Progress and trend of PbTe based Thermoelectric Materials

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Abstract—Energy shortage and environmental pollution have become severe problems that cannot be ignored in every country. As a new energy conversion material, thermoelectric material can realize thermoelectric conversion with the advantages of safety, energy saving and environmental protection. This paper summarizes the progress of some PbTe based thermoelectric materials in recent ten years, including the influence of doping elements such as Na, S, Sr and I on their thermoelectric properties, and introduces a method to balance their mechanical and thermoelectric properties. It can be seen that PbTe based thermoelectric materials have good development and broad application prospects in the future.

1. Introduction

Thermoelectric material is a functional material. It transfers heat and electric energy to each other. The Seebeck effect (revealed in 1821) and the Peltier effect (revealed in 1834) pave the way for the application of thermoelectric energy converters and thermoelectric refrigeration. Therefore, the material is very promising in market applications. Today, environmental pollution and energy crises are also threatening the survival of mankind at all times, which also shows that the research on this new type of thermoelectric material has very important practical significance.

The purpose of this paper is to summarize the previous methods to improve the properties of lead telluride based thermoelectric materials and the mechanism of performance improvement. This study promotes the understanding of the mechanism of thermoelectric materials and contributes to the further exploration of the mechanism of improving the properties of thermoelectric materials.

2. Thermoelectric effect

It shows three main principles of thermoelectric effect: Seebeck effect, Peltier effect and Thompson effect[1-6]. In practical application, "thermoelectric merit" (ZT) which is dimensionless is used to measure the thermoelectric properties of thermoelectric materials. The higher the ZT value, the higher the energy conversion efficiency of thermoelectric devices. The expression of ZT is as follows:

\[
ZT = \frac{\sigma S^2}{\kappa T} = \frac{PF}{\kappa T}
\]

Where: \(\sigma\) is conductivity; \(S\) is Seebeck coefficient; \(\kappa\) is the thermal conductivity; \(T\) is the temperature; \(PF\) is a power factor used to characterize the electrical properties of thermoelectric materials.

The three parameters, including Seebeck coefficient, conductivity and thermal conductivity, affecting the thermoelectric properties of materials are not independent. They all depend on the electronic structure of materials as well as the transport and scattering of carriers. Therefore, scientists tend to look for materials with a high Seebeck coefficient, and while improving their conductivity, they expect to reduce their thermal conductivity to obtain a higher ZT value. Generally, researchers will dope
thermoelectric materials with excellent properties. That helps to advance the carrier concentration and carrier mobility of the materials, improve their phonon scattering ability to some degrees, and cut down the thermal conductivity of these materials.

As a traditional thermoelectric material in the middle temperature range, PbTe based thermoelectric material has isotropic electrical and thermal properties, and the band gap is only 0.32ev, making it easy to show p-type or n-type conductivity after doping. It has been a research hotspot in thermoelectric materials since the middle of the 20th century. In the last two decades, both n-type and p-type PbTe based thermoelectric materials have made good development, as shown in Figure 1. Several doping improvements for lead telluride based thermoelectric materials will be introduced below.

![Figure 1: The developments of n-type and p-type PbTe based thermoelectric materials](image)

3. Several Doping of lead telluride based thermoelectric materials

3.1. Na-doped PbTe–PbS Thermoelectric Materials

Steven’s work[8] confirms that by adding PbS and Na to PbTe, there are two effects: the change of the electronic structure and the decrease of the lattice thermal conductivity, which together contribute to an excellent quality factor. They build a successful thermoelectric material system that combined nanostructure to reduce lattice thermal conductivity and density-of-states(DOS) engineering to enhance electronic transport properties. The highest ZT value of 2% Na doped PbTe and PbTe PbS 12% is 1.8(shown in Figure 2).

![Figure 2: High-temperature (A) total and lattice thermal conductivity and (B) ZT of 2% Na-doped PbTe and PbTePbS 12%.](image)
3.2. Na-Doped PbTe–SrTe Thermoelectric Material

In He’s work[9], some conduct chalcogenide semiconductors, such as PbTe, PbSe, and PbS doped with various concentrations of Na lead to Na-rich precipitates, and boost the power factor. Later, the highest ZT of Na doped PbTe–SrTe system reached 2.2 in several researches[10-12] (Figure 3 shows Biswas’s work[10]). Recently, a research[13] studied the effect of annealing on the thermoelectric properties of PbTe–4Sr–2Na samples in detail. They proved that in addition to the correlation between the properties of the PbTe–4mol%SrTe sample and the thermoelectric properties, APT can also perform quantitative analysis in three dimensions.

![Figure 3 ZT of three methods in Biswas’s work[10]](image)

3.3. Effect of iodine doping on n-type PbTe based thermoelectric material

N-type iodine doped PbTe based thermoelectric materials are a hot direction in recent years as well. However, considering the intense sintering process, the sample in its final composition is often very different from the initial standard.

In 2011, Aaron et al. combined with the careful control of carrier density through iodine doping, revealed a significantly larger quality factor ZT of 1.4, which is higher than the previously reported n-type PbTe[14].

Later, the work of Juan et al. showed that in PbTe1-xIx, when x is 0.004 and 0.005, the ZT value is higher, and at this time it also has high conductivity, high power factor and low lattice thermal conductivity. They confirmed that iodine as valid donor in PbTe offers adequate carrier concentration with a handful of dopant. In addition, because the radii of I- and Te2- are similar, doping iodine has no significant effect on the lattice structure[15]. Figure 4 shows the ZT value and the comparison of others in their work.

![Figure 4 Comparison of the (a) ZT values and (b) average ZT values of Juan et al.’ samples with other reported n-type PbTe samples doped with halides[15-18].](image)
3.4. **Balance the strong mechanical properties and high thermoelectric properties**

Both p-type and n-type PbTe based thermoelectric materials enjoy perfect thermoelectric properties, although the mechanical properties are on the low side. In Fu’s work, they chose to dope n-type PbTe-3%Sb material and improve the mechanical properties of the material by alloying it with PbS. According to their data, after alloying, the hardness of the sample increased by more than 60%, the microhardness increased from 54.2 kg mm\(^{-2}\) to about 88 kg mm\(^{-2}\) while the relative ZT value decreased by only 7.4%, still about 1.5 (shown in Figure 5)[19]. It shows that a relatively good balance is achieved between the mechanical properties and thermoelectric properties of PbTe materials. And this balance is conducive to the practical application in the thermoelectric power generation. The good balance between the mechanical properties and thermoelectric properties of PbTe materials is conducive to the practical application in the thermoelectric power generation field.

![Figure 5](image)

**Figure 5** (a) Temperature dependence of the dimensionless figure of merit of PbTe\(_{1-x}\)S\(_x\)–3% Sb–I\(_{0.004}\) (x = 0.00, 0.05, 0.10, 0.15, and 0.20) samples. (b) Vickers microhardness of PbTe\(_{1-x}\)S\(_x\)–3% Sb–I\(_{0.004}\) (x = 0.00, 0.05, 0.10, 0.15, and 0.20) samples[19].

4. **Conclusion**

This paper discusses the changes of several doping methods on the properties of PbTe based thermoelectric materials. One method is Na-doped PbTe–PbS Thermoelectric Materials, in which way the ZT value of the material is improved by changing the electronic structure and reducing the lattice thermal conductivity. Other studies about Na-Doped PbTe–SrTe Thermoelectric Material showed that Na-rich precipitates can improve the power factor, resulting in a significantly high ZT value of PbTe – 4sr – 2Na system sample. Another method is iodine doping, which can greatly improve the carrier concentration of the sample without changing the crystal structure since the structure of I\(^{-}\) and Te\(^{2-}\) are similar. Additionally, alloying n-type PbTe-3%Sb with PbS can greatly improve the mechanical properties with little influence on the thermoelectric properties, which is beneficial to the practical application of thermoelectric devices in thermoelectric power generation.

As a new type of energy conversion material, thermoelectric materials can cleanly convert heat energy and electric energy into each other, and play an important role in reducing the consumption of fossil energy. In recent years, PbTe based thermoelectric materials have developed rapidly, and the ZT value has increased year by year. It is expected to achieve higher performance breakthroughs and large-scale commercial applications in the future.

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