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X-ray Identification of n-PbTe Sublimate and the Dependence of the Rate of Sublimation on the Cover Gas Pressure

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Abstract. Lead telluride and its related materials sublimate at high temperature. This could result in a change in stoichiometry due to the preferential loss of one of the constituents, which in turn alters the carrier concentration hence the thermoelectric properties of the material. The onset of sublimation started at 838K and a cover gas pressure of $1.38X10^5Nm^{-2}$. Negligible mass losses ($<10^{-8}$kg) were noticed during the heating cycle below 838K, but became detectable above 923K. Losses increased as the temperature approached 973K. X-ray studies showed that PbTe sublimes as molecular PbTe and not as Pb or Te atoms, accompanied by a slight shift in stoichiometry towards Te-deficiency. The rate of sublimation decreased significantly with increasing cover gas pressure when heated at 973K. A reduction of 50% in the rate of sublimation is achieved when the cover gas pressure varied from $1.722X10^5Nm^{-2}$ to $3.79x10^5Nm^{-2}$. A further reduction in the rate of sublimation could be achieved by applying higher gas pressures provided the equipment can withstand it. The measured rate of sublimation at 973K is 30 per cent lower than the calculated rate as predicted by theory.

Introduction

Lead telluride (PbTe) and its solid solutions, as a bulk material or thin films, are promising materials for use in thermoelectric generation [2-12,22], laser industry and micro-electronics [23-27]. PbTe is a semiconductor with an energy gap of 0.3 eV. Its crystal structure is face centered cubic (FCC) with a lattice constant $a_0=6.50\pm0.02$ [1-2]. The melting point of un-doped PbTe is 1190K for 50 at. % Te and has a density of $8.15x10^3kgm^{-3}$. The electrical properties of PbTe are greatly affected by adding foreign atoms to its lattice. PbTe can be made n-type or p-type semiconductor by slightly changing its stoichiometry, (Pb-rich PbTe is n-type, while Te-rich PbTe is p-type) or by introducing some impurities to the matrix [3-12].

A thermoelectric power generator consists of many thermocouples. A thermocouple consists of n-type and p-type arms joined at a junction and produces a low voltage and a high current. To obtain a high voltage a number of thermocouples are connected electrically in series and thermally in parallel to form a module. The module is heated at one end (hot side) and a temperature gradient maintained with respect to the other end (cold side).

The efficiency of a thermoelectric power generator in converting heat energy into electrical energy depends upon the figure -of-merit Z of the thermocouple material [13-14]:

$$Z = \frac{\alpha^2}{\lambda}\sigma \tag{1}$$

where α is the Seebeck coefficient, σ the electrical conductivity and λ the thermal conductivity. All these parameters are functions of the carrier concentration.

PbTe sublimes at high temperatures, and may thus results in a change in its stoichiometry. This change could be attributed to a preferential loss of one of its constituents which alters the carrier concentration and hence affects the thermoelectric properties of the material.

Field and Bunde [15] derived the following formula to calculate the rate of sublimation of PbTe under the application of a positive gas pressure:

$$\Gamma = \frac{2\pi r_0}{p\eta}\alpha_0 T^{1/2}\exp(-E_a / R_0 T) \tag{2}$$

where Γ is the rate of sublimation (kg/m^2.s), r_o is the radius of a cylinder shape specimen (m), α_o is the proportionality constant, T is the absolute temperature, P is the surrounding gas pressure (N/m^2), E_a is the activation energy of sublimation of n-PbTe (6.56x10^{5}J/kg), R_0 is the universal gas constant (24.81 J/kg.K), and η is a constant that depends on the inert gas, and it equals unity in the case of argon gas.

The aim of our study is to identify the n-PbTe sublimate and to suppress or minimize the rate of its sublimation. This aim can be achieved by applying different positive gas pressures of argon in order to keep the thermoelectric properties of the material unchanged when heated at high temperature. Also it aims to verify the validity of the predicted formula of Field and Bunde [15].

Experimental

(a) Identification of the PbTe sublimate:

A sample of n-PbTe was heated in an evacuated silica ampule at 973K for 8h in a vertical tube furnace along which was established a temperature gradient. The sublimate was collected and ground to a fine powder. Sample identification was carried out by an x-ray diffractometer with Co-K$_\alpha$ line(−1.79021 Å) operated at 40 kV and 20 mA with a graphite monochromator. X-ray diffraction patterns of the original starting material and of the PbTe sublimate were obtained.

(b) Dependence of the rate of sublimation of n-PbTe on cover gas pressure:

Parallelopiped shaped samples were cut from the n-PbTe ingot using a low speed diamond saw. The specimen was weighed and its dimensions measured using a precision micrometer before it was put in a silica tube inside the furnace. The silica tube was connected to a vacuum system with a facility which enabled it to be evacuated then filled with argon gas to the desired pressure. The temperature of the furnace was raised to 973K using an Eurotherm programer/controller. The temperature was measured with S-type thermocouple with accuracy of ± 1K. After two hours of heating at 973K, the furnace was switched off and left to cool to about 393K. The specimen was then taken out of the furnace, weighed and the loss in weight was calculated.

The above procedure was repeated four times using the same specimen to give a total heating time of 8h. The same procedure was repeated under different cover gas pressures. A new specimen is being used in each experiment. The rate of sublimation is readily calculated from the slopes of the graphs of weight loss versus time of annealing and the total surface area of the corresponding specimen.

The following cover gas pressures were used: $0.6886\text{x}10^5$, $1.033\text{x}10^5$, $1.337\text{x}10^5$, $1.722\text{x}10^5$, $2.754\text{x}10^5$ and $2.4\text{x}10^5 \text{N/m}^2$.

Results and Discussion

The x-ray diffraction patterns of the n-PbTe sublimate and the n-PbTe original starting material are shown in Fig.1. It shows that the sublimate has the same lines as the starting material with a very slight shift towards smaller angles, i.e., towards Te-deficiency. No lines that correspond to any of the constituents were detected. This indicates that PbTe evaporation from the surface of PbTe occurs as molecular PbTe and not as atomic Pb or Te. The lattice parameters are calculated. Corrected values of the lattice parameters were obtained using the Nelson-Reily extrapolation function [16]. The corrected values of our measured lattice parameters are shown in Table 1 together with published values for PbTe. Table 1 shows that our data are in close agreement with that reported by Rustamov et al [7], and Rosi [17], and differs slightly from those given by Reimer [18] and Pashinkin and Novoselova [19]. This difference could be due to the purity of the starting material used in preparing PbTe. Pashinkin and Novoselova [19] used a 99.99% purity starting materials which had been further purified, while Rustamov et al [7] used a 99.999% purity materials. From their chemical analysis data of PbTe and its sublimates, Pashinkin et al [19] showed that the sublimate has slightly more Te than the original materials and slightly less Pb, which again is in agreement with our x-ray measurement.

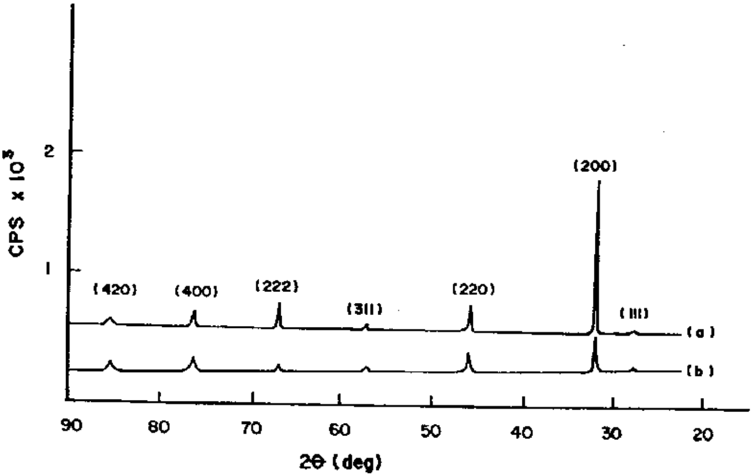

Fig.1. X-ray diffraction patterns of: a) n-PbTe starting material (original); b) n-PbTe sublimate.

Table 1. Comparison of the lattice constant of n-PbTe original material and the n-PbTe sublimate with the published data

Material	Lattice constant	Reference
PbTe (Original)	6.464	Present work
	6.464	ref.7
	6.50 ± 0.02	ref.18
	6.44	ref.19
	6.439 ± 0.006	ref.21
	6.46	ref.17
PbTe (Sublimate)	6.4584	Present work
	6.44	ref.19

Evaporation of PbTe started at 838K at a cover gas pressure of $1.337 \times 10^5 Nm^{-2}$. Negligible mass losses ($<10^{-8}$kg) were observed during the heating cycle below 838K, and became more detectable above 923K. The losses increased as the temperature approached 973K, as shown in Fig.2. The loss in mass at 973K, after equal heating time intervals of two hours from the beginning of experiment was determined at different cover gas pressures and is shown in Fig.3. The calculated rate of sublimation using equation (2) and the measured rate of sublimation as a function of cover gas pressure are presented in Fig.4. The calculated rate is based on a fixed sample radius of 0.318x10^{-2}m. The temperature which was used in the calculation is the same temperature used in the experiments (973K).

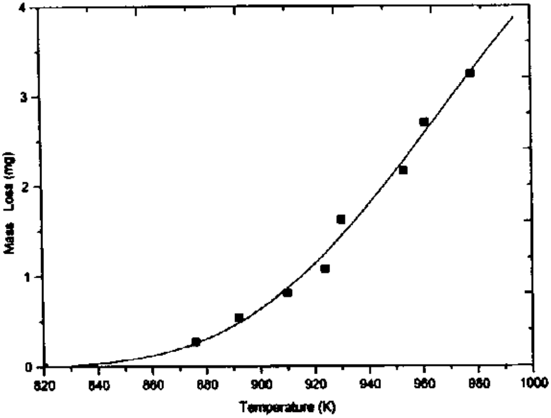

Fig. 2. Variation of the mass loss of n-PbTe material with temperature taken at a cover gas pressure of 1.38x10^{5}Nm^{-2}.

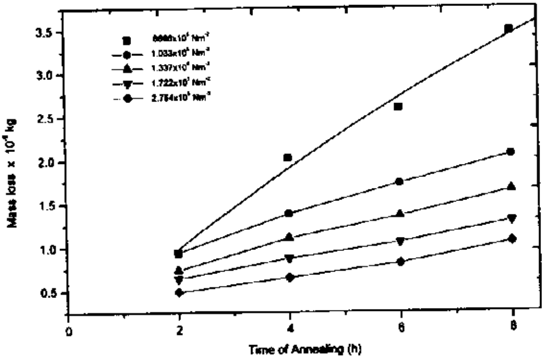

Fig. 3. Variation of the mass loss of n-PbTe material with cover gas pressure and time of annealing at 973K.

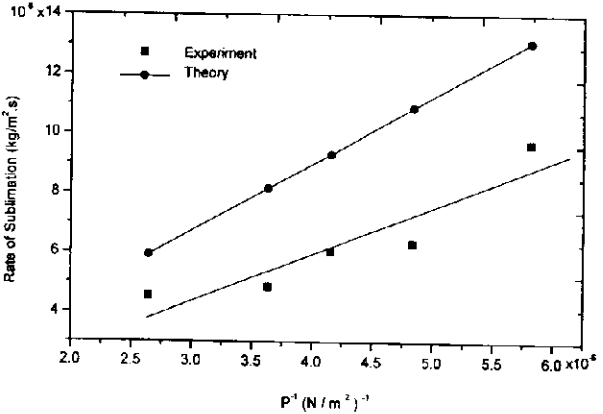

Fig. 4. Variation of the rate of sublimation of n-PbTe material with cover gas pressure P, at 973K.

Field and Bunde [15] calculated the rate of sublimation at 873K for n-PbTe. It was $2.1x10^{-7}$ kg/m^2.s at $1.722x10^5$Nm^{-2}. Killian [20] showed that the rate of sublimation for n-PbTe ranged from $9x10^{-8}$kg/m^2.s at 673K to $6x10^{-4}$kg/m^2.s at 873K in vacuum.

For p-PbTe, the rate of sublimation varied from $1.9x10^{-6}$kg/m^2.s at 723K to $7x10^{-3}$kg/m^2.s at 873K in vacuum, i.e. one order of magnitude higher than n-PbTe under the same conditions [20].

Our measured rate of sublimation varied significantly with increasing cover gas pressure as shown in Fig.4. It decreased from $9.69x10^{-6}$kg/m^2.s at $1.722x10^5$N/m^2 to $4.52x10^{-6}$kg/m^2.s at $3.79x10^5$N/m^2; a reduction of 50% was achieved. A further reduction in the rate of sublimation could be attained by applying higher gas pressures provided the equipment can withstand it. Also, we found that the measured rate of sublimation is about 30 per cent lower than the calculated rate from equation (2), as shown in Fig.4. A Good agreement of eq.2 with experimental curve is achieved by choosing a value of $1.3555x10^{12}$ for the proportionality constant α_o in eq.2, as shown in Fig.5.

From this study, the vacuum deposition of PbTe layers on proper substrates for thermoelectric applications [21] could be a useful technique as sputtering deposition of superlattices of semiconductors [22] and using molecular beam epitaxy to grow epitaxial layers of PbTe doped with Bi on BaF_2 (111) substrates [23]. Degradation of the structure at high Bi-concentrations in PbTe occurs due to the formation of a ternary $Pb_{1-x}Bi_xTe$ and this degradation was indicated by surface images obtained by atomic force microscopy.

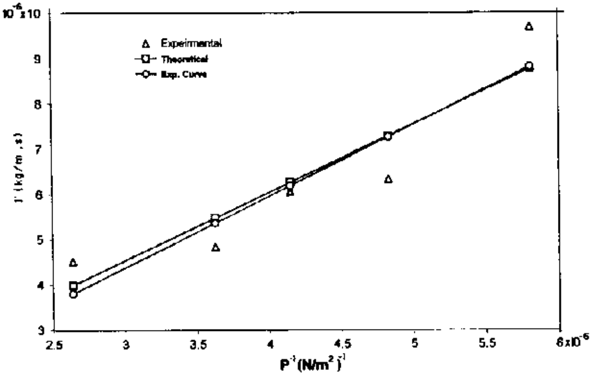

Fig. 5. Variation of the rate of sublimation of n-PbTe material with cover gas pressure P, at 973K. Best fitting of the experimental results with eq.2.

Yardanov [24,25] has taken into account the scattering by composition fluctuations according to the band structure of the system p-$Pb_{1-x}Sn_xTe$ solid solution. The peculiarities in the dependence of the hole mobility on the composition existing at 77K were interpreted by band inversion and scattering by the composition fluctuations.

Recent study to improve the oxidation resistance of PbTe was by coating PbTe by SiO_2-ZnO-B_2O_3-Na_2O system glass with various composition [26]. It showed that PbTe coated by the glass containing 60 mass% PbO.TeO_2 exhibited excellent oxidation resistance and showed no mass changes at 773K for 360ks.

The decrease in carrier mobility of PbTe thin films with fine grains fabricated by gas evaporation method was greatly decreased by the grain boundaries and of the oxidation [27].

Conclusion

It is concluded that PbTe evaporation from the surface of PbTe occurs as molecular PbTe and not as atomic Pb or Te. Applying positive cover gas pressure of an inert gas during the preparation and annealing processes of PbTe has proved to minimize the rate of sublimation at high temperatures. Consequently, the transport properties of this material will not deteriorate due to sublimation of dopant or any of the alloy constituents.

References

[1] Rowe D.M. and Bahandari, C.M. *Modern Thermoelectrics*. London: Holt Technology, 1983.

[2] Shunk, A. *Constituents of Binary Alloys*. New York: McGraw Hill, 1969.

[3] Borrisova, L., Decheva, St. and Dimintrova, St. "Preparation and Properties of the System (Ag x/2 Pb 1-x Bi x/2)Te." *Bulg.J. Phys*., 3 (1976) 307-310.

[4] Borrisova, L. Dimitrova, S.K., Histakudis, H. and Histakudi, T.A. "On Some Kinetic Parameters of the (PbTe)1-x (BiTe)x Systems At 0<x<0.02." *Bulg. J. Phys*., 9 (1982), 284-291.

[5] Borrisova, D., Berchenko, M.A. and Vulchev,V.D. "Electric Properties of n-Type Lead Telluride Doped with Chromium." *Bulg. J. Phys*., 9 (1962) 642-649.

[6] Brebrick, R.F. and Gubner, E. "Composition Stability of PbTe." *J. Chem. Phys*., 36 (1962), 1283-1289.

[7] Rustamov, P.G., Alidzhanov, M.A. and Abilov, Ch.I. "Effect of Partially Substitution of Lead by Gallium, Indium, and Thallium on Thermoelectric Properties of PbTe." *Phys.Sat.Sol*., 12 (1972), K103-K107.

[8] Strauss, A.J. "Effect of Pb- and Te-Saturation on Carrier Concentrations in Impurity-doped PbTe." *J. Electronic Materials*, 2 (1973), 553-569.

[9] Borrisova, L.D. "Thermoelectric Properties of Impurities Doped PbTe." *Phys. Stat. Sol*., 53 (1979), K19-K23.

[10] Weiser, K. "Doping of PbTe with Group III Elements: An Ionic Lattice Approach." *Phys. Rev., B*. 23 (1981), 2741-2751.

[11] Borrisova, L.D., Vulchev, V.D., Dimitrova, S.K. and Histakudis, G.Kh. "Thermoelectric Properties of Lead Telluride with Bismuth Impurities." *Bulg. J. Phys*. 9 (1982), 634-641.

[12] Koval'Chik, T.L. and Maslakovets, Iu P. "Effect of Impurities on the Electric Properties of Lead Telluride." *Sov.Phys. Tech.Phys*.,1 (1957), 2337-2349.

[13] Ioffe, F. *Semiconductor Thermoelements and Thermoelectric Cooling*. London: *Infosearch*, 1957.

[14] Goldsmid, J. *Applications of Thermoelectricity*. London: Methuen Monograph, 1960.

[15] Field, D.R. and Bunde, G.W. "A Model to Describe Long Term Performance Characteristics of Pressure Contacted Lead-Telluride Thermoelectric Generators." Space and Defence Products Department, 3M Company, St. Paul, Minnesota, U.S.A., (1968 Record) 425-430.

[16] Nelson, J.B. and Riley, D.P. "An Experimental Investigation of Extrapolation Methods in the Deviation of Accurate Unit-Cell Dimensions of Crystals." *Proc. Phys. Soc*., London, 7(1945), 160-177.

[17] Rosi, F.D. "Semiconducting Materials for Thermoelectric Power Generation." *RCA Review*, 22 (1961) 82-121.

[18] Reimer, L. "The Structure of PbTe Evaporated Layers." *Naturwissenschaften*, 44 (1957), 416-17.

[19] Pashinkin, A.S. and Novoselova, A.V. "Determination of the Standard Vapour Pressure of Solid Lead Telluride." *Russ J. Inorg.Chem*., 4 (1959), 1229-1231.

[20] Killian, J.W. "A Method to Asset the Weight Loss of PbTe. "Intersociety Energy Conversion Engineering Conference, " 1968 Record, August 13-17 (1968), 272-276.

[21] Parris, P.K., Mukherjee, D, Hogarth, C.A. "Electrical and Optical Properties of Vacuum Deposited Lead Telluride Layers. " *Phys. Stat. Solidi, A*, 152, 2 (1995), 461-6.

[22] Wagner, A.V., Foreman, R.J., Farmer, J.C., Barbee,Jr, T.W. "Sputtering Deposition of Semiconductor Superlattices for Thermoelectric Applications. " *Mater. Res. Soc*. (Philadelphia, PA,USA) (1997), 465-72.

[23] Ueta, A.Y., Springholz, G., Schinagl, F., Marschner, G., Bauer, G. "Doping Studies for Molecular Beam Epitaxy of PbTe and Pb$_{1-x}$Eu$_x$Te. " *Thin Solid Films*, 306, 2 (1997), 321-6.

[24] Yordanov, S.P. "Transport Phenomena in p-Pb$_{1-x}$Sn$_x$Te Solid Solutions. I. " *Bulg. J. Phys*., 17, 1 (1990), 6.

[25] Yordanov, S.P. "Transport Phenomena in p-Pb$_{1-x}$Sn$_x$Te Solid Solutions.II. Two Band Kane Model-Analysis of the Results. " *Bulg. J. Phys*., 18, 1 (1991), 15-28.

[26] Chen, L., Goto, T. Yu, Hirai, R.Tu.T. "Oxidation Resistance of Glass Coated PbTe. " *IEEE* (USA) (1998), 539-42.

[27] Ito, O., Won-Son Seo, Kounoto, K. "Thermoelectric Properties of PbTe Thin Films Prepared by Gas Evaporation Method. " *J. Mater. Res*., 14, 1 (1999), 209-12.

التعرف على بخار n-PbTe باستخدام الأشعة السينية

اعتماد معدل التبخر على ضغط الغاز المحيط

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ملخص البحث. يتبخرتوليريد الرصاص والمواد المشتقة منه عند درجات الحرارة المرتفعة مما يؤدي إلى تغير في نسبة المكونات نظرا لإمكانية الفقد المفضل لأحد هذه المكونات والتي تؤدي بدورها إلى تغير في تركيز النواقل وبالتالي في الصفات الكهروحرارية للمادة. يبدأ التبخر عند ٨٣٨ كلفن وضغط غاز خارجي ١,٣٨ × ١٠^{٥} ن م^{٢}.

بينت التجربة أن الكتلة المفقودة قليلة جدا (أصغر من ١٠$^{-٨}$ كجم) أثناء عملية التسخين عند أقل من ٨٣٨ كلفن، لكنه أصبح محسوسا أكثر فوق ٩٢٣ كلفن. إزداد الفقد عندما اقتربت درجة الحرارة من ٩٧٣ كلفن. بينت الدراسة، باستخدام حيود الأشعة السينية، أن PbTe يتبخر كجزيء PbTe وليس كذرات من Pb أو Te مصحوبا بميل قليل في نسبة مكوناته نحو نقص في Te. انخفض معدل التبخر بشكل ملحوظ مع زيادة ضغط الغاز المحيط عندما سخنت عند ٩٧٣ كلفن. حصل انخفاض قدره ٥٠٪ من معدل التبخر عندما غير ضغط الغاز من ١,٧٢٢ × ١٠^{٥} ن م$^{-٢}$ إلى ٣,٧٩ × ١٠^{٥} ن م$^{-٢}$. يمكن الحصول على انخفاض أكبر في معدل التبخر بتطبيق ضغوط أعلى من الغاز بشرط أن يستطيع الجهاز تحمل هذا الضغط. إن معدل التبخر المقاس عند ٩٧٣ كلفن يقل بمقدار ٣٠٪ عن المعدل الذي تتنبأ به الحسابات النظرية.