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STUDY OF SOME PHYSICAL PROPERTIES OF BULK $Cu_{1.8}Se_{1-x}S_x$

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The alloys of $Cu_{1.8}Se_{1-x}S_x$ ($0.25\leq x\leq 0.7$) are prepared within the composition range of homogeneous solid solution by direct reaction of the elements. The composition of the constituent is tested using energy dispersive X-ray analysis (EDAX). X-ray diffraction pattern for prepared samples showed polycrystalline cubic structure, the lattice parameter a, vary linearly with the change of sulfur content but the crystallite size D depart from a linear relation. At room temperature all investigated samples are p-type and the electrical conductivity, carrier concentration, Hall mobility and thermoelectric power Q decreases as the S content (x) increases and this can be attributed to intrinsic lattice defects on the solid solution. The energy gap values obtained from diffused reflection measurements, exhibit bowing behavior expressed by the relation:
E_g (x) = 1.23 +0.29x+0.11x^2 and this is consistent with the behavior of the disorder effect in the alloy lattice due to the difference in electronegativites of Se and S.

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1. Introduction

Recently, $Cu_{1.8}Se$ has been studied due to its interesting properties and potential application in solar cell converter [1-5],window material [6]super ionic conductor ,optical filter [7], electro optical devices [8,9] and thermo electric converter [10,11]. It is usually existed in the wide homogeneity range allowing high concentration of native defects (10^{20} -10^{21}) which are copper vacancies , it is typically p-type, highly conducting, semitransparent, semiconductors with band gap varying between 1.2 and1.6 eV suitable for solar energy conversion and a semitransparent layer in high speed detectors working in the visible range [12,13].

It has many phases and structural forms: stoichiometric α–CuSe, Cu_3Se_2, CuSe as well as a non-stoichiometric $Cu_{2-x}Se$ [14-16].The thermal stability of this compound varies depending on its composition. By gradually substituting S by Se, this can allows tailoring of the band gap (1.2-1.6) eV and other material properties.

In order to optimize the use of $Cu_{1.8}Se_{1-x}S_x$ as an absorber material in solar cells and other applications an understanding of the basic properties is required.

In the present work as the first study, the preparation and some physical properties (composition, structural, optical and transport properties) of bulk alloys of $Cu_{1.8}Se_{1-x}S_x$ are studied.

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2. Preparation

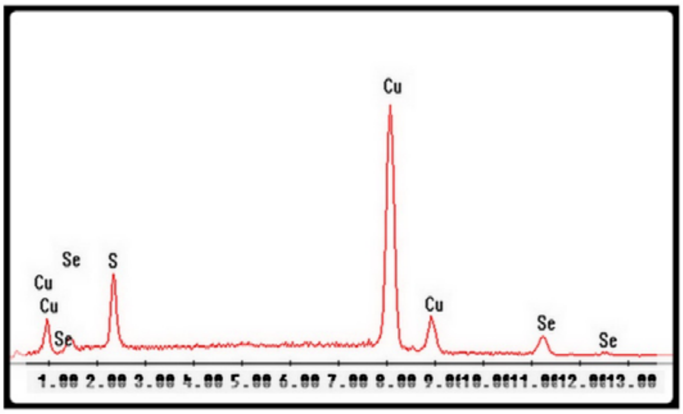
$Cu_{1.8}Se_{1-x}S_x$ ($0.25 \leq x \leq 0.7$) compound was prepared by fusion method, which is generally used when the melting points of the reacting compounds differ largely. In this method the constituent elements of 5N copper, selenium and sulfur were weighted in stoichiometric ratio. The mixture was sealed in a silica tube under vacuum (10^{-6} mbar). A silica tube was prepared by annealing in oxygen atmosphere to remove any active silica on the surface. The tube was then graphitized using paraffin oil. Graphitization was necessary to prevent oxidation, which causes sticking of the product to the tube surface. The sealed tube was placed in a furnace and the temperature was slowly increased at the rate of 30 K h^{-1} up to 473 K. The tube was maintained at that temperature for a period of 24 to minimize pressure build-up and to avoid possible strong exothermic reactions. The temperature was then increased at the rate of 60 Kh^{-1} up to 973 K, beyond which a slow heating process was used to minimize the risk of cracking. The tube was kept at 1400 K for a period of 24 h and was rotated intermittently for 2 hr to ensure complete mixing and reaction of the constituents. It was then cooled slowly in the furnace to 973 K and annealed at that temperature for 3-4 days and finally the current to furnace is switched off and the tube was left to cool down to room temperature. The materials prepared were obtained in the form of the polycrystalline with bluish grey color and metallic luster.

Spectroscopic analysis of the prepared materials revealed the presence of traces of Si, Mg, Al and Ga.

3. Results and discussion

3.1. Composition Analysis

The composition of he alloys $Cu_{1.8}Se_{1-x}S_x$ ($0.25<x<0.7$) were determined by energy-dispersive X-ray analysis (EDAX) Philips (XL 30 attached with EDX unit) the calculated contents with copper, selenium and sulfur %wt were comparable with % Wt of the starting materials. Fig.1 shows EDAX profile of $Cu_{1.8}Se_{0.3}S_{0.7}$ composition and the results of the EDAX of all Compositions were listed in table 1. It is found that the composition of alloys has approximately the composition of starting material with error about 0.03%.



Element	Wt%	At%	K-Ratio	z	A	F
S K	13.89	24.83	0.0597	1.1109	0.3872	1.000
Cu K	71.73	64.73	0.7137	0.9889	0.9909	1.0153
Se K	14.38	10.44	0.1228	0.9223	0.9261	1.000
total	100.00	100.00				

Fig.1. EADX of $Cu_{1.8}Se_{0.3}S_{0.7}$ compound: Profile (top) and table (below).

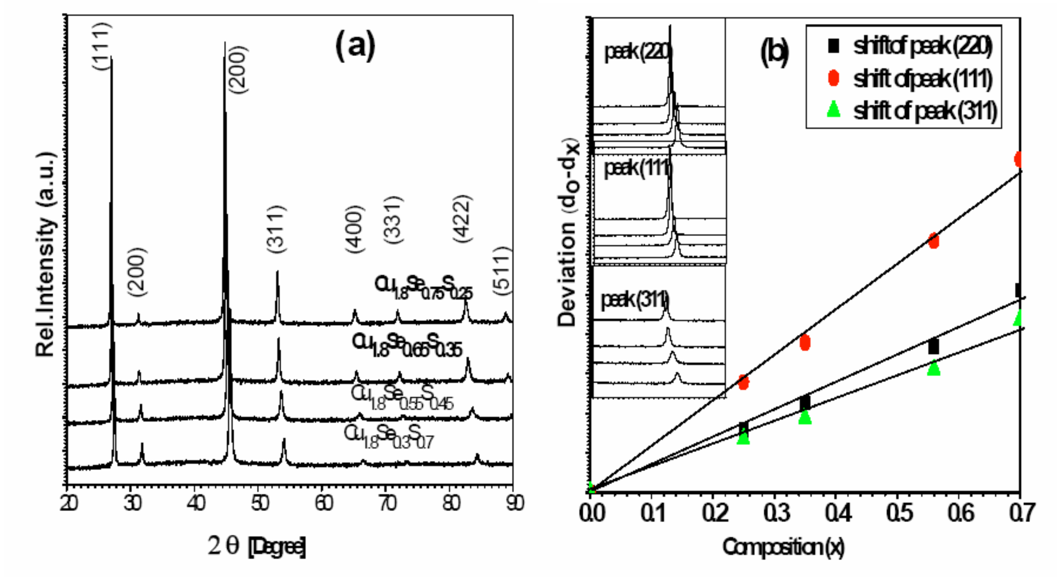
Table 1. Results of EDAX of $Cu_{1.8}Se_{1-x}S_x$.

Cu (Atomic%)		Se (Atomic %)		S (Atomic %)		x
Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
64.16	64.29	26.39	26.79	9.45	8.92	0.25
65.17	64.29	23.48	23.21	11.35	12.501	0.35
63..94	64.29	16.55	16.07	20.51	19.64	0.55
64.33	64.29	10.44	10.71	24.83	25.00	0.70

3.2. Structural Characterization

X-ray analysis was carried out at room temperature using an X-ray diffractometer (Philips type PW1373diffractometer).

Typical diffraction patterns of four different compositions of $Cu_{1.8}Se_{1-x}S_x$ alloys are shown in Fig.2a. It is clear that there is a small deviation of d values from the standard card (JCPDS-card 71-0044) towards higher theta angles. In addition, it is found that the deviation of the three strongest peaks (220), (111) and (311) of each compound from d_o (d_o is d value of standard card) vary linearly with the increasing in sulfur as shown in Fig.2b (the onset figures show this shift in peaks). This can be explained as: XRD pattern show isostructure with the compound $Cu_{1.8}Se$ because all d values of the prepared samples nearly matching with the d value of $Cu_{1.8}Se$ and there are no excess peaks to reveal other phases. The difference in the d values may be attributed to the difference between ionic radii of sulfur (0.102 nm) and selenium (0.116nm). This means that the increase in sulfur content may affect the d values of the prepared alloys.



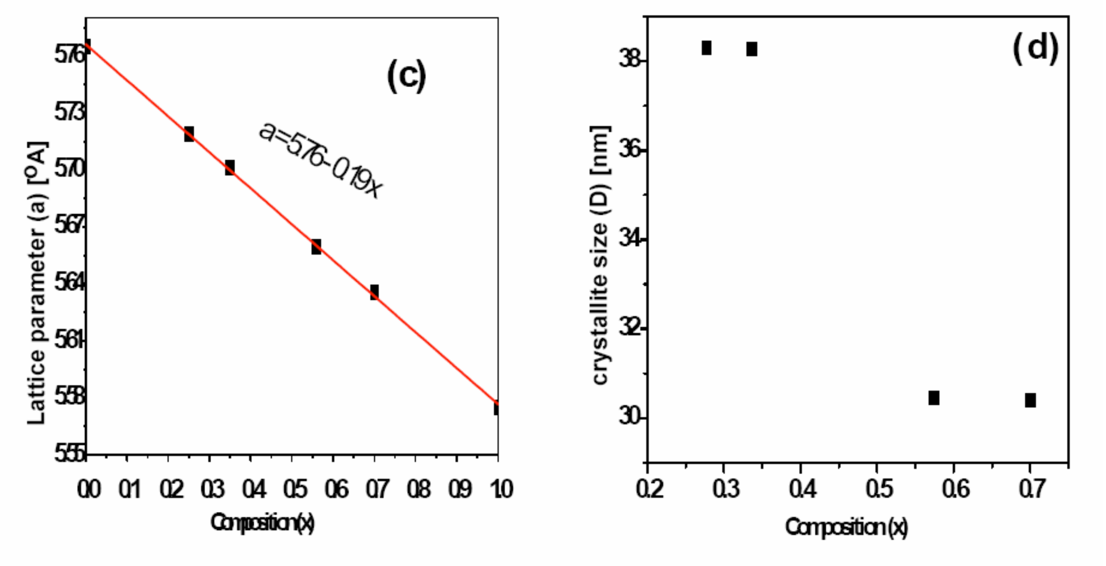


Fig.2. (a) X ray diffractgram for $Cu_{1.8}Se_{1-x}S_x$, (b) Shift from d_o for the three strongest peaks for $Cu_{1.8}Se_{1-x}S_x$. (c) Relation between sulfur content(x), and lattice parameter (a) for $Cu_{1.8}Se_{1-x}S_x$ (d) Relation between x and crystallite size(D) for $Cu_{1.8}Se_{1-x}S_x$, where x=0.25, 35, 55 and 0.7 respectively.

Now it worth mentioning that all prepared samples are formed in cubic system with a space group $Fm\bar{3}m$ with deviation in cell parameter depending on the S content.

The lattice parameter, a, was determined by the usual least-square fit method from the obtained data. It is found that, over the whole composition range, the relation between lattice parameter and x can be represented by a straight line as shown in Fig.2c. , i.e. $Cu_{1.8}Se_{1-x}S_x$ samples form a solid solution. Thus, Vegard's law is verified. From the full-width at half maximum (FWHM) β, the grain size (D) is calculated using the Scherer's formula:

$$D = \frac{0.9\lambda}{\beta \cos\varphi}$$

Where λ: is wavelength of X-ray used; θ: is Bragg's angle.

The lattice parameter (a) together with volumes of unit cell (a^3) and grain size (D) are reported in Table 2.

Table2. Show lattice parameter, volume of unit cell and crystallite size of different composition.

Composition	Lattice parameter(a) (A°)	Volume of unit cell (a^3) (A°)	Crystallite size (D) (nm)
$Cu_{1.8}Se_{0.75}S_{0.25}$	5.718	187.015	38.285
$Cu_{1.8}Se_{0.65}S_{0.35}$	5.701	185.293	38.263
$Cu_{1.8}Se_{0.45}S_{0.55}$	5.659	181.288	30.446
$Cu_{1.8}Se_{0.30}S_{0.70}$	5.623	178.96	30.408

3.3. Optical properties

The energy gap E_g values of $Cu_{1.8}Se_{1-x}S_x$ as a function of sulfur content (x) at 300 K were determined from the diffused reflectance in the wave length (λ) range (400-2500)nm .The spectra in the band gap region are shown in figure (3a). E_g values were determined from the onset of the linear increase in the diffused reflectance [17, 18]. Fig. (3b) shows the obtained values of E_g as a function of S content (x). These values of E_g correspond to an allowed direct transition between parabolic bands. E_g increased with the increase of x, and definite bowing behavior is observed. The variation of E_g with x can be fitted to a parabolic form, $E_g=a+bx+cx^2$ where a is the transition energy of the sample with x=0. This curve is shown in Fig.3b and can expressed by the relationship

$$E_g(x) = 1.23+0.29x+0.11x^2 \tag{2}$$

The experimental data yield bowing parameter c=0.11eV and there is no data reported on the value of E_g for $Cu_{1.8}Se_{1-x}S_x$ and bowing parameter.

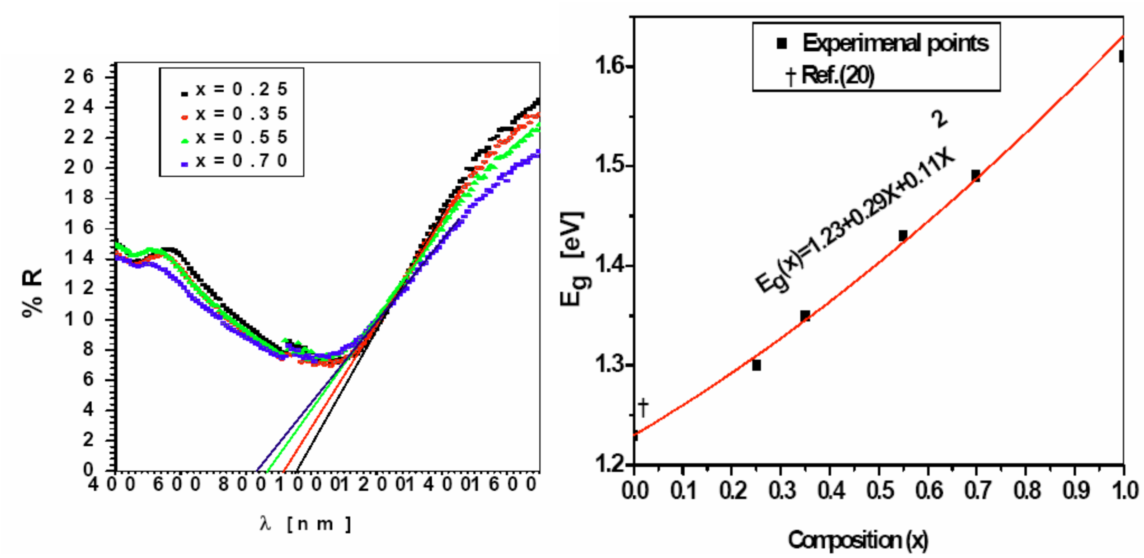


Fig.3. (a) Variation of the value of the diffuse reflection percentage (R) with the wave length (λ) for different compositions.(b) Variation of energy gap as a function of Composition for $Cu_{1.8}Se_{1-x}S_x$ Where x=0.25, 0.35.0.55 and 0.7.

Optical bowing behavior in a mixed system of $Cu_{1.8}Se_{1-x}S_x$ alloys is believed to be due to the difference in the electronegativity of the cations and / or anions constituting the mixed pseudo-system [19].

3.4 Transport properties

The electrical conductivity σ, Hall coefficient R_H, and thermoelectric power Q, were measured at room temperature for $Cu_{1.8}Se_{1-x}S_x$ as function of S content.

For electrical and thermoelectric measurement, the samples were cut mechanically from the middle part of the ingot, which was usually more homogenous than the extremes. Before carrying out the measurements, the samples were annealed in an evacuated tube for 24 hr at 437 K in order to remove any mechanical strain during cutting and polishing process. Liquid silver was used to improve the contacts between specimen and potential leads, copper belt thermocouples, and copper sinks.

The electrical conductivity was measured by the conventional four-probe method. The Hall voltage was measured potentiometrically with the usual precautions of reversing both the magnetic and current direction. The thermoelectric power was measured simultaneously against copper while establishing a maximum temperature gradient of 10 K along the sample.

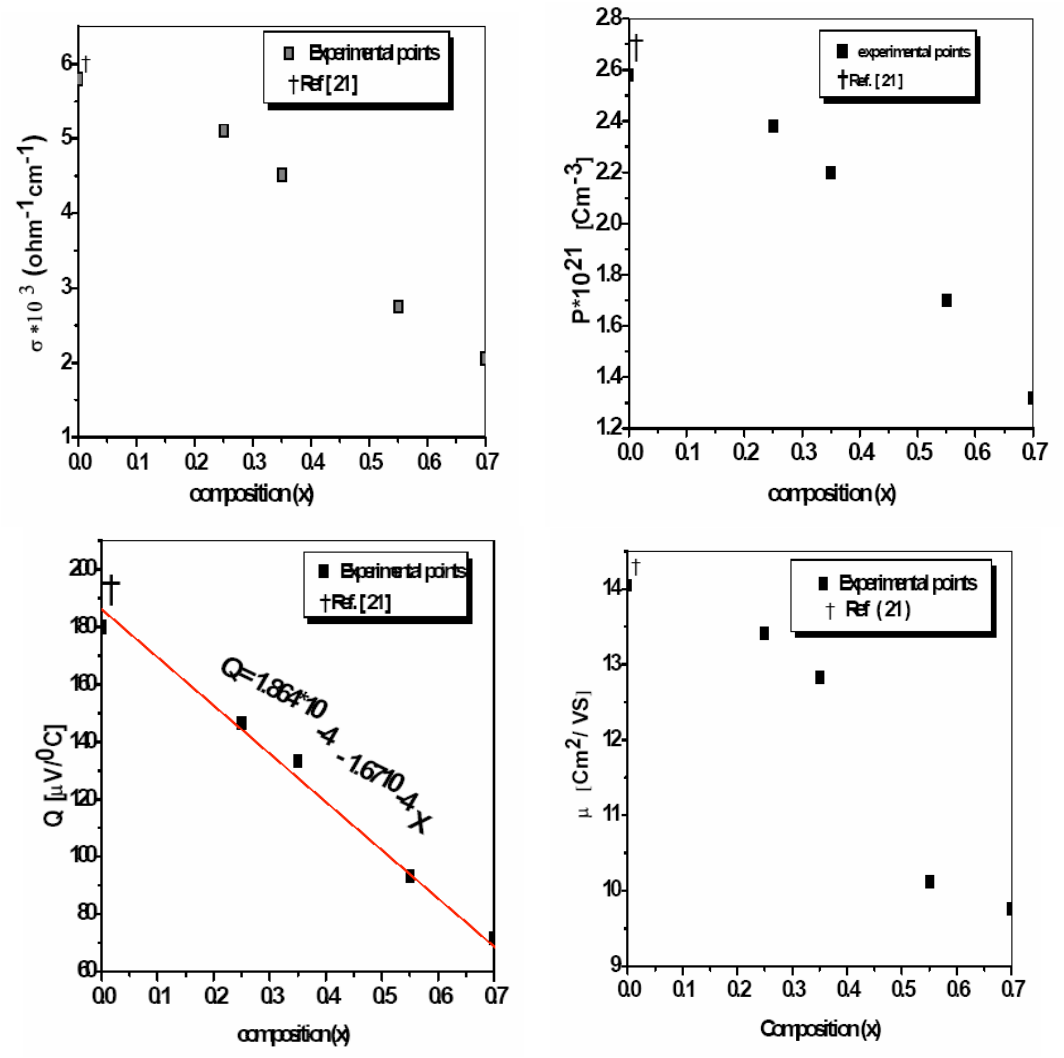


Fig.4. Variation of: (a) conductivity σ, (b) carrier concentration P, (c) thermoelectric power Q and (d) Hall mobility μ_H *as a function of composition for* $Cu_{1.8}Se_{1-x}S_x$ *compounds.*

Fig. (4a, b & c) shows the composition dependence of conductivity σ, carrier concentration $P = 1/R_H e$ and thermoelectric power (Q), respectively, at room temperature (300 K). The sign of R_H and Q are positive (+) for all values of x indicating p-type conduction, which may be due to the copper vacancies.

It is observed that, as sulfur content (x) increases σ, P, μ_H and Q increase. This can be attributed to the intrinsic lattice defects in the solid solution. The electrical efficiency $\alpha = Q^2\sigma$ as a function of composition(x), is reported in Table 3, the high values of α indicate that the $Cu_{1.8}Se_{1-x}S_x$ can be used in the field of thermoelectric converters.

Table (3): show data of σ, Q, α, P and μ for $Cu_{1.8}Se_{1-x}S_x$, where x=0.0, 0.25, 35, 55 and 0.7 respectively.

Compositions (x)	$\sigma*10^3$ $(\Omega. Cm)^{-1}$	Q (μV/°C)	α (W/CmK^2)	$P*10^{21}$ Cm^3	μ
$0^{Ref[21]}$	5.8E3	180	1.87E-4	2.58	14.05
0.25	5.11	146.67	1.098E-4	2.38	13.4
0.35	4.51	133.33	8.026E-5	2.2	12.8
0.55	2.75	93.33	2.398E-5	1.7	10.12
0.70	2.05	71.65	1.057E-5	1.32	9.76

4. Conclusions

Structural, electrical, and optical properties of a polycrystalline bulk $Cu_{1.8}Se_{1-x}S_x$ ($0.25 \leq x \leq 0.7$) were studied as a function of composition .The composition and structure of the bulk was determined using EDAX and XRD techniques.

Energy dispersive X-ray analysis [EDAX] measurements confirmed that composition of alloys has approximately the composition of starting material with an error of about ± 0.03%. X-ray diffraction data confirmed that a cubic single–phase solid solution with the chalcogenite structure occurs through the whole composition range. The lattice parameter (a) decreases linearly as the sulfur content(x) increases.

The energy gap values deduced from diffused reflectance curves can be fitted to a second –order equation in x (sulfur content) giving a downward bowing parameter of about 0.11 eV. This is consistent with the behavior of the disorder effect in alloys lattice due to the difference in electronegativites of Se and S atoms.

The electrical data revealed that the samples show p-type conduction and σ, P, Q and μ_H decrease as the S content (x) increases.

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