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Effects of sintering temperature and time on the electrical properties of pellets made from beneficiated galena ore

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The effects of sintering temperature and time of PbS pellets made by cold pressing of beneficiated galena ore on the room temperature resistivity and room temperature thermoelectric power are reported. The increased resistivity of such pellets with increasing sintering time has been explained in terms of a possible reaction between PbS and PbO leading to compensation of "p"-type conductivity. The increase in thermoelectric power with sintering temperature and time has been explained on the basis of inhomogeneity in the sample following Kwok's approach.

1. Introduction

The present work is an extension of our earlier works [1–6] on the possibility of utilizing naturally occurring galena and beneficiated galena ore for the purpose of making low-cost thermoelectric generators (TEGs). During the work, it became apparent that the conditions of forming the pellets by cold pressing and sintering have a profound influence on their electrical properties. Similar studies were carried out by Bear and Barclay [7 – 9] on the possibility of utilizing such compacts for electrowinning of the metals and other electrochemical work. Our preliminary studies indicated that sintering at higher temperatures, of the order of 950 K, gives better properties to the pellets to be used for thermoelectric generators; data for the effect of sintering at such temperatures was not available. It was thus considered worthwhile to study the effect of sintering temperature up to 950 K and sintering time on the electrical properties of pellets made from beneficiated galena ore collected from Zawar Mines, Rajasthan, India. A model based on inhomogeneity of such a sample is used to explain some of its electrical properties [10, 11].

2. Experimental details

2.1. Materials

Beneficiated galena (concentrated galena) was used in this study. This is the same as that used for manufacturing lead; the ore is beneficiated by separating galena by a froth flotation technique. The beneficiated galena has the general chemical composition (as supplied by Hindustan Zinc Limited, Zawar Mines, Rajasthan, India) shown in Table I.

2.2. Pellet formation by cold pressing and sintering

The beneficiated galena was cold pressed to cylindrical pellets of size 1.27×10^{-2} m ($\frac{1}{2}$ in.) diameter and 1.91×10^{-2} m ($\frac{3}{4}$ in.) length by a hand-operated remote-controlled hydraulic press applying a pressure up to 77.6×10^{6} N m^{-2} (5 ton in.$^{-2}$) maintained constant for 60 sec in a H.S. steel die. These samples were sintered in a nitrogen atmosphere at different temperatures ranging from 350 to 950 K and times varying from 10 min to 12 h. The thermocouple used to measure temperature was placed just above the sample and close to it, inside a tubular quartz furnace and the temperature was maintained constant with the help of a temperature controller.

2.3. Electrical measurement

The resistivity and thermoelectric power (TEP) of the pellets were measured by applying graphite contacts to the two plane surfaces. The sample was placed in a special type of sample holder described elsewhere [12]. In the sample holder, the sample was kept in position by a U-shaped steel clamp with two elongated studs protruding inside. One is a fixed stud while the other can be screwed in and out with the help of a knurled head. The TEP at a desired mean temperature is measured by creating a temperature difference of the order of 10 K between the two ends of the sample using an auxiliary heater. The temperatures of the two ends of the sample were measured using thermocouples brazed to two nickel electrodes. The resistance was measured using an LCR bridge and the thermo e.m.f. was measured with a d.c. microvoltmeter with an input impedance of 1 MΩ.

2.4. X-ray line profile measurement

The X-ray diffractograms of the samples were recorded with the help of a Norelco X-ray diffractometer employing Cu$K\alpha$ radiation from a tube operated at 35 kV and 10 mA and a scanning speed of $\frac{1}{4}°$ min^{-1}. The integral breadths of the X-ray line-profiles were measured by dividing the area of the peak by the intensity.

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TABLE I Composition of beneficiated galena, collected from three different places in the Zawar Mines, Rajasthan, India

Elements/compounds	Mochia Mongra lodes	Barai Magra lodes	Zawar Mala lodes
Pb (%)	68.2	66.5	62.2
Zn (%)	5.7	1.9	4.5
Fe (%)	2.1	2.01	4.0
Insoluble (%)	1.1	3.5	1.57
Ca (present in the form of $CaCO_3$) (%)	2.0	1.65	0.88
Mg (present in the form of $MgCO_3$) (%)	0.65	1.34	0.48
Co (p.p.m.)	8	–	24
Ni (p.p.m.)	26	0.9%	28
Mn (%)	0.04	0.087	0.076
Cu (p.p.m.)	380	680	260
Cd (p.p.m.)	320	50	238
S (%)	12.9	11.78	14.3
Sb (p.p.m.)	560	–	–
Ag (p.p.m.)	1020	130	1150
Al_2O_3 (%)	1.77	1.14	0.24

3. Results

3.1. Effect of sintering temperature on room temperature resistivity of pellets for a fixed sintering time

The room-temperature resistivity of the pellets made from beneficiated galena by cold pressing at $77.6 \times 10^6\,N\,m^{-2}$ (5 ton in.$^{-2}$) and pressed for 60 sec was of the order of $6.8 \times 10^3\,\Omega\,cm$. When such pellets were sintered for 1 h at different temperatures, ranging from 350 to 850 K, the room-temperature resistivity decreased. The variation of log room temperature resistivity (log ϱ) with reciprocal sintering temperature is shown in Fig. 1. The figure shows that the curve has three regions, AB, BC and CD. In the first range AB (350 to 430 K), the curve has an activation energy of $E_{AB} = 0.410\,eV$. In the second range BC (430 to 525 K), the activation energy is $E_{BC} = 0.022\,eV$. In the third region CD (525 to 850 K), E_{CD} rises to 0.660 eV.

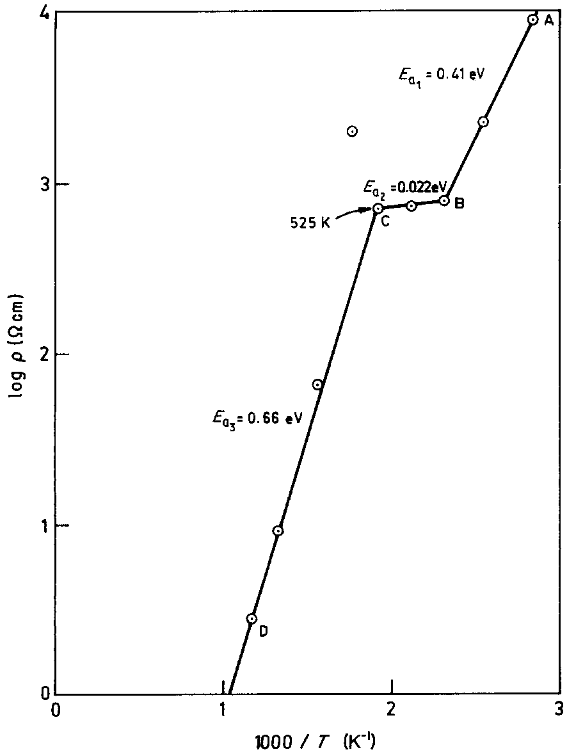

Figure 1 The variation of room temperature resistivity of pellets made from beneficiated galena with sintering temperatures for a fixed sintering time (1 h).

3.2. Effect of time of sintering on room temperature resistivity for a fixed sintering temperature

The pellets prepared in a similar manner, were sintered at 700 K for 10 to 60 min. It was seen that the resistivity decreases with increasing the sintering time. The log–log plot of room-temperature resistivity against sintering time as shown in Fig. 2, indicates that the resistivity decreases rapidly up to 30 min (AB) and after that the rate of decrease is reduced. The gradient of the two lines "AB" and "BC" is −2.30 and −0.66, respectively. Similar plots for another set of pellets which were sintered at 950 K for 10 min to 12 h, show that resistivity first decreases up to 30 min and after that it starts increasing. The log–log plot of room-temperature resistivity against sintering time (Fig. 3) shows that the resistivity decreases up to 30 min (AB), where the slope of the line AB = −0.703 and after 30 min, the resistivity starts increasing continuously. The slope of this line BC = +1.26.

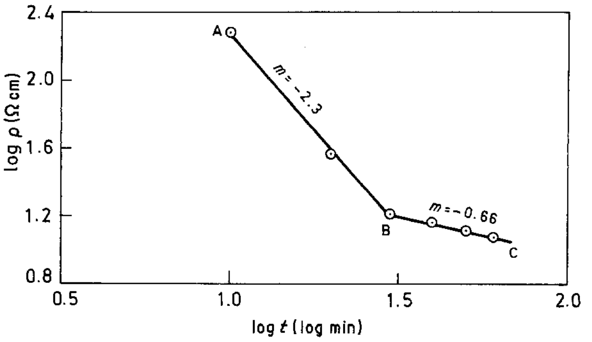

Figure 2 The variation of room-temperature resistivity of pellets made from beneficiated galena with sintering time for a fixed temperature of 700 K.

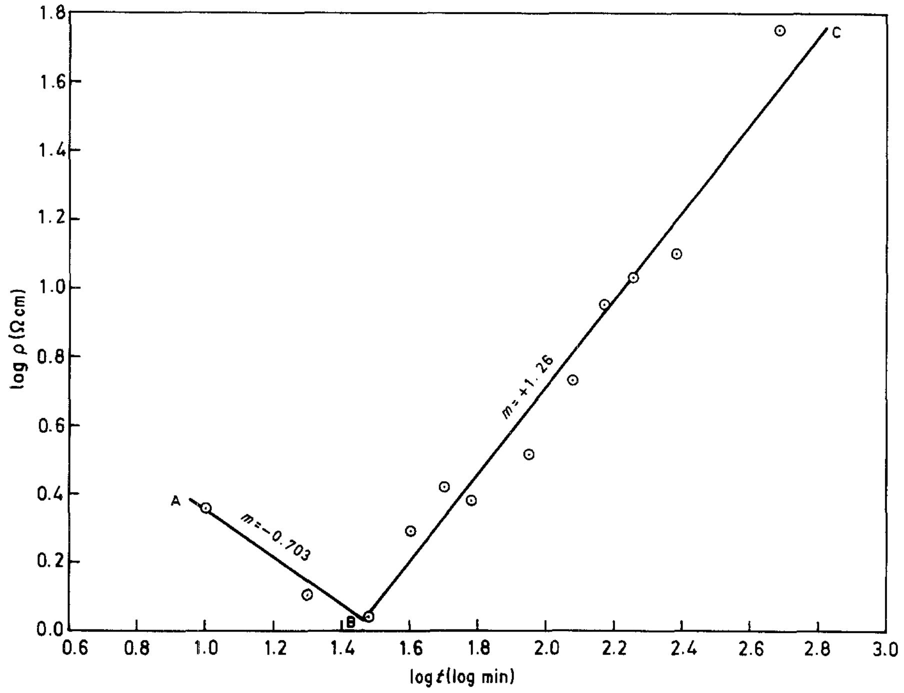

Figure 3 The variation of room-temperature resistivity of pellets made from beneficiated galena with sintering time for a fixed temperature of 950 K.

3.3. Effect of sintering temperature for a fixed sintering time on room-temperature thermoelectric power

From the thermoelectric power measurement, it was found that the cold-pressed beneficiated galena sintered at any temperature and for any duration showed "p"-type conduction only. The variation of room-temperature thermoelectric power (TEP) of pellets as a function of sintering temperature, with the sintering time kept constant at 1 h, is shown in Fig. 4a. In Fig. 4b, log α is plotted against reciprocal of sintering temperature. It shows that TEP decreases with increasing sintering temperature up to 575 K, with an activation energy of 0.025 eV. After about 575 K the increase in sintering temperature increases TEP with an activation energy of 0.077 eV.

3.4. Effect of time of sintering on room temperature thermoelectric power for a fixed sintering temperature

The variation of thermoelectric power (TEP) with sintering time at 700 K is shown in Fig. 5. It shows that up to a time of 20 min the TEP decreases with increasing time. After this TEP begins to rise slowly

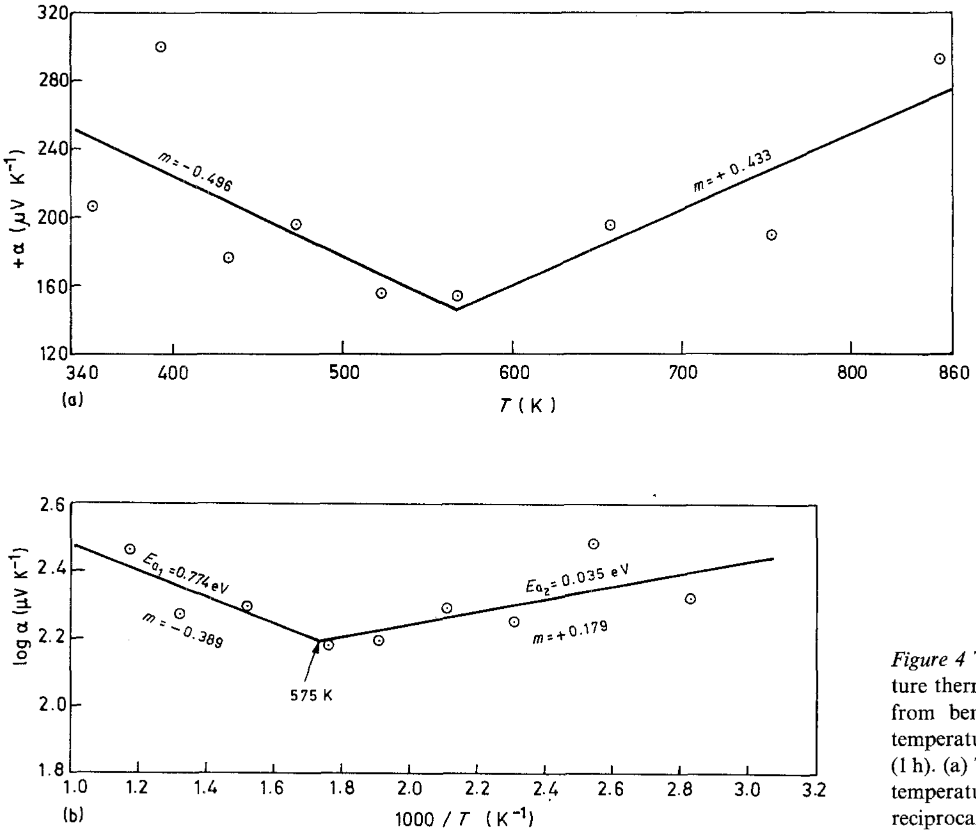

Figure 4 The variation of room temperature thermoelectric power of pellets made from beneficiated galena with sintering temperatures for a fixed sintering time (1 h). (a) TEP (α) plotted against sintering temperature. (b) log α plotted against reciprocal of sintering temperature.

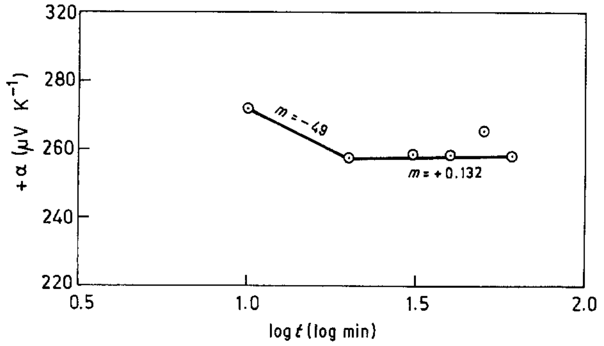

Figure 5 The variation of room-temperature thermoelectric power of pellets made from beneficiated galena with sintering time for a fixed temperature of 700 K.

with increasing time. The variation of TEP with sintering time at 950 K is shown in Fig. 6. At this temperature (950 K) too, TEP decreases with increasing time up to 20 min, but with a higher rate of decrease (slope $m = -140$) compared to sintering at 700 K (slope $m = -49.0$). After 20 min TEP begins to increase with increasing time. Here also the rate of increase is faster compared to sintering at 700 K. The slopes are $m_{950} = +8.00$ and $m_{700} = +0.132$.

3.5. X-ray analysis data on the effect of sintering

The value of lattice parameter a calculated from X-ray diffractograms indicates a value of 0.594 nm, which agrees well with the standard value for PbS [13]. The effect of sintering at 950 K for 12 h on the structure of pellets as monitored by the width of various X-ray diffraction lines is shown in Table II. It is seen that the sintering temperature increases the integral width of the diffraction lines, suggesting an increased concentration of lattice defects when sintered at 950 K for 12 h.

4. Discussion

When the beneficiated ore of galena is cold-pressed, the resistivity of the pellet is very high, of the order of $7 \times 10^3\,\Omega\,\mathrm{cm}$. This high value of resistivity is supposed to be associated with resistance offered by grain boundaries. On sintering, a "neck" is formed between grains by a diffusion process which may be either surface diffusion, grain-boundary diffusion or volume diffusion depending upon the temperature range [14]. It has been stated [15] that surface diffusion operates above $0.23T_m$, where T_m is the melting point of powder on an absolute scale, (its value is 319 K for beneficiated galena ore), whereas the volume diffusion proceeds at an appreciable rate above $0.33T_m$ (458 K in the case of beneficiated ore). Bear and Barclay [8] studied in detail the mechanism of sintering in hot-pressed PbS compacts. According to them resistivity decrease with temperature can be accounted for by the increase in the radius of the "neck" between the particles [7, 8, 16, 17]. This change in resistivity for a constant pressure and fixed sintering time is given by an expression of the type

$$\varrho = A e^{-E/KT} \qquad (1)$$

where A is a constant and E is the activation energy appropriate to the type of diffusion process in operation.

The experimental curve of variation of resistivity as a function of temperature can be represented by an equation of the form

$$\varrho = A_1 e^{-E_1/KT} + A_2 e^{-E_2/KT} + A_3 e^{-E_3/KT} \qquad (2)$$

where $E_1 = 0.41\,\mathrm{eV}$, $E_2 = 0.022\,\mathrm{eV}$ and $E_3 = 0.66\,\mathrm{eV}$. This suggests that three different types of mechanism are in operation, depending on the temperature. Generally, activation energy for volume diffusion is more than grain boundary diffusion which is more than surface diffusion [15, 20] and so in the range beyond 450 K the volume diffusion mechanism seems to predominate.

In such a model, the variation of resistivity with sintering time at a given temperature is given by

$$\varrho = a t^{2/m} \qquad (3)$$

where m is a constant depending on the mechanism of diffusion.

The results of the present work on the variation of room-temperature resistivity with sintering time for two different sintering temperatures, show that in the log–log plot of resistivity against time of sintering, two different slopes occur, depending on the sintering time and the sintering temperature, indicating two different mechanisms of change of resistivity with sintering time. Because sintering temperature is the same for a given curve, the diffusion mechanism would not change with sintering time. As such the change in slope of these curves should be due to some other mechanism by which resistivity changes occur, in addition to the decrease in resistivity due to increase in

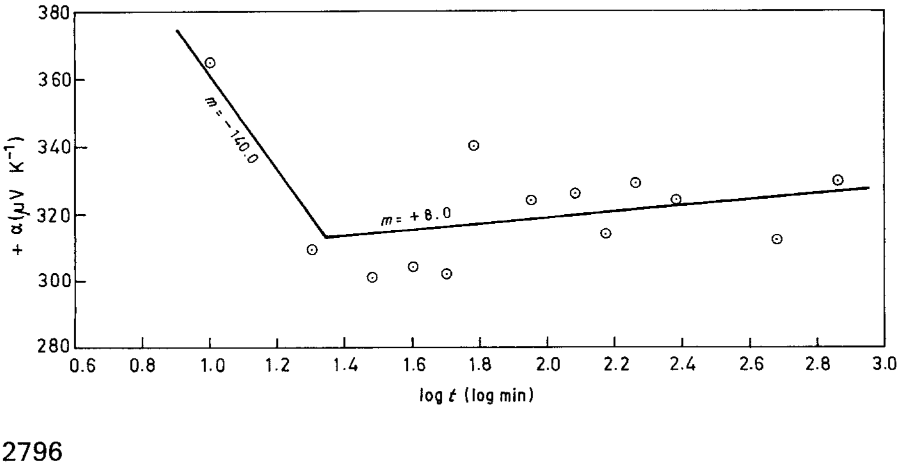

Figure 6 The variation of room-temperature thermoelectric power of pellets made from beneficiated galena with sintering time for a fixed temperature of 950 K.

TABLE II X-ray analysis for beneficiated galena, before and after sintering (950 K)

Standard values of lead sulphide		1st set of pellets prepared from beneficiated galena				2nd set of pellets prepared from beneficiated galena			
		Before sintering		After sintering		Before sintering		After sintering	
Corresponding planes ($h\,k\,l$)	d (nm)	d (nm)	$\beta_{2\theta}$* (10^{-3} rad)	d (nm)	$\beta_{2\theta}$ (10^{-3} rad)	d (nm)	$\beta_{2\theta}$ (10^{-3} rad)	d (nm)	$\beta_{2\theta}$ (10^{-3} rad)
1 1 1	0.3429	0.3433	4.19	0.3419	6.11	0.3480	5.59	0.3410	6.98
2 0 0	0.2969	0.2963	5.24	0.2964	5.24	0.2953	4.89	0.2959	5.41
2 2 2	0.1714	0.1715	7.16	0.1713	8.20	0.1718	7.85	0.1710	7.85
4 0 0	0.1484	0.1485	6.11	0.1479	8.90	0.1489	7.33	0.1482	10.12

*The integral breadth of the X-ray line profile.

"neck" radius. The clue for such a mechanism is given by the curve obtained after sintering at 950 K. In this case (Fig. 3) the resistivity decreases up to 30 min after which it begins to increase with increasing time. As increasing sintering time would always increase the "neck radius" this mechanism tries to reduce the resistance of the compacts with increasing time. The increase in resistance with time might be due to compensation effects of lead atoms produced by the reaction of the following type in the "p"-type concentrate particles:

$$PbS + 2PbO = 3Pb + SO_2 \qquad (4)$$

The rate of this reaction would increase with temperature hence the slope of log ϱ against log t changes slowly in the case of sintering at lower temperature (700 K), because it is not possible to neutralize fully the decrease in resistivity due to increase in neck radius. However, when the temperature is increased to 950 K the reaction proceeds at a faster rate so that it is not only able to compensate the decrease in resistivity due to neck formation but leads to a net increase in resistivity.

Support for such a picture is provided by the fact that the width of the X-ray diffraction lines from sintered pellets is greater than that of those from as-formed pellets. The width of X-ray lines increases when defects in crystallites are increased (as shown in Table II) from which one can conclude that the sintered pellets have larger defects. Larger defects could have been produced by the reaction stated in Equation 4, leading to evolution of SO_2 and the formation of lead atoms. It is well known that the introduction of defects increases the resistivity, so this may be another mechanism of increase of resistance with sintering time.

The room-temperature thermoelectric power of the pellets sintered at different temperatures (from 350 to 950 K for 1 h), decreases with increasing sintering temperature up to 575 K (Fig. 4). This behaviour is quite similar to that of a homogeneous semiconductor for which

$$\alpha_p = \frac{K}{e}\left[A + \ln\left(\frac{N_v}{p}\right)\right] \qquad (5)$$

where N_v is the effective density of states in the valency band and p is the carrier concentration. But above 575 K, TEP begins to increase, whereas the corresponding resistivity decreases (Fig. 1). Such a contradiction can be explained if one considers the actual structure of compacts and the fact that such a change starts above the critical temperature, above which volume diffusion begins to predominate.

The lead sulphide particles in the compact are likely to be covered by a layer of PbO due to surface oxidation. When a compact with such particles is sintered, the PbO on the surface of the particles reacts with PbS leading to formation of lead and evolution of SO_2. These lead atoms are initially incorporated in "p"-type PbS particles by diffusion, leading to compensation. Thus the outer layer of PbS particles would have a lower concentration of holes compared to the inner core. As time proceeds or temperature increases for a given time, the length of the outer core would increase.

Thus the compact can be considered to consist of PbS particles having an inner core of length L_2 and carrier concentration p_2 and an outer core of carrier concentration p_1 of length L_1. The thermoelectric power of such a system has been considered by Kwok [10]. According to him the measured thermoelectric power, α_{av}, of such an inhomogeneous sample is given by:

$$\alpha_{av} = \frac{K}{q}\left[A + \ln N_v - \frac{1}{1 + L_2/L_1}\ln p_1 - \frac{1}{1 + L_1/L_2}\ln p_2\right] \qquad (6)$$

where A is a constant whose value lies between 2 and 4 depending on the type of scattering mechanism. In the case of PbS we take $A = 4$ [21].

Fig. 7 shows a plot of the calculated value of α_{av} for various values of L_1/L_2; for different values of p_1 and p_2. The value of p_1 has been taken as $10^{17}\,cm^{-3}$ and p_2 has been varied from 1.18×10^{18} to $1.03 \times 10^{19}\,cm^{-3}$. The graph shows that for all these cases, which are likely to occur due to the reaction given in Equation 4, the measured TEP should increase with increase in the ratio L_1/L_2. As mentioned earlier, the ratio of L_1/L_2 will increase due to compensation of the "p"-type layer by the incorporation of lead atoms, when either the sintering temperature is increased or when the sintering time is increased at a fixed temperature. However, the increase in TEP with increasing sintering temperature for a fixed time would be much faster, compared to the increase of TEP with sintering time at a fixed temperature.

5. Conclusions

From the above discussion it can be concluded that in order to produce compacts having low resistivity in the shortest possible time, they should be sintered at

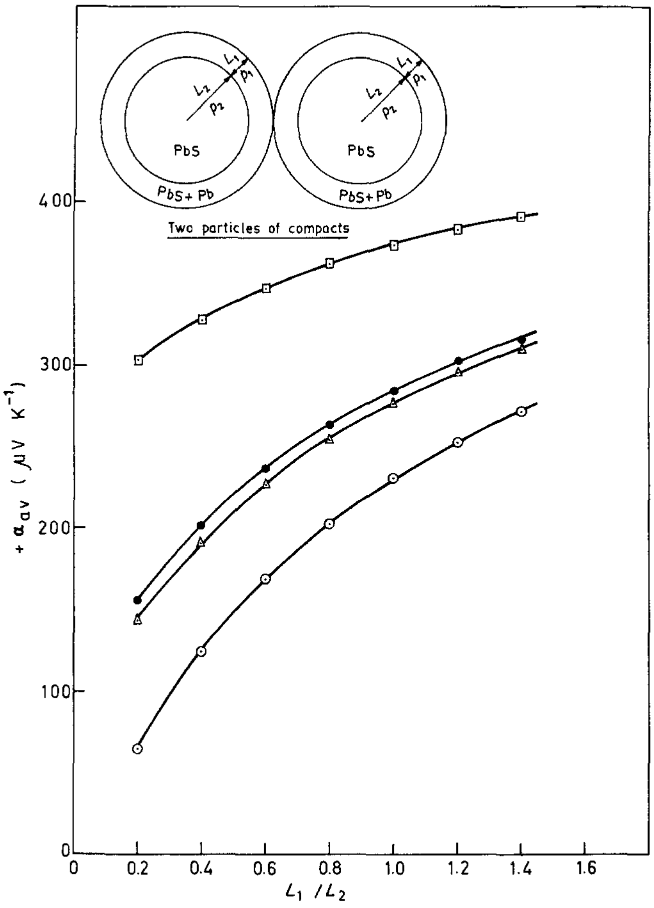

Figure 7 Variation of theoretically calculated thermoelectric power with L_1/L_2 for different values of p_2 and fixed value of $p_1 = 10^{17}\,\mathrm{cm}^{-3}$. p_1 = Surface carrier concentration of holes. p_2 = Bulk carrier concentration of holes. $p_1 < p_2$. $p_1 = 10^{17}\,\mathrm{cm}^{-3}$, (●) $p_2 = 8.858 \times 10^{18}\,\mathrm{cm}^{-3}$, (□) $p_2 = 1.12 \times 10^{18}\,\mathrm{cm}^{-3}$, (○) $p_2 = 3.12 \times 10^{19}\,\mathrm{cm}^{-3}$, (△) $p_2 = 1.038 \times 10^{19}\,\mathrm{cm}^{-3}$.

high temperature (950 K) but for a time less than 30 min. The change in resistivity and TEP with sintering temperature and time suggests that the resistance of compacts is changed by two effects: the increase in neck radius leads to a decrease in resistance whereas incorporation of lead atoms from a reaction between PbS and PbO leads to an increase in resistance. The inhomogeneous structure produced by this reaction would lead to an increase in TEP with sintering temperature and time.

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