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Impurity effects on the lattice thermal Conductivity in the Ternary $CuGe_2P_3$ Semiconductor

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Abstract

The callaway model is used to calculate lattice thermal conductivity for the doped $CuGe_2P_3$ semiconductor between 1 and 300K. Generally, the effects of doping with S, Se, Zn, are increase this phenomena except for that of In-Zn doped which is reduces thermal conductivity from that of the undoped samples. The highest values of K is found for the Zn-doped sample to be 0.57W/cm.K while the lowest is found for In-Zn doped to be 0.15 W/cm.K. The effects of the impurity concentrations N at K_{max} is changes according to $N^{0.622}$ and the K_{max} for all concentrations does not affected by the temperature.

Results are analysed according to; first, the Rayleih scattering process with the longe wave length effect as well as the resonance scattering process and, second is the dependence on the chemical formation of the compound.

Keywards:-Lattice thermal conductivity, Semiconductors, $CuGe_2P_3$, Ternary compounds.

Introduction

The ternary semiconducting compound $CuGe_2P_3$ has increasingly an attracting attention beginning from 1960th of the last century[1]. That's due to the limitation of the research activities on this compound in which it gives a good chance for achieving many important research works regarding the technological as well as academic point of view. The crystal structure for this compound is a zinc-tlend diamond like type with Cu and Ge are randomly distributed on the cation lattice while P is occupy the anion lattice[2]. The study of semiconducting properties for $CuGe_2P_3$ will also provides a foundation for the study of many other compounds from its ternary group I-IV_2V_3 as well as many other similar compounds such as Cu_2GeS_3 and Cu_2GeSe_3[3].

This compound has been first prepared as a polycristalline by Goryunova[4], then as a single crystals it was prepared by using a modification achieved on the Bridgman technique for crystal growth by Omar[5]. In regards of the crystallographical point of view, a high quality thin films have been prepared by using a direct evaporation technique with that of the annealing process[2]. The elastic behaviour[6], the solid solution with other semiconductors[7], its Lattice thermal expansion[6,8,9], the heat capacity and the Deby temperature[10], thermoelectric power[11], the infrared

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reflectivity[12], optical properties[13], electrical and DTA, as well as many other physical properties have been investigated for this compound[14].

In recent years, thermal properties of semiconductors have attracted a lot of attentions[15], this is due to continuos scaling down of the feature sizes in microelectronic device and circuits, which is leads to an increase in power dissipation per unit area of the semiconductor chip. Another resion is the rebirth of the field of thermoelectric materials in such away that, engineer material parameters or material geometry will be quite important for thermal conductivity in a particular direction[15]. A microstructure limit of lattice thermal conductivity limited by umklapp, impurity as well as boundary scattering effects has interested due to the increase in the application in the highly advanced integrated circuits[16]. Thermal management is also important in device design as well as photonic devices such as vertical cavity surface emitting lasers[17].

Electrically active impurity atoms provides an attractive defects in semiconductors, in which can be studied by thermal conductivity measurements[18]. The purity and structure perfection of the host lattice and the ease with which definite amounts of known impurities can be added over a wide range of concentrations.However, many articles have been reported[19,20], describing thermal conductivity measurements and analysis for both elementary and multinary semiconducting compounds and insulators.

In this work, Lattice thermal conductivity for the compound $CuGe_2P_3$ will be calculated by using the Callaway formula and the results will be analyzed in regards of the temperature and the doping effects.

Methods of calculation

The Calaway model was used to calculate the Lattice thermal conductivity for several doped semiconducting compound samples of $CuGe_2P_3$. This model is suitable to calculate this phenomenon for this type of compounds at temperatures from very low up to near their Deby temperature θ_D[21]. The mathematical model which has been proved by Callaway is;

$$K=\frac{k_B}{2\pi^2\upsilon}\left(\frac{k_BT}{\hbar}\right)^3\int_0^{\theta_D/T}\frac{\tau_c\cdot x^4\cdot e^x}{(e^x-1)^2}dx \quad -(1)$$

where $x=\frac{\hbar w}{k_BT}$, is the reduced phonon energy parameter, $\hbar$ is the Dirac constant, w is the phonon frequency, k_B is the Boltzmann constant and T is the interested absolute temperature. v is the speed of sound and can be calculated from the following relation[22];

$$v=\frac{k_B\theta_D}{\hbar}\left(\frac{V}{6\pi^2}\right)^{\frac{1}{3}} \quad ----(2)$$

hence, θ_D is the Deby temperature and it is equal to 429K for $CuGe_2P_3$[6], V is the average atomic unit volume. The unit-cell lattice parameter for this compound is 5.3678A° in which give V to be equal to 1.933×10^{-29} m^3. Equation 2 will give the value of v to be equal to 816455(cm/s). The phonon scattering τ_c, which is the most important parameter in this work, will be given by the relation;

$$\tau_c^{-1}= Aw^4 + (B_u+B_N)w^2T^3+ v/L \quad ----(3)$$

The parameters in this equation are represents the contributions to the scattering rate from the point imperfection (Aw^4), Umclapp and Normal process as well as the boundaries respectively. The parameter A is the sum for the isotope

(A_{iso}) and the imperfection (A_{imp}) scattering processes. For the compound $CuGe_2P_3$ the former will be given by[23]:

$$A_{iso} = \frac{V}{4\pi v^3}\left[\left(\frac{\bar{M}_{cu}}{\bar{M}}\right)^2\Gamma(Cu)+\left(\frac{2\bar{M}_{Ge}}{\bar{M}}\right)^2\Gamma(Ge)+\left(\frac{3\bar{M}_{p}}{\bar{M}}\right)^2\Gamma(P)\right] \quad \text{---- (4)}$$

$$\Gamma(cu)=\sum_i f_i \frac{(M_i-\bar{M}_{cu})}{\bar{M}_{cu}} \quad \text{----(5)}$$

$$\bar{M}_{cu}=\sum_i f_i M_i, \bar{M}_{Ge}=\sum_j f_j M_j \quad \text{and}$$

$$\bar{M}_p=\sum_k f_k M_k \quad \text{---- (6)}$$

$$\bar{M}=\bar{M}_{cu}+2\bar{M}_{Ge}+3\bar{M}_p \quad \text{---- (7)}$$

and if f_k is the fractional concentration of the i^{th} isotope of mass M[24], then calculations through equ.(4) will give A_{iso} to be equal to 4.96×10^{-42} sec^3. The parameter A_{imp} can be calculated by the relation[25]:

$$A_{imp}=\frac{3V^2s^2}{\pi v^3}N_{imp} \quad \text{---- (8)}$$

where s is the scattering factor which is usually has the value near unity and hence s=1[23], N_{imp} is the concentration of imperfections and it is regarded as the carrier concentration of the sample which is taken from reference[2], values of v and V as indicated earlier are used, then values of A_{imp} will be calculated for all investigated samples in this work. The total scattering is

$$A = A_{iso} + A_{imp} \quad \text{---- (9)}$$

However, calculated values for A have been always comparable with that found by the experimental method with the exceptions for that concerning the uncertainties in the values of s and v[26].

The parameter B which is the sum of B_v and B_n is given by:

$$B_u+B_n=\frac{\gamma^2 k_B^5}{4(0.318)^2\hbar^2 v^5 MV} \quad \text{----(10)}$$

hence γ is the Gruneisen parameter and is equal to 1.2 for the compound $CuGe_2P_3$[27] then, with the values calculated above, this parameter will be equal to 1.15×10^{-22} sec deg^{-3}. In the third part of equation 3, L is the characteristic length for the investigated samples, which is calculated by the Casmir's formula[28] as; $L=1.12\,(L_1L_2)^{1/2}$ when L_1L_2 regards the sample cross section.

To make this effect unchanged for different doping samples, which are interested in this work, a fixed value for L as 0.137 cm is used for calculations. Figure(1) shows the calculated lattice thermal conductivity versus temperature for five different doped samples of $CuGe_2P_3$.

Discussion

In the limit of long wave length, the scattering by a point defect can be described as an elastic scattering of the plane wave $(w, \vec{q}_1)$ in to another plane

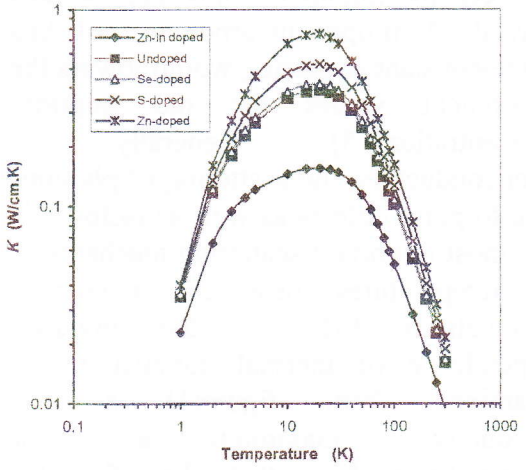

Fig.(1): Variation of lattice thermal conductivity as a function of temperature.

wave (w, $\vec{q}_2$)with a phonon relaxation rate proportional to w^4 as indicated in Eq.(3). If mass defect scattering alone or the isotope effect is considered, the perturbation is simply will be given by the kinetic energy of the excess mass, this process is called the Rayleigh scattering strength[18]. This is ideally the only effect for the point defects on thermal conductivity at the temperature range 10-40K, were it will be in the form of the resonance scattering of phonons. For temperatures below that, the Rayleigh scattering will only be caused by the mass difference which, could be controlled by impurities[29]. Hence, because the long wave length phonons are very weakly scattered by impurities, the conductivity will become infinite, and therefore the integral in which it expresses the heat flows diverges at k=0 limit (k is the wave vector of scattered phonons)[30]. The change in A in Eq.(3) is also will be due to the effects of the mass difference between the impurity atoms and that of the host ones. However, in reality, Rayleigh scattering could also be arise due to the change in the force constant between the impurity atoms and the host crystal. A proper incorporation of this force-constant scattering would lowers the theoretical values for the impurity concentration[18]. Generally in semiconductors, the scattering of phonons due to point defects as well as isotopes is the most important scattering mechanisms at temperatures near the maximum conductivity [31]. If the impurity dependence of thermal conductivity is examined from figure(1) at the conductivity maximum and for temperatures above that, then figure(2) will be obtained. This gives K to be changes according to N^{-x}, where N is the impurity concentration and X is the impurity strength parameter which is for the conductivity maximum equal to 0.622. However this value for X are represents the limitation of a strong scattering process. Others found this dependence to be as $N^{-0.75}$[32] and $N^{-0.55}$[33] for a wide range of concentrations which they have been carried out under a strong impurity scattering conditions. It is clear that for temperatures lower than 50K, a weak impurity scattering condition will be controlling the process as discussed in the first paragraph.

For temperatures above K_{max}, the resonant scattering will has a pronounced effect of thermal conductivity[34]. As the temperature is raised the proportional of phonons with energy is exceeding the threshold increase and they participate in the resonant scattering. However, the periodic lattice distortion is due to the crystal field modulations by phonons, which in turn causes transitions among different spin sub-levels[34]. There fore the thermal conductivities at temperatures above T(K_{max}) will be

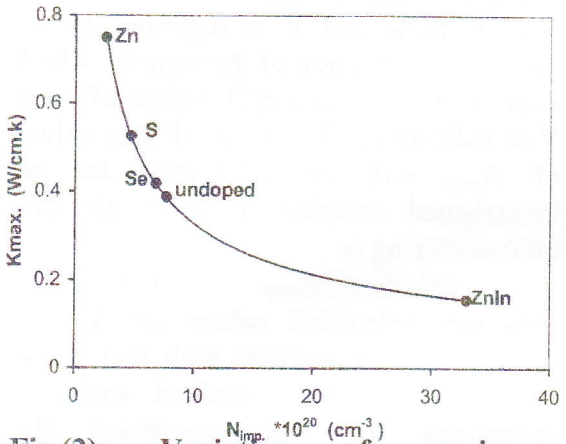

Fig.(2): Variation of maximum conductivity as a function of impurity concentration.

reduced with increasing temperature, and that's in contrast to ordinary impurity scatters which is roughly temperature independent. Hence from figure(1) and for this range of temperature the higher the concentration is, the lower the slop will be for thermal conductivity. This can be represented by the scattering strength parameter X as a temperature dependent shown in figure(3) which is changes according to the relation:-

$$X = -0.0906\text{Ln}(T)+0.8707$$

In regard of the dependence of the impurity type and its concentration for thermal conductivity the conclusions below may be helpful;

A second phase of the binary CuP_2 has been reported in the as grown samples of $CuGe_2P_3$ semiconductor[2]. This will creates a case of a high impurity concentration which is consequently causes to reduce the lattice thermal conductivity compared to that, if there are intrinsic samples[23]. The as grown samples of $CuGe_2P_3$ doped with Zn, will give this element to have the probability of taking the positions of the cation sites which is formerly occupied by Cu and Ge[2].

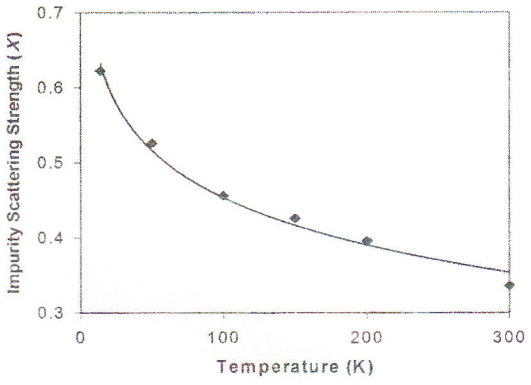

Fig.(3): Temperature dependence of the scattering strength X for $CuGe_2P_3$.

If there are some extra P atoms during the growth, which is always the case for the high volatile materials, then the probability of having a short range solid solutions in the form of $CuZnGe_3P_5$ will be possible and that consequently effects to create a certain degree of an ordered lattice structure. However, the latter will reduces the degree of the amount of the CuP_2 phases as well as the extra P atoms in the sample[5]. These three phenomenous will reduce the impurity and that consequently with the effects of Lattice ordering are reduces the phonon scattering. The effects of impurity on the lattice thermal conductivity at K_{max} is shown in figure(2) and it is found to be changes according to the relation.

$$K_{max} = 1.3702N_{imp}^{-0.622}$$

When In atoms are used in doping during the growth, an extra second phase of InP will be formed. However, possibilities of a solid solution between $CuGe_2P_3$ and InP has not been found[2]. Atoms of Zn, Cu as well as the binary InP are possible to be found in between the $CuGe_2P_3$ crystal lattices and these consequently increases the impurity concentrations. The latter will produce a higher lattice scattering process which means a lower thermal conductivity. Solid solutions between $CuGe_2P_3$ and that of Cu_2GeSe_3 and Cu_2GeS_3 have been reported in the form of superlattice structures, in which they have a partial solid solutions for the first and a complete one for the second[35,36]. Both results will effect to reduce the concentrations of impurities, this is due to the breaking of the Cu-P bonding which is consequently release the atomic bonds to form an ordered structure for the composition in the range $CuGe_2P_3$-Cu_2GeS_3[6]. The latter will reduce the phonon scattering due to

the reduce of both the impurities as well as lattice imperfections and that consequently increases the Lattice thermal conductivity for both types of the doping. But, the possibilities of forming $CuGe_2P_3$ with a more ordered lattice with the excess of S is a more probable than that of Se[7]. Then a higher impurity concentration for Se is a more probable which consequently gives a higher phonon scattering. The larger size for Se atoms will also give a higher lattice scattering, which is with the former effects are both produces a less thermal conductivity for Se doped samples compared to that of the S doped.

Conclusions

From the theoretical calculations of the lattice thermal conductivity for $CuGe_2P_3$ semiconductor, the following conclusions have indicated;

Callaway's formulation, which is based on both of the Deby'es approximation of the phonon spectrum and the use of the relaxation time for phono-phonon scattering which is valid for longitudinal phonons will give a good thermal conductivity curves for the temperature range 1-300K.

The effects of impurity scattering on the maximum lattice thermal conductivity are decreases with increasing its concentrations according to the relation.

$$K_{max} = 1.3702N_{imp}^{-0.622}$$

The conductivity maximum temperature does not affects by the doping elements as well as their concentrations. At the region of the K_{max}, the Rayleih scattering mechanism is controlling the conductivity by the process of the long wavelength scattering below the K_{max} temperature while above that by the resonance scattering.

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هۆکاری خلتی لەسەر گەیەنەری تۆری گەرمی لە نیمچە گەیەنەری سیانی $CuGe_2P_3$

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پوختە

مۆدیلی کالاوی بەکارهات بۆ لێکدانەوەی گەیەنەری تۆری گەرمی لە پلەی گەرمی نێوان K(1-300). هۆکاری پیس کردن بە Zn, Se, S ئەم تایبەتیە زۆر دەکات بێجگە لە پیس کردن بە In-Zn کە گەیەنەری گەرمیەکە کەم دەکات بەرامبەر بە نموونە پیس نەکراوەکان. بەرزترین بڕی K دۆزرایەوە بۆ نموونەی پیس کراو بە Zn کە دەکاتە 0.57 W/cm.K بەلام نزمترین بڕ دۆزرایەوە بۆ نموونەی پیس کراو بە In-Zn کە دەکاتە 0.15 W/cm.K . هۆکاری چڕی پیسی N لە K_{max} دەگۆڕێ بە پێی $N^{-0.622}$ بەلام K_{max} بۆ هەموو چڕیەکان ناگۆڕێت بە هۆکاری پلەی گەرمی.

تأثير الشوائب على التوصيلية الحرارية الشبيكية في الشبه الموصل الثلاثي $CuGe_2P_3$

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الخلاصة

تم استخدام نموذج كالاوي في حساب التوصيلية الحرارية الشبيكية للشبه الموصل الثلاثي المشوب $CuGe_2P_3$ في مدى درجات الحرارة K(1-300) . بشكل عام، تأثير التشويب بـ Zn, Se, S تزيد من هذه الخاصية ما عدا التشويب بـ In-Zn والتي تقلل التوصيلية الحرارية بالمقارنة مع النماذج الغير المشوبة. تم ايجاد اكبر قيمة لـ K للنماذج المشوبه بـ Zn و بقيمة 0.57 W/cm.K بينما أقل قيمة هي للنموذج المشوب بـ In-Zn والتي هي 0.15 W/cm.K . تأثير تركيز الشوائب N عند K_{max} تتغير حسب $N^{-0.622}$ وان K_{max} لنماذج ذات تراكيز محتلفة تكون غير متأثرة بدرجات الحرارة.

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