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STUDIES ON FEASIBILITIES OF USING GALENA FOR PREPARING THERMOELEMENTS

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ABSTRACT

The potentialities of galena for thermoelectric device applications having been established, the feasibility of using the mineral galena as it is i.e. without any further treatment has been explored.

Semiconductor thermocouples were used as a basic device of a thermoelement. With pellets made out of the natural galena as one arm of this semiconductor thermocouple and pellets made out of beneficiated ore was used as the second arm during the preparating of thermoelectric device. The latter was prepared out of cold pressed beneficiated ore and was sintered in nitrogen atmosphere at the temperature ranging from 350°C to 750°C. The length of the time used this process was one hour.

These optimised conditions gave a better performance in the matter of power obtainable.

INTRODUCTION

Investigations on the thermoelectric properties of lead chalcogenides date back to the latter half of the 19^{th} century. The virute of the thermoelectric devices made of these lead chalcogenides arises out of their high thermoelectric power (1-3). But their exploitation for device application has not received due attention. It had been first reported the potentialities of the galena occuring in fair abondance in the Zawar Mines of India, in the 4^{th} and 5^{th} International Conference on Thermoelectric Energy Conversion (4-5). In those papers had been given some points the feasibility of using the mineral galena as it is i.e. without any further treatments for the fabrication of thermoelectric devices.

The avoidance of the necessity of using high purity startîng material is important point. From considerations of cost in purifying the starting material as in the case with the present material is an obvious advantage of these thermoelectric generators. Consideration on cost involved in growing single crystals necessitated us to think of alternatives. This resulted in our successful exploitation of cold pressed and sintered pellets for this purpose. The electrical, thermal and thermoelectric properties of these sintered pellets were studied. Sintering has helped bring dwon the resistance without much impairing thermoelectric property. In an attempt to understand the causes for the changes taking place during this sintering process we have undertaken studies of the microstructural changes occuring there in X-ray diffraction and SEM studies were used as a tool for this purpose.

EXPERIMENTAL DETAILS

Electrical Conductivity and Thermoelectric Power Measurement.

Electrical resistance measurement was given detail in elsewhere (6–7). After resistance measurement using the relation, $R=\rho l/A$, we found ρ and then conductivity.

The measurement of thermoelectric power also can be found in the given references above. 10 degrees of temperature difference was produced by heating only one side of the sample. The relation $S = \frac{\Delta V}{\Delta T}$ is used to find thermoelectric power, S. The results were given in Table 1 and Table 2.

Thermal Conductivity Measurement

The equation of heat flow under steady state condition is given (8) by $Q/t = \frac{KA}{d} \Delta t$. Where K is the thermal conductivity coefficient, A is the cross section area, d is the length of the sample, Δt is the temperature difference between two ends of the sample and t is the

Table 1. Conductivity And Thermoelectric Power of Galena.

Pressure (tons)	σ ($ohm^{-1}cm^{-1}$)	S ($\mu V/K$)
4	2.40×10^{-3}	225
5	4.25	220
6	6.10	210
7	6.16	205
8	8.57	200

Table 2. Variation Of Thermoelectric Voltage (V) With Temperature Difference.

$\Delta T \rightarrow$	3	5	7	9	13	15	18	20
S_A	0.20	0.10	0.15	0.18	0.20	0.24	0.27	0.29
S_B	0.42	1.30	1.60	1.85	2.30	2.30	2.60	2.80
S_C	0.40	0.85	1.10	1.55	1.80	2.20	2.60	2.90
S_D	0.08	0.20	0.25	0.35	0.52	0.62	0.70	0.78

Sample S_A: Applied pressure 8T Sintering 2 hrs at 400°C
S_B: Applied pressure 6T Sintering 1 hrs at 750°C
S_C: Applied pressure 6T Sintering 2hrs at 650°C
S_D: Applied pressure 7T Sintering 3 hrs at 350°C

time. The heat current Q/t through the heat source namely copper rod is

$$\frac{Q_1}{t} = \frac{K\,C_u\,A_1\,(T_1-T_2)}{d_1}$$

where T_1 is the temperature of the copper rod at the end in contact with the sample and T_1, at a distance d_1 above it up the rod. The current through the sample when its ends are maintained at temperatures T_2 and T_3 is

$$\frac{Q_1}{t} = \frac{K_S\,A_2\,(T_2-T_3)}{d_S}$$

where d_S is length of the sample rod.

Thus at steady state when the heat flow is linear and convection and other losses are negligible compared to linear heat flow

$$Q_1 = Q_2 \text{ and } A_1 = A_2$$

Then

$$\frac{K_{Cu}\,A\,(T_1-T_2)}{d_1} = \frac{K_S\,A\,(T_2-T_3)}{d_S}$$

Thus from the above expression the thermal conductivity of the unknown sample is given by

$$K_S = \frac{d_S}{d_1}\,K_{Cu}\,\frac{T_1-T_2}{T_2-T_3}\,.$$

Thermal measurement system is given in Figure 1. As seen in this figure the sample is put between two similar copper blocks. The system was covered with a graphite material for heat insulation and reducing

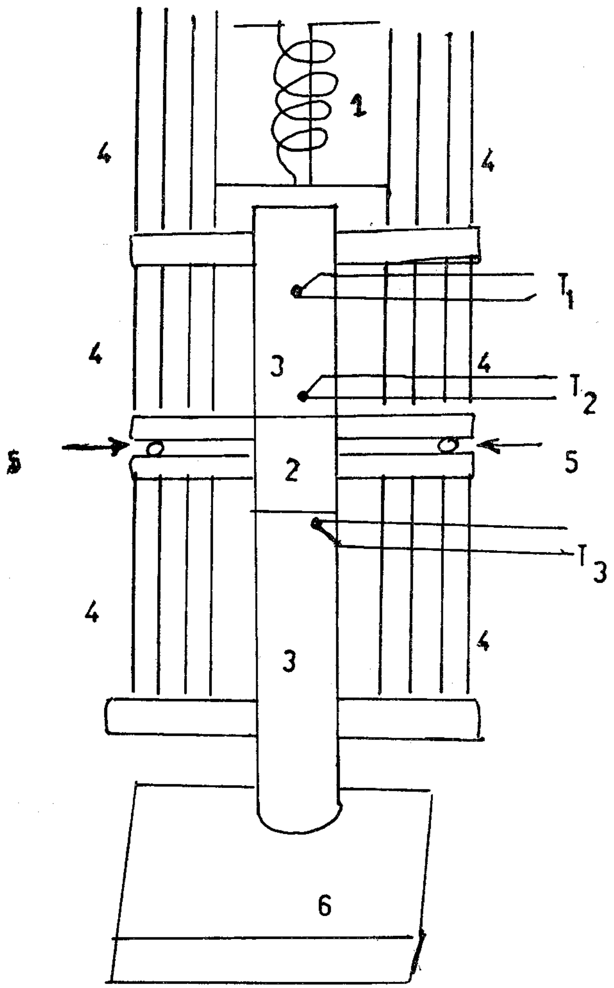

Figure 1. Schematic drawing of a thermal conductivity measurement system. 1: nichrom heater, 2: sample, 3: copper rod, 4: two layers of graphite belt, 5: oring and 6: heat sink.

heat loss. The temperature of T_1, T_2 and T_3 were measured by the three thermocouples. The system was calibrated with known reference sample before going through measurement. Some results are shown in Figure 2 and Table 3.

Thermoelectric Generator Construction

The p-type legs of a thermocouple were prepared with natural galena or galena aggregate by cold pressing. The n-type legs were prepared by dopping galena aggregate with PbCl+Pb. After having made legs they were joined to form thermocouples.

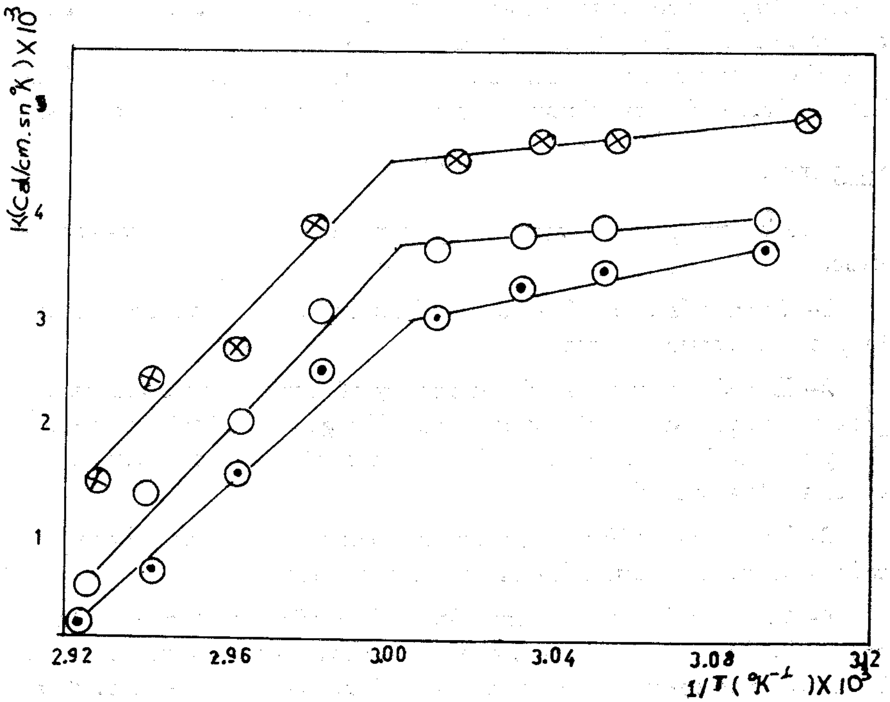

Figure 2. Thermal conductivity versus reciprocal of temperature. +: Pellet prepared from $104x10^3$nm powder, 0: Pellet prepared from $(76–60)x10^3$nm powder, +: Pellet prepared from $53x10^3$nm powder.

Table 3. Variation Of Thermal Conductivity With Hot Surface Temperature.

T (°K)	$\frac{1}{T}$ ($°K^{-3}$)	K (Cal/cm.sn°K)
324.7	$3.08x10^{-3}$	$3.8x10^{-3}$
328.9	3.04	3.2
331.1	3.02	2.5
334.4	2.99	2.0
337.8	2.96	1.2
240.0	2.94	0.8
342.5	2.92	0.5

For the joint procedure the follows: the contact to the n and p type elements were made by first cleaning the end surfaces with emery paper and then applying colloidal graphite paint. The hotside consisted of a thick aluminum plate ower which a thin sheet of mica was placed for electrical insulation. Aluminum foils of proper size were than posted on the mica sheet. A similar arrangement was done on the coldside. The n and p type elements were then placed position over aluminum foils on the hotside. The cold side with pasted aluminum foils was placed over the pellets so as to make series connections of four couples. The hot and cold ends were clamped together with the help of four screws.

RESULTS

The following results were to be obvious after this study was completed.

1– Thermoelectric effects are utilization a thermoelectric circuit to produce power generation.

2– In order to increase the efficiency of thermoelectric generators pellets were prepared different mesh size. We got higher efficiency from the pellets which were made with big size mesh than the pellets were made small size mesh.

3– In achieving final optimum properties doping and alloying to reduce thermal conductivity are important factors.

4– The overall open circuit voltage, V_{0C}, of our system was of the order of 0.15 V and the short circuit current, I_{Sn} was of the order of 25mA for a temperature differences of 200°K. The low values of short circuit current was associated with high contact resistance.

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