Preparation of Cu_3SbSe_4 Doping with Aluminum and Studying on its Thermoelectrical Properties

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Abstract

The electrical transport and thermoelectric properties of **$Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 &0.07)** compounds are investigated in the temperature range of **(298 – 553) K**. The results indicate that with increasing Al content from **(x=0)** to **(x=0.07),** hole concentration increases monotonically from (**2.03×10^{18} to 2.82×10^{18} cm^{-3})** due to the substitution of **Al^{3+}** for **Sb^{5+}**, thus leading to a large decrease in the electrical resistivity of **$Cu_3Sb_{1-x}Al_xSe_4$**. Meanwhile, the increase in hole concentration leads to a transition from a non-degenerate **(x = 0)** to a partial degenerate **(x = 0.05, 0.07)** and then to a degenerate state **(x=0.07**). The power factor **(PF)** of all the Al-doped **$Cu_3Sb_{1-x}Al_xSe_4$** samples is remarkably improved due to the optimization of hole concentration. Lattice thermal conductivity **k_L** of the heavily doped sample**(x=0.07)** is reduced. As a result, a large thermoelectric figure of merit **ZT = 1.28** is obtained for **$Cu_3Sb_{0.97}Al_{0.03}Se_4$** at **458K**, which is around 5 times as large as that of the un-doped **Cu_3SbSe_4** sample.

Key Words: Electrical properties, thermal conductivity, XRD, RHP.

الخلاصة

في هذا البحث تمت دراسة خصائص الانتقال الكهربائي الحراري والناقلية الكهربائية للمركب $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 and 0.07) ولمدى من درجات الحرارة المطبقة K (553 – 298) وقد اظهرت النتائج ان الزيادة في قيمة (x = 0) to (x =0.07), زيادة في تركيز الفجوات من(2.03×10^{18} الى 2.82×10^{18} cm^{-3}) تبعا لتغير احلال او استبدال Al^{3+} مكان Sb^{5+} والذي سوف يؤدي الى نقصان كبير في قيم المقاومية الكهربائية للمركب $Cu_3Sb_{1-x}Al_xSe_4$ ، وفي نفس الوقت فان الزيادة الحاصلة في تركيز الفجوات سوف تؤدي الى انتقال من حالة الهبوط الحاد عند (x = 0)الى النزول التدريجي او الجزئي عند(x = 0.05, 0.07) وان حالة الاستقرار ستكون عند (x = 0.07) وان عامل القدرة(PF) لكل النماذج المشوبة$Cu_3Sb_{1-x}Al_xSe_4$ ظهر هنالك تحسن فيما يخص تركيز الفجوات .وان العامل k_L , والذي يمثل عامل التوصلية الحرارية للشبيكة يتناقص في حالة الزيادة العالية من التشويب أي عند النموذج (x =0.07)، وكنتيجة نهائية فان المؤشر الكبير لقيمة ZT= 1.28 والتي تم الحصول عليها للمركب ذو الصيغة $Cu_3Sb_{0.97}Al_{0.03}Se_4$ في درجة ,458K كبيرة بقدر خمسة مرات كما لو في النموذج Cu_3SbSe_4والذي يمثل المركب بدون تشويب.

الكلمات المفتاحية: الخصائص الكهربائية ،تحليل حيود الاشعة السينية، التوصيلية الحرارية

1. Introduction

Thermoelectric materials (TE) have a huge attention because of their potential applications as power generators and heat pumps [Poudel, *et al.,* **2008**]. The efficiency of a TE material is generally characterized by the dimensionless figure of merit ZT, defined as:

$$ZT = \frac{(S^2T)}{\rho\,(k_C + k_L)} \quad \ldots\ldots\ldots\ldots \quad (1)$$

Where **ρ, S, k_C , k_L** and **T** are the electrical resistivity, Seebeck coefficient, thermal conductivity from carrier contribution, lattice thermal conductivity and absolute temperature, respectively [Heremans; *et al.,* **2008**] . Copper-based multinary semiconductors have recently received much attention due to their good electronic transport properties and relatively low intrinsic thermal conductivity, which contributes to being good TE materials (e.g. $Cu_{2.10}Cd_{0.90}SnSe_4$, ZT = 0.65 at 700 K, $Cu_2Sn_{0.90}In_{0.10}Se_3$, **ZT= 1.14** at 850 K , $Cu_3Sb_{0.97}Ge_{0.03}Se_{2.8}S_{1.2}$, **ZT = 0.89** at 650 K) [Liu, *et al.* **2009**–10]. The ternary semiconductor of Cu_3SbSe_4, as a narrow bandgap semiconductor (0.13 – 0.42 eV)[Wei, *et al.* **2014**] with a unit cell four times larger than ZnSe (n = 8 for Cu_3SbSe_4 versus n = 2 for ZnSe) [An. *et al* . **2003**] ,with high Seebeck coefficient and low thermal conductivity at room temperature (the Cu/Se atoms form the structural framework and the rest Sb atoms have the rattling behaviors similar to the resonators [Yang *et al.* **2011**]).

However, the un-doped Cu_3SbSe_4 compound has low hole concentration and relatively large electrical resistivity, which leads to low TE performance .The ZT of Cu_3SbSe_4 is too small to be used in practice. Hence, it is a key issue to reduce its electrical resistivity and to optimize its PF defined as:

$$\mathbf{PF} = \frac{S^2}{\rho} \quad \mathbf{\ldots\ldots\ldots(2)}$$

In This work , Al a cheap, environment-friendly and abundant element, is used as the dopant and the inequitable substitution of $\mathbf{Al^{3+}}$ for $\mathbf{Sb^{5+}}$ will introduce hole into the host, giving rise to a large increase in hole concentration in this p-type compound Cu_3SbSe_4 .And the Samples of bulk of Cu_3SbSe_4 and $Cu_3Sb_{0.97}Al_{0.03}Se_4$ were prepared using **Rapid Hot Press (RHP) system**. structural properties of Cu_3SbSe_4 and $Cu_3Sb_{0.97}Al_{0.03}Se_4$has been studied by X-ray diffraction (X.R.D) , DC , Hal effects, Seebeck effects, Power factor, thermal conductivity, ZT , electrical resistivity measurements were carried out .

2. Experimental

2.1. Chemicals:

(EDA) (99.7%), CuCl (97%), $SbCl_3$ (99%), $AlCl_3$ (99%), and selenium powder (99.0%)

2.2. bulk preparation:

For preparation of Cu_3SbSe_4 and $Cu_3Sb_{0.97}Al_{0.03}Se_4$, 2 mmol ($SbCl_3$), 8 mmol Se and 40 mL (EDA) were put into a 100 mL glass beaker. After mixing uniformly, 60 mmol CuCl was then put into the Same beaker .The solution was stirred by a magnetic stirrer at the speed of 1700 r s^{-1}maintaining a temperature at **150 °C** during the synthesis; after about two hours, a large quantity of powders was precipitated . Then the precipitates were collected, filtered and washed with anhydrous ethanol and distilled water until a PH value close to 7 was obtained, and then dried at 60 °C for nearly 6 h. The formed powder was milling by a ceramic mortar, pressed under (9219 Pa /cm^2) as disks of **(3.11) Cm** diameter and 3.5mm thickness .Then $Cu_3Sb_{0.97}Al_{0.03}Se_4$ material

pressed at **(280°C)** for (**30 min**) with rapid hot press system (R.H.P). The technique is demonstrated by consolidating dense Cu_3SbSe_4 based thermoelectric materials at 458 K for 30 min.

3. Results and discussion:

3.1 structural studies:

The XRD patterns of all the samples **$Cu_3Sb_{1-x}Al_xSe_4$** (x = 0, 0.03,0.05 and 0.07) at room temperature are shown in Fig (1). The main diffraction peaks correspond well to the standard JCPDS card (no. 01-085-0003) of **Cu_3SbSe_4**with tetragonal structure. The lattice constant calculated was found to be **(a = 5.655Å)** for **(112)** plane.

Where $$a = d\sqrt{h^2 + k^2 + l^2} \quad \ldots\ldots \quad (3)$$

$$2\,d \sin\theta = n\lambda \quad (4)$$

(Bragg's Law) [Neha, *et al.*, **2004**].

The crystallite sizes of **Cu_3SbSe_4** is estimated by using Scherrer's formula [Neha, *et al.* **2004**, Obida, *et al.*2005]:

$$D = \frac{K\lambda}{(\beta_{2\theta}\cos\theta)} \quad \ldots\ldots\ldots \quad (5)$$

Where : **K = 0.94** and λ is the wavelength of X-ray used which is Cu Kα radiation **(λ = 1.54Å)** and $\beta_{2\theta}$ is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane. The strain (ε) was calculated using the formula [Obida, *et al.*, 2005**]**:

$$\varepsilon = \frac{\beta\cos\theta}{4} \quad \ldots\ldots\ldots\ldots \quad (6)$$

The dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the following [Obida, *et al* . 2005]:

$$\delta = \frac{1}{D^2} \quad \ldots\ldots\ldots\ldots \quad (7)$$

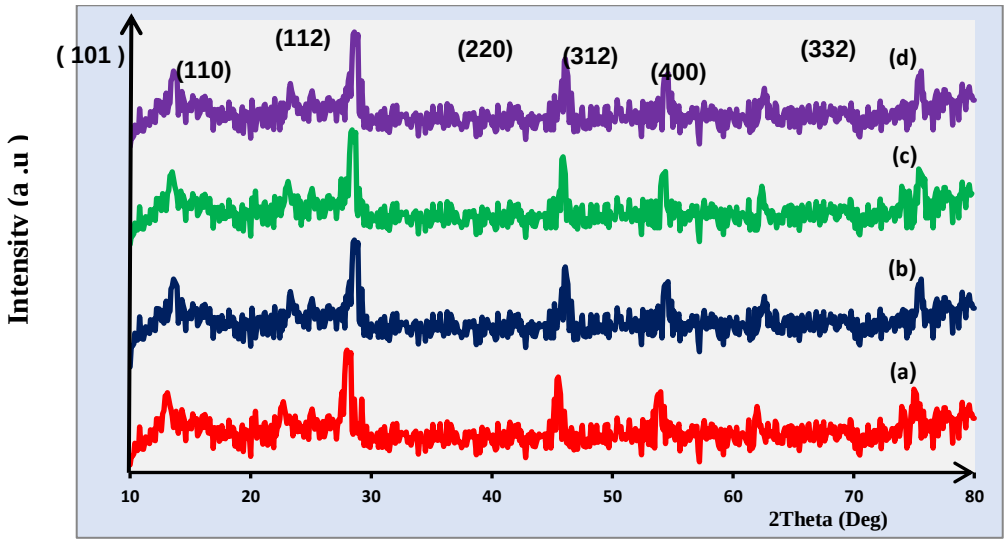

Fig (1): Shows the XRD profile of all the samples $Cu_3Sb_{1-x}Al_xSe_4$ a (x = 0) , b (x =0.03) ,c (x =0.05) and d(x = 0.07) at room temperature.

Indicating that the doped specimens have the same crystallographic structure as that of the **Cu_3SbSe_4** phase and no obvious impurity phase is observed. A reitveld re-finement approach is employed to calculate the lattice parameters from the XRD data.

The result reveals that lattice parameters (a, d) decrease monotonically with increasing Al content, as shown in Table (1), which is due to the substitution of Al^{3+} with smaller ionic radius **(0.39 Å)** for Sb^{5+} possessing larger ionic radius **(0.62 Å) .**

Table (1): Structural parameters of $Cu_3Sb_{1-x}Al_xSe_4$ bulk at room temperature (x = 0, 0.03, 0.05 and 0.07) .

$Cu_3Sb_{1-x}Al_xSe_4$	(hkl)	a(Å)	d (Å)	D (nm)
X = 0	(112)	5.674	2.325	23
X = 0.03	(112)	5.655	2.317	25
X = 0.05	(112)	5.630	2.307	28
X = 0.07	(112)	5.611	2.299	32

Strain (ε x 10^{-4}) ($lines^{-2}$ m^{-4})	Dislocation Density ($\delta x10^{13}$) ($lines/m^2$)
82.5	20
59.9	16
52.2	13
44.8	9

3.4. Electrical Measurements

The thermoelectric properties of **$Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.01, 0.02 and 0.03)** are shown in Fig (2) it is clear that electrical resistivity **ρ** of **Cu_3SbSe_4** decreases with increasing temperature, indicating that the un-doped bulk materials exhibit non-generate semiconductor-like behavior. However, in the case of the **Al** doped compounds, **ρ** are different temperature dependences and have higher resistivity of non doped sample.

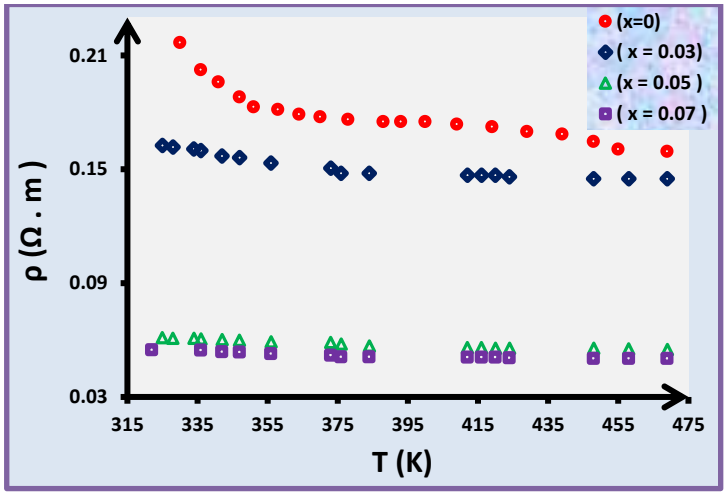

Fig (2) shows the Temperature dependences of electrical resistivity For $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0 , 0.03, 0.05, 0.07).

And when (**x = 0.03**) **ρ** decreases with increasing temperature. With increasing Al content to **(x = 0.05), ρ** almost has in average same value in temperature range (**325 - 373) K** and then decreases with further increasing temperature, reaching (**5.03×10^{-2} Ω m (at 469 K)**). However, **ρ** in the case with **(x = 0.07)** almost remains unchanged in the whole temperature range. In addition, **Al** doping causes the decrease in the magnitude of the electrical resistivity.

4.2.2. Determine the activation energy of $Cu_3Sb_{1-x}Al_xSe_4$:

In order to examine the temperature behavior of the resistivity for **Cu_3SbSe_4,** logarithm of the resistivity **ρ** as a function of reciprocal of temperature is given in the in Fig.(2). It can be seen that good linear relationships between **Ln ρ** and **1/T** exist in the high temperature range for **Cu_3SbSe_4** . The existence of a linear relationship between ln ρ and **1/T** means that the resistivity can be described by using a thermally activated expression in corresponding temperature regimes, written as:

$$\mathbf{Ln\ \rho = C + \frac{E_g}{2K_BT}} \qquad \mathbf{(8)}$$

Where C is an constant and k_B Boltzmann constant (8.62×10^{-5} eV/K)., E_g band gap. By best fitting of the experimental data to formula (8). Table (2) shows the variation of activation energy with quantity doping .We note that the conductivity of the samples increases with increasing of quantity doping.

Table (2): Shows variation activation energy with ratio of doping

Sample	Doping quantity	Ea. (eV)
1	(x = 0)	0.216
2	(x = 0.03)	0.120
3	(x = 0.05)	0.119
4	(x = 0.07)	0.115

Our further measurements (see following text) demonstrate that Seebeck coefficient and Hall coefficient of Cu_3SbSe_4 are positive in the whole temperature investigated, indicating the major carriers are holes. Since the substitution of Al^{3+} for Sb^{5+}occurs, the doping of Al is expected to introduce holes into the host. Therefore, the Al substitution for Sb will give rise to a large increase in hole concentration. The hole concentrations p at room temperature for $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 and 0.07) are calculated according to the measured Hall coefficient and the results are listed in Table 3. One can see that the hole concentration increases from (5.91×10^{17} cm^{-3}) for (x =0) to (2.03×10^{18} cm^{-3}) for (x = 0.03) , (2.5×10^{18} cm^{-3}) for (x = 0.05) and (2.82×10^{19} cm^{-3}) for(x = 0.07) , respectively. Al-doping leads to the increase in hole concentration, which explains the smaller resistivity upon doping.

3.4.3. Hall Effect Measurement:

The variation of Hall voltage V_H with the current for $Cu_3Sb_{1-x}Al_xSe_4$ bulk at room temperature shown in fig (3).

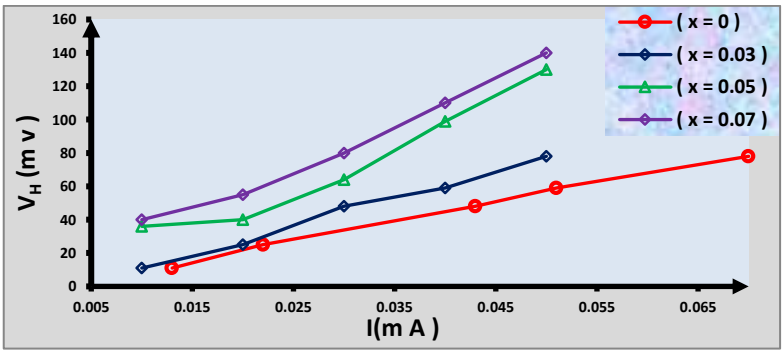

Fig (3) The variation of Hall voltage (V_H) with the current for $Cu_3Sb_{1-x}Al_xSe_4$.

The lattice structure may be un stochiometric , and the interstitials control the conductivity type[Almatooq, **2010**]. So that the prepared $Cu_3Sb_{1-x}Al_xSe_4$ are p-type .According to the relationship [Salem & Hamid , **2001**]:

$$V_H = \frac{R_H I_x B_Y}{d} \quad (9)$$

Due to the vacancies of sulfide ion [Stancu *et al.*, **2008**] that means the conduction is dominated by holes [Ubale *et al* . **2007**].

Table (3) show values of resulting parameters from Hall Effect studies. It was found that the carrieres concentration and Hall mobility increase with increasing of the Doping quantity [Salem & Hamid , **2001**], where carriers concentration P, Resistivity ρ and Hall mobility μ are Calculated According to the relationships [Salem & Hamid , **2001**]:

$$R_H = \frac{3\pi}{8}\frac{1}{ep} \quad \text{.....(10)} \ ,$$

$$\mu = \frac{R_H}{\rho} \quad \text{..... (11)} \ ,$$

$$\frac{1}{\rho} = \frac{a}{R_x bd} \quad \text{..... (12)}$$

Where: a, b, d The dimensions of the **$Cu_3Sb_{1-x}AlxSe_4$** sample, R_H Hall coefficient

Table 3: Values of resulting parameters from Hall Effect studies.

Sample (x)	0	0.03	0.05	0.07
Hall coefficient $R_H \times 10^{-6}$ (m^3/C)	1.05	2.89	1.84	2.08
carrier density $P_H \times 10^{18}$ (Cm^{-3})	0.591	2.032	2.50	2.82
resisitivity ρ $\times 10^{-7}$ (Ω .m)	0.97	0.73	0.55	0.12
Hall mobility μ × 10^{-2} (m^2/V s)	117	157	100	114

All the samples are p-type semiconductors, as verified by the positive Seebeck coefficients and Hall coefficient, which are shown in Fig. (3,4).

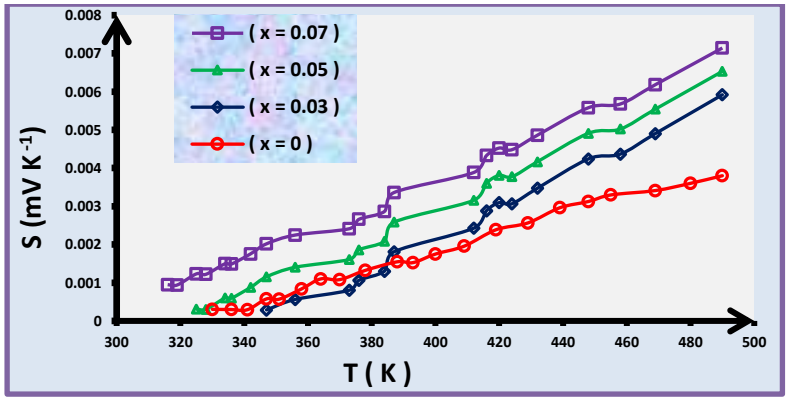

Fig (4) shows the Temperature dependences of Seebeck coefficient For $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0 , 0.03, 0.05, 0.07).

The Seebeck coefficient S for Cu_3SbSe_4 decreases with the increasing temperature. In contrast, S for samples with x =0.03, 0.05 and 0.07 increases much with increasing temperature and increase with X value. This is the typically characteristic of a heavily degenerate semiconductor.

The temperature dependences of power factor of $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 and 0.07) are shown in Fig (5) The values of PF for all the Al-doped compounds are larger than that for the un-doped one. Specially, the PF of sample with x = 0.07 nearly increases linearly with temperature, and it reaches 66×10^{-3} Wm^{-1} K^{-2} at 480 K, which is about 9 as large as that of Cu_3SbSe_4.

The temperature dependences of lattice thermal conductivity k_L for $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 and 0.07) compounds are presented in Fig. (6), respectively .for all the samples, k decreases with increasing temperature in the whole temperature range investigated.

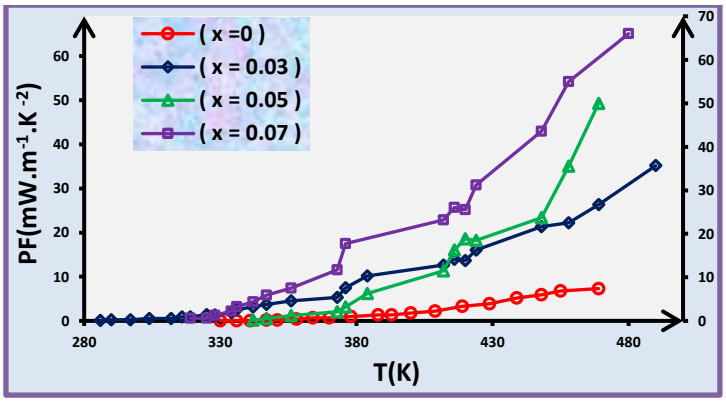

Fig (5) Shows the Temperature dependences of power factor For $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03,0.05 ,0.07) .

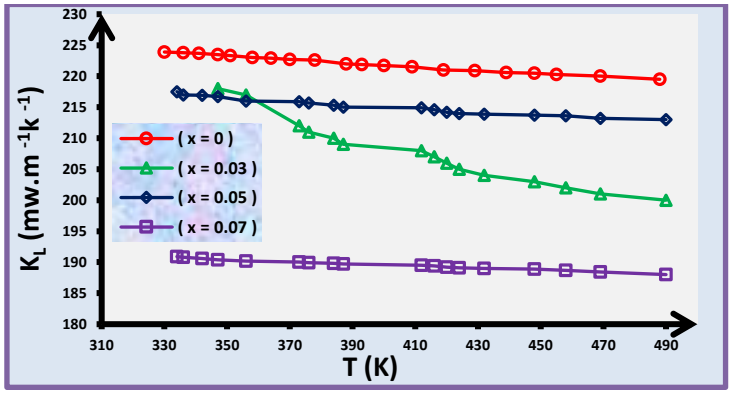

Fig (6) shows the Temperature dependences of the lattice thermal Conductivity k_L for $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 , 0.07) .

In comparison, k_L of the Al-doped samples is slightly lower at room temperature and then becomes higher than that of the undoped Cu_3SbSe_4 with the increasing temperature due to the increased contribution from k_c (Fig 6). Lattice thermal conductivity k_L is estimated by subtracting the carrier thermal conductivity k_c from k:

$K_c = L_0T/\rho$……..(13)
$k_L = k - k_c$ ……(14)
$k = \sigma . S$ ……(15)

Here, L_0 is set to (2×10^{-8} V^2 K^2) [Salem & Hamid , **2001**; Stancu *et al.* **2008**]. As shown in Fig (6), k_L of samples with x = 0.03 and 0.05 is similar to that of the un-doped sample. However, k_L for x = 0.07 is smaller than that of the pure sample especially at high temperatures. Fig (7) shows the temperature dependence of ZT for $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 and 0.07). ZT of the Al-doped compounds $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0.03, 0.05 and 0.07) is larger than that of un-doped Cu_3SbSe4. The maximum ZT reaches 1.28 for $Cu_3Sb_{0.97}Al_{0.03}Se_4$ at 458 K , which is around 5 times as large as that of the un-doped Cu_3SbSe_4 (ZT = 0.84). The elevation of ZT for $Cu_3Sb_{0.97}Al_{0.03}Se_4$ results mainly from both its enhanced PF due to the optimization of hole concentration and reduced $k_{L..}$

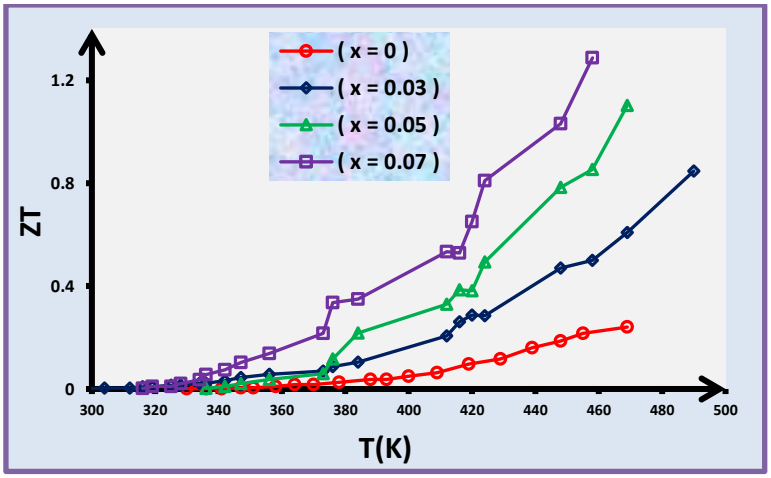

Fig (7) Shows Temperature dependence of ZT for $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05, 0.07).

Conclusions

The effects of Al-doping on the thermoelectric properties of $Cu_3Sb_{1-x}Al_xSe_4$ (x = 0, 0.03, 0.05 and 0.07) compounds obtained by rapid hot press system (R.H.P) investigated in this work. Experiments show that Al-doping leads to large decreases in the electrical resistivity due to great increase in hole concentration. With increasing Al-doping content the samples transform from non-degenerate (x = 0) to partial degenerate (x = 0.03, 0.05) and then to degenerate state (x = 0.07). Hall measurements confirmed *p*-type conduction for $Cu_3Sb_{1-x}Al_xSe_4$.The carrier concentration was estimated to be ($2.82\times10^{18)}$ Cm^{-3} and the mobility is about ($157\times10^{-2)}$ m^2/Vs. PF of all the Al-doped samples is remarkably improved. Moreover, heavy Al-doping (x = 0.07) leads to reduced lattice thermal conductivity .The largest ZT_{max} = 1.28 is achieved at 458 K for $Cu_3Sb_{0.97}Al_{0.03}Se_4$, which is about 5 times larger than that of the un-doped compounds. Our study demonstrates that Al-doping is an effective and environment-friendly way to improve the thermoelectric performance of $Cu_3SbSe_{4.}$

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