machine (Tuopu, Tianjin, China) with a pressing pressure of 100 kN, a loading speed of 2 kN/s, and a duration of 10 min. The press blank was then placed in a crucible and subjected to melting treatment in a muffle furnace at 900 °C for 4 h. Upon completion of melting, the crucible was cooled to room temperature before being removed. A graphite crucible was secured in a fixture and the molten material was poured into a graphite mould for casting, producing a sample.
The physical structure of the alloys was examined and analyzed by X-ray diffraction (XRD, D/max-RB, Rigaku, Tokyo, Japan), with a Cu target as the X-ray source, a scanning angle from 10° to 90°, and a scanning speed of 10°/min. A scanning electron microscope (SEM, Zeiss, Oberkochen, Germany) was used for the observation of the microstructures in conjunction with the energy spectrometer (EDS) to analyze the elemental distribution of the alloy. The hardness of the alloys was measured by a Vickers hardness tester, model AHVD-1000 (Miange, Suzhou, China), with a load of 200 g and a retention time of 20 s. Ten different positions were selected for each sample.

The crystal structure models of η’-Cu₅Sn₃ and η-Cu₆Sn₅ are depicted in Figure 1. A dopant atom Ag was introduced to replace Cu atoms, forming the (Cu, Ag)₅Sn₃ structural model. These structures underwent geometry optimization using a first-principles approach based on density-functional theory with the CASTEP procedure to calculate elastic constants [21–23]. The elastic properties of Cu positions in Ag-substituted Cu₅Sn₃ were then determined. An OTFG ultrasonic pseudopotential was utilized to describe ionic nuclei and valence electron interactions, with the exchange correlation equation following GGA-PBE [24]. Parameters such as k-point (7 × 7 × 2), cut-off energy (408.2 eV), and internal structure calculations using the BFGS algorithm were specified. Convergence criteria included a maximum ion Hellmann–Feynman force of 0.03 eV/Å, total energy tolerance of 5 × 10⁻⁵ eV/atom, maximum ion displacement of 0.001 Å, and maximum stress tolerance of 0.05 GPa.

<table>
<thead>
<tr>
<th>No.</th>
<th>Composite</th>
<th>Sn</th>
<th>Cu</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>Cu₅Sn₃-0Ag</td>
<td>61</td>
<td>39</td>
<td>0</td>
</tr>
<tr>
<td>S1</td>
<td>Cu₅Sn₃-3Ag</td>
<td>59.17</td>
<td>37.83</td>
<td>3</td>
</tr>
<tr>
<td>S2</td>
<td>Cu₅Sn₃-6Ag</td>
<td>57.34</td>
<td>36.66</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 1. Composition of Cu₅Sn₃-xAg alloys.

3. Results and Discussion

3.1. Effect of Ag Content on the Microstructure of Alloys

Figure 2 displays the X-ray diffraction (XRD) spectra of Cu₅Sn₃-Ag alloy samples with varying Ag powder content (0%, 3%, and 6%). The physical phase characterization of the Cu₅Sn₃-xAg (x = 0%, 3%, 6%) alloy was conducted, as depicted in Figure 2. The 2θ values of the main peaks in the Cu₅Sn₃-Ag alloy were found to be 30.093° and 42.973°. The lattice constants of Cu₅Sn₃ in the Cu₅Sn₃-xAg alloy were determined using Jade9.0 software and are presented in Table 2. The experimentally obtained XRD data were fitted to the full peaks of the physical phases in Jade software and the magnitude of the lattice constant was calculated. Following geometry optimization, the structural information of η’-Cu₅Sn₃ was compiled. The calculated results, obtained using Generalized Gradient
Approximation (GGA), closely matched the experimental values, with lattice constant errors falling within acceptable limits. Error analysis confirmed the reasonableness of the optimization results. Table 2 illustrates that upon Ag atom doping, the lattice constants of \( \eta'-\text{CuSn}_5 \) increased in the a and b directions and decreased in the c direction, resulting in a more uniform volume and reduced anisotropy of the \( \eta'-\text{CuSn}_5 \) structure.

Figure 2. XRD patterns of Cu_6Sn_5-Ag alloy samples.

**Table 2. Effect of Ag addition on the lattice constant of Cu_6Sn_5.**

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta'-\text{CuSn}_5 )</td>
<td>10.994</td>
<td>7.267</td>
<td>9.862</td>
</tr>
<tr>
<td>( \eta'-\text{CuSn}_5 ) (GGA)</td>
<td>11.039</td>
<td>7.305</td>
<td>9.903</td>
</tr>
<tr>
<td>Doped with 3 wt% Ag</td>
<td>11.036</td>
<td>7.273</td>
<td>9.751</td>
</tr>
<tr>
<td>Doped with 6 wt% Ag</td>
<td>11.006</td>
<td>7.284</td>
<td>9.687</td>
</tr>
</tbody>
</table>

Figure 3 displays the SEM images of Cu_6Sn_5-Ag alloys containing 0%, 3%, and 6% Ag. The micro-morphology of the alloy exhibited three distinct compositions: white zone, light grey zone, and grey zone. Voids appeared on the surface of the alloy, which gradually decreased with the increase in Ag addition. The SEM image reveals the presence of three different substances, with intermetallic compounds appearing as relatively large lumps and no other impurities or precipitates.

The distribution of elements was analyzed using energy dispersive X-ray spectroscopy (EDS) point scans attached to the scanning electron microscope (SEM). As shown in Figure 4 (a) and (b) for SEM image of Cu_6Sn_5-3%Ag alloy and Cu_6Sn_5-6%Ag alloy respectively, the analysis revealed the main components to be elemental Sn, Cu_6Sn_5 intermetallic compounds, Cu_6Sn_5 intermetallic compounds, and Ag_3Sn intermetallic compounds, as depicted in Figure 4. Tables 3 and 4 present the results of the EDS point scan specifically for the Cu_6Sn_5-Ag alloy. 1-4 in Tables 3 corresponds to 1-4 in Figure 4(a), indicating the EDS results for each point, 1-4 in Tables 4 corresponds to 1-4 in Figure 4(b), indicating the EDS results for each point. The addition of Ag had a notable impact on the microstructure and morphology of the alloy. Compared to the alloy without Ag, the surface grain became more uniform the presence of Ag_3Sn intermetallic compounds helped to refine the structure of the alloy and enhance its mechanical properties. The elemental distribution analysis conducted through EDS surface scanning is depicted in Figure 5. EDS analysis reflects...
that the green component represents the Sn element, the red component represents the Cu element, and the blue component represents the Ag element.

Figure 3. SEM images of Cu₆Sn₅-xAg alloys: (a) 0%; (b) 3%; (c) 6%.

Figure 4. SEM image of Cu₆Sn₅-3%Ag alloy (a) and Cu₆Sn₅-6%Ag alloy (b).

Table 3. Cu₆Sn₅-3%Ag alloy spot scan elemental results (at%).

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<th>2</th>
<th>3</th>
<th>4</th>
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<td>Sn</td>
<td>25.99</td>
<td>45.19</td>
<td>23.69</td>
<td>94.82</td>
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<tr>
<td>Cu</td>
<td>73.55</td>
<td>54.59</td>
<td>2.300</td>
<td>5.14</td>
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<tr>
<td>Ag</td>
<td>0.44</td>
<td>0.21</td>
<td>74.00</td>
<td>0.04</td>
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<table>
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<tr>
<th>Phase name</th>
<th>Cu₆Sn</th>
<th>Cu₆Sn₃</th>
<th>Ag₃Sn</th>
<th>Sn</th>
</tr>
</thead>
</table>

Table 4. Cu₆Sn₅-6%Ag alloy spot scan elemental results (at%).

<table>
<thead>
<tr>
<th>elemental</th>
<th>1</th>
<th>2</th>
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<th>4</th>
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</thead>
<tbody>
<tr>
<td>Sn</td>
<td>81.19</td>
<td>24.40</td>
<td>42.60</td>
<td>24.78</td>
</tr>
<tr>
<td>Cu</td>
<td>1.140</td>
<td>3.090</td>
<td>56.83</td>
<td>74.19</td>
</tr>
<tr>
<td>Ag</td>
<td>17.67</td>
<td>72.51</td>
<td>0.57</td>
<td>1.03</td>
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<table>
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<tr>
<th>Phase name</th>
<th>Sn</th>
<th>Ag₃Sn</th>
<th>Cu₆Sn₃</th>
<th>Cu₆Sn</th>
</tr>
</thead>
</table>
3.2. Microhardness of Alloys

The Vickers hardness test results of Cu₆Sn₅-xAg alloys are presented in Figure 6. In Figure 6a, the Vickers hardness of the Cu₆Sn₅ alloy ranges from approximately 200 HV to 510 HV. Figure 6b illustrates that the Vickers hardness of the alloy doped with 3% Ag falls within the range of 240 HV to 360 HV, while in Figure 6c, the Vickers hardness of the alloy doped with 6% Ag ranges from 180 HV to 300 HV. The addition of Ag to the alloy narrows the range between the maximum and minimum values compared to the Cu₆Sn₅ alloy. This phenomenon is attributed to the formation of new phases in the alloy with the addition of Ag, as evidenced by the SEM test results shown in Figure 4.

Figure 6. Hardness test plots of Cu₆Sn₅-xAg alloy: (a) 0%; (b) 3%; (c) 6%.

3.3. Mechanical Property Analysis

The stiffness coefficients of the crystal structures for both the low-temperature phase η’-Cu₆Sn₅ and the high-temperature phase η- Cu₆Sn₅ were determined through simulation. The stiffness coefficient represents the amount of deformation generated by a unit stress when an object is subjected to force. A higher stiffness coefficient suggests that the object can deform more easily under force and is more resistant to external forces [25–27]. This coefficient is closely linked to performance parameters like the material’s modulus of elasticity [28]. The elastic constant of the crystalline solid is calculated by the CASTEP code according to the stress–strain method. In this method, three normal strains (ε₁, ε₂, and ε₃) and three shear strains (γ₄, γ₅, and γ₆) act on the crystal. The corresponding stress (σ₁, σ₂, σ₃ and τ₄, τ₅, τ₆) is obtained after deformation of the crystal; then, the independent elastic constants can be obtained from Hooker’s law. Tables 5 and 6 shows the elastic
constants of $\eta$-Cu$_6$Sn$_5$ and $\eta'$-Cu$_6$Sn$_5$. This coefficient is closely linked to the material’s modulus of elasticity and other performance parameters, allowing for the calculation of related properties. Tables 7 and 8 present the mechanical properties of both crystal structures, calculated using the first-nature principle.

Table 5. Calculated elastic constants $C_{ij}$ (in GPa) of $\eta$-Cu$_6$Sn$_5$.

<table>
<thead>
<tr>
<th>i</th>
<th>$C_{i1}$</th>
<th>$C_{i2}$</th>
<th>$C_{i3}$</th>
<th>$C_{i4}$</th>
<th>$C_{i5}$</th>
<th>$C_{i6}$</th>
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<tbody>
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<td>1</td>
<td>124.6</td>
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<td>62.5</td>
<td>0.0</td>
<td>-7.9</td>
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<tr>
<td>2</td>
<td>55.6</td>
<td>115.7</td>
<td>45.0</td>
<td>0.0</td>
<td>10.4</td>
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</tr>
<tr>
<td>3</td>
<td>62.5</td>
<td>45.0</td>
<td>112.3</td>
<td>0.0</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
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<td>0.0</td>
<td>0.0</td>
<td>29.4</td>
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<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>-7.9</td>
<td>10.4</td>
<td>-1.0</td>
<td>0.0</td>
<td>38.2</td>
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<tr>
<td>6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>3.5</td>
<td>0.0</td>
<td>30.5</td>
</tr>
</tbody>
</table>

Table 6. Calculated elastic constants $C_{ij}$ (in GPa) of $\eta'$-Cu$_6$Sn$_5$.

<table>
<thead>
<tr>
<th>i</th>
<th>$C_{i1}$</th>
<th>$C_{i2}$</th>
<th>$C_{i3}$</th>
<th>$C_{i4}$</th>
<th>$C_{i5}$</th>
<th>$C_{i6}$</th>
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<tbody>
<tr>
<td>1</td>
<td>145.0</td>
<td>52.8</td>
<td>51.9</td>
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<td>0.0</td>
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<tr>
<td>2</td>
<td>52.8</td>
<td>145.0</td>
<td>51.9</td>
<td>0.0</td>
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<tr>
<td>3</td>
<td>51.9</td>
<td>51.9</td>
<td>160.5</td>
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<td>0.0</td>
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<td>0.0</td>
<td>43.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>43.8</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>46.1</td>
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</table>

The mechanical stability of the monoclinic system can be assessed using the following criteria [29]: the system is stable when $C_{ij} > 0$ (i = 1 – 6), $[C_{11} + C_{22} + C_{33} + 2 (C_{12} + C_{13} + C_{23})] > 0$, $C_{23} C_{33} - C_{22} > 0$, $(C_{44} C_{66} - C_{46}) > 0$, and $(C_{33} C_{22} - 2C_{23}) > 0$. It is evident that $\eta'$-Cu$_6$Sn$_5$ and its variants with different levels of Ag doping meet the stability requirements based on elastic constants, indicating mechanical stability. In practical scenarios, the polycrystalline elastic modulus is often more relevant than single-crystal constants. The elastic properties of $\eta'$-Cu$_6$Sn$_5$ in its low-temperature phase, high-temperature phase $\eta$-Cu$_6$Sn$_5$, and various Ag-doped systems, including bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$), and Poisson’s ratio ($\nu$), were determined using the Voigt-Reuss-Hill (VRH) approximation. The calculations for these properties are conducted as follows [30–33]:

$$B_H = \frac{1}{2} (B_R + B_V)$$

$$G_H = \frac{1}{2} (G_R + G_V)$$

$$E = \frac{9G_H B_H}{G_H + 3B_H}$$

$$\nu = \frac{3B_H - E}{6B_H}$$

The Vickers hardness of polycrystalline materials is typically determined using a theoretical model that relies on the material’s bulk modulus and shear modulus, as expressed in the following equation [34]:

$$H_V = 0.92 \left( \frac{G}{B} \right)^{1.137} G^{0.708}$$
Figures 7 and 8 display three-dimensional graphs illustrating the bulk modulus ($B$), Young’s modulus ($E$), and hardness ($H$) of the crystal structures of the low-temperature phase $\eta'$-Cu$_6$Sn$_5$ and the high-temperature phase $\eta$-Cu$_6$Sn$_5$.

Table 7. Mechanical properties of the low-temperature phase $\eta'$-Cu$_6$Sn$_5$.

<table>
<thead>
<tr>
<th></th>
<th>Voigt</th>
<th>Reuss</th>
<th>Hill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Modulus ($B$, GPa)</td>
<td>75.417</td>
<td>74.541</td>
<td>74.979</td>
</tr>
<tr>
<td>Shear Modulus ($G$, GPa)</td>
<td>32.256</td>
<td>30.722</td>
<td>31.489</td>
</tr>
<tr>
<td>Young’s Modulus ($E$, GPa)</td>
<td>84.695</td>
<td>81.032</td>
<td>82.867</td>
</tr>
<tr>
<td>Hardness ($H$, GPa)</td>
<td>4.007</td>
<td>3.693</td>
<td>3.849</td>
</tr>
<tr>
<td>Poisson ratio ($v$)</td>
<td>0.313</td>
<td>0.319</td>
<td>0.316</td>
</tr>
<tr>
<td>$B/G$</td>
<td>2.338</td>
<td>2.426</td>
<td>2.381</td>
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</table>

Table 8. Mechanical properties of the high-temperature phase $\eta$-Cu$_6$Sn$_5$.

<table>
<thead>
<tr>
<th></th>
<th>Voigt</th>
<th>Reuss</th>
<th>Hill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Modulus ($B$, GPa)</td>
<td>84.855</td>
<td>84.701</td>
<td>84.778</td>
</tr>
<tr>
<td>Shear Modulus ($G$, GPa)</td>
<td>46.326</td>
<td>46.134</td>
<td>46.230</td>
</tr>
<tr>
<td>Young’s Modulus ($E$, GPa)</td>
<td>117.580</td>
<td>117.135</td>
<td>117.358</td>
</tr>
<tr>
<td>Hardness ($H$, GPa)</td>
<td>7.008</td>
<td>6.967</td>
<td>6.987</td>
</tr>
<tr>
<td>Poisson ratio ($v$)</td>
<td>0.269</td>
<td>0.270</td>
<td>0.269</td>
</tr>
<tr>
<td>$B/G$</td>
<td>1.832</td>
<td>1.836</td>
<td>1.834</td>
</tr>
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</table>

Figure 7. Three-dimensional graphs of bulk modulus, Young’s modulus, and hardness of $\eta'$-Cu$_6$Sn$_5$ and $\eta$-Cu$_6$Sn$_5$. The units are in GPa.

The 3D graphs illustrate the anisotropy in the structure of the low-temperature phase $\eta'$-Cu$_6$Sn$_5$, showing variations in the Young’s modulus and hardness across different directions compared to the high-temperature phase $\eta$-Cu$_6$Sn$_5$. Pugh [35] introduced the ductility index ($B/G$) to quantify a material’s ductility, where higher values indicate greater ductility. Both phases of Cu$_6$Sn$_5$ have $B/G$ values above 1.75, signifying ductility. Moreover, Poisson’s ratio ($v$) is associated with $B/G$, with $v$ values above 0.26 indicating ductility. In both phases, $v$ exceeds 0.26, confirming their ductile nature.
To visually compare the differences between the maximum and minimum values, face projections were conducted in three directions. Figures 8–10 illustrate the projections of the bulk modulus (B), Young’s modulus (E), and hardness (H) in these directions.

**Figure 8.** Projections of \(\eta'\)-Cu\(\text{Sn}_5\)'s and \(\eta\)-Cu\(\text{Sn}_5\)'s bulk modulus.

**Figure 9.** Projections of \(\eta'\)-Cu\(\text{Sn}_5\)'s and \(\eta\)-Cu\(\text{Sn}_5\)'s Young’s modulus.

**Figure 10.** Projections of the hardness of \(\eta'\)-Cu\(\text{Sn}_5\) and \(\eta\)-Cu\(\text{Sn}_5\).

The mechanical properties of the high-temperature phase \(\eta\)-Cu\(\text{Sn}_5\) structure are typically isotropic, while those of the low-temperature phase \(\eta'\)-Cu\(\text{Sn}_5\) structure tend to be anisotropic, as evident from projection diagrams. It has been established that the mechanical properties of the intermetallic compound Cu\(\text{Sn}_5\) undergo changes during the structural transformation from high-temperature phase \(\eta\)-Cu\(\text{Sn}_5\) to low-temperature phase \(\eta'\)-Cu\(\text{Sn}_5\). This alteration is attributed to the anisotropic transformation of the elastic modulus and hardness of Cu\(\text{Sn}_5\), which also contributes to the formation of microcracks during the structural shift from \(\eta'\)-Cu\(\text{Sn}_5\) to \(\eta\)-Cu\(\text{Sn}_5\).

The low-temperature phase \(\eta'\)-Cu\(\text{Sn}_5\) crystals exhibit a monoclinic crystal structure and are classified under the C2/C space group. Each \(\eta'\)-Cu\(\text{Sn}_5\) crystal contains seven
atoms at distinct positions: Cu1 (4a), Cu2 (4e), Cu3 (8f1), Cu4 (8f2), Sn1 (4e), Sn2 (8f1), and Sn3 (8f2). Doping calculations were conducted for seven potential doping positions. The bulk modulus ($B$) is a common measure of a material’s resistance to compressive deformation. When subjected to external pressure, a material’s volume is compressed, making it compressible. The bulk modulus is the reciprocal of compressibility, indicating that materials with higher $B$ values have greater compression resistance and are harder to compress. The bulk modulus ($B$) values were determined based on the single-crystal elastic constants. Tables 9 and 10 illustrate the stress deformation resistance magnitude of $\eta'$-Cu$_3$Sn$_5$ and Ag-elemental substitution doped $\eta'$-Cu$_3$Sn$_5$, with the ranking as follows: Ag-Cu$_3$ > Ag-Cu$_2$ > Ag-Cu$_4$ > Ag-Sn$_3$ > Ag-Sn$_1$ > Ag-Sn$_2$ > $\eta'$-Cu$_3$Sn$_5$ > Ag-Cu$_1$. Specifically, Ag-Cu$_3$ has a bulk modulus of 112.9 GPa, while Ag-Cu$_1$ has a bulk modulus of 74.1 GPa, indicating that Ag exhibits the highest resistance to volume change when replacing Cu$_3$ in $\eta'$-Cu$_3$Sn$_5$ and the lowest resistance when replacing Cu$_1$ in $\eta'$-Cu$_3$Sn$_5$. Young’s modulus ($E$) is a common indicator of elasticity that reflects mechanical properties, with higher values corresponding to greater stiffness. The stiffness ranking for $\eta'$-Cu$_3$Sn$_5$ and Ag-element substitution doped $\eta'$-Cu$_3$Sn$_5$ is Ag-Cu$_3$ > Ag-Cu$_2$ > Ag-Sn$_3$ > Ag-Cu$_4$ > Ag-Sn$_1$ > Ag-Sn$_2$ > Ag-Cu$_1$ > $\eta'$-Cu$_3$Sn$_5$. The modulus of elasticity for Ag-Cu$_3$ is 126.0 GPa, which is 43.1 GPa higher than that of $\eta'$-Cu$_3$Sn$_5$, indicating that Ag replacement at the Cu$_3$ position results in the greatest hardness.

Hardness ($H$) refers to a material’s ability to resist localized surface pressure from a hard object. The hardness ranking in Tables 7 and 8 is as follows: Ag-Sn$_3$ > Ag-Cu$_1$ > Ag-Sn$_1$ > Ag-Cu$_3$ > Ag-Sn$_2$ > Ag-Cu$_2$ > Ag-Cu$_4$ > $\eta'$-Cu$_3$Sn$_5$, showing that replacing Ag at the Sn$_3$ position results in the highest hardness. Figures 11–13 illustrate that when Ag replaces doped Cu and Sn atoms at the Cu$_1$, Cu$_3$, Cu$_4$, Sn$_1$, and Sn$_3$ sites, it reduces the anisotropy of the bulk modulus. However, replacing the Cu$_2$ and Sn$_2$ sites does not have a significant effect. Similarly, replacing Ag at doped Cu$_1$, Cu$_3$, Sn$_1$, and Sn$_3$ sites reduces the anisotropy of Young’s modulus, while replacing the Cu$_2$, Cu$_4$, and Sn$_2$ sites does not show a noticeable impact.

Table 9. Mechanical properties of $\eta'$-Cu$_3$Sn$_5$ and Ag-element substitute-doped $\eta'$-Cu$_3$Sn$_5$ (Cu1, Cu2, Cu3).

<table>
<thead>
<tr>
<th>$\eta'$-Cu$_3$Sn$_5$</th>
<th>Ag-Cu1</th>
<th>Ag-Cu2</th>
<th>Ag-Cu3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Voigt</strong></td>
<td>75.4</td>
<td>74.5</td>
<td>75.0</td>
</tr>
<tr>
<td><strong>Reuss</strong></td>
<td>84.7</td>
<td>81.0</td>
<td>82.9</td>
</tr>
<tr>
<td><strong>Hill</strong></td>
<td>4.0</td>
<td>3.7</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 10. Mechanical properties of $\eta'$-Cu$_3$Sn$_5$ and Ag-element substitute-doped $\eta'$-Cu$_3$Sn$_5$ (Cu4, Sn1, Sn2, Sn3).

<table>
<thead>
<tr>
<th>Ag-Cu4</th>
<th>Ag-Sn1</th>
<th>Ag-Sn2</th>
<th>Ag-Sn3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Voigt</strong></td>
<td>111.4</td>
<td>110.5</td>
<td>111.0</td>
</tr>
<tr>
<td><strong>Reuss</strong></td>
<td>121.7</td>
<td>108.7</td>
<td>115.2</td>
</tr>
<tr>
<td><strong>Hill</strong></td>
<td>5.0</td>
<td>3.9</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Figure 11. Schematic of the bulk modulus of $\eta'$-Cu$_6$Sn$_5$ doped with Ag elements. The units are in GPa.

Figure 12. Schematic of Young’s modulus of $\eta'$-Cu$_6$Sn$_5$ doped with Ag elements. The units are in GPa.
The distribution of the bulk modulus bottom projection in the [010] direction becomes more homogeneous when the Ag element is substituted at the Cu1, Cu3, Cu4, Sn1, and Sn3 sites, as illustrated in Figures 14–16. This demonstrates a reduction in the anisotropy of Cu₆Sn₅ following Ag element doping. Similarly, the anisotropy of Young’s modulus was also suppressed with the introduction of Ag element through substitution at the Cu1, Cu3, Sn1, and Sn3 sites.

The anisotropy ratio $E_{\text{max}}/E_{\text{min}}$ was utilized to quantify the degree of anisotropy, where a larger ratio indicates higher anisotropy. Specifically, for $\eta’$-Cu₆Sn₅, $E_{\text{max}} = 84.7$ GPa and $E_{\text{min}} = 81.0$ GPa, resulting in an anisotropy ratio of 1.045. In the case of Ag-Cu1, $E_{\text{max}} = 98.0$ Gpa and $E_{\text{min}} = 94.7$ GPa, leading to an anisotropy ratio of 1.034. Lastly, for Ag-Sn3, $E_{\text{max}} = 119.7$ Gpa and $E_{\text{min}} = 118.9$ GPa, yielding an anisotropy ratio of 1.006. This suggests that the substitution of Ag for Cu1 and Sn3 in $\eta’$-Cu₆Sn₅ results in a lower elastic modulus of anisotropy.

Figure 13. $\eta’$-schematic of the hardness of Cu₆Sn₅ doped with Ag elements. The units are in GPa.

Figure 14. $\eta’$-bulk modulus projection of Cu₆Sn₅ doped with Ag elements.
3.4. Calculation of the Density of States of Alloys

The total and fractional density of states of $\eta'$-$\text{Cu}_6\text{Sn}_5$ and its doped systems were analyzed using first principles. Figure 17 presents the TDOS and PDOS diagrams of $\eta'$-$\text{Cu}_6\text{Sn}_5$ and its doped system. The TDOS in the valence band of $\eta'$-$\text{Cu}_6\text{Sn}_5$ exhibits two main peaks at energy levels of $-3.24$ eV and $-7.55$ eV, contributed by Cu-$d$ and Sn-$s$ states, respectively. Furthermore, a strong covalent bond structure is formed by Cu-$d$ and Sn-$p$ hybridisation at $-3.24$ eV. The main peaks in the doped systems shift to $-3.53$ eV and $-7.85$ eV with Ag doping, indicating an effect on the density of states. Ag doping enhances the metallic properties of $\eta'$-$\text{Cu}_6\text{Sn}_5$, consistent with previous studies [36,37]. Additionally, a
new main peak at 2.47 eV in the doped system is attributed to the interaction of Ag-p with Sn-p and Cu-d, leading to increased stability of $\eta'\text{-Cu}_{6}\text{Sn}_{5}$. For $\eta\text{-Cu}_{6}\text{Sn}_{5}$, there are two main energy peaks below the Fermi energy level. The strong peak at $-3.11$ eV coincides with the partial density of states of the Cu-d orbitals; it is formed by the hybridisation of Cu-d orbital electrons at different positions, and at the same time, in this region, the cu-d orbital electrons are weakly hybridised with Sn-p orbital electrons. In the same region, the electrons in the Cu-d orbitals are weakly hybridised with the electrons in the Sn-p orbitals.

This newly introduced hybridisation reduces the formation energy of the intermetallic compound system and strengthens the chemical bond due to higher electron density distribution in the bonding orbitals. Consequently, (Cu, Ag)$_6$Sn$_5$ exhibits improved bonding ability and force, contributing to a stable structure and enhanced physical and mechanical properties.

![Diagram](image)

Figure 17. (a) DOS and (b) PDOS plots of Cu$_6$Sn$_5$ and (c) its doping system.

4. Conclusions

In this study, the physical and morphological characterization of the Cu$_{6}$Sn$_{5-x}$Ag ($x = 0, 3, 6$; %, mass fraction) alloy was conducted by adjusting the addition of Ag elemental content, followed by testing the hardness of the alloy. First-principle calculations were utilized to simulate the crystal structure and mechanical properties of Cu$_6$Sn$_5$ intermetallic compounds. Additionally, the mechanical properties of Ag were examined when replacing Cu and Sn in Cu$_6$Sn$_5$. The resulting alloys with Ag addition exhibited three main phases: Sn, Cu$_6$Sn$_5$, Cu$_6$Sn$_5$ intermetallic compounds, and Ag$_3$Sn intermetallic compounds.
The introduction of Ag led to an increase in the Cu₅Sn₃ lattice constants in the a and b directions, while decreasing in the c direction, resulting in a more uniform bulk and reducing the anisotropy of the η'-Cu₅Sn₃ structure. The low-temperature phase η'-Cu₅Sn₃ structure displayed noticeable anisotropy, with the Young’s modulus and hardness varying significantly in different directions compared to the high-temperature phase η'-Cu₅Sn₃. Through Ag substitution doping, it was found that Ag element substitution at the Cu₁, Cu₃, Cu₄, Sn₁, and Sn₃ sites helped mitigate the anisotropy of the bulk modulus, while substitution at the Cu₂ and Sn₂ sites had minimal impact. Similarly, Ag element substitution at the Cu₁, Cu₃, Sn₁, and Sn₃ sites reduced the anisotropy of the Young’s modulus, with substitution at the Cu₂, Cu₄, and Sn₂ sites showing little effect. For Ag-Cu₁, $E_{\text{max}} = 98.0$ GPa and $E_{\text{min}} = 94.7$ GPa, with an anisotropy ratio of 1.034, and for Ag-Sn₃, $E_{\text{max}} = 119.7$ GPa and $E_{\text{min}} = 118.9$ GPa, with an anisotropy ratio of 1.006. This suggests that Ag substitution at Cu₁ and Sn₃ in η'-Cu₅Sn₃ results in less elastic modulus anisotropy. Additionally, a new main peak at an energy value of 2.47 eV was observed in the doped system, indicating that the stability of η'-Cu₅Sn₃ is enhanced by Ag doping due to the strong interaction of Ag-p with Sn-p and Cu-d. Overall, this study offers valuable insights and theoretical guidance for future applications of the Cu₅Sn₃ alloy.

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Conflicts of Interest: Lingyan Zhao is employed by Yunnan Tin New Material Co. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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