Effect of band structure adjustment based of Cu site on the thermoelectric properties of BiCuSeO

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Original Research

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Abstract

The effect of Ti doped at Cu site on the thermoelectric properties of BiCuSeO was studied by experimental method and first principles calculation. The results show that Ti doping can cause the lattice contraction and decrease the lattice constant. Ti doping can increase the band gap and lengthen the Cu/Ti-Se bond, resulting in the decrease of carrier concentration. Ti doping can reduce the effective mass and the Bi-Se bond length, correspondingly improve the carrier mobility. Ti doping can decrease the density of states of Cu-3d and Se-4p orbitals at the top of valence band, but Ti-4p orbitals can obviously increase the density of states at the top of valence band and finally increase the electrical conductivity in the whole temperature range. With the decrease of effective mass, Ti doping would reduce the Seebeck coefficient, but the gain effect caused by the increase of electrical conductivity is more than the benefit reduction effect caused by the decrease of Seebeck coefficient, and the power factor shows an upward trend. Ti doping can reduce Young's modulus, lead to the increase of defect scattering and strain field, correspondingly reduce the lattice thermal conductivity and total thermal conductivity. It is greatly increased for the ZT values in the middle and high temperature range, with the highest value of 1.04 at 873 K.

1. Introduction

With the rapid development of industrialization in today's society, the standards for the energy industry that support the industrial operation are correspondingly getting higher and higher. Energy materials are the basis of energy industry. The structure and performance of raw energy materials have determined the performances and parameters of energy industry. Thermoelectric material is a kind of important energy raw material, which has lots of applications in the field of thermal power generation and micro refrigeration [1], [2]. The early thermoelectric research and applications are mainly based on alloy materials, because the thermoelectric conversion efficiency of alloy materials is relatively high [3, 4]. However, due to the problems of raw material cost and pollution, thermoelectric research of low-cost oxygen-containing materials has been paid more and more attention in recent years [5, 6].

Traditional oxygen-containing materials have low power factor, high thermal conductivity, and correspondingly low thermoelectric conversion efficiency due to crystal structure or the large difference in electronegativity of O and cations [7, 8]. In 2010, scholars found that BiCuSeO with layered natural superlattice structure has higher Seebeck coefficient and lower thermal conductivity, which is obviously different from traditional oxygen-containing materials due to the confinement effect of special structure [9, 10]. The disadvantage of this material system is its low electrical conductivity. In the past decade, scholars have done a lot of research work to improve the electrical conductivity and the thermoelectric conversion efficiency, such as Pb doping [11, 12], Ba doping [13, 14], Na doping [15, 16], Ca doping [17, 18] based on the acceptor effect. The thermoelectric performance has been improved due to the increase of carrier concentration. But these doping studies are mainly focused on the Bi site in $(\text{Bi}_2\text{O}_2)^{2+}$ layer. The density of states near the top of BiCuSeO valence band is mainly contributed by Cu-3d and Se-4p orbitals

in $(\text{Cu}_2\text{Se}_2)^{2-}$ layer [9]. Here, we adjust the Cu sites in the $(\text{Cu}_2\text{Se}_2)^{2-}$ layer based on the idea of energy band adjustment [19, 20], in order to investigate the effect mechanism of Cu site doping on the thermoelectric properties of BiCuSeO. Based on the position rule of doped atoms and the principle of defect chemistry and the radius of Bi^{3+} (1.03 Å) and Cu^+ (0.77 Å) ions, we chose the high-valence Ti^{4+} ions (0.605 Å) with smaller radius than Cu ions to dope at Cu sites in order to adjust the band structure of BiCuSeO. Powder samples were prepared by high temperature solid state reaction combined with mechanical alloying, and bulk samples were prepared by self-made spark plasma sintering furnace. The crystal structure parameters, energy band and density of states were calculated and analyzed by Materials Studio software based on the first principles, and the properties were tested by the thermoelectric related equipments. The Cu site doping mechanism of BiCuSeO was studied from two aspects of material calculation science and experimental science .

2. Sample Preparation And Performance Testing Process

The sample preparation process is similar to the previous work related to BiCuSeO [21, 22]. Firstly, the raw materials with purity above 99.99 % are prepared according to the mole ratio of Ti element as 0, 0.02, 0.04, 0.06, 0.08, 0.10, and then mixed it in agate mortar, put it into quartz glass tube, vacuumed, sealed it with hydrogen oxygen machine, put it into heating furnace, raise the temperature to 1073 K, keep the temperature for 8 h. After cooling, crushed the sample, ball milled it for 6 h (dry grinding for 5 h at 400 rpm with argon atmosphere, wet grinding for 1 h at 300 rpm with anhydrous ethanol), and then take the sample out in drying oven for vacuum drying at 343 K. Then the powder was put into the graphite mold and sintered in the spark plasma sintering furnace. The sintering temperature was 873 K and the pressure was 50 MPa. The bulk samples with diameter of 20 mm and height of 13 mm was obtained.

The detection of samples includes phase analysis (by X-ray diffraction), micro morphology analysis (by field emission scanning electron microscope), element distribution analysis (by energy dispersive spectrometer), electrical performance test (by ZEM-3 thermoelectric performance tester), thermal performance test (the thermal diffusivity is measured by laser thermal conductivity meter, the specific heat is measured by differential scanning calorimeter, and the density is measured by self-made Archimedes equipment). The specific model of the instruments and the size of the testing samples can be found in the previous works [21, 22]. The crystal model of undoped/doped superlattice is established by Materials Studio software. The crystal structure parameters (such as lattice constant, bond length), the band structure, density of states, and fractional density of states are obtained by first principles calculation of castep module in Materials Studio. The calculation function used is the plane wave pseudopotential (PBE) in the generalized gradient approximation (GGA), and the cutoff energy is 440.0 eV. The specific parameters of software calculation can be found in our previous works [19, 23].

3. Testing And Calculation Results And Related Discussion

The X-ray diffraction results of the series of samples are shown in Fig. 1 (a). The diffraction peaks of the series of samples correspond to the BiCuSeO reference peaks, and no heteropeak is detected. The refined lattice constants of the series of samples are shown in Fig. 1 (b), the lattice constants **a** and **c** both decrease with the increase of Ti content. The lattice contraction is related to the the smaller radius of Ti^{4+} than that of Cu^{+} . In order to analyze and verify the results of crystallographic parameter changes, the $1 \times 5 \times 1$ superlattice of BiCuSeO and the corresponding superlattice of Ti doped sample were established by materials studio. Through the structural optimization calculation based on the generalized gradient approximation principle, we obtained the crystallographic parameters as shown in Table 1. It can be seen that the lattice constants calculated by the first principle also shows a downward trend with Ti doping, which is consistent with the experimental results.

Fig. 2 shows the microstructure of natural fracture of the Ti doped sample with $x = 0.06$ obtained by SEM and the scanning element distribution map by EDS for sample with $x = 0.06$ handled by smoothing and polishing. The sample exhibits the typical lath structure, tightly stacked. The distribution of matrix elements and Ti elements is uniform after Ti doping, and no local segregation is found.

Fig. 3 (a) shows the relationship between the electrical conductivity (σ) of the series of samples and temperature. It can be seen that the electrical conductivity of Ti doped samples increase significantly in the temperature range from room temperature to 873 K, with the highest value of $\sim 200 \text{ Scm}^{-1}$. The hall testing results show that the carrier concentration (n) decreases with the increase of Ti content, so the increase of electrical conductivity should be due to the increase of carrier mobility (μ). The change of bond length after Ti doping is listed in Table 1. It can be seen that the Cu/ Ti-Se bond becomes longer after Ti doping. Because the electrical transporting performance of BiCuSeO is mainly determined by Cu 3d-Se 4p, it may lead to the decrease of carrier concentration. At the same time, the Bi-Se bond becomes longer, because the Bi-Se bond is the carrier transporting channel from the $(\text{Bi}_2\text{O}_2)^{2+}$ layer (carrier storage layer) to the $(\text{Cu}_2\text{Se}_2)^{2-}$ layer (conductive layer), it may lead to the increase of carrier mobility.

In order to further analyze the reason of the change for electrical conductivity, we calculated the energy band structure and density of states (DOS) before and after doping through the CASTEP module in Materials Studio as shown in Fig 4. It can be seen that the band gap becomes wider after Ti doping, which makes it more difficult for carriers to excited from the valence band to the conduction band, resulting in the decrease of carrier concentration. In addition, it can be seen that the top of the valence band has a downward trend, which will lead to the decrease of the effective mass (consistent with the change trend of the calculated value in Fig. 3 (b)) and the corresponding increase of the carrier mobility. Fig. 5 shows the partials density of states (PDOS) before and after Ti doping. It can be seen that although Ti doping causes the decrease of the density of states of Cu 3d orbit and Se 4p orbit and the valence band top to move down, which would make the density of states near the valence band top decrease, but the 3d orbit of Ti would contribute obviously the density of states at the valence band top, which makes the total density of states at the valence band top increase, thus causing the increase of the electrical conductivity.

Fig. 6 (a) shows the relationship between the Seebeck coefficient (S) of the series of samples and temperature. Since the Seebeck coefficient has a positive correlation with the carrier concentration and a negative correlation with the effective mass of the density of states, and the carrier concentration decreased after doping, the decrease of the Seebeck coefficient should be caused by the decrease of the effective mass (as shown in Fig. 3 (b)). The relationship between the power factor ($PF = \sigma S^2$) of the series of samples and temperature is shown in Fig. 6 (b). The increase of power factor in the middle and high temperature range is mainly due to the gain effect caused by the increase of the electrical conductivity overpowered the benefit reduction effect caused by the decrease of Seebeck coefficient.

Fig. 7 (a) shows the relationship between the thermal conductivity (κ) of the series of samples and temperature. It can be seen that with the increase of Ti content, the thermal conductivity ($\kappa = \kappa_e + \kappa_l$) decreases in the whole temperature range, especially in the low and medium temperature range. Because the electrical thermal conductivity has a positive relationship with the electrical conductivity, it increases with the increase of Ti content (as shown in Fig. 7 (b)). The decrease of thermal conductivity is due to the decrease of lattice thermal conductivity as shown in Fig. 7 (c). The decrease of the lattice thermal conductivity should be due to the point defects produced by Ti doping at Cu site, which leads to the increase of lattice distortion and strain field, thus increasing the anharmonicity of the lattice vibration, increasing phonon scattering and decreasing the lattice thermal conductivity. In order to further analyze the reason for the decrease of lattice thermal conductivity, we calculated the elastic constants before and after Ti doping by Materials Studio software according to the first principle. As shown in Fig. 7 (d), after Ti doping, Young's modulus exhibits a downward trend, and low Young's modulus is the main reason for the low thermal conductivity of BiCuSeO [9]. The further decrease of Young's modulus promotes the further decrease of lattice thermal conductivity.

Fig. 8 shows the relationship between the dimensionless figure of merit (ZT) of the series of samples and temperature. It can be seen that the increase of ZT ($ZT = PFT/\kappa$, T is the temperature) value is obvious in the middle and high temperature range after Ti doping, which is mainly due to the increase of power factor (PF) and the decrease of thermal conductivity (κ). The maximum ZT value is 1.04 at 873 K, which was obtained from 4 % Ti doped sample.

4. Conclusion

In summary, Ti is used to dope at Cu site to improve the thermoelectric properties of BiCuSeO. A series of samples were prepared by high temperature vacuum reaction, high energy ball milling and spark plasma sintering. The performances were tested by thermoelectric equipments, and the crystallographic structure parameters, energy band, density of states and elastic constants were calculated by first principles. The results show that Ti doping can cause the lattice contraction and decrease the lattice constant; Ti doping can increase the band gap and lengthen the Cu/Ti-Se bond, resulting in the decrease of carrier concentration; Ti doping can reduce the effective mass and the Bi-Se bond length, thus improve the carrier mobility, and finally increase the electrical conductivity; Ti doping would reduce the Seebeck coefficient, and increase the power factor; Ti doping can reduce Young's modulus, lead to the increase of

defect scattering and strain field, thus reduce the thermal conductivity. It is greatly increased for the ZT values in the middle and high temperature range, with the highest value of 1.04 at 873 K.

Declarations

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Declaration of Interest Statement

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Tables

Table 1. The simulated crystallographic parameters of BiCuSeO and Ti doped BiCuSeO.

	BiCuSeO	Ti doped BiCuSeO
Lattice constant	a= 3.922 Å c= 8.920 Å	a= 3.904 Å c= 8.893 Å
Length of Bi-Se bond	3.162 Å	3.127 Å
Length of Cu/Ti-Se bond	2.471 Å	2.500 Å

Figures

Figure 1

(a) the X-ray diffraction results of the series of samples; (b) the refined lattice constants of the series of samples; (c) the crystal lattice structure of BiCuSeO built by materials studio; (c) the crystal lattice structure of Ti doped BiCuSeO built by materials studio.

Figure 2

The microstructure of natural fracture of the Ti doped sample with $x = 0.06$ obtained by SEM and the scanning element distribution map by EDS for sample with $x = 0.06$ handled by smoothing and polishing.

Figure 3

(a) The relationship between the electrical conductivity of the series of samples and temperature; (b) the carrier concentration (n), carrier mobility (μ) and effective mass (m^*) of the series of samples.

Figure 4

(a) the calculated band structure of BiCuSeO by the castep module of materials studio; (b) the calculated band structure of Ti doped BiCuSeO; (c) the calculated density of states (DOS) of BiCuSeO by the castep module of materials studio; (d) the calculated density of states (DOS) of Ti doped BiCuSeO.

Figure 5

(a) the calculated calculated partial density of states (PDOS) of Cu 3d in BiCuSeO by the castep module of materials studio; (b) the calculated partial density of states (PDOS) of Cu 3d in Ti doped BiCuSeO; (c) the calculated partial density of states (PDOS) of Se 4p in BiCuSeO; (d) the calculated partial density of states (PDOS) of Se 4p in Ti doped BiCuSeO; (e) the calculated density of states (DOS) of Ti in Ti doped BiCuSeO; (f) the calculated partial density of states (PDOS) of Ti 3d in Ti doped BiCuSeO.

Figure 6

(a) The relationship between the Seebeck coefficient (S) of the series of samples and temperature; (b) The relationship between the power factor (PW) of the series of samples and temperature.

Figure 7

(a) The relationship between the thermal conductivity (κ) of the series of samples and temperature; (b) The relationship between the electrical thermal conductivity (κ_e) of the series of samples and temperature; (c) The relationship between the electrical thermal conductivity (κ_l) of the series of samples and temperature; (d) the calculated elastic constants of the pristine sample and Ti doped sample by castep of materials studio.

Figure 8

The relationship between the dimensionless figure of merit (ZT) of the series of samples and temperature.