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Thermoelectric Figure of Merit in Degenerate Cu_7Se_4 and Non Degenerate InSe Thin Films

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***Abstract*— The thermoelectric figure of merit in reactive evaporated thin films of degenerate Cu_7Se_4 and non degenerate InSe are evaluated in view of their use in thermoelectric devices. The power factor exhibited by the films was comparable to those reported for certain potential thermoelectric materials. Also the films exhibited a figure of merit close to unity which is suitable for use in thermoelectric devices. This suggests the potential of the as prepared Cu_7Se_4 and InSe thin films for thermoelectric applications.**

***Keywords*— Cu_7Se_4, InSe, thin films, reactive evaporation, thermoelectric figure of merit.**

I. INTRODUCTION

Thermoelectric represents a novel method of power generation and refrigeration for specific applications and it has now emerged into an active area of research in science and technology. Subsequently, the development of thermoelectric materials that can assure high performance for power generation and refrigeration has become the current scientific and technical issue.

Thermoelectric materials are capable of converting waste heat into useful electricity and also serve as heat pumps to provide local cooling. The efficiency of a thermoelectric material is denoted by a dimensionless quantity called figure of merit (ZT) and it is given by Eq. (1)

$$ZT = \frac{S^2 \sigma T}{k} \tag{1}$$

where S is the seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and k is the thermal conductivity [1]. The term $S^2\sigma$ is referred to as the power factor and it is proportional to the maximum power [2]. Therefore, in order to enhance ZT, the power factor has to be maximized and k must be minimized. The power factor can be optimized as a function of the carrier concentration. However, the interdependence of S, σ and k makes it difficult to achieve high ZT values and is a challenging task for researchers.

Today, several materials such as skutterudites, clathrates, cobalties, manganites and titanates are being used as efficient thermoelectric materials. Among them, semiconducting compounds based on chalcogens (especially sulphides, selenides and tellurides) are extensively being investigated for thermoelectric applications owing to their favourable thermoelectric properties that can be tuned in a desired manner to meet specific need in thermoelectric devices.

Among the chalcogens, tellurium based compounds such Bi_2Te_3 [3], PbTe [4] and Sb_2Te_3 [5] are already commercialized for thermoelectric applications while thermoelectric devices based on sulphides and selenides is still a subject of ongoing research. However, due to the scarcity and toxicity of tellurium, much research is diverted in search for thermoelectric materials based on sulphides and selenides which are more abundant and less toxic than tellurium.

Hence the present work, evaluates the thermoelectric power factor and figure of merit in compound semiconducting thin films based on selenides, namely; Cu_7Se_4 and InSe. The as prepared Cu_7Se_4 is a p-type degenerate semiconductor and InSe is a p-type non degenerate semiconductor.

II. EXPERIMENTAL DETAILS

Cu_7Se_4 and InSe thin films were prepared by reactive evaporation, a variant of Gunther's three temperature method [6]. The experimental details, optimized deposition conditions, structural analysis using X-ray diffraction (XRD) and compositional analysis using energy dispersive analysis of X-rays (EDAX) of Cu_7Se_4 and InSe thin films has been described in reference [7] and [8] respectively.

The electrical conductivity of the film was measured at a constant voltage in the temperature range 300–425K by DC four probe method. The details of thermal conductivity and thermoelectric power measurement setup in the temperature range 300–425K are given in the reference [9]. The measurement of electrical conductivity and thermoelectric power was also carried out at low temperatures in the range 4-300K using liquid helium as the coolant. The details of the experimental setup and procedure are given in the reference [10]. The thermal conductivity of the film in the temperature range 4-300 K is measured using the experimental setup described in the reference [11]. Silver paste was applied at the ends of the film for ohmic contact.

III. RESULTS AND DISCUSSION

A. Determination of power factor in the temperature range 300-425K

Being a degenerate semiconductor, Cu_7Se_4 possess a very high carrier concentration ≈ $8 \times 10^{21} cm^{-3}$ [7]. Due to the degenerate nature, the seebeck coefficient (S) observed in Cu_7Se_4 was very low ≈ $6 \mu V K^{-1}$ at 300K, just like that of metals [7]. However the electrical conductivity (σ) exhibited by the film was high ≈ $10^3 Scm^{-1}$ which is well within the optimum range of materials for thermoelectric applications [12]. The variation of S and σ with temperature of Cu_7Se_4 thin film is depicted in Fig. 1 and Fig. 2 respectively. The increase in S with temperature validates the degenerate semiconducting nature of the as prepared Cu_7Se_4 thin film.

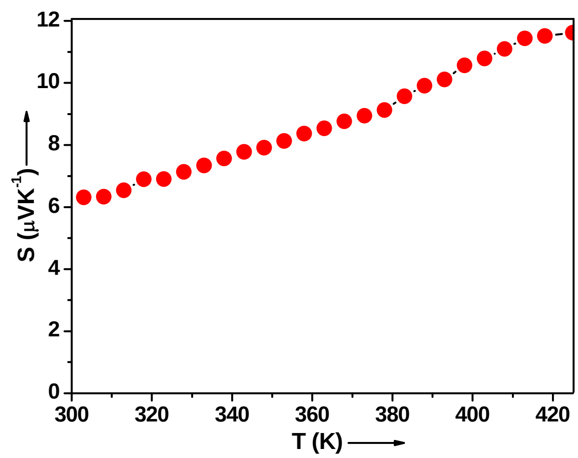

Fig. 1 Variation of S with temperature of Cu_7Se_4 film

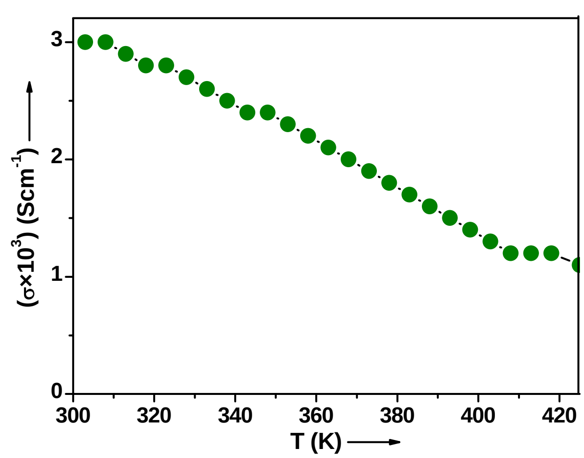

Fig. 2 Variation of σ with temperature of Cu_7Se_4 film

The variation of power factor ($S^2\sigma$) with temperature is shown in Fig. 3.

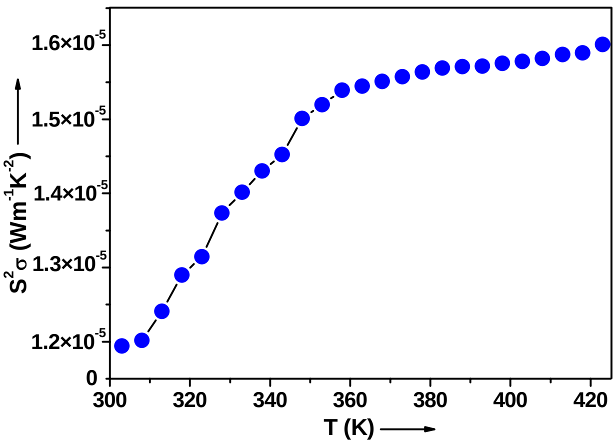

Fig. 3 Variation of $S^2\sigma$ with temperature of Cu_7Se_4 film

As observed from Fig. 3, the power factor of the film was ≈ $10^{-5}Wm^{-1}K^{-2}$ with a room temperature value ≈ $1.2x10^{-5}Wm^{-1}K^{-2}$. This is rather low compared to the useful range (≈ 10^{-3}–$10^{-5}Wm^{-1}K^{-2}$) for applications in thermoelectric devices. But the observed values are close to those reported for certain potential thermoelectric materials such as Bi_2Te_3 based composite thin films (≈ $3.2x10^{-5}Wm^{-1}K^{-2}$) [13], Bi_2Se_3 nanostructures (≈ $2.8x10^{-5}Wm^{-1}K^{-2}$) [14] and $CuAl_{1-x}Ca_xO_2$ (≈ $7.8x10^{-5}Wm^{-1}K^{-2}$) [15] that are recently being developed. Since Cu_7Se_4 possess high σ suitable for thermoelectric devices, an increase in S will enhance $S^2\sigma$. This suggests the potential of Cu_7Se_4 and hence that of degenerate semiconductors for thermoelectric applications, on further work.

On the other hand, the as deposited InSe thin film was found to possess a carrier concentration ≈ $9.8\times 10^{16}cm^{-3}$ [8] which is very much less than the calculated value of density of states ≈ $5.7\times10^{17}cm^{-3}$, suggesting the non degenerate nature of the film.

Being a non degenerate semiconductor, InSe exhibits a high value of S ≈ $198\mu VK^{-1}$ at 300K, which is well within the optimum range of materials for thermoelectric applications [12]. However σ of the film was low ≈ $0.21Scm^{-1}$ at 300K because of its non degenerate semiconducting nature. The variation of S and σ with temperature of InSe thin film is depicted in Fig. 4 and Fig. 5 respectively. As observed from Fig. 4, the decrease in seebeck coefficient with temperature confirms the non degenerate semiconducting nature of the as prepared InSe thin film.

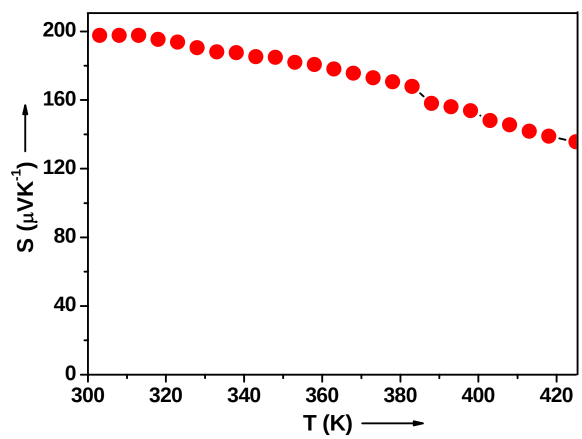

Fig. 4 Variation of S with temperature of InSe film

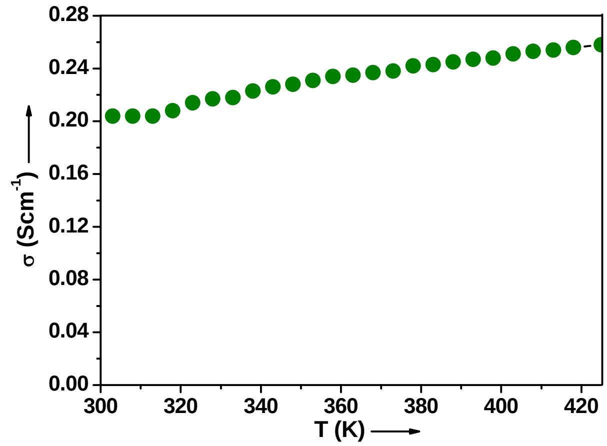

Fig. 5 Variation of σ with temperature of InSe film

The variation of $S^2\sigma$ with temperature is shown in Fig. 6.

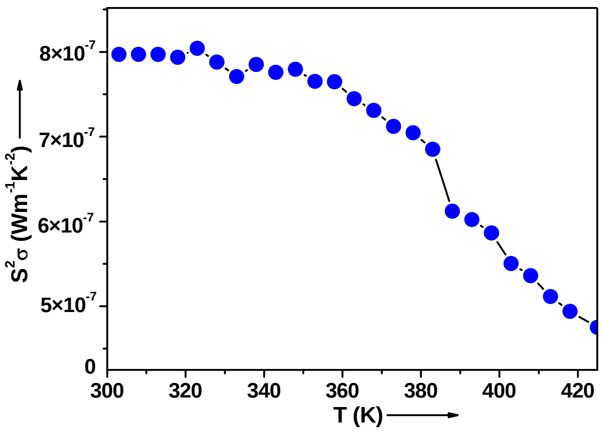

Fig. 6 Variation of $S^2\sigma$ with temperature of InSe film

The $S^2\sigma$ of the film was low and was of the order of $10^{-7}Wm^{-1}K^{-2}$, but comparable to certain materials such as rutile TiO_2 [16], organic conducting polymers [17] and perovskite–type Co doped $BaSnO_3$ [18] that are currently being investigated for their thermoelectric properties. The reasonably high value of S observed in InSe shows its potential for use in thermoelectric devices on further enhancement of σ and hence $S^2\sigma$, as a function of carrier concentration through doping and nano structuring [19].

B. Determination of power factor in the temperature range 4-300K

The variation of S with temperature of Cu_7Se_4 in the temperature range 4-300K has been described elsewhere [7]. The variation of σ and $S^2\sigma$ of Cu_7Se_4 thin film in the temperature range 4-300K is shown in Fig. 7 and Fig. 8 respectively. The value of σ was high ≈ 10^3Scm^{-1}, due to the degenerate nature.

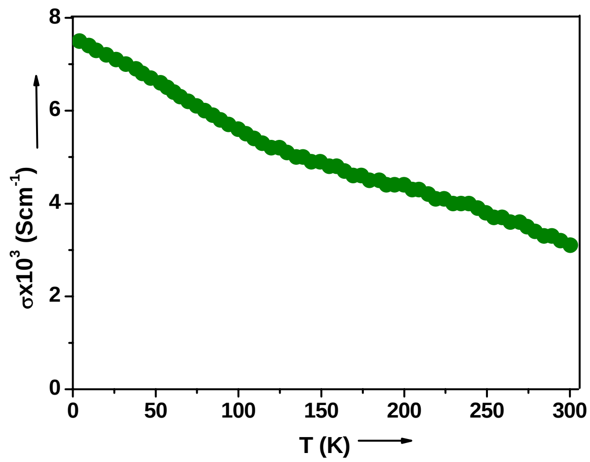

Fig. 7 Variation of σ with temperature of Cu_7Se_4 film

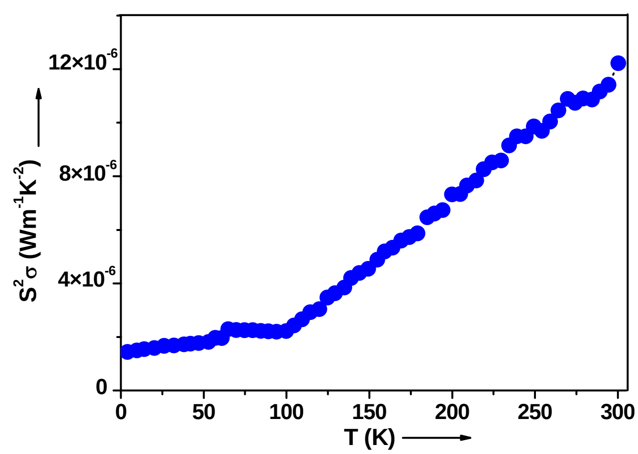

Fig. 8 Variation of $S^2\sigma$ with temperature of Cu_7Se_4 film

As seen from Fig. 8, the power factor of the film was in the range 10^{-5}-$10^{-6}Wm^{-1}K^{-2}$, which agree to those reported for good thermoelectric materials such as ZnO [20], TiO_2 ceramics [21] and La doped $BaSnO_3$ [22]. This indicates the possible use of Cu_7Se_4 thin films also for low temperature thermoelectric applications on further enhancement of power factor.

On the other hand, InSe thin films exhibited high value of S ≈ 2626μVK^{-1} at 38K, typical values of efficient materials used for thermoelectric applications [8]. The variation of S in temperature range 4-300K has been described elsewhere [8]. The variation of σ and $S^2\sigma$ of InSe thin film is shown in Fig. 9 and Fig. 10 respectively.

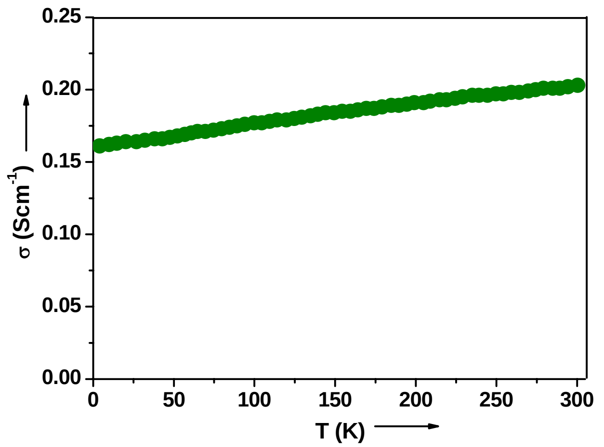

Fig. 9 Variation of σ with temperature of InSe film

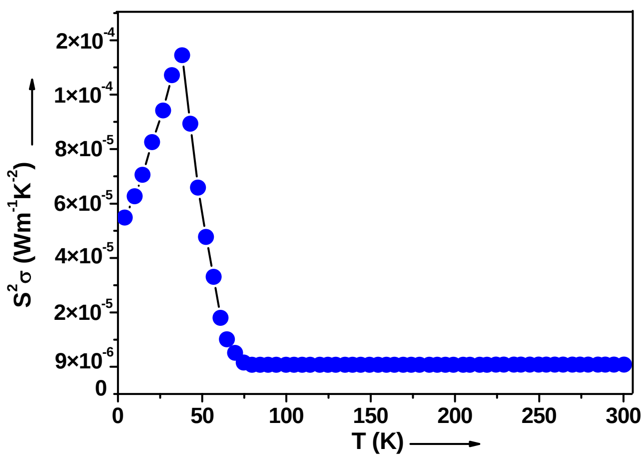

Fig. 10 Variation of $S^2\sigma$ with temperature of InSe film

As observed from Fig 10, the value of $S^2\sigma$ varies from 10^{-4} to 10^{-7} $Wm^{-1}K^{-2}$ with a maximum ≈ 1.1x$10^{-4}$$Wm^{-1}K^{-2}$ at 38K, approaching the optimum range ($10^{-3}$$Wm^{-1}K^{-2}$) for applications in thermoelectric devices [23]. A similar power factor has been reported for $Ca_{3-x}Cu_xCo_4O_9$ ceramics [24], Li and Na doped NiO compacts [25] and Bi substituted $Ca_3Co_4O_9$ ceramics [26]. This confirms the promising property of InSe for low temperature thermoelectric devices.

C. Determination of thermal conductivity and figure of merit in the temperature range 4-425K

The thermal conductivity (k) of the as prepared Cu_7Se_4 and InSe thin films is measured and is shown in Fig. 11 and Fig. 12 respectively.

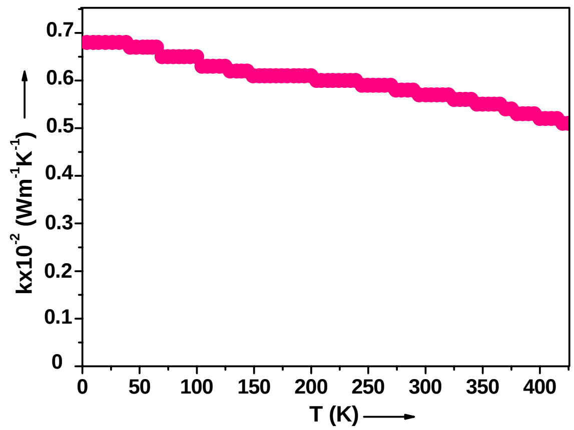

Fig. 11 Variation of k with temperature of Cu_7Se_4 film

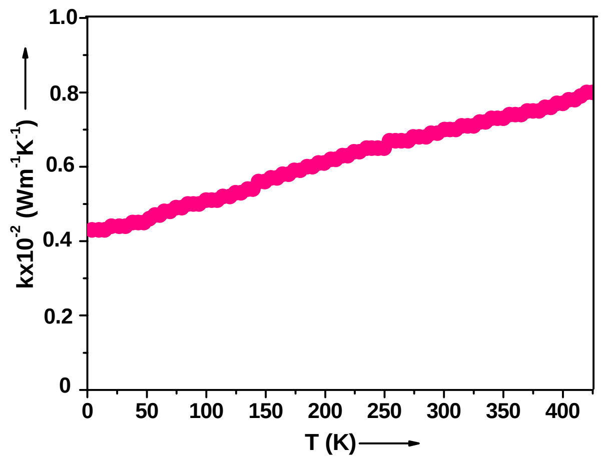

Fig. 12 Variation of k with temperature of InSe film

The thermal conductivity of Cu_7Se_4 was found to vary from 0.0068 to 0.0051$Wm^{-1}K^{-1}$ and that of InSe was found to vary from 0.0043 to 0.008$Wm^{-1}K^{-1}$. These values of k are reasonably good enough to yield high figure of merit (ZT) or efficiency for thermoelectric applications. The ZT observed in Cu_7Se_4 and InSe thin films are depicted in Fig. 13 and Fig. 14 respectively.

In the temperature range 4-425K, the ZT of Cu_7Se_4 varied from 0.008 to 1.3 with a maximum ZT ≈ 1.3 at 425 K. The ZT values of InSe varied from 0.02 to 0.97 with a maximum ZT ≈ 0.97 at 38K.

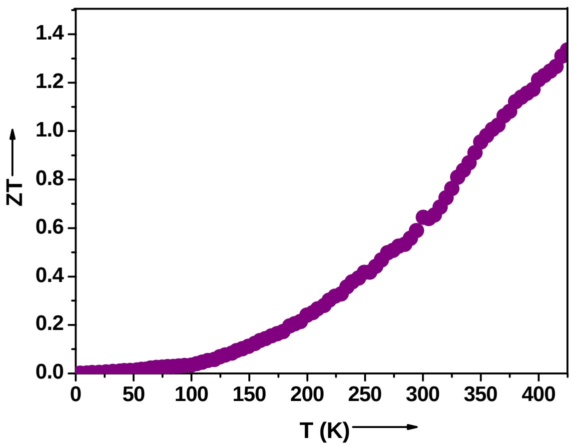

Fig. 13 Variation of ZT with temperature of Cu_7Se_4 film

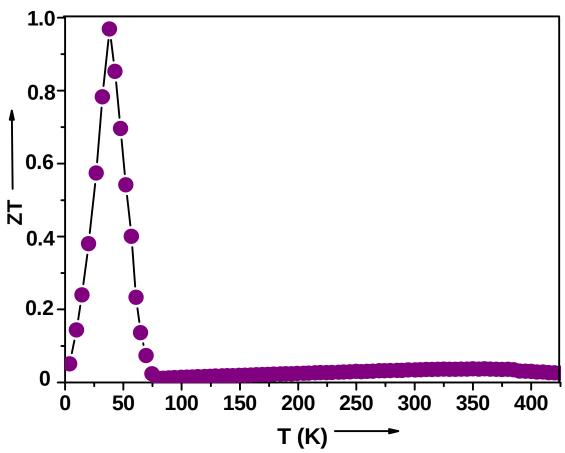

Fig. 14 Variation of ZT with temperature of InSe film

The observed values of ZT are higher than those reported for certain emerging potential thermoelectric materials such as Bi_2Se_3 [14]. Materials with ZT ≥ 1 are found to be efficient candidates for use in thermoelectric devices [12]. Hence the as prepared Cu_7Se_4 thin film with ZT ≈ 1 at 425K can be considered as a potential candidate for high temperature thermoelectric applications whereas InSe thin film with ZT ≈ 0.97 at 38K can be regarded as a promising material for cryogenic thermoelectric applications.

IV. CONCLUSIONS

Thin films of Cu_7Se_4 and InSe were prepared by reactive evaporation and their figure of merit is evaluated in view of their use in thermoelectric devices. The degenerate Cu_7Se_4 thin films exhibit high value of σ ≈ 10^3 Scm^{-1} and ZT ≈ 1.3 at 425K optimum for high temperature thermoelectric applications. The non degenerate InSe thin films demonstrate high value of S ≈ 2626μVK^{-1} and ZT ≈ 0.97 at 38K, indicating its potential for cryogenic thermoelectric applications. Thus the evaluation of ZT of the as prepared Cu_7Se_4 and InSe thin films reveals their promising property for thermoelectric applications. These materials demand further research on the optimization of ZT to enhance their thermoelectric efficiency to a larger extent suitable for use in thermoelectric devices.

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