

## THERMOELECTRIC MATERIALS BASED ON SnTe BINARY COMPOUNDS

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**Abstract.** In recent years, many researches have been focused on developing both thermoelectric structures and materials that have high efficiency. In general, thermoelectric research is two-pronged with (1) experiments focused on finding new materials and structures with enhanced thermoelectric performance and (2) analytical models that predict thermoelectric behavior to enable better design and optimization of materials and structures. In this paper we present a theoretical study about thermoelectric materials based on tin telluride (SnTe) and their applications in different fields.

**Keywords:** semiconductors, tin telluride, thermoelectric devices.

### 1. Introduction

A semiconductor is a material that has a resistivity value between that of a conductor and an insulator. The conductivity of a semiconductor material can be varied under an external electrical field. In a metallic conductor, current is carried by the flow of electrons. In semiconductors, current can be carried either by the flow of electrons or by the flow of positively-charged "holes" in the electron structure of the material.

Semiconductor nanocrystals are of great interest for both fundamental research and technical applications [1]. In particular, researches on semiconductor nanostructures with size-dependent optical and electronic properties are motivated by potential applications. Current attention has focused on the preparation of nanocrystalline semiconductors under mild conditions. SnTe has found applications in mid-IR (3–14  $\mu\text{m}$ ) detection photodetectors, radiation receiving, and thermoelectric devices [2].

Like in other solids, the electrons in semiconductors can have energies only within certain bands (i.e. ranges of levels of energy) between the energy of the ground state, corresponding to electrons tightly bound to the atomic nucleus of the material, and the free electron energy, which is the energy required for an electron to escape entirely from the material. The energy bands each correspond to a large number of discrete quantum states of the electrons, and most of the states with low energy (closer to the nucleus) are full, up to a particular band called the

valence band. The ease with which electrons in a semiconductor can be excited from the valence band to the conduction band depends on the band gap between the bands, and it is the size of this energy band gap that serves as an arbitrary dividing line (roughly 4 eV) between semiconductors and insulators [3-4].

Thermoelectric materials can be used to convert heat directly to electricity for power generators, or reversely in refrigeration devices [5]. Novel compounds and nanostructured materials based on SnTe have been of interest recently and intensively investigated [6-8]. The property of a thermoelectric material is characterized with the figure of merit,  $Z = S^2\sigma/\kappa$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity and  $\kappa$  is the thermal conductivity. Among them  $S$  is the most significant parameter since  $Z$  is proportional to the square of  $S$ .

## 2. Thermoelectric properties

Initial thermoelectric materials studied were metals, which display Seebeck coefficients of a few tens of  $\mu\text{V/K}$ . However, in the middle of the 20th century, interest turned towards semiconductors as thermoelectric materials despite small ratios of electrical to thermal conductivity, due to their high Seebeck coefficients and heat conduction dominated by phonon transport. In 1952 Ioffe studied the change in semiconductor thermal conductivity of a material relative to its position in the periodic table. He found that for larger mean atomic weight, the thermal conductivity was lower. The voltage between the two ends is proportional to the temperature difference across the wire provided the temperature gradient is small.

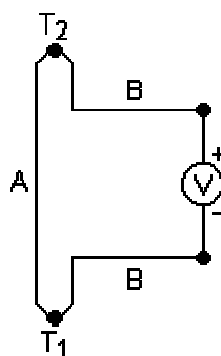


Figure 1. Circuit diagram

The proportionality constant is defined as the Seebeck coefficient or thermoelectric power and is obtained from the ratio of the voltage generated and the applied temperature difference,

which can be in several different configuration and be governed by the same equations), the voltage developed can be derived from:

$$V = \int_{T_1}^{T_2} (S_B(T) - S_A(T)) dT$$

$S_A$  and  $S_B$  are the Seebeck coefficients (also called thermoelectric power or thermopower) of the metals A and B as a function of temperature, and  $T_1$  and  $T_2$  are the temperatures of the two junctions. The Seebeck coefficients are non-linear as a function of temperature, and depend on the conductor's absolute temperature, material, and molecular structure. If the Seebeck coefficient is effectively constant for the measured temperature range, the above formula can be approximated as:

$$V = (S_B - S_A) \times (T_2 - T_1)$$

The Seebeck effect is due to two effects: charge carrier diffusion and photon drag. If both connections are held at the same temperature, but one connection is periodically opened and closed, an AC voltage is measured, which is also temperature dependent. This application of the Kelvin probe is sometimes used to argue that the underlying physics only needs one junction. And this effect is still visible if the wires only come close, but do not touch, thus no diffusion is needed [10-11].

In 1834, the Peltier effect, a companion to the Seebeck effect, was discovered [12]. This effect occurs when a current passes through a wire. The current will carry thermal energy so that the temperature of one end of the wire decreases and the other increases. The Peltier coefficient  $\Pi_{12}$  is defined as the heat emitted per unit time per unit current flow from conductor 1 to 2. Therefore, this heat is directly proportional to the current passing through the junction as described by Eq.

$$dQ = \Pi dI$$

The Peltier effect is often overwhelmed by irreversible Joule heating, which also originates from electronic current. The Thomson effect was predicted in 1854 and found experimentally in 1856. The Thomson effect occurs when a current flows across two points of a homogeneous wire having a temperature gradient along its length and heat is emitted or absorbed in addition to the Joule heat. The Thomson coefficient  $\mu T$  is positive if heat is generated when positive current flows from a higher temperature to lower temperature.

The three thermoelectrical properties provide the basis for modern direct energy conversion devices and their exploitation has been the subject of considerable research. In 1912, Altenkirch introduced the concept of a figure of merit when he showed that good

thermoelectric materials should possess large Seebeck coefficients, high electrical conductivity to minimize Joule heating and low thermal conductivity to retain heat at the junctions that will help maintain a large temperature gradient. Ioffe in 1957 [13] presented the figure of merit as  $Z=S^2\sigma/k$  which he used to qualify the efficiency of thermoelectric materials. The present day dimensionless figure of merit is commonly represented as  $ZT=S^2\sigma T/k$ . Good thermoelectric materials have high electrical conductivity and Seebeck coefficients and low thermal conductivities, but these properties are not independent.

Many research groups are looking for new materials, with better figures of merit, and compatible with solid-state electronics.

### 3. Thermoelectric devices

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely when a voltage is applied to it, it creates a temperature difference (it is known as Peltier effect). At atomic scale (specifically, charge carriers), an applied temperature gradient causes charged carriers in the material, whether they are electrons or holes, to diffuse from the hot side to the cold side, similar to a classical gas expands when heated; hence, the thermally-induced current. This effect can be used to generate electricity, to measure temperature, to cool objects, or to heat them or cook them. Because the direction of heating and cooling is determined by the sign of applied voltage, thermoelectric devices make very convenient temperature controllers [14].

Traditionally, the term thermoelectric effect or thermoelectricity encompasses three separately identified effects, the Seebeck effect, the Peltier effect, and the Thomson effect. In many textbooks, thermoelectric effect may also be called the Peltier- Seebeck effect. This separation derives from the independent discoveries of French physicist Jean Charles Athanase Peltier and Estonian-German physicist Thomas Johann Seebeck. Joule heating, the heat that is generated whenever a voltage is applied across a resistive material, is somewhat related, though is it not generally termed a thermoelectric effect (and it is usually regarded as being a loss mechanism due to non-ideality in thermoelectric devices). The Peltier- Seebeck and Thomson effect can in principle be thermodynamically reversible, whereas Joule heating is not [15].

Thermoelectric generators convert heat directly into electricity, using the voltage generated at the junction of two different metals. The history begins in 1821 when Thomas Johann Seebeck found that an electrical current would flow in a circuit made from two

dissimilar metals, with the junctions at different temperatures. This is called the Seebeck effect. Apart from power generation, it is the basis for the thermocouple, a widely used method of temperature measurement. The voltage produced is proportional to the temperature difference between the two junctions. The proportionality constant  $S$  is called the Seebeck coefficient.

Thermoelectric devices are made from alternating p-type and n-type semiconductor elements connected by metallic interconnect as pictured in the figures below. Semiconductor junctions are especially common in power generation devices, while metallic junctions are more common in temperature measurement. Charge flows through the n-type element, crosses a metallic interconnect, and passes into the p-type element. If a power source is provided, the thermoelectric device may act as a cooler, as in the figure 2. This is the Peltier effect, described in the next section. Electrons in the n-type element will move opposite the direction of current and holes in the p-type element will move in the direction of current, both removing heat from one side of the device. If a heat source is provided, the thermoelectric device may function as a power generator, as in the figure 2.

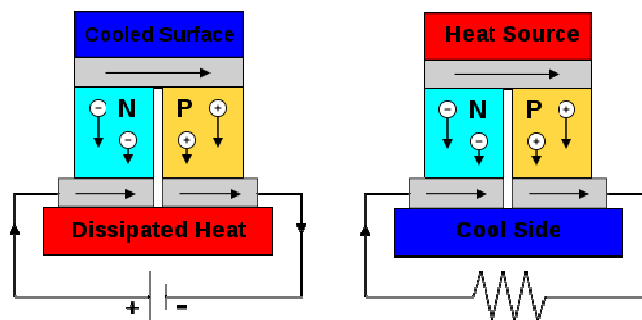


Figure 2. Thermoelectric device

The heat source will drive electrons in n-type element toward the cooler region, thus creating a current through the circuit. Holes in the p-type element will then flow in the direction of the current. The current can then be used to power a load, thus converting the thermal energy into electrical energy [16].

#### 4. Thermoelectric materials based on SnTe

Tin telluride is a compound of tin and tellurium (SnTe) and is often alloyed with lead to make lead tin telluride, which is used as an infrared detector material. Tin telluride is a cubic crystal with lattice constant 0.63 nm, specific heat capacity  $185 \text{ J.kg}^{-1}.\text{K}^{-1}$  and enthalpy of sublimation  $222 \text{ kJ.mol}^{-1}$ . Tin telluride is a small band gap semiconductor with a direct gap of

0.18 eV [17]. It is known that SnTe undergoes a ferroelectric phase transition with the displacement type from a cubic structure of NaCl to that of rhombohedral at a transition temperature near 100K [18].

Tellurides elements and alloys based on them have find wide application in the construction of thermoelectric generators. Sodium-doped tintelluride, and solid solutions based on GeTe are the most efficient thermoelectric materials of *p*-type in the intermediate temperature range with figure of merit  $ZT=1.1-1.4$ . For SnTe this value does not exceed 0.35, but thanks to such attributes as its chemical compatibility with many metals, it continues to be one of the widely used materials. In view of this circumstance, raising the thermoelectric efficiency of SnTe is still a task of current importance [19].

Tin telluride is a semiconductor compound with a wide (~1%) one-sided homogeneity region and a high concentration of nonstoichiometric defects ( $10^{20}-10^{21} \text{ cm}^{-3}$ ) [20]. It is known that SnTe undergoes a ferroelectric phase transition (PT) at  $T_c \sim 100\text{K}$ : It was shown that an increase in the hole concentration *p* leads to a decrease in  $T_c$  and at  $p > (7-8) \times 10^{20} \text{ cm}^{-3}$ , the phase transition is not observed. There are a limited number of experimental works, reporting the possibility of the existence of other phase transitions in bulk SnTe [21]. Temperature anomalies of the electrical resistivity *r* and the Hall coefficient  $R_H$  were revealed in the ranges of 135–150 and 200–215K in monocrystalline SnTe thin films with  $p = (3.5-4.5) \times 10^{20} \text{ cm}^{-3}$ . These anomalies were attributed to phase transitions connected with cation vacancy redistribution over the crystal lattice under changing temperature [21].

#### **4. 1. Experimental**

A mixture of fine tellurium powder (21.6 m mol, purity: 99.999%),  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (10.1 m mol), the chemical compounds with analytical grade and without further purification, was loaded into a 70-ml Teflon liner autoclave, which was then filled with anhydrous ethylenediamine up to 95% of the total volume. The autoclave was sealed and maintained at different temperatures 180°C for 24 h, and then cooled to room temperature naturally. The products were filtrated and washed first with distilled water for three times and then with absolute ethanol for two times to remove by-products. Finally, the dark products were dried in vacuum at 50°C for 5 h [22].

The morphologies of SnTe crystallites were observed to be spherical, examined with JSM-6700F (Field Emission Scanning Electron Microscope) scanner, and the average grain sizes are about 50–60 nm.

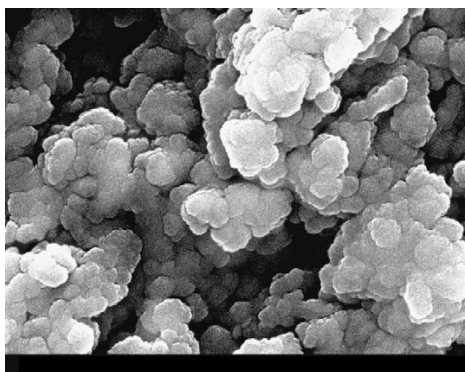


Figure 3. The morphology of nanocrystalline SnTe prepared at 180°C for 24 h

The XRD patterns of synthesized powders, prepared at temperature 180°C using ethylenediamine as a solvent, is shown in Fig. 4.

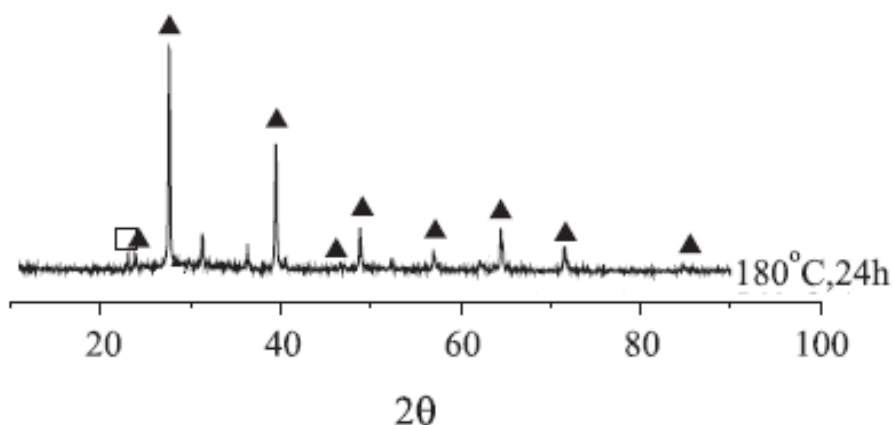


Figure 4. XRD patterns of powder products prepared at 24h using ethylenediamine as a solvent

#### 4. 2. Summary

The average grain sizes of SnTe are about 50–60 nm at 180°C, no rapid increment of grain size with reaction time was observed in this work. Relatively pure ternary compound SnTe can be synthesized via solvothermal route using ethylenediamine as a solvent, and the stoichiometric ratio  $x \sim 0.5$  can be obtained when the reaction temperature and time were controlled to be 180 °C [22, 23].

After the bibliographic study performed, result that nanocrystals materials based on tin telluride are promising materials for our next research.

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