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Electrical Conductivity Studies in Polycrystalline $(CuSe)_{1-x}Se_x$

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ABSTRACT

This studies are directed towards measuring the electrical conductivity of the $(CuSe)_{1-x}Se_x$ metal chalcogenide semi-conductor composites, with different stoichiometric compositions of Se (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8,1.0) in bulk form. The electrical conductivity measurement was carried out at room temperature, using the parallel plate technique. The $(CuSe)_{1-x}Se_x$ composites were prepared using solid state reaction, by varying the ratio of CuSe:Se, in the reaction mixture. The electrical conductivity of $(CuSe)_{1-x}Se_x$ was determined to be in the range of 1.17×10^{-8} to 1.02×10^{-1} S/cm. The finding indicated that the electrical conductivity value tended to decrease as the concentration of Se increased. The effect of the concentration of Se, on electrical conductivity of $(CuSe)_{1-x}Se_x$ composites, is discussed in this paper.

Keywords: Electrical conductivity, $(CuSe)_{1-x}Se_x$ metal chalcogenide semi-conductor, stoichiometric, parallel plate techniques, solid state reaction

INTRODUCTION

Copper selenide (CuSe) is an interesting semi-conductor compound, with various applications in solar cells, super ionic conductors, photo-detectors, photovoltaic cells and Shottky-diodes (Lippkow and Strehblow, 1998; Pathan, Lokhande *et al.*, 2003). The attraction of copper selenide also lies in the feasibility of producing ternary material, i.e. $CuInSe_2$, by incorporating indium into this binary compound (Dhanam *et al.*, 2005). Copper selenide is a metal chalcogenide semi-conductor, with a wide range of stoichiometric compositions (CuSe, Cu_2Se, Cu_3Se_2, Cu_7Se_4, Cu_5Se_4, Cu_2Se) and non-stoichiometric composition ($Cu_{2-x}Se$) (Deevi, 2000; Dhanam *et al.*, 2005). $Cu_{2-x}Se$ or Cu_2Se is treated as copper (I) selenide, while CuSe, Cu_3Se_2 and $CuSe_2$ are treated as copper (II) selenide (Shafizade *et al.*, 1978; Nandakumar *et al.*, 1998; Hankare *et al.*, 2006). Copper (II) selenide, in the form of Cu_3Se_2, is often reported as an impurity phase, along with CuSe (Shafizade *et al.*, 1978; Pathan *et al.*, 2003). The copper selenide exists in various crystallographic forms, even at the room temperature. These include orthorhombic, monoclinic (Heyding and Murray, 1976), cubic (Grozdanov, 1994; Hankare *et al.*, 2006), tetragonal and hexagonal (Heyding and Murray, 1976; Perez-Robles *et al.*, 1999) forms, depending on the method of preparation used.

Selenium has good photovoltaic and photoconductive properties. It exhibits both photovoltaic action (where light is converted directly into electricity) and photoconductive action (where the electrical resistance decreases with the increasing illumination). These properties make selenium useful in the production of photocells and exposure meters for

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photographic use, as well as solar cells. In addition, selenium is extensively used in rectifiers to convert ac to dc electricity. Just like carbon and silicon, selenium is also known as a structuring element. It was expected that the mixture of the CuSe-Se composite material would affect the electrical properties, which have been extensively used in electronics, such as photocells, light meters as well as solar cells and solid-state applications. The investigation of the electrical transport phenomena, in those materials, is an important topic which is closely linked to their basic fundamental and physical properties.

In this paper, the electrical conductivity measurement of the $(CuSe)_{1-x}Se_x$ metal chalcogenide semi-conductor composites in bulk form, using the parallel plate technique, is presented to further fill in the information gap in the literature on the electrical properties of polycrystalline, $(CuSe)_{1-x}Se_x$ composites.

MATERIALS AND METHODS

The samples of $(CuSe)_{1-x}Se_x$ (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8,1.0) were prepared using the solid state reaction method, with the stoichiometric mixtures of CuSe and Se. The starting CuSe (purity 99.5%) and Se (99.5%) were weighed based on the stoichiometric amount, and milled in the volumetric flasks for 24 hours with a magnetic stirrer. For this, ethanol was used as the mixing medium. The mixtures were then dried overnight in an oven, at the temperature around 75°C. After that, the dried $(CuSe)_{1-x}Se_x$ powder was weighed and placed into an 8 mm diameter mould, to form a pellet shape sample, using a hydraulic press (SPECAC USA, model 15011) of 3 tonne pressure.

The electrical conductivity of the samples used in this study was measured using the parallel plate technique. In this system, copper wires were attached to both ends of the pellet sample. Silver paint was applied to the surfaces of the pellet to serve as electrodes. The current I, which flowed through the sample, was measured by the Keithley 236 source measure unit consisting of a voltage source and current detector. The *I-V* characteristic showed a linear relationship; this indicated that a good ohmic junction was formed between the electrodes and the sample. The resistivity of the material was obtained by measuring the resistance and physical dimension of a material, based on the following expression:

$$\sigma = \frac{RA}{L} \tag{1}$$

where R is the resistance of the sample, A is surface area and L is the thickness of the sample. The electrical conductivity, σ was calculated from $\sigma = 1/\rho$.

RESULTS AND DISCUSSION

The XRD spectra of the polycrystalline $(CuSe)_{1-x}Se_x$ compounds (*Fig. 1*) show that the compound is a polycrystalline material. It can clearly be observed that the diffraction peaks corresponded to only the planes of CuSe and Se phase.

Fig. 2 shows the *I–V* curves for the $(CuSe)_{1-x}Se_x$ sample, with compositions x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1. The *I-V* behaviour of this sample shows a linear behaviour for both forward and reverse bias conditions. The slope of the curve provides the conductance value which can be used to calculate the electrical conductivity of the sample.

Fig. 3 shows the electrical conductivity σ, as a function of composition x of the $(CuSe)_{1-x}Se_x$ samples. The conductivity was found to decrease drastically as Se replaced the CuSe in the $(CuSe)_{1-x}Se_x$ compound, from x = 0 to 1. The bulk electrical conductivity values of

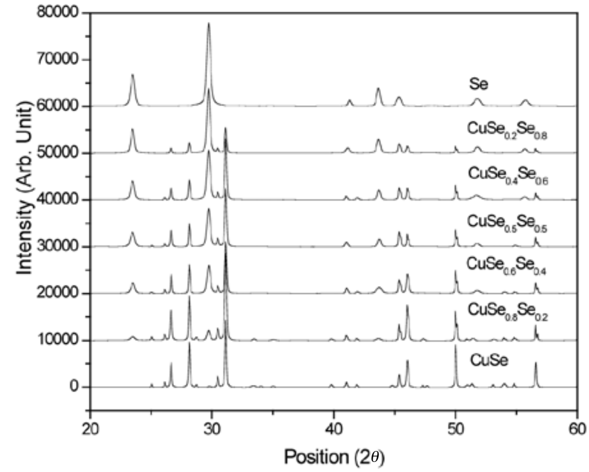
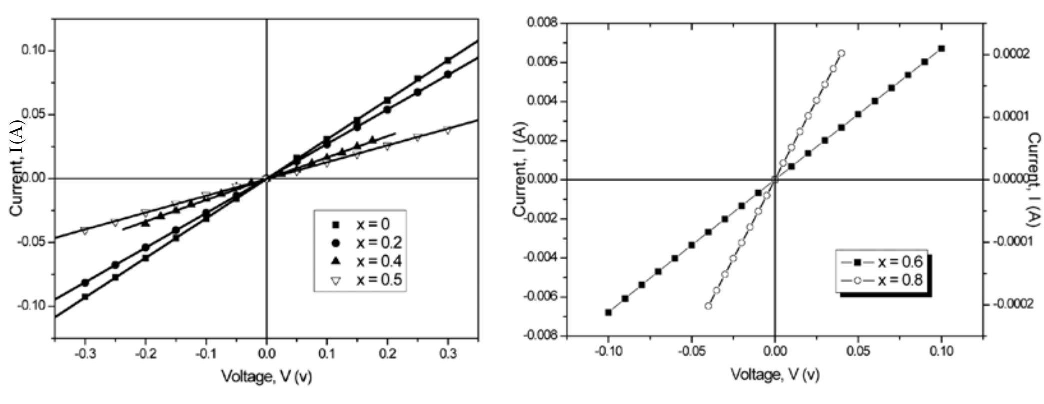
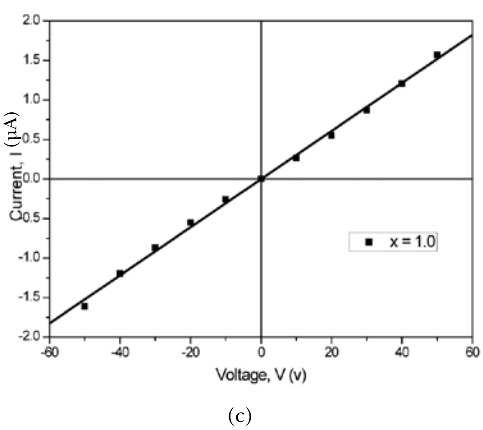


Fig.1: The XRD pattern of the $(CuSe)_{1-x}Se_x$ composites





(c)

Fig. 2: The I-V characteristics for the $(CuSe)_{1-x}Se_x$ sample (a) x = 0, 0.2, 0.4, 0.5; (b) x = 0.6, 0.8; (c) x = 1

$(CuSe)_{1-x}Se_x$ were determined to be in the range of 1.17 x 10^{-8} to 1.02 x 10^{-1}S/cm. A larger value of electrical conductivity was observed at low Se content, suggesting that the electrons in the CuSe do play a role in the electrical conductivity. This is because the CuSe contains metallic copper inclusion, which positively contributes to the conductivity. The samples with higher Cu concentration were found to show a remarkably larger electrical conductivity as compared to the sample with higher Se concentration. When Se was added to $(CuSe)_{1-x}Se_x$, the Cu concentration decreased, and this in turn decreased the electrical conductivity of the composites.

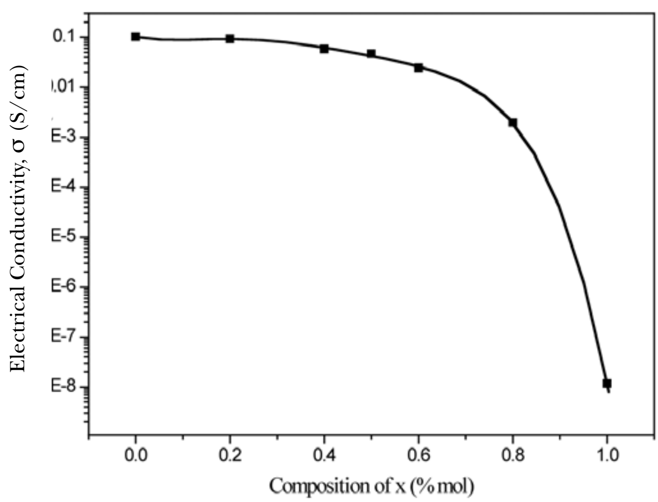


Fig. 3: The electrical conductivity σ for $(CuSe)_{1-x}Se_x$ at different compositions of x

CONCLUSIONS

$(CuSe)_{1-x}Se_x$ metal chalcogenide compounds had been successfully prepared using a solid state reaction, by varying the ratio of CuSe:Se in the reaction mixture. The electrical conductivity of $(CuSe)_{1-x}Se_x$ compounds, with different stoichiometric compositions of Se (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8,1.0), was investigated using the parallel plate technique. The electrical conductivity values of the $(CuSe)_{1-x}Se_x$ compounds were determined to be in the range of 1.17 x 10^{-8} to 1.02 x 10^{-1} to S/cm, which corresponded to the compositions of Se, i.e. from x = 0 to 1.0. The electrical conductivity of the $(CuSe)_{1-x}Se_x$ composites was found to decrease when the composition of Se increased.

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