A Method for Thermoelectric Figure of Merit Reaching 100 or higher

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Since several decades, many efforts have been made all over the world to achieve the highly efficient conversion from low-grade thermal energy into electrical energy and the conversion efficiency is usually described by Thermoelectric Figure of Merit, *i.e.*, *ZT* coefficient. However, the highest *ZT* coefficient have not reached 4 in spite of worldwide scientific researches for many years. In this work, a method for reaching an unprecedented *ZT* coefficient was proposed by utilizing phase-transition induced sudden change of electric potential for the oxidation-reduction couple at an electrode material in a thermogalvanic cell (TGCs). It was found that such TGCs could exhibit *ZT* coefficient of the order 100 and even higher, and this new type of thermogalvanic cell was named phase-transition thermogalvanic cell (PT-TGCs). By optimizing the experimental design, the PT-TGCs may convert waste heat into electrical power more effectively and would be applied in various areas in the future.

keywords: figure of merit; *ZT* coefficient; thermogalvanic cell; phase transition

1. Introduction

Thermoelectric (TE) materials can produce electricity from waste heat and are expected to provide an alternative route for power generation, reducing dependence on fossil fuels and cutting down greenhouse gas emissions. Their energy conversion efficiency, *i.e.*, TE efficiency, can be characterized by a dimensionless figure of merit, defined as $ZT=\sigma S^2T/\kappa$, where σ, S, κ and T are electrical conductivity, Seebeck coefficient, thermal conductivity and absolute temperature, respectively [1]. *ZT* coefficient is a key parameter to determine whether the TE materials accomplish industrial applications or not. Over the past tens of years, people have made many efforts to explore high *ZT* coefficient of TE materials. The strategies are to improve the Seebeck coefficient, electrical conductivity and decrease the thermal conductivity. But they are conflicting properties in materials. Insulators and some semiconductors possess large Seebeck coefficient, but their electrical conductivity is small. Metals display huge electrical conductivity, however, they have low Seebeck coefficient and great thermal conductivity. To realize high *ZT* coefficient, the route may be search for appropriate materials where these conflicting properties can be optimized to some extent.

In recent several decades, as motivated by Slack [2], the high-performance TE materials should be “phonon glass electron crystal”. In these materials, phonons are scattered, resulting in reduction of thermal conductivity, nevertheless, the conduction electrons are not blocked, maintaining electrical conductivity. So they are expected to give large *ZT* coefficient. Upon exploring this type of high-performance TE materials,

main efforts focused on two approaches, one was bulk materials with complex crystalline structures (such as skutterudites [3], clathrates [4] and Zintl phases [5]), the other were materials with specially engineered nanostructures [6] (such as mosaic crystals [7], Bi2Te3/Sn2Te3 superlattices [8], dense dislocation arrays in grain boundaries [9]). Owing to concerted worldwide efforts, inspiring advances has been reached. For example, the unprecedented record ZT coefficient ~2.6 at 923 *K*, is realized in single crystal SnSe along b-axis of the room-temperature orthorhombic unit cell [10]. Further investigation indicate that this is caused by the intrinsically giant anharmonic and anisotropic bonding of SnSe, which lead to ultralow lattice thermal conductivity in SnSe [10]. In a recent work, the hole-doped polycrystalline SnSe samples were reported to display an upmost *ZT* coefficient of roughly 3.1 at 783 K [11]. Up to now, so many attempts have been made to reach industrial application of TE materials. However, as far as is known, all these TE materials are nevertheless inefficient to be cost-effective in applications.

An alternative strategy is thermogalvanic cells (TGCs) where a cell voltage is yielded by means of a single electrochemical reaction occurring at electrodes with different temperatures. It can convert low-grade thermal energy into electrical energy without net emission and consumption of any materials [12, 13, 14, 15]. For a TGCs, the temperature dependence of the open-circuit potential difference may be monitored by the Seebeck coefficient [12]

$$S = \frac{\partial V}{\partial T} \tag{1}$$

where V is the measured open-circuit potential difference (OCPD) between the cold and hot electrodes, S the Seebeck coefficient. In general, Seebeck coefficients of various TGCs usually present the order of 1 mV/K, and the corresponding figure of merit Z may only reach the order of 10^{-5} K^{-1}[12, 14], a value much smaller than that of some high-performance thermoelectric semiconductors 10^{-3} K^{-1}. Despite remarkable improvements in power and conversion efficiencies for related devices in recent years, their key performance may be still very limited and prohibit their wide commercial applications [12, 15].

In this work, enlightened by series of theoretical work and experimental work on phase transitions [16-21], a new universal method for achieving ZT coefficient 100 or even higher may be proposed by means of phase transition.

2. Results and discussion

As is known, when the temperature is varied, many materials exhibit different kinds of phase transitions such as structural phase transition, magnetic phase transition and so on. Upon phase transitions, several theoretical work and experimental work showed that the Fermi surface energy (FSE) of a material, *i.e.*, the electron chemical potential, may usually display a sudden alteration and the altered FSE could cause an electric potential between the different phases [16-21]. It may be conceived that this electric potential may be employed to create an ultrahigh-performance TGCs. As is schematically shown in Figure 1, two identical materials act as the two electrodes in TGCs. A material in phase I (colored blue) at a cold temperature T_1 acts as an electrode. At a warm temperature higher than the phase transition temperature (PTT) T_c, the other material may undergo a phase transition and become phase II (colored magenta) which

shows a lifted FSE and behaves as another electrode in the TGCs. Owing to the lifted FSE induced by phase transition, the potential of related oxidation-reduction couple $V(M^{n+}/M)$ may be changed accordingly so that the same oxidation-reduction couple $V(M^{n+}/M)$ in difference phases could yield an OCPD, *i.e.*,

$$V = V(M^{n+}/M1) - V(M^{n+}/M2) \quad (2)$$

where $V(M^{n+}/M\mathrm{I})$ is the oxidation-reduction couple formed by the ion and the material in phase I, while $V(M^{n+}/M\mathrm{II})$ the oxidation-reduction couple composed of ion and the materials in phase II. The correlated oxidation and reduction reactions at anode and cathode may be

$$M - ne \rightarrow M^{n+}$$

$$M^{n+} + ne \rightarrow M$$

The generated OCPD between the anode and cathode may sensitively depend on the temperature and give rise to a temperature dependence of Seebeck coefficient base on Equation (1). As shown in Figure 2, when both the temperatures of the two electrodes are either below or above the PTT T_c, this TGCs may be a common TGCs where the yielded OCPD and correlated Seebeck coefficient may be very small. However, the temperature of cold electrode could be below PTT T_c while the warm electrode can be heated up to a temperature higher than T_c and the electrode material may enter phase II. In this case, the potential of the related oxidation-reduction couple may be subject to a notable alteration which may result in a drastically improved OCPD shown in Figure 3. According to Equation (1), the induced Seebeck coefficient may exhibit remarkable non-linear behaviors and display a largest value close to the PTT T_c, as is schematically

shown in Figure 3. This point could be proved by the well-designed experiments [21] on such a half-cell. As shown by the experiments [21] on a half cell, the temperature dependence of electromotive force between the reference electrode and working electrode was indeed found to exhibit a conspicuous change near the PTT T_c of the electrode material. Serial connection of such a half cell below PTT T_c and another half cell above PTT T_c may form a complete TGCs. This type of TGCs may give birth to an ultra-large Seebeck coefficient and thereby result in an unprecedented *ZT* coefficient. In view of experimental data [21] on such a half cell, Figure 4 gives three cases of such TGCs based on the electrode material with phase transition, *i.e.*, chromium (Cr) exhibiting a antiferromagnetic-paramagnetic phase transition at Neel temperature 311.65 K [22], gadolinium (Gd) displaying a ferromagnetic-paramagnetic transition at Curie temperature 294 K [23], and TiNi alloy experiencing a *R* phase transition in the temperature range 310-316 K [24]. For the electrolytes within these TGCs, the electrical conductivity might reach an order of 20 S/m and the thermal conductivity could be the order of 0.5 $W/m{\cdot}K$ which are the typical values for some electrolytes [25, 26, 27]. So, these TGCs may exhibit ultra-large *ZT* coefficients which might approach the order of 10^2 and even higher, as is shown in Figure 5. This kind of TGCs may take advantage of the sudden change of electric potential for oxidation-reduction couple at the PTT T_c of the electrode material and could be named phase-transition thermogalvanic cell (PT-TGCs).

For the PT-TGCs, several points should be noted. First, PT-TGCs may be a special type of TGCs. It is the phase transition of the electrode material that induces great

variations (~0.1 V) of electric potential of oxidation-reduction couple within a narrow temperature zone (~ 1 K) at the electrode and leads to ultra-large ZT coefficients. So, only in the situation that one electrode is under the PTT T_c and another electrode is above the PTT T_c it can work well. Second, in actual applications the anode material may be consumed but the cathode material may accumulate due to continuous deposition. To improve the output power, one may need to reduce the internal resistance of PT-TGCs and a possible method may be selecting appropriate metals and alloys to work as electrode materials. Third, the appropriate electrolyte in PT-TGCs may be very important. It may dominate both the ZT efficient and output power of PT-TGCs. Once the electrode material PT-TGCs is determined, the optimization of electrolyte may be an important task for people.

3. Conclusion

In summary, a new type of TGCs was proposed in this work by taking into account of sudden change of electric potential of oxidation-reduction couple at electrode material upon phase transition and it was named PT-TGCs. This new kind of PT-TGCs may exhibit an unprecedented ZT coefficient 10^2 and ever higher in their right working temperature zone. To be expected, these PT-TGCs may convert low-grade thermal energy into electrical energy effectively and find important applications in various areas in the future.

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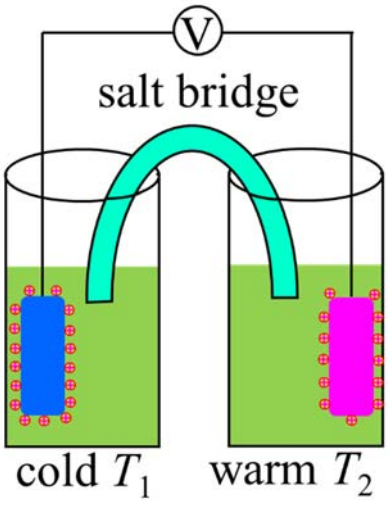

Figure 1 Sketch of a thermogalvanic cell consisting of two half cells bridged by a salt bridge.

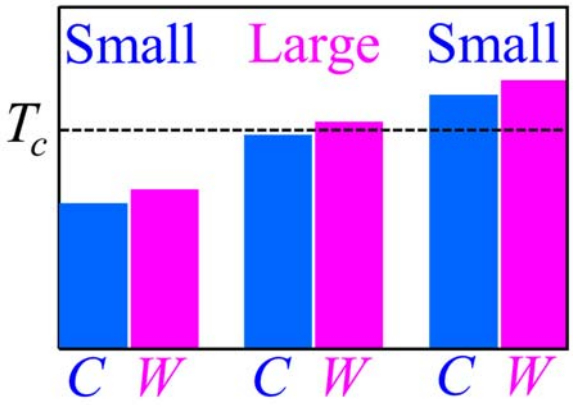

Figure 2 Three typical situations for the electrodes of a thermogalvanic cell at different temperatures.

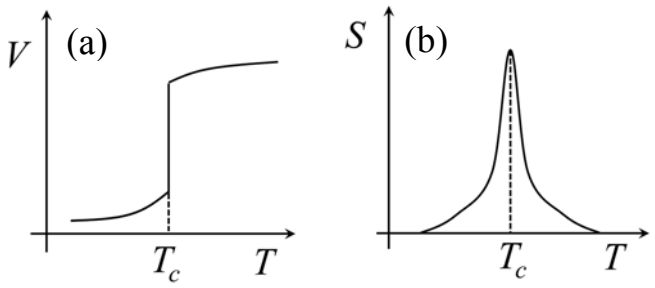

Figure 3 Schematic diagrams for temperature dependence of electric potential (a) and the generated Seebeck coefficient (b) for a thermogalvanic cell with its electrode material experiencing a phase transition at temperature T_c.

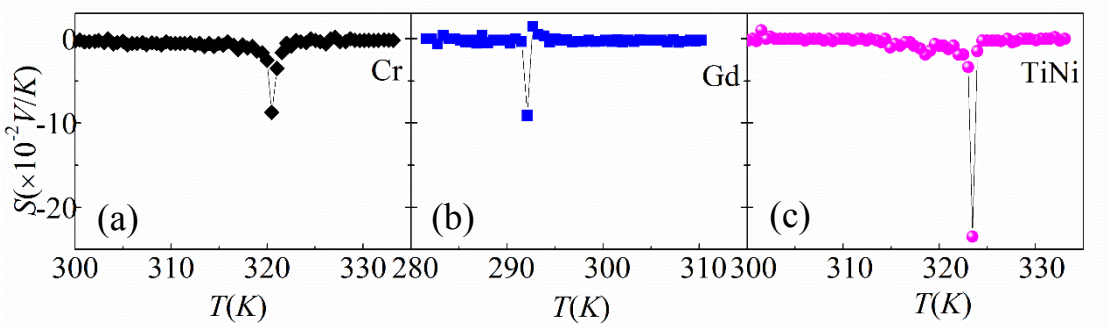

Figure 4 Temperature dependence of Seebeck coefficients generated by phase-transition thermogalvanic cell according to experimental data [21] on a half cell using chromium (a), gadolinium (b) and TiNi alloy (c) as electrode materials.

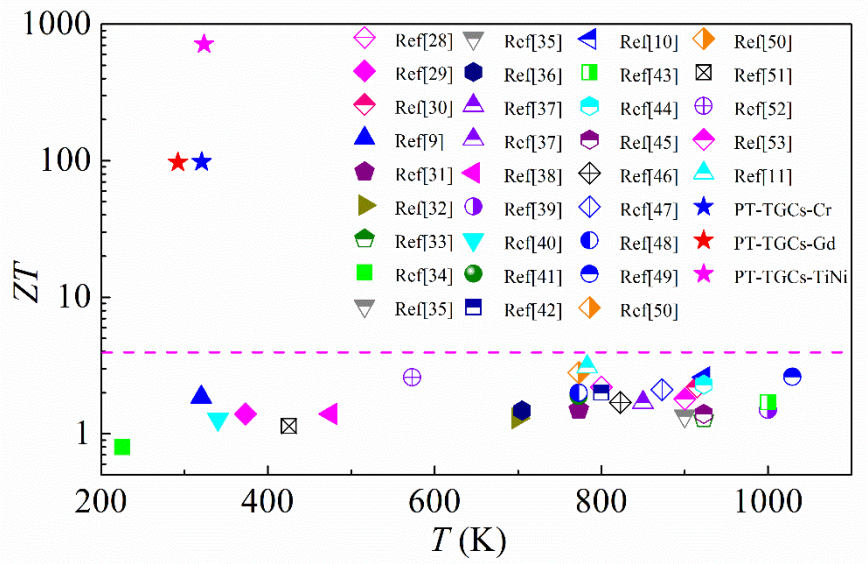

Figure 5 Reported peak values of dimensionless figure of merit (*ZT* coefficient) and the related working temperatures. The stars are given by phase-transition Thermogalvanic cell (PT-TGCs).