Ab Initio Calculations on the Structural and Electronic Properties of AgAu Alloys

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ABSTRACT: In our paper, we study the effects of pseudopotential and concentration of Au doping (0, 25, 50, 75, 100%) on the geometric structure and electronic structures of AgAu alloys. For this purpose, we use ab initio quantum calculations in the Material Studios software. The geometric structures of materials are confirmed through the lattice constant, crystal structure, and total energy of the unit cells ($E_{\text{tot}}$). Electronic structures of the materials are confirmed by band gap ($E_g$), projected density of states (PDOS), and total density of states (DOS). The obtained results show that the pseudopotential and concentration of Au doping on AgAu alloys play an important role in the origin of the physical properties of AgAu alloys.

1. INTRODUCTION

Gold (Au) is one of the precious metals that show inertia, biocompatibility, and stability, which are used widely in coinage, ornaments, jewelry, and for clinical techniques. Gold (Au) is soft, flexible, and ductile, and it belongs to the class of high thermal and electrical conductive metals. To increase the plasticity and electrical conductivity of Ag, one can phase Au into metals such as silver (Ag), copper (Cu), nickel (Ni), manganese (Mn), chromium (Cr), etc. The possibility of fabricating pure metallic NPs with controllable size and shape enables modulation of the LSPR from the UV region to the IR region of the electromagnetic spectrum. Among them, Ag and Au metals are applied many in areas such as nanophotonics, energy harvesting, molecular detection, biomedicine, and catalysis. Almost all of these studies use experimental methods, and only a few theoretical studies use density functional theory to investigate the properties of AgAu alloys. For example, Du et al. have successfully determined the effect of Au impurity concentration on the shape of NPs, and Ag atoms are always located in the shell of the AgAu alloy. Similarly, Yang et al. have successfully determined the effect of the concentration of impurity Au on the linear expansion coefficient, melting point, and volume heat capacity of AgAu alloy with lattice constants $a = b = 4.09$ Å and $c = 4.08$ Å. Guisbiers et al. have successfully fabricated AgAu alloy nanoparticles in different shapes and sizes and shown that the surface segregation of silver had an effect on the optical properties of materials. Also, Gong et al. have successfully investigated the effect of Au dopant concentration on the optical properties of AgAu alloy.

Besides, in recent years, we have also studied the effects of heating rate, doping concentration, atom number, temperature of the structure, electronic structure, phase transition, and crystallization of alloys AuCu, AlNi, NiCu, and FeNi. The results obtained show that when the heating rate increases, the alloy changes from liquid state to amorphous state and vice versa, and that when the atom number increases, size increases and the energy of the system decreases. Increase (or decrease) of temperature leads to phase transition, from which the phase-transition temperature ($T_m$), glass-transition temperature ($T_g$), and density of the dictionary state changes have been determined. Moreover, increasing the symmetrical impurity concentration leads to a change in the number of structural units (FCC, HCP, Amor), and then electron density becomes very large. Then, a question arises: what happens to the electronic structure of the alloy when the doping concentration changes? To answer this question, we consider the influence of the force field, the concentration of impurity on the electronic structure, and the general structure of the AgAu alloy. In this paper, we use ab initio calculation.
through DMol3 tools in the Materials Studio software to study the effects of pseudopotential and concentration of Au doping on the geometric structure and electronic structure of AgAu alloy.

2. RESULTS AND DISCUSSION

2.1. Effect of Pseudopotential. The effect of pseudopotential on the lattice constant of Ag and Au is presented in Figure 1.

It follows from these results that the lattice constants of Ag and Au metals have been optimized using different pseudopotentials: generalized gradient approximation-Perdew–Burke–Erzernhof (GGA-PBE), GGA-Perdew–Wang (GGA-PW91), GGA-revised PBE (GGA-RPBE), local density approximation-Perdew–Wang (LDA-PWC), and LDA-Vosko–Wilk–Nusair (LDA-VWN). The lattice constants values of Ag are $a = b = c = 4.1761$, 4.1745, 4.2069, 4.0630, and 4.0623 Å, which correspond to the values of total energy of the unit cells ($E_{\text{tot}}$), $E_{\text{tot}} = -2286.53$, -2289.97, -2287.28, -2277.43, and -2277.43 eV (Figure 1). For Au, we have $a = b = c = 4.1724$, 4.1735, 4.1924, 4.0908, and 4.0910 Å, which correspond to $E_{\text{tot}} = -1996.11$, -1998.60, -1996.85, -1988.41, and -1988.41 eV. We see that different hypotheses lead to changes of lattice constants of Ag and Au (Figure 1). In the obtained results, the LDA-PWC hypothesis gives a result of 4.0630 with Ag and 4.0908 with Au. The results are in good accordance with the experimental results: $a = b = c = 4.0630$ Å with Ag and $a = b = c = 4.0782$ Å with Au, which are almost 3 times larger than the valence radii of Ag (1.36 Å) and Au (1.45 Å). These results show that pseudopotential LDA-PWC gives the values of lattice constant for Ag and Au, which are in good accordance with experimental results, so we choose it for calculations.

2.2. Effects of Concentration of Impurities. 2.2.1. On Lattice Constants. The effects of the concentration of Au impurity on the unit cell shape, the lattice constant, and the total energy of the unit cells ($E_{\text{tot}}$) of AgAu alloy are demonstrated in Figures 2 and 3 and Table 1.

The obtained results show that Ag and Au are metals with surface center cubic structure (FCC) with lattice constants of the base cell of Ag and Au of $a = b = c = 4.0630$ Å, $E_{\text{tot}} = -2277.43$ eV and $a = b = c = 4.0908$ Å, $E_{\text{tot}} = -1988.41$ eV, respectively. When Au was doped into the AgAu alloy with doping concentrations of 0.0, 25, 50, 75, and 100%, we obtain alloys Ag (Figure 2a), Ag$_{0.25}$Au$_{0.75}$ (Figure 2b), Ag$_{0.5}$Au$_{0.5}$ (Figure 2c), Ag$_{0.75}$Au$_{0.25}$ (Figure 2d), and Au (Figure 2e). Then, the lattice constant values increase correspondingly with Ag$_{0.75}$Au$_{0.25}$ for $a = b = c = 4.0806$ Å, total energy of the unit cells ($E_{\text{tot}}$), $E_{\text{tot}} = -2205.19$ eV; for Ag$_{0.5}$Au$_{0.5}$, $a = b = c = 4.0955$ Å, $E_{\text{tot}} = -2132.94$ eV; and for Ag$_{0.25}$Au$_{0.75}$, $a = b$
It follows that when the concentration of Au doping in Ag is increased, the lattice constants \( a, b, \) and \( c \) increase. This is the consequence of size effect and surface effect. When the Au atom was doped with a lattice constant greater than the lattice constant of the Ag atom, the center of the Ag lattice is deformed, leading to a change of the Ag structure and then an increase in the size of AgAu. The results obtained are perfectly consistent with simulation results with \( a = b = 4.0955 \) Å and \( c = 4.0854 \) Å.\(^{15}\)

The lattice constant value changes increase 1% higher than the lattice constants of Ag and Au. The changes of lattice constants \( a, b, \) and \( c \) in the Ag\(_{0.5}\)Au\(_{0.5}\) alloy are shown in Figure 3 and Table 1. Due to the asymmetry of Ag atoms, the crystal status of Ag\(_{0.5}\)Au\(_{0.5}\) alloy are shown in Figure 3 and Table 1. Due to the asymmetry of Ag atoms, the crystal status of Ag\(_{0.5}\)Au\(_{0.5}\) changed from cubic structure to triclinic structure. In these models, substitution of the Au atom into the Ag atom leads to the formation of interleaved layers of Ag and Au, with the periodic arrangement of atoms in each layer. This structure increases the space between atoms, so it increases the lattice constant and changes the lattice system from cubic in intrinsic Ag to tetragonal in Ag\(_{0.5}\)Au\(_{0.5}\).

### Table 1. Crystal Information of Ag, Ag\(_{0.75}\)Au\(_{0.25}\), Ag\(_{0.5}\)Au\(_{0.5}\), Ag\(_{0.25}\)Au\(_{0.75}\), and Au Calculated Using LDA-PWC Functional

| alloy     | Bravais lattice | Ag  | Ag\(_{0.75}\)Au\(_{0.25}\) | Ag\(_{0.5}\)Au\(_{0.5}\) | Ag\(_{0.25}\)Au\(_{0.75}\) | Au  |
|-----------|-----------------|-----|---------------------------|--------------------------|--------------------------|-----|
| \( a = b \) (Å) | 4.0630 | 4.0806 | 4.0955 | 4.0959 | 4.0908 |
| \( c \) (Å) | 4.0630 | 4.0806 | 4.0854 | 4.0959 | 4.0908 |
| total energy \( E_{\text{tot}} \) (eV) | \(-2277.43\) | \(-2205.19\) | \(-2132.94\) | \(-2060.68\) | \(-1988.41\) |
| result     | 4.0630\(^{24}\) | \(4.09\) | \(4.0815\) | \(4.0782\) | \(4.09\) | \(4.08\) | \(4.0782\) | \(4.09\) | \(4.08\) | \(4.0782\) |

Figure 4. Electronic structures (a) and partial density of states (b) of Ag; electronic structures (c) and partial density of states (d) of Au calculated using LDA-PWC.

\( = c = 4.0959 \) Å, \( E_{\text{tot}} = -2060.68 \) eV. It follows that when the concentration of Au doping in Ag is increased, the lattice constants \( a, b, \) and \( c \) increase. This is the consequence of size effect and surface effect. When the Au atom was doped with a lattice constant greater than the lattice constant of the Ag atom, the center of the Ag lattice is deformed, leading to a change of the Ag structure and then an increase in the size of AgAu. The results obtained are perfectly consistent with simulation results with \( a = b = 4.0955 \) Å and \( c = 4.0854 \) Å.\(^{15}\) The lattice constant value changes increase 1% higher than the lattice constants of Ag and Au. The changes of lattice constants \( a, b, \) and \( c \) in the Ag\(_{0.5}\)Au\(_{0.5}\) alloy are shown in Figure 3 and Table 1. Due to the asymmetry of Ag atoms, the crystal status of Ag\(_{0.5}\)Au\(_{0.5}\) changed from cubic structure to triclinic structure. In these models, substitution of the Au atom into the Ag atom leads to the formation of interleaved layers of Ag and Au, with the periodic arrangement of atoms in each layer. This structure increases the space between atoms, so it increases the lattice constant and changes the lattice system from cubic in intrinsic Ag to tetragonal in Ag\(_{0.5}\)Au\(_{0.5}\).

#### 2.2.2. On the Electronic Structures.

The electronic structure characteristics of Au and Ag are shown in Figure 4. It follows from the obtained results that band structures and density of states of Ag and Au metal are shown with the horizontal dotted line representing the Fermi level, which corresponds to band gap \( E_g = 0.0 \) eV. We see that the band structures and density of states of Ag and Au between energy state \( (E) \), \( E = -10 \) eV to 20 eV, are changed. The density of states in valence bands is higher but narrower than that in the conduction bands, in good agreement with the results of projected density of states (PDOS) calculation. This is evident in the band structures of Ag and Au calculated by PDOS; the conduction and valence bands overlap, so there is no band gap in these materials. In other words, they are metals, because for metals, the forbidden area width is always \( E_g = 0.0 \) eV. This result is completely consistent with the experimental results. We observed similar results with the PDOS of s, p, d, and f...
Orbitals to the formation of the band structure of Ag and Au metals (Figure 4b,d). The contribution of orbital f is 0.0 in both materials, which is consistent with the absence of this orbital in the valence electron configuration of Ag and Au. The orbitals s and p only contribute a small portion to their tight bonding with the core. The d orbitals play the most important role in the formation of the band structure of Ag and Au metals; this result is completely consistent with the valence electron configurations of Ag and Au, 5d^{10}6s^{1} and 3d^{10}5s^{1}, respectively. Also, the densities of states (DOS) of the subclasses s, p, d, and f are mainly concentrated in the energy state range from $E = 0.0$ eV to $-10$ eV (Figure 4a,c), which corresponds to the valence region of metal. This shows that metal electrons are mainly concentrated in the valence region and the conduction region has very few electrons, with band gap ($E_{g}$), $E_{g} = 0.0$ eV. When the concentration of Au doping into AgAu alloy increases, the results obtained are shown in Figure 5.

The results showed the band structures of the alloys Ag_{0.75}Au_{0.25} (Figure 5a,b), Ag_{0.5}Au_{0.5} (Figure 5c,d), and...
Ag0.25Au0.75 (Figure 5e,f) with a horizontal dotted line for Fermi level at 0.0 eV. One can see no band gap in these band structures, which suggests that all AgAu alloys are metals. The energy state levels lie between $E = -10$ eV and 20 eV, and the valence bands have a higher density of states, similar to Ag and Au results. One can see that almost all of the states below Fermi levels are filled; therefore, the electrons from valence bands can easily jump to conduction bands for increasing their mobility. This, in consequence, enhances the thermal and electrical conductivities of Ag, Au, and their alloys. The details of the density of states of Ag and Au and their alloys are shown in Figure 6.

![Figure 6. Total density of states with Au, Ag, and alloys calculated using LDA-PWC.](image)

The results obtained show, when Au atoms are doped into the Ag lattice, that the total electronic density of states of Ag has significant changes. In Ag, the width of the bands with a high density below the Fermi level is between $E = -10$ eV and 0.0 eV and the values of this width increase with a decrease of Au concentration: at $E = -10$ eV, the value of electron density remains unchanged (0.0%); at $E = -7.25$ eV, the electron density decreases, then increases, and finally decreases to reach the extreme value in the valence area, which tends to change from 0.74% to 0.18, 0.32, 0.0, and 1.25%; at $E = -5.0$ eV, the electron density decreased, then increased, and finally decreased from 0.22% to 0.36, 7.69, 0.0, and 8.27%; at $E = -4.42$ eV, the electron density decreased, then increased, and finally decreased from 0.31% to 0.50, 10.72, 0.0, and 0.53%; at $E = -2.5$ eV, the electron density decreased, then increased, and finally decreased from 0.16% to 0.20, 9.0, 0.0, and 9.36%; at $E = 0.0$ eV, the electron density increased and then decreased from 0.38% to 0.60, 0.66, 0.0, and 1.64%. This is a consequence of the fact that changes in the s and p subclasses of 5d106s1 with Ag and 3d105s1 with Au lead to changes in the density of electrons in the s, p, d, and f subclasses. With energy larger $E > 0.0$ eV, electronic density has a very small, almost constant value (Figure 6). This shows that in the valence region, the electron density has the largest percentage, extending the maximum value to $E = -4.42$ eV. This result suggests that the mobility of an electron in AgAu alloys increases and the conductivity of AgAu alloy is higher than in Ag metal. The reason is that the electronic interaction between Ag and Au atoms, when the concentration of Au doping in Ag increases, leads to an increase in the conductivity of AgAu alloy and reaches the maximum value with Ag0.5Au0.5. The results obtained are very useful and would be served as a basis for future experimental studies.

### 2.2.3. On the Energy Formation

The formation of AgAu alloys can be fixed using the formation energies of the materials. The formation energies ($\Delta E_{\text{form}}$) of AgAu alloys are calculated by formula 1

$$\Delta E_{\text{form}} = E_{\text{tot}}(\text{models}) - E_{\text{tot}}(\text{Au}) - m\mu_{\text{Au}} + n\mu_{\text{Ag}}$$

(1)

where $E_{\text{tot}}(\text{models})$ and $E_{\text{tot}}(\text{Au})$ are the total energies of AgAu alloy and intrinsic Au metal, respectively; $\mu_{\text{Ag}}$ and $\mu_{\text{Au}}$ are the chemical potentials of intrinsic Ag and Au, respectively, and m and n represent the numbers of substituted and removed Ag atoms in the corresponding models, respectively. The details are listed in Table 2. The values of chemical potentials $\mu_{\text{Ag}}$ and $\mu_{\text{Au}}$ are determined via the energy of a single Ag and Au atom in bulk material, and the accepted values of $\mu_{\text{Ag}}$ and $\mu_{\text{Au}}$ in this research are $-497.103$ eV and $-569.356$ eV, respectively. We list the calculated formation energies of all models in Table 2.

The results show that all almost formation energies of AgAu alloys are negative and small, but the energy of Ag0.25Au0.75 is negative and has the smallest value. Negative and small formation energies suggest that AgAu alloys can be easily formed by doping Au into Ag with different ratios (0.25:0.75, 0.5:0.5, and 0.75:0.25) for creating alloys (Table 2). In general, one can predict this fact because AgAu alloys can form in distinct mass or atom ratios and Ag0.25Au0.75 is more difficult to form because it has smaller lattice constants with more negative and small total energy.

### 2.2.4. On the Radial Distribution Function

The radial distribution function (RDF) $g(r)$ is defined as follows:

$$g(r) = \frac{4\pi r^2 \rho(r)}{\rho}$$

where $\rho(r)$ is the local density of the material at coordinate $r$ and $\rho$ is the density of the material. The results are demonstrated in Figure 7.

The obtained results show that the separated peaks at different distances of all RDF are the consequences of the periodic distribution of Ag and Au atoms and AgAu alloy in the

![Figure 7. Values of the radial distribution function $g(r)$ of Ag, Ag0.25Au0.75, Ag0.5Au0.5, and Au calculated using LDA-PWC.](image)
space. The similarity of lattice constants and ionic radii of Ag, Au, and AgAu can explain the unchanged positions of RDF peaks of all models. When Au atoms are doped into the Ag lattice, the lattice constants and structure of AgAu alloys exhibit insignificant changes.

3. CONCLUSIONS

In this paper, the geometric structures and electronic structures, formation process, and radial distribution function of Ag, Au metal, and AgAu alloys with different dopings of Au have been studied by calculating ab initio via the DMol3 package in the Materials Studio software. The calculated results show that AgAu alloys have been created. The substitution of Au atoms into Ag atoms gives insignificant changes of lattice constant and leads to insignificant changes in the structural and electronic properties of AgAu alloys. The lattice constant of the alloys varies slightly when the Au concentration is increased, and a Ag/Au ratio of 0.5:0.5 leads to the change of the lattice structure from cubic to tetragonal. The density of state (DOS) of AgAu is always greater than that of metal. When Au atoms are doped in Ag atoms, there is a maximum value for Ag$_{0.5}$Au$_{0.5}$. Besides, the RDF result shows insignificant changes in lattice constants, which are characterized by the similarity of the peaks.

4. COMPUTATIONAL METHODS

All ab initio calculations were carried out using DMol$^3$ — a widely used module in Materials Studio, a copyrighted software for materials simulation designed by Biovia (formerly Accelrys). Different exchange—correlation functionals for local density approximation (LDA) (Perdew–Wang (PWC)) and generalized gradient approximation (GGA) (Perdew–Burke–Ernzerhof (PBE), revised PBE (RPBE), and Perdew–Wang (PW91)) had been used to optimize and identify the stable unit cells of materials. The accepted Monkhorst-Pack k-point grid sampling for all of the calculation is $5 \times 5 \times 4$, while the valence electron configurations of intrinsic Ag and Au are 4d$^{10}$5s$^1$ and 5d$^{10}$6s$^1$, respectively. The density functional semicore pseudopotential (DSPS) was used to describe the interactions of valence electrons and the core. The self-consistent iterations convergence was fixed when the change of total energy reaches the value of $1 \times 10^{-6}$ eV. The tolerances of maximum force and maximum displacement in the geometry optimization processes were established at $5.4 \times 10^{-3}$ eV/Å and $5 \times 10^{-3}$ Å, respectively. Initially, Ag and Au metals are placed at different pseudopotentials and AgAu alloy with Au doping concentrations of 0% (0.0), 25% (0.25), 50% (0.5), 75% (0.75), and 100% (1.0). The obtained results, geometric structures, are determined through lattice constant, total energy ($E_{\text{tot}}$), and radial distribution function (RDF), and electronic structures through band gap ($E_{\text{g}}$), projected density of states (PDOS), and total density of states (DOS) of Ag and Au metals and AgAu alloys. To check the accuracy of the results, we compare the simulation results with the results of previous studies.

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Notes

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