CHAPTER 1

INTRODUCTION

1.1 Introduction

In the last decade, green power sources have catched a big attention due to a severe environmental problem. Among the green power sources, there are solar energy, ocean wave, geothermal heat, waste heat, body heat and others. The demand for alternative energy technologies to reduce our dependence on fossil fuels is becoming an ever more important regime of research, including that of high temperature energy harvesting via the direct recovery of waste heat and its conversion into useful electrical energy. Using thermoelectric power generations, the energies are transformed to electric power with great efficiency. They have a long working life (over 20 years) in a wide temperature range with highly stable performance [1]. The power generation efficiency mainly depends on thermoelectric materials. It is determined by thermoelectric figure of merit (Z) which can be typically expressed by dimensionless quantity ZT, $ZT = T\alpha^2\sigma/\lambda$. In this equation, T is the temperature, α is the Seebeck coefficient, σ is the electrical conductivity, and λ is the thermal conductivity. Thermoelectric materials are usually made of semiconductor. The main purpose to produce thermoelectric materials is having ZT>1 at room temperature. Many studies have been done to improve ZT value of thermoelectric materials in recent years [2]. In addition, semiconductors that used as thermoelectric materials require small band gaps [3]. For all of these properties are recognized to be great importance to guarantee the performance of the thermoelectric materials.

There are many kinds of thermoelectric materials which can be classified by the number of elements composing phases such as binary, tertiary and quaternary [4]. As a result, there are many synthetic thermoelectric materials of binary and tertiary phases, such as TiO_2, Bi_2Te_3, $CuInS_2$ and $PbTiO_3$ [3, 5, 6]. Quaternary composition is the new interesting one. In recent years, there were many reports on quaternary compound for using as thermoelectric materials.

Thermoelectric materials are normally made from a semiconductor because of their physical properties. A semiconductor is a material which its electrical conductivity is in between that of a conductor and an insulator. The semiconductor has small band gap which allows electrons in the valence band to be activated to the conduction band easily. A large number of semiconductor materials were being investigated by the late 1950's and early 1960’s, several of which emerged with Z values significantly higher than in metals or metal alloys. No single compound semiconductor evolved that exhibited a uniform high figure-of-merit over a wide temperature range, so most researches have focused on developing materials with high figure-of-merit values over relatively narrow temperature ranges. Of the great number of materials investigated, those based on bismuth telluride, lead telluride and silicon germanium alloys emerged as the best for operating to temperatures of about 450K, 900K and 1400K respectively. Moreover, semiconductors are grouped in two types; intrinsic and extrinsic semiconductors. A pure semiconductor is often called an “Intrinsic semiconductor” and a doped semiconductor is often referred to as extrinsic.

$Cu_{0.5}Ag_{1.5}InSe_3$ (CAIS) is extrinsic semiconductor which is doped with silver as acceptor [7]. The hole of electron was found in CAIS structure. So, CAIS was called a p-type semiconductor.

Various methods are used to prepare thermoelectric materials e.g. deposition method (electro deposition, chemical deposition etc.)[8], templating and chemistry process [5], sol-gel method [9], and spark plasma sintering [2]. Deposition method and theirs applications are used widely, but theirs instrument are specifically and higher cost than other techniques. The major interesting characteristics of these materials should be small and uniform particles. Hence sol-gel method is monitored because it can be generally used to prepare nano-particles with monodispersion[10]. Moreover, most of the reports were concentrating on thin films, because of thin films technology breakthroughs in microelectronic, optics and nanotechnology [11]. Thin films are prepared by coating semiconductor material on a substrate. There are varieties of thin-film preparation methods, such as spin coating method and dip-coating method [3, 12].

In this research, sol-gel dip-coating method will be used to prepare $Cu_{0.5}Ag_{1.5}InSe_3$; CAIS (quaternary thermoelectric material) thin film on glass substrate and powder by annealing process.

The details of thermoelectric properties of material were described in the next parts. It will show the meaning of thermoelectric, properties of thermoelectric materials (Seebeck, Figure-of-merit) and the applications of thermoelectric devices.

1.2 Thermoelectric properties

The thermoelectric is the direct way to convert electrical energy into heat transfer and vice versa. While traditional cooling systems use gas or liquids to transfer heat, the thermoelectric system uses the electrons themselves as the means of transportation. The cold side of the thermoelectric module is connected to a heat exchanger which helps the heat absorption from the object to be cooled. The warm side is connected to a heat sink which helps to transfer the absorbed heat to the surrounding environment [13].

The properties of thermoelectric were shown how beneficial of thermoelectric. There were seebeck coefficient and figure-of-merit as a parameter. Seebeck coefficient was reported in Seebeck Effect that described how much of electrical potential in the thermoelectric materials. And the figure-of-merit was shown in Thermoelectric Figure-of- merit that described how good of thermoelectric materials.

The following sections will focus on a brief introduction to parameters which influence the properties, applications of thermoelectric and finally some of the latest achievements trend of materials in this field.

1.2.1 Seebeck Effect

In 1821, German physicist Thomas Johann Seebeck found the temperature difference at the junctions [14], which induced a current along the closed loop. Such phenomenon is called the Seebeck effect. It can be considered that the free electrons with enough kinetic energy (thermal energy) tend to travel from one junction to the other, and therefore a potential difference is created between the two junctions [13]. The two metals can be characterized as n-type (electron carriers) or p-type (holes)

Seebeck effect was the magnitude of the magnetic field was proportional to the temperature difference and dependent on the type of conducting material, but did not depend on the temperature distribution along the conductors. This meant that the produced voltage difference (ΔV) was directly proportional to the temperature difference between the hot side and the cold side ($\Delta T = T_H - T_C$):

The proportionality is called the Seebeck coefficient (S), which is also known as thermopower. The generation of this effect, where an applied temperature difference causes charge carriers in a thermoelectric material to diffuse from the hot side to the cold side. Charge carriers at the hot end, such as electrons, gain higher side and the oppositely charged nuclei are left behind at the hot side, as shown in Figure 1.1 This charge separation results in a potential difference between the junctions, hence an electrical current flows when the two sides are connected. This current will be maintained as long as the temperature gradient exists.

Figure 1.1 The electrical potential induced by the temperature gradient.

(In this schematic the charge carriers are electrons.)

http://kleinke.uwaterloo.ca/te.html (2 July 2011)

1.2.2 Thermoelectric Figure-of- merit

The figure of merit is the thermoelectric property that showed how good thermoelectric materials. High electrical conductivity to minimize Joule heating, low thermal conductivity to retain heat at the junctions and maintain a large temperature gradient, and large Seebeck coefficients for maximum conversion of heat to electrical power or electrical power to cooling performance[15]. These three properties were later incorporated mathematically into one formula [16]. The commonly used figure-of-merit (FOM) of a thermoelectric material is defined as:

$$Z = \alpha^2\sigma/\lambda$$

Where α is the Seebeck coefficient
σ is the electrical conductivity
λ is the thermal conductivity

Since *Z* has a unit of K^{-1}, one often uses dimensionless figure-of-merit defined as *ZT*. The figure of merit (*ZT*) is the standard measure of a single material's thermoelectric performance.

1.2.3 Application of Thermoelectric

The thermoelectric effect for power generation was developed in 1950s by Ioffe[17]. His colleagues found thermoelectric conversion theory, which provided the basis for modern thermoelectric theory and led to the prospering of thermoelectric applications [18]. Since then, thermoelectric devices have been well investigated. To convert thermal energy into electricity, the Seebeck effect is utilized, as shown in Figure 1.2.a Heat is being pumped from the hot *p-n* junction and rejected from the cold junction, thus producing an electrical current, which amounts to power generation. If an electric current is applied to the *p-n* junction, heat is pumped from the cold junction to the hot junction. A typical thermoelectric module consists of many pairs of p-type and n-type semiconducting, which are connected electrically in series and thermally in parallel.

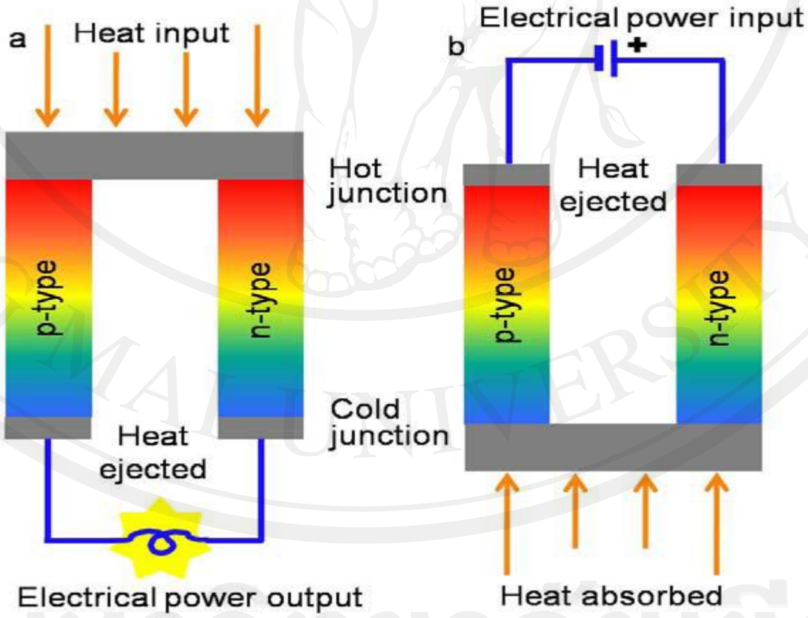

Figure 1.2 a) Power generator module; b) Refrigerator module.

http://www.laserfocusworld.com (4 July 2011)

Recently, there has been a rapid increase in the use of thermoelectric devices for power generation in remote telecommunication sites, space probes, and waste heat recovery for automobiles, portable refrigerators, electronic component coolers, and metal alloy sorting devices. Some examples are shown in Figure 1.3.

In thermoelectric devices consists of thermoelectric materials. There are many materials that use as thermoelectric materials. Some of these materials were used at high temperature and some were used at low temperature. The following section will describe on the development of thermoelectric materials that use in thermoelectric applications in recently.

Figure 1.3 a) Global TEG on a natural gas line, b) BMW TEG in the car exhaust system, c) Lunch box with TE technologies.

http://www.flickr.com (4 July 2011)

http://www.greencar.com (4 July 2011)

1.3 Thermoelectric Materials

Among the vast number of materials known to date, only a relatively few are identified as thermoelectric materials. In Figure 3 is displayed the figure-of-merit Z of a number of thermoelectric materials together with potential generating applications.

Thermoelectric materials can be conveniently divided into three groupings with each dependent upon the temperature range of operation (Figure1.4). Alloys based on bismuth in combinations with antimony, tellurium or selenium are referred to as low temperature materials and can be used at temperatures up to around 450K

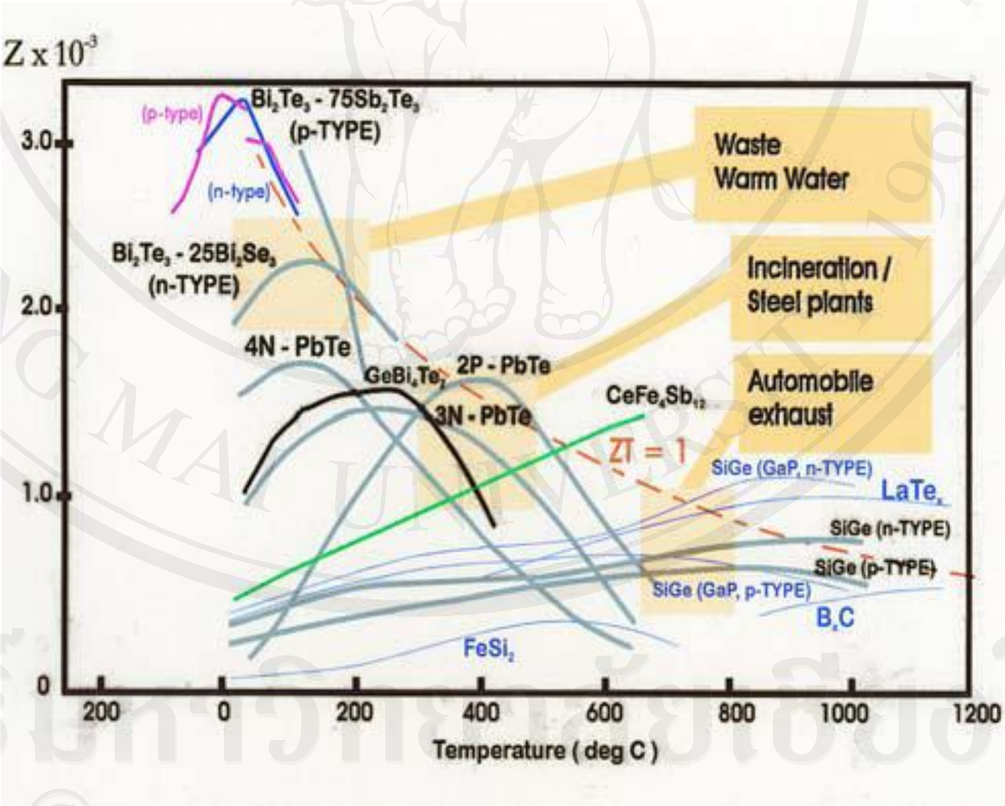

Figure 1.4 Figure-of-Merit of a selection of materials

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These are the materials which are universally employed in thermoelectric refrigeration and have no serious contenders for applications over this temperature regime. The highest figure-of-merit for a thermocouple fabricated from n- and p-bismuth telluride is around $2.0\text{x}10^{-3}$ K^{-1} [19]. The intermediate temperature range – up to around 850K is the regime of materials based on alloys of lead while thermo elements employed at the highest temperatures are fabricated from silicon germanium alloys and operate up to 1300K.

Although the above mentioned materials still remain the basis for commercial/practical applications in thermoelectric generation, significant advances have been made in synthesizing new materials and fabricating material structures with improved thermoelectric performance. Efforts have focused primarily on improving the material’s figure-of-merit, and hence the conversion efficiency, by reducing the lattice thermal conductivity [20].

Most of thermoelectric materials used as a semiconductor because of their physical properties. In addition, the physical properties of semiconductor will show in following section.

1.4 Semiconductor

A semiconductor is a material which its electrical conductivity is in between that of a conductor and an insulator. The semiconductor has small band gap which allows electrons in the valence band to be activated to the conduction band easily (Figure 1.5) [7]. Moreover, semiconductors are grouped in two types; intrinsic and extrinsic semiconductors.

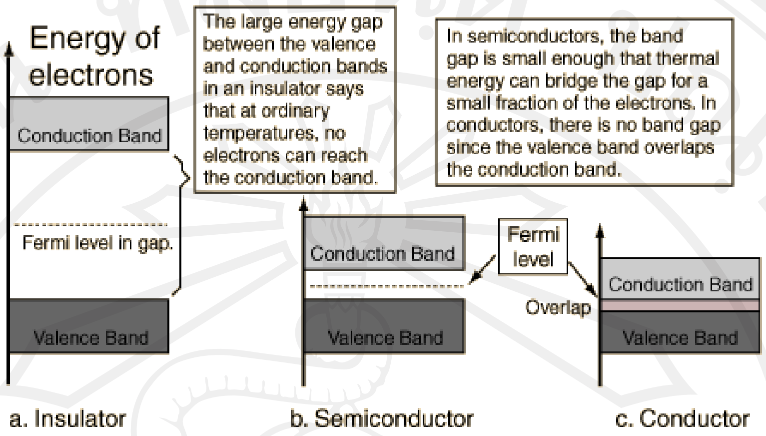

Figure 1.5 The conduction band of a) insulator, b) Semiconductor and c) Conductor

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- **Intrinsic semiconductor** [21] (Figure 1.6) is a pure semiconductor without any significant dopant species present. The number of charge carriers is therefore determined by the properties of the material itself instead of the amount of impurities. In intrinsic semiconductors the number of excited electrons and the number of holes are equal: n = p

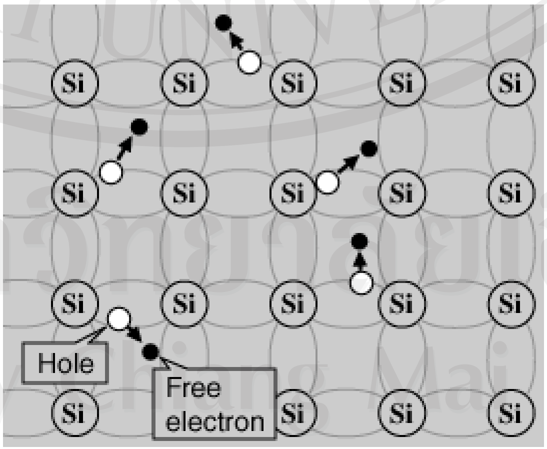

Figure 1.6 The intrinsic semiconductor

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- **Extrinsic semiconductor** (Figure 1.7) is a semiconductor that has been *doped*, that is, into which a doping agent has been introduced, giving it different electrical properties than the intrinsic (pure) semiconductor. Doping involves adding dopant atoms to an intrinsic semiconductor, which changes the electron and hole carrier concentrations of the semiconductor at thermal equilibrium. Dominant carrier concentrations in an extrinsic semiconductor classify it as either an n-type or p-type semiconductor. The electrical properties of extrinsic semiconductors make them essential components of many electronic devices.

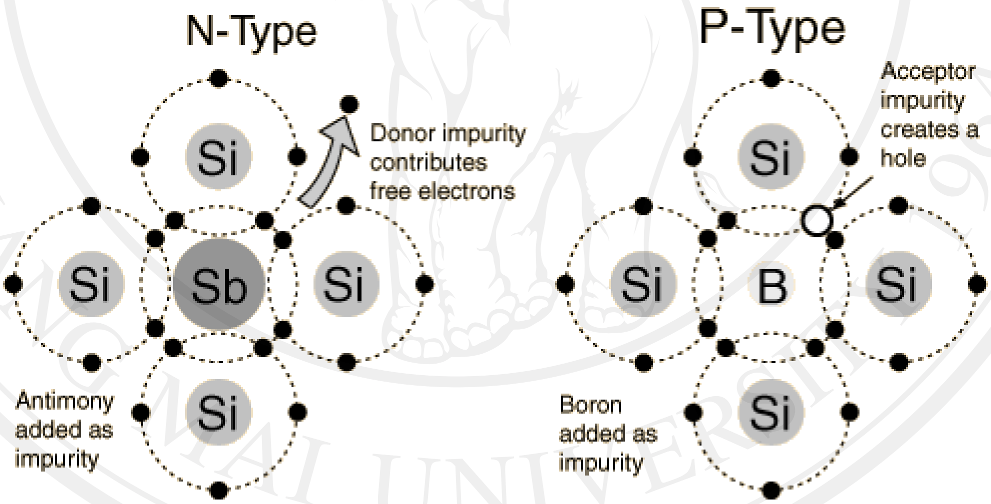

Figure 1.7 The extrinsic semiconductor.

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Acceptor impurity atoms have less valence electron than the atoms they replace in the intrinsic semiconductor. They "accept" electrons from the semiconductor's valence band. This provides excess holes to the intrinsic semiconductor. Excess holes increase the hole carrier concentration (p_0) of the semiconductor, creating a p-type semiconductor.

Semiconductors and dopant atoms are defined by the column of the periodic table of elements they fall in. The column definition of the semiconductor determines how many valence electrons its atoms have and whether dopant atoms act as the semiconductor's donors or acceptors. Group IV semiconductors use group V atoms as donors and group III atoms as acceptors.

Group III-V semiconductors use group VI atoms as donors and group II atoms as acceptors. Group III-V semiconductors can also use group IV atoms as either donors or acceptors. When a group IV atom replaces the group III element in the semiconductor lattice, the group IV atom acts as a donor. Conversely, when a group IV atom replaces the group V element, the group IV atom acts as an acceptor. Group IV atoms can act as both donors and acceptors; therefore, they are known as amphoteric impurities.

The two types of extrinsic semiconductor

- **N-type semiconductors**

Extrinsic semiconductors with a larger electron concentration than hole concentration are known as n-type semiconductors (Figure 1.7). The phrase 'n-type' comes from the negative charge of the electron. In n-type semiconductors, electrons are the majority carriers and holes are the minority carriers [21]. N-type semiconductors are created by doping an intrinsic semiconductor with donor impurities. In an n-type semiconductor, the Fermi energy level is greater than that of the intrinsic semiconductor and lies closer to the conduction band than the valence band.

- **P-type semiconductors**

As opposed to n-type semiconductors, p-type semiconductors have a larger hole concentration than electron concentration. The phrase 'p-type' refers to the positive charge of the hole. In p-type semiconductors, holes are the majority carriers and electrons are the minority carriers (Figure 1.7). P-type semiconductors are created by doping an intrinsic semiconductor with acceptor impurities. P-type semiconductors have Fermi energy levels below the intrinsic Fermi energy level. The Fermi energy level lies closer to the valence band than the conduction band in a p-type semiconductor.

There are many methods that use to prepare thermoelectric materials and semiconductor. In this research was studied on one method that usually prepare at low temperature and many people take an interest. This method will be brief in next part.

1.5 Sol-gel Method

Sol–gel processing is a relatively new method for the preparation of oxide materials at low temperature. The lower temperatures involved, near room temperature for the formation of the gel precursor to the oxide, are in stark contrast to the traditional method used to prepare oxide materials by mixing fine-grained solid powders of oxides and firing at high temperature: the so-called ‘‘grind-and-fire’’ method. Since the uses of oxide materials are multitudinous from refractory oxides and the ceramics industry to silica glass to superconductors. The advent of sol–gel processing has had a significant impact over the years [22].

Sol–gel processing involves the controlled hydrolysis and condensation of a soluble precursor to form a sol, a homogeneous suspension of submicroscopic solid oxide particles in a liquid. In turn, the sol particles can grow and condense to form a continuous network polymer or gel containing trapped solvent particles. The method of drying then determines the nature of the final product: the gel can either be heated to drive off the trapped solvent molecules leading to capillary pressure and a collapse of the gel network; or, alternatively, the gel may be dried supercritically, which allows solvent removal without network collapse (Figure 1.8) . The final product obtained from supercritical drying is called an aerogel that from heating is called a xerogel [23]. Gels are not the only form for the final product obtainable. Figure 1.9 shows the various routes to the different product types.

There are four principal advantages to using sol–gel processing techniques over traditional methods of preparing ceramic materials [24]:

- **Purity of the final product**. As the process uses molecular precursors rather than bulk materials, standard purification techniques such as distillation, sublimation, chromatography, and recrystallization can be applied.

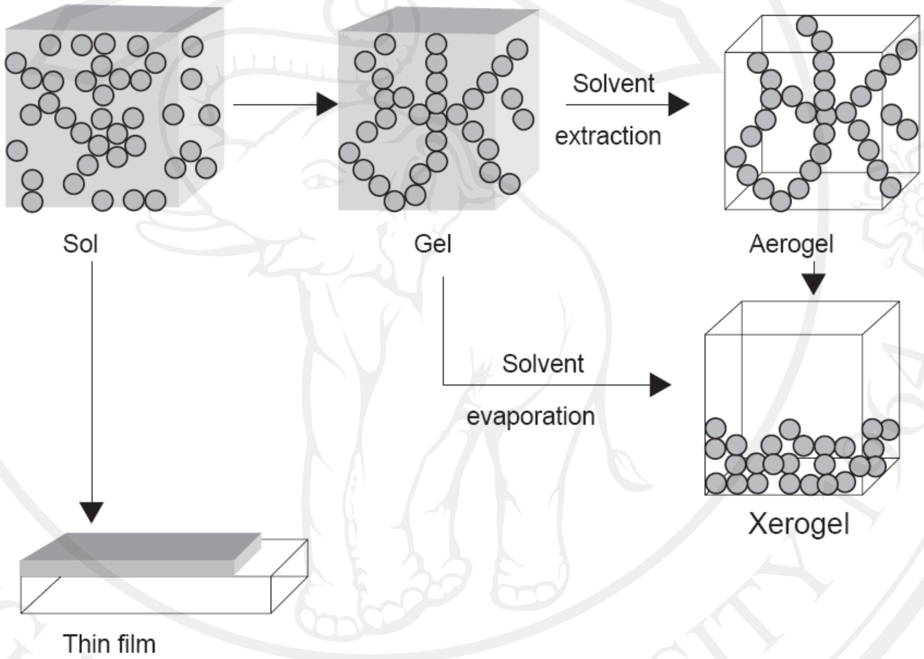

Figure 1.8 Outline of Sol-gel process.

Sol-gel, J. A. CRAYSTON University of St. Andrews, Scotland

- **Greater stoichiometric control.** The use of molecular precursors: sol–gel processing allows precise amounts of starting materials to be mixed together in solution with control of the exact stoichiometry and thus the desired final properties upon calcination. This aspect of the technique is particularly important for the production of complex oxides such as the materials used for high-T_c superconductors.

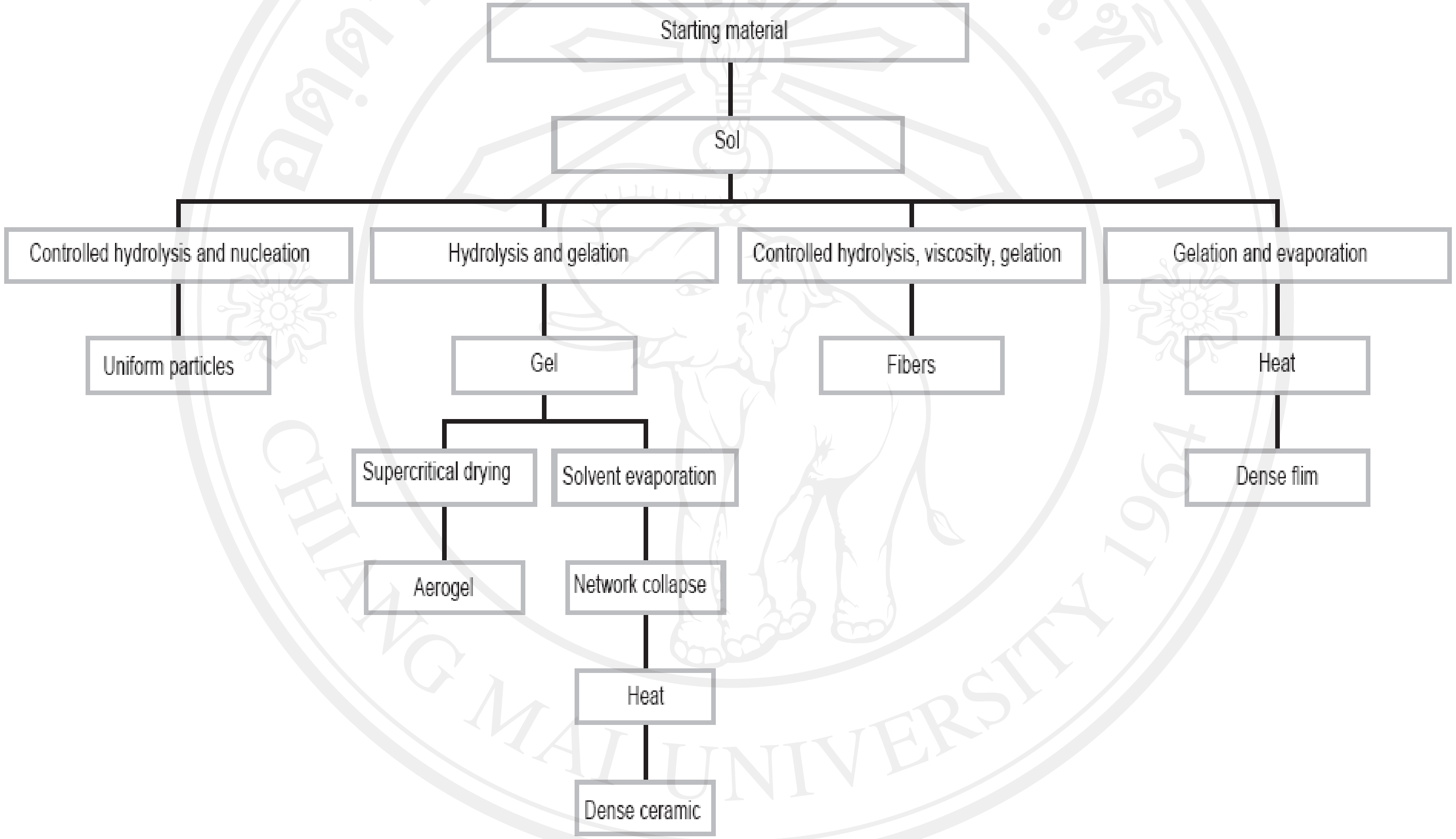

Figure 1.9 Variation of product type under different sol–gel condition.

http://www.chemat.com/chemattechnology/SolGel.aspx (15 November 2010)

- **Low-temperature synthesis.** Due to the homogeneity of the dried powder/gel product and the smaller particle size when compared to grind-and-fire methods, nucleation and growth of crystalline phases can occur at lower temperatures. This also allows the synthesis of metastable phases and the inclusion of organic or other compounds with low thermal stability into the final product. Volatile materials are no longer lost and amorphous phases can be formed. Lower temperatures avoid the effects of particle sintering.
- **Control of ceramic properties through control of parameters**. Variation of the reaction conditions affects product morphologies and bulk properties. Variation of pH, temperature, concentration, and chemical control of the rates of hydrolysis and condensation dramatically affect the final product. The complexity of the reactions involved often precludes a complete mechanistic understanding but the use of computer simulation and mathematical models to predict the behavior of the precursors under different conditions allows an insight into how the reaction might proceed and thus how the nature of the final product can be controlled.

Sol–gel processing holds many of these advantages in common with other so-called ‘‘chimiedouce’’ methods such as hydrothermal synthesis. However, we shall focus on sol–gel processing only in this section. The area of sol–gel processing has been extensively reviewed. A key summary of work until 1990 is the comprehensive book by Brinker and Scherer.1 Since then, more general reviews have appeared, as well as reviews specializingin electroceramics, electrochromic,6 and electrode materials, optical and electro-optical materials,10 anti-reflective coatings,11 and high-T_c superconductors. Reviews have also covered chemical applications in catalysis, includingaerog els16 and mesoporous solids and in membranes for gas separations.

From the synthesis point of view, reviews have addressed the use of heterometallic alkoxides, lanthanide precursors and the issue of homogeneity of the oxide products.

Sol–gel processing can be roughly divided into two areas based on the type of precursor used:the alkoxide route, i.e., the controlled hydrolysis and condensation of a hydrolytically unstable precursor (usually based upon a metal alkoxide species) soluble in non-aqueous solvents; and the colloidal route, the peptidization of a water-soluble precursor (also known as colloidal processing). Hydrolysis of an aqueous metal precursor occurs on changing the pH of the precursor solution. These types are usually discussed separately.

Sol-gel processing is widely use in coating process to prepare thin films products. Because of there are many advantages of this. For example:

- The chemical reactants for sol-gel process can be conveniently purified by distillation and crystallization.
- All Starting materials are mixed at the molecular level in the solution so that a higher degree of homogeneity of films can be expected.
- The trace elements in the form of organometallic compound or soluble organic or inorganic salts can be added to adjust the micro-structure or to improve the structural, optical and electrical properties of oxide films.
- The viscosity, surface tension and concentration of polymeric solution can be easily adjusted.
- Large-area films of desired composition and thickness can be easily formed on a complex geometry substrate.
- It facilitates to form films of complex oxides and eases to control of composition and microstructure of the deposited films.

Because of the advantages of sol-gel method. In many studies selected sol-gel method in preparation method. Also with this research, sol-gel method was selected to prepared $Cu_{0.5}Ag_{1.5}$ $InSe_3$; p-type semiconductor use as thermoelectric materials.

1.6 $Cu_{0.5}Ag_{1.5}InSe_3$

The structure of $Cu_{0.5}Ag_{1.5}$ $InSe_3$; CAIS (Figure 1.11) was simulated from face-centered structure of Cu_2GeSe_3 (space group: I42d) using Carine V 3.1 program. Germaniums were replaced by indium positions and some positions of copper atoms were replaced by silver atoms. The radius of composition atoms was showed in Table.1

Table 1.1 The radius of composition atoms of $Cu_{0.5}Ag_{1.5}$ $InSe_3$.

Atom	Atomic radius(A^o)
Cu	1.28
Ag	1.44
In	1.36
Se	1.16

$Cu_{0.5}Ag_{1.5}$ $InSe_3$ is a p-type thermoelectric material that adapted from Ag_2InSe_3 structure (applied Cu_2GeSe_3 structure) from by doping copper atoms in the structure. The result from doping copper atoms make holes in the structure. The structure of $Cu_{0.5}Ag_{1.5}$ $InSe_3$ was showed is in Figure 1.10.

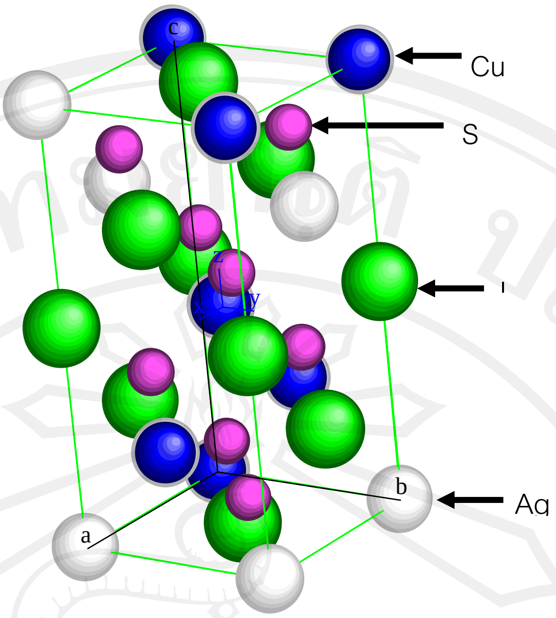

Figure 1.10 The unit cell of $Cu_{0.5}Ag_{1.5}InSe_3$.

1.7. Literature Review

Thermoelectric materials are useful and widely used in recent technology. They have long been recognized that original thermoelectric materials are material-oxide group e.g. Sb_2O_3, $Cd(OH)_2$, CdO, CuO_2, In_2O_3, PbO_2, SnO_2,TiO_2 and ZnO [4], [5], [12], [34]. Titanium dioxide (TiO_2) was usually investigated, since their applications are high value for using in opto-electronic industry [6]. Then, new methods that were used to improve the performance of TiO_2 were interested. There were many studies on the improvement of TiO_2 efficiency. The Cu/TiO_2 is thermoelectric materials that effective elements were added to TiO_2 structure and were reported as the efficiency improved of TiO_2 one [6]. After improving of TiO_2 efficiency was populated. There was the new trial as a tertiary phase thermoelectric semiconductors e.g. $PbTiO_3$ and Cu_2SrO_2 [25]. Moreover, non-oxide thermoelectric materials were investigated, such as CdSe, ZnS, Sb_2S_3, Bi_2Se_3, (Cd,Zn)S, $CuInSe_2$, $CuInS_2$, $CuFeS_2$ and $AgInSe_2$ [6],[12],[26],[27].

In recent years, many reports have concentrated on quaternary phase semiconductor (used as thermoelectric materials). For example, the studies on preparation of $CuIn_xGa_{1-x}Se_2$(CIGS) desirable in photovoltaic materials. The CIGS was developed from $CuInS_2$ because CIGS reduced the band gaps of $CuInS_2$ by incorporation of Gallium (Ga) in this structure. $Cu_{0.5}Ag_{1.5}$ $InSe_3$ (CAIS) is one of the important semiconductors used as thermoelectric materials. Its properties are similar to $CuInSe_2$. Besides, its properties are most likely to CIGS by smaller band gaps than $CuInSe_2$. The silver atoms substitute some position of the copper atoms in CAIS structure, so quaternary phase of materials will present.

It has been reported that $CuInS_2$ and $CuIn_xGa_{1-x}Se_2$(CIGS) can be prepared by sol-gel method[6], electro deposition method[8], solution route method [27], electron beam evaporation[28] and colloidal route method[29] etc. These methods can be used to prepare $CuInS_2$ and CIGS, but the most interesting method is sol-gel. Sol-gel method is simpler than other methods. Its advantages such as low temperature of preparation control of particle size, better product from special properties of gel and special products (films). The major advantages of this process are the low processing temperature and simple preparation for thin films products. Thus, there are many researches that use sol-gel method to prepare semiconductors and new materials, for example, the preparation of TiO_2 [5, 30], $CuInS_2$ thin films [3] and sulfurization precursors deposited of Cu_2ZnSnS_4 [31] etc.

Various methods can be used to prepare thin films e.g. dip-coating, spin coating, meniscus coating and electro-deposition on substrate [3],[8],[32],[33]. The most popular method that has been reported is dip-coating method. By this simple process and equipment, leads to low cost to prepare and it can prepare uniform film thickness. Processing in dip-coating method has six forces to concern, these are list in Table.1. All of forces must take more attentions among investigation [34].

Table 1.2 The determined forces during films deposition.

1. Viscous drag upward on the liquid by moving substrate.
2. Force of gravity.
3. Resultant force of surface tension in the concavely curved meniscus.
4. Inertial force of the boundary liquid layer arriving at the deposition region.
5. Surface tension gradient.
6. The disjoining or conjoining pressure (important for film less than 1 μm. thick).

Not only dip-coating is the most common method, but also the easiest way to deposit sol-gel film on a substrate. Comparison of dip-coating method and several coating methods (meniscus coating and spin coating) were summarized. The dip-coating method is the best method because of its good thickness uniformity, excellent scale-up capability and low cost of equipment. The hybridization of the techniques (sol-gel dip-coating method) is still tendency to develop thin films-materials. Recently, there are many reports that present this hybrid technique as common preparation method e.g. nanostructure of TiO_2[34] thin films, ZnO_2 thin films and silver dispersed $PbTiO_3$ thin films [35,36]. In this research, preparation of $Cu_{0.5}Ag_{1.5}InSe_3$, thermoelectric material, will be reported for the first time by using sol-gel dip-coating method. In addition, this thermoelectric material will also successful in its thermoelectric properties.

1.8 Research objectives

The research objective was studied on preparation thin film and powder of $Cu_{0.5}Ag_{1.5}InSe_3$(CAIS) by sol-gel method. By concentrated on the temperature effect, pH effect, annealing atmosphere effect, mole ratio of metal precursor: solvent: stabilizer: water, drying time and annealing time.

In additions, this research studied on physical properties and thermoelectric properties by various techniques.

- The X-ray diffraction technique use for confirmation of CAIS structure.
- Scanning electron microscopy technique use for analyzes size, morphology of CAIS powder and thickness of CAIS thin films.
- Energy dispersive x-ray spectroscopy technique use for analyzes percent of elements in CAIS.
- Transmission electron microscopy technique use for analyzes particles size, morphology of CAIS powder.
- Four Point Probe technique use for analyzes electrical conductivity of CAIS.
- Seebeck analyzer use for analyzes Seebeck coefficient of CAIS.