# CHAPTER 1

# INTRODUCTION

Providing a sustainable supply of energy to the world's population will become a major society problem for the 21st century as fossil fuel supplies decrease and demand increases. One of the types of energy conversion technologies that have received renewed attention is thermoelectric (TE) energy conversion, where heat is converted directly into electricity using a class of materials known as thermoelectric materials. Thermoelectric phenomena, involving the conversion between thermal and electrical energy, and providing a method for heating and cooling materials, are expected to play an increasingly important role in meeting the energy challenge for the future [1-3]. Thermoelectrics materials are also capable of acting as solid state refrigerators or heat pumps which do not use any moving parts and environmentally harmful fluids. Because of their high reliability and simplicity, thermoelectrics are used extensively in fields such as space power generation and a variety of cooling applications [4]. The efficiency of a material used in TE devices is determined by the dimensionless figure of merit, $ZT = \alpha^2 \sigma T/\kappa$, where Z is the figure of merit, $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the total thermal conductivity ($\kappa = \kappa_{lat} + \kappa_{el}$, the lattice and the electronic contributions). In order to maximize $ZT$ of the material since $\alpha$, $\sigma$, and $\kappa_{el}$ in bulk materials are interrelated, $\alpha$ is required to be the highest, but electrical resistivity $\rho$ ($\rho = 1/\sigma$) and $\kappa$ are the lowest. Due to their transport property interrelation, they are needed to be optimized to achieve maximum $ZT$ [5].

The advanced bulk-materials approach focused on new categories of materials that contained heavy-ion species with large vibrational amplitudes (rattlers) at partially filled structural sites, thereby providing effective phonon-scattering centers. The most prominent of these advanced bulk materials are the so-called phonon-glass/electron-crystal (PGEC) materials such as the partially filled skutterudites based on alloys of $CoSb_3$ [3,6]. Regarding the low-dimensional materials approach, two ideas were dominant. Firstly the introduction of nanoscale constituents would introduce quantum-confinement effects to enhance the power factor $\alpha^2\sigma$. Secondly, the many internal interfaces found in nanostructures would be designed so that the thermal conductivity would be reduced more than the electrical conductivity, based on differences in their respective scattering lengths [1].

During the 1990s these two approaches developed independently and mostly in different directions. More recently, the two approaches seem to be coming together again. Firstly, the most successful new bulk thermoelectric materials are host materials containing nanoscale inclusions that are prepared by using chemical approaches [7]. Secondly, low-dimensional materials systems are now being assembled as nanocomposites containing a coupled assembly of nanoclusters showing short-range low dimensionality embedded in host materials [6], thereby producing a bulk material with nanostructures and many interfaces that scatter phonons more effectively than electrons [1].

The main advantage of using nanotechonologies in the design of thermoelectric materials lies in the fact that the addition of the dimensionality of the system as a new parameter can influence the interdependence of the transport coefficients. There are two basic mechanisms which $ZT$ is improved in low-dimensional systems [1-2,8]:

1. An increase in the power factor $\alpha^2\sigma$, or at least the avoidance of decrease in $\alpha^2\sigma$ with the decrease in $\kappa$, through size quantization or energy filtering of the electrons.
2. A reduction in the lattice thermal conductivity due to the scattering and the refraction of phonons on the physical boundaries of the nanoscale structure.

To the best assess of the recent progress and prospects in thermoelectric materials, the decades of research and development of the established state-of-the art materials should also be considered. By far the most widely used thermoelectric materials are alloys of $Bi_2Te_3$ and $Sb_2Te_3$. For near-room-temperature applications, such as refrigeration and waste heat recovery up to 200°C, $Bi_2Te_3$ alloys have been proved to possess the greatest figure of merit for both *n*- and *p*- type thermoelectric systems. It was quickly realized that alloying with $Sb_2Te_3$ and $Bi_2Se_3$ allowed for the fine tuning of the carrier concentration alongside reduction in lattice thermal conductivity. The most commonly studied *p*-type compositions are near $(Sb_{0.8}Bi_{0.2})_2Te_3$, whereas *n*-type compositions are close to $Bi_2(Te_{0.8}Se_{0.2})_3$ [8].

ZnTe is a II-VI semiconductor material which has a direct wide band gap of 2.26 eV at 300 K [9], and an exciton Bohr radius of 6.2 nm [10]. It has a great deal of potential applications, such as green-light-emitting diodes, solar cells, waveguides, modulators [9], and other optoelectronic and thermoelectric devices [11,12].

Based on these interesting electrical properties, the TE properties such as $\alpha$, $\rho$, and $\kappa$ of GaSb and InSb have been examined [13-16]. For example, Su et al. investigated the TE properties of Zn-doped InSb single crystals and reported the maximum *ZT* value to be around 0.27 at 700 K [15]. The TE properties of $In_2Te_3$-InSb solid solutions were also examined [16]. Ebnalwaled investigated the TE properties of GaSb bulk crystals and reported the power factor value of $8.82\times10^{-3}$ $mWm^{-1}K^{-2}$ at 322 K [13]. However, as for ternary compounds containing Ga, In, and Sb, the TE properties have scarcely reported. As for *M*-(Ga or In)-Sb ternary compounds, the existing of $Ni_3GaSb$ and $Ni_3InSb$ have been reported by Jan and Chang [17]. These compounds exhibit the hexagonal, P63/mmc crystal structure - similar to that of $Ni_3GaAs$ [18]. The melting points were determined to be >1339 K and >1364 K for $Ni_3GaSb$ and $Ni_3InSb$, respectively [17].

Synthesis and characterization of nanostructured materials have been major research activities for over ten years. Many interesting problems have been thrown up because of unusual properties of these materials. Nanoscale electronics is a fast developing field and is predicted to play a significant role in future device technology [19]. At the present time, nanotechnologies are the key indicator to determine the level of development of world technologies and economics. Many areas of researches are in rapid advance owing to the combined efforts of science and engineering. However, the methods of access, investigation, and properties of nanoparticles still have no answer for the main questions on the reason for their specific features [28, 29]. As with all materials that have the prospect of widespread usage, thus preparation methods of thermoelectric materials are desired to improve. For example, new synthetic routes to prepare these compounds may lower production costs, shorten reaction time or enhance physical properties [30].

Microwave radiations with the frequency of 2.45 GHz are coherent and polarized [9]. They are able to couple with atomic materials, and cause them to be heated up very rapidly. In general, materials are classified into three groups: reflectors: bulk metals and alloys, transparency: fused-silica and fluoropolymers, and absorbers: inorganic materials, powdered metals, metal oxides and metal halides [31]. The use of microwaves in analytical sample preparation, materials processing and organic synthesis is becoming increasingly attractive; however, the utilization of microwaves for solid-state inorganic synthesis is limited to some extents. This is due to, in part the lack of understanding the interactions of microwaves with solids in dry media and the effect of reaction variables have on these interaction. Solid-state microwave reactions are able to access high temperatures rapidly and no requirement of a long time for completion. Reactions, which normally require hour or days via conventional heating, can be carried out in the microwave within an order of minutes. Shorter reaction procedures are advantageous, not only because they save time and are money, but also because they may allow for the synthesis of kinetically stable or meta-stable compounds, which are difficult to synthesize via other methods. Another advantage is that, unlike other alternative methods to traditional, high-temperature solid-state preparation, such as solvothermal synthesis, no solvent waste is generate in these reactions. These advantages allow solid-state microwave synthesis to be considered as a relatively green technique. Solid-state microwave irradiation has been used to prepare a variety of different materials, such as carbides, oxides, silicides, phosphides and borides [31].

The purpose of the present research was to find the way to save the energy consumption for producing purified $Sb_2Te_3$ and ZnTe nanocrystals by a microwave plasma under 4.3±1 kPa argon absolute pressure. This synthetic process required a pressure that is not as low as previously done by Bhunia et al [9]. It is inexpensive, shorten reaction time, and environmentally benign appropriate for green environment.

**Research objective**

1. To build and develops the solid-state synthetic technique by using a microwave induced plasma system which is able to offer several advantages over other conventional heating techniques.
2. To synthesize and characterize the properties of ZnTe and $Sb_2Te_3$ using microwave induced plasma system with nanometer and micrometer structures.
3. To synthesize and characterize the properties of $Ni_3GaSb$ and $Ni_3InSb$ ternary compounds by alloying preparation in furnace with bulk thermoelectric materials.
4. To study and investigate thermoelectric properties of $Ni_3GaSb$ and $Ni_3InSb$ compounds.