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Synthesis of new sulphides of transition metal ions in presence of sun light

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New sulphides of transition metal ions [$M^{+n} = Cu^{+1}$, Cu^{+2} and Zn^{+2}] have been synthesised in sunlight. XRD patterns show that these compounds are not MxSy but are mercaptyl, hydroxyl metal sulphides [$M(SH)(OH)(H_2O)_2$] which is further ascertained by I.R. spectra showing bands due to T_d-symmetry. ESCA of compound of copper in solid state shows presence of Cu^{1+} and Cu^{2+} ion. The presence of hydroxyl, mercaptyl, aqua and S^{-2} groups has finally been confirmed with TGA, DTA and ESCA. Conductivity and Seebeck coefficient measurements show that compound of copper is *p*-type semiconductor and compound of zinc is *n*-type semiconductor. The production of these low cost materials opens an interesting area of research and development for their use in solar cell devices.

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1. Introduction

Generally M_xS_y are not formed when H_2S reacts with aqueous solution of metal ions instead SH-group act as ligand [1]. The synthesis of the complex, $[Cr(H_2O)_5(SH)]^{+2}$, has been reported by Ramasami and Sykes [2]. In order to synthesize such materials the photosensitive [3] reactant, Na_2S7H_2O, has been selected which lowers the cost of production of materials. The synthesis of low cost materials is useful for industry and technology. Therefore the synthesis of new sulfides has been carried out in presence of sunlight, which has entirely different route than earlier one. The present paper reports the preliminary studies, such as XRD pattern, FT-I.R spectra, ESCA, TGA, DTA, conductivity and Seebeck coefficient measurements of final products which are potentially important materials for solar cell and can be obtained by very simple methods. In order to compare the structure and reactivity, compounds of transition metal ions have been prepared in solid state as well as in solution with a mixture (1:1 molar) of $Na_2S{\cdot}7H_2O$ and $MSO_4X{\cdot}H_2O$ ($M^{2+} = Cu^{2+}$, Zn^{2+}) in sunlight. Compound of Cu^{2+} ion prepared in solution shows possibility of only one type of structure, square planar in XRD pattern while the compound of Cu^{2+} ion prepared in solid state shows mixture of tetrahedral and square planar structures as deduced by the presence of two strong lines. These compounds are different from reported [6] M_xS_y compounds.

2. Experimental

Copper sulphate ($CuSO_4{\cdot}5H_2O$) A.R grade, purity 99.98 (BDH), sodium sulphide ($Na_2S{\cdot}7H_2O$), purity 99.98 (Emerk) and zinc sulphate ($ZnSO_46H_2O$), 99.98 pure (BDH) were used for preparing final product from a mixture of $Na_2S{\cdot}7H_2O$ and MSO_4XH_2O in solid state as well as in solution in 1:1 molar ratio in sun light.

$$CuSO_45H_2O + Na_2S7H_2O \rightarrow [Cu(SH)(OH)(H_2O)_2] + Na_2SO_4 + 9H_2O$$

$$ZnSO_46H_2O + Na_2S7H_2O \rightarrow [ZnS(H_2O)_3] + Na_2SO_4 + 10H_2O$$

Rise in temperature during solid state reactions is shown in Fig. 1. Rise in voltage and current are given in Fig. 2a and b. The final products [$M(SH)(OH)(H_2O)_2$] were purified through vigorous washing with distilled water for several times. The final washing was completed with the removal of SO_4^{2-} and S^{2-} ions. The compounds were prepared thrice and the reproducibility was checked by ESCA. These reactions were not successful in the dark. These reactions were carried out in the solid state as well as in solution in the presence of sun light. The elemental analysis was carried out with the help of ESCA-750 spectrometer, Shimadzu Corporation, Japan. Results are given below.

Chemical analysis of the copper compound, [$Cu(SH)(OH)(H_2O)_2$], from ESCA

	Cu	S	O	H
Calc (%)	42.97	17.29	34.31	5.41
Obs. (%)	42.91	17.28	34.30	5.45

Chemical analysis of the structure of zinc compound, [($ZnS(H_2O)_3$)], ESCA

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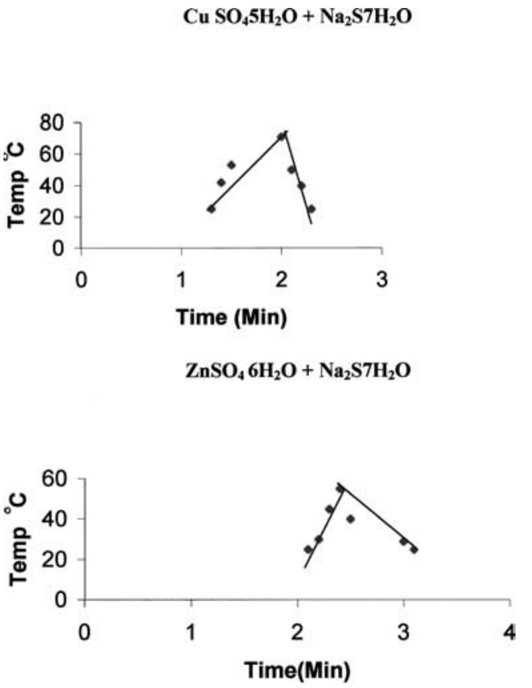
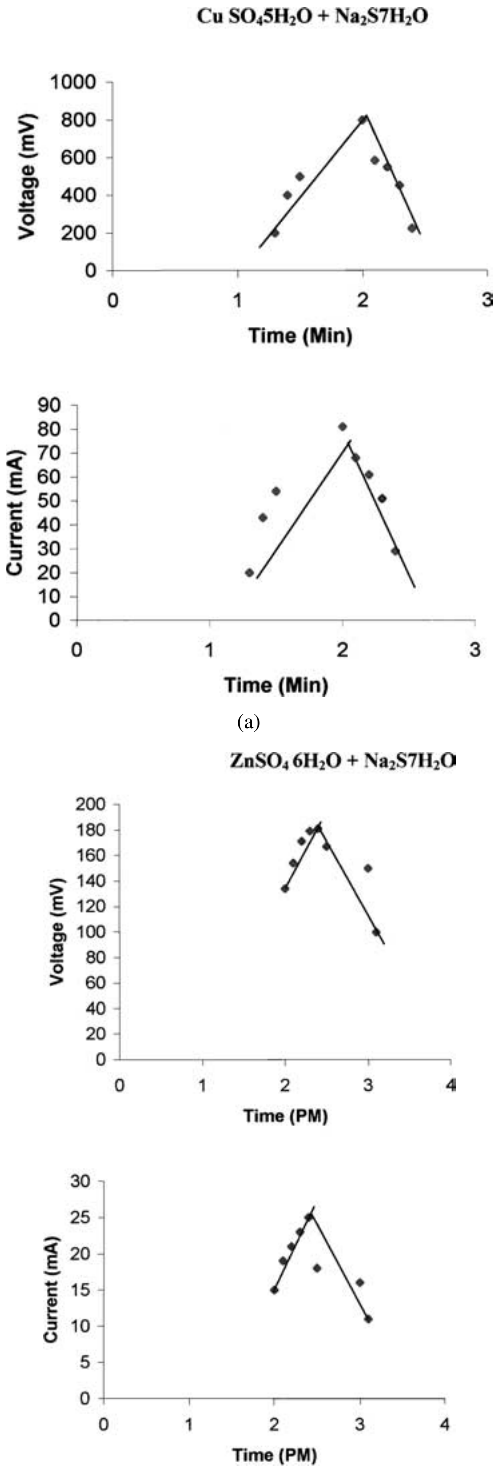


Figure 1 Rise in temperature during solid-state reaction in presence of sunlight.

	Zn	S	O	H
Calc (%)	43.2	21.1	31.5	3.9
Obs. (%)	43.1	20.9	31.3	3.7



(a)

(b)

Figure 2 (a) Rise in Current and voltage during solid reaction in presence of sun light. (b) Rise in Current and voltage during solid reaction in presence of sun light.

The IR spectra were recorded in nitrogen purge by FT-I.R model-1710, Perkin Elmer. TG-DTA was carried out by RIGAKU 8150. Electrical conductivity and thermoelectric power were measured with the help of a digital multimeter PM 2522/90, Philips, India. Seebeck coefficient measurement and fabrication of solar cell have been done at Delhi University, Delhi, India. For thermoelectric power (Seebeck cofficient) measurements a temperature difference $\Delta T \sim 20^{\circ}\mathrm{C}$ was produced across the pellet with the help of a microfurnace fitted with the sample holder assembly. The temperature of both the surfaces of the pellet were measured with the help of chromel/alumel thermocouple wires firmly attached with the platinum electrodes and the ambient temperature has been taken as average of the temperature of both the surfaces of the pellet. The thermoelectric power, $S(T)$, was calculated using the following relation.

$$S(T) = \frac{\Delta E}{\Delta T}; \quad (\Delta T \to 0)$$

where ΔE is the thermo em.f. developed across the pellet due to the temperature difference, ΔT. A temperature difference $\Delta T \sim 20^{\circ}\mathrm{C}$ was held across the pellet, in order to reduce errors in measuring thermo e.m.f. E.

Solar cell was fabricated by pinning up n-p junctions that is placing pellet of n-type compound of zinc on the pellet (6×10^6 gm cm^{-2}, diameter = 0.5 cm.) of p-type compound of copper. Surface of the pellets were cleaned by ion beam sputtering techniques to get better contact. A conventional three electrode configuration was used where nickel plate is acting as counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Copper leads were soldered on the back surface and a common epoxy was applied on the back side. Gold dot was used as front contact. The voltage and current were measured with the help of digital multimeter (PM 2522/90 Philips India) in presence of sunlight. The glass body cell was packed with an electrolyte which is solid mixture of Na$_2$S, S$_8$ and NaOH in 1:1:1, molar ratio.

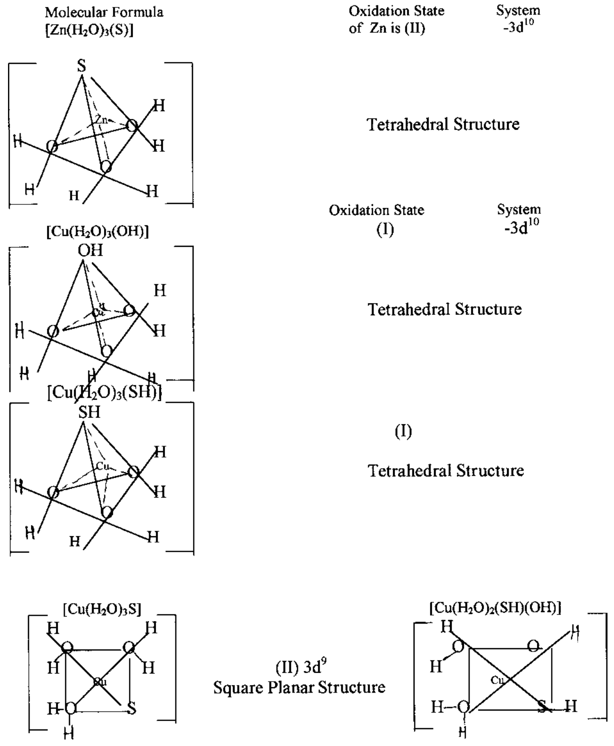


Figure 3 Structure of zinc and copper compounds.

3. Results and discussion

3.1. Infra red spectra

The interesting point of this work is that the presence of IR bands in finger print region can not be due to M_xS_y structure [7, 5–8]. The IR spectrum of $[CuSO_45H_2O]$ having Cu^{2+} ion in D_{4h} symmetry in $[Cu(H_2O)_4]^{++}$ cation shows band at 581 cm^{-1} [8]. The mercaptyl, hydroxyl compound, $[Cu(H_2O)_2(SH)(OH)]$ of Cu^{2+} ion, in present investigation, also shows bands at 590 cm^{-1} (Fig. 3) due to D_{4h} symmetry. The Infrared bands of SO_4^{-2} ion in T_d symmetry occur at 1105 and 611 cm^{-1} [8]. The mixture of tetrahedral and square planar structure of copper compound [5, 9] is the only possibility instead of ionic M_xS_y structure. Therefore Raman spectrum of copper compound can not help in predicting pure structure. The compound of Zn^{2+} ion shows IR bands of T_d-symmetry [8] at 1120 and 621 cm^{-1}. The bands due to SH, OH are absent in zinc compound. Bands at 3468 cm^{-1}, 2556 cm^{-1}, 1960 cm^{-1}, 430 cm^{-1} and 405 cm^{-1} occur due to $\nu O{-}H(H_2O)$, ν-SH, ν-OH, $\nu M{-}O$ and $\nu(M{-}S)$ [9–13, 14–18] respectively in copper compound.

3.2. Thermal analysis

The exotherm in DTA at 248.7 and 251.8°C showed detachment of aqua and S^{-2} group (Table I) indicating coordination number four in the compound, $[ZnS(H_2O)_3]$.

TABLE I Exotherm and Endotherm in DTA of both the compounds

Compound from solid state	Compound from solution	
Exotherm		
248.7°C	251.8°C	Zinc compound
233.6°C	362,390.450°C	Copper compound
Endotherm		
–	90.4°C	Zinc compound
101.2°C, 217.3°C	–	Copper compound

Three exotherms of copper compound prepared from solution showed detachment of $2H_2O$, (OH)- and (SH)-groups indicating coordination number four in $[Cu(SH)(OH)\ (H_2O)_2]$ with a total weight loss of 73.09% in TGA while in compound of Cu^{2+} ion obtained from solid state reaction only one exotherm at 233.6°C is observed due to difference in structures [5, 8] $[Cu(OH)(H_2O)_3]$, $[Cu(SH)(H_2O)_3]$ or $[CuS(H_2O)_3]$, explaining coordination number four (Fig. 3).

3.3. Measurement of magnetic moment

The presence of Cu^{+1} $(3d^{10})$ ion in the complex makes the complex magnetically dilute and exhibits magnetic moment, 1.4 + 0.03 B.M., which is quite low w.r.t. spin only value 1.73 B.M. for $(3d^9)$ Cu^{+2} ion. The low value of magnetic moment may ascertain the possibility of antifero spin exchange [19].

3.4. ESCA Analysis: (XPS)

ESCA of zinc compound showed only one peak for $O(2P_{1/2})$ and one for $S(2P_{1/2})$ (Table II) in both the compounds, prepared in solution as well as in solid state. Hence the presence of aqua and S^{-2} group is confirmed. There is a peak at 1029.5 ev for Zn $(3d_{3/2})$ in both the compounds. Since the compounds are found to be diamagnetic, structure $[Zn(H_2O)_3S]$ is further confirmed. ESCA of copper compound shows two peaks for sulfur, which might be due to presence of (SH)- and S^{-2} ions (Table III). Similarly, two peaks for oxygen might be due to presence of OH- and H_2O groups and two peaks for Cu $(3d_{3/2})$ and $(3d_{1/2})$ might be due to presence of Cu^{2+} and Cu^{1+} ions in the compound.

3.5. XRD pattern

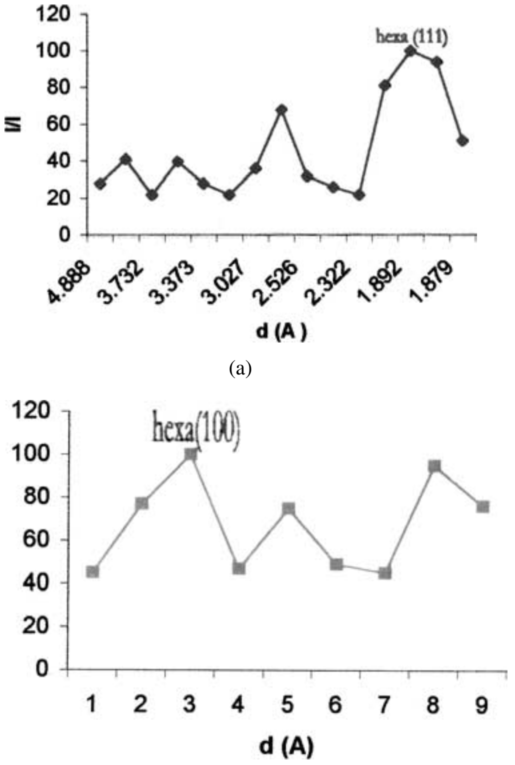
The copper compounds (Fig. 4a and b) contain other ions $(SH)^-$ or $(OH)^-$ instead of sulphide (S^{-2}) ion, which has been confirmed by the comparison of reported d-value (2.81 A°) for CuS [6]. Two strong lines in XRD. Pattern ascertain the presence of two type of ions, Cu^{+2}, and Cu^{+1}, in solid state (Fig. 4b).

TABLE II ESCA of the compound of zinc prepared in solid state as well as in solution

Element	Compound from solid state	Compound from solution
Zn (3d 3/2)	1029.5 ev	1030.0 ev
S (2P 1/2)	168.5 ev	169.5 ev
O (2P 1/2)	539.5 ev	539.5 ev

TABLE III ESCA of the compounds of Cu^{2+} ion prepared in solid state as well as in solution

Element	Compound from solid state	Compound from solution
Cu^{2+}	939 ev	935 ev
Cu^{1+}	932 ev	
SH^-	169 ev	164.5 ev
S^{-2}	189 ev	
OH^-	514 ev	533.5 ev
H_2O	530 ev	534.5 ev



(a)

(b)

Figure 4 (a) Plot of d-values (A°) versus I/I_o for copper compound prepared in solution. (b) Plot of d-values (A°) versus I/I_o for copper compound prepared in solid state.

Thus, compound of copper is not a simple copper (II) compound but contains Cu(I) and Cu(II) [14] units. It has been reported [12–15] that CuS has hexagonal structure with six CuS formula units in the unit cell, better formulated as Cu^{I} Cu^{II} S_2, where four atoms are tetrahedraly and two are triangularly coordinated by S-atom. The compound, $[Cu^{II}(SH)(OH)(H_2O)_2]$ has hexagonal structure with plane 111 and the compound, $[Cu^{I}(SH)(H_2O)_3]$, has hexagonal structure with plane 100. The compound, $[Zn(S)(H_2O)_3]$, has hexagonal structure. The XPS of copper compound also shows a doublet structure for two types of copper ions Cu^{I} and Cu^{II}. The compounds are paramagnetic with magnetic moment $1.4^{+} - 0.03$ B.M.

3.6. Electrical conductivity measurement

The electrical conductivity of copper compound upto 370°K seems to be due to p-type nature with an activation energy 1.66 ev. The activation energy 1.66 ev, calculated in the temperature range 200–370°K, (Fig. 5) is in reasonable agreement with the intrinsic activation energy of NiO (1.9 ev) estimated by Ksendsov and Drabkin [7, 16] Electrical conductivity of zinc compound (Fig. 6) shows n-type nature with an activation energy 1.29 ev.

The positive increase in thermoelectric power with a positive value over the entire range of temperature shows that majority charge carriers are holes. Therefore, the compound of copper is p-type semiconductor. The negative increase in thermoelectric power with a negative value over the entire range of temperature shows that majority charge carriers are electrons. Thus, compound of zinc ion is n-type semiconductor (Fig. 6).

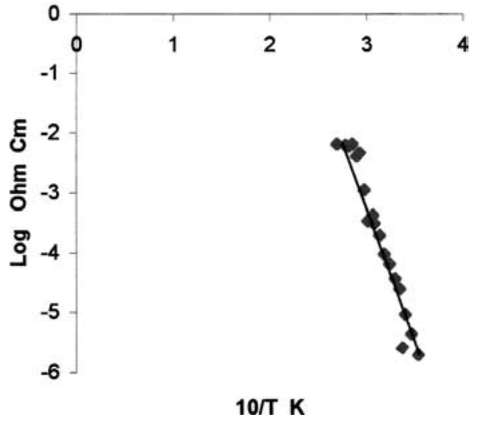


Figure 5 Plot of electrical conductivity for Copper compound.

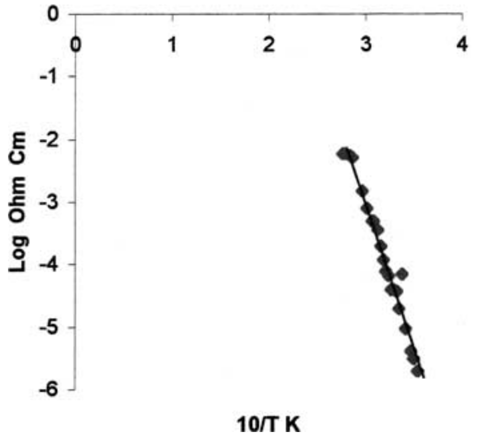


Figure 6 Plot of electrical conductivity for Zinc compound.

4. Conclusion

These new compounds synthesized in presence of sunlight do not require furnace and pressure assembly etc., thus reduce the cost of production. The n-type and p-type behaviour of the materials (Fig. 7) opens an interesting area of research and development for their use in solar cell devices.

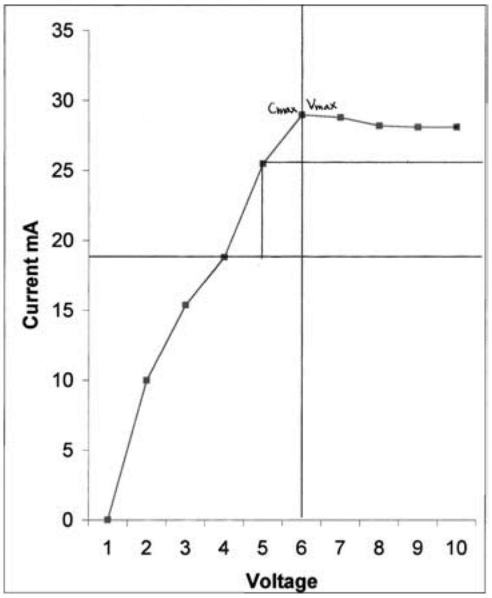


Figure 7 Current-voltage plot for n-p junction (□).

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