

Title	Deviation from Stoichiometry in PbSe and its Stable Range
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Editor(s)	
Citation	Bulletin of University of Osaka Prefecture. Series A, Engineering and natural sciences. 1962, 11(1), p.89-98
Issue Date	1962-09-28
URL	http://hdl.handle.net/10466/8008
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Deviation from Stoichiometry in PbSe and its Stable Range

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(Received June 30, 1962)

Deviation from stoichiometry in PbSe is controlled by the heat treatment under a specified selenium pressure. Cooling along the p - n transition boundary (i boundary) is found to be efficacious in order to obtain uniform specimen with low carrier concentration. Melting point of PbSe with deviation from stoichiometry is determined by the thermal analysis of the freezing process under a specified selenium pressure. Stability limit with excess lead is obtained through a thermochemical calculation of standard free energy of formation. Stable range of PbSe is given on P-T-x diagram including equi-composition contours.

1. Introduction

Different from the case for elemental semiconductors, in the case of compound semiconductors with volatile constituent there are additional difficulties for their synthesis, purification and crystal growth. One of the main causes for these difficulties is the deviation from stoichiometric composition and this deviation plays very significant roles on the electrical properties. The vapor pressure of the more volatile component is often fairly high at the temperatures required during the process of preparation and adequate precautions must be taken to maintain the compound in stoichiometric or in some specified composition. The purpose of this work is to check the possibility of controlling the deviation from stoichiometry by regulating the partial pressure of the more volatile constituent.

There are many investigations^{1)~8)} on the properties of lead sulphide group of semiconductors, especially on PbS very elaborate results were reported by J. Bloem *et al.*²⁾ But on PbSe there are few studies which pay attentions for the deviation from stoichiometry. Recent approach by R. F. Brebrick *et al.*⁹⁾ gives some information on its stability limits. P-T-x (pressure-temperature-composition) diagram can afford the most fundamental information on the deviation from stoichiometry, in this work efforts are made to establish P-T-x diagram for PbSe and to define its stability limits as a function of selenium pressure and temperature.

PbSe is a compound semiconductor, stable over a narrow composition range, it may take up either excess lead resulting in n -type specimen or excess selenium giving p -type material. Component elements can be obtained in very pure state and single crystal of this compound can be grown fairly easily by Bridgman technique. One of the characteristic properties of this compound is its high carrier mobility and this high mobility

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can be used as a measure of the high purity of the prepared specimen. After equilibrating the specimen at a given temperature to a given selenium pressure, it is water quenched and carrier concentration and carrier mobility are determined from Hall effect and conductivity measurements. The stability limit in equilibrium with lead on P-T-x diagram is obtained through thermochemical calculation of standard free energy of formation of PbSe, and melting point of PbSe with deviation from stoichiometry is determined by thermal analysis of freezing process under a specified selenium pressure.

2. Experimental

Single crystal bowl of PbSe is grown from nearly stoichiometric melt which is vacuum sealed into a quartz tube. Starting materials are 5-nine selenium (American Smelting and Refining Co.) and zone refined 6-nine lead (Asahi Metal Manufacturing Co.). Thin specimen approximately 2 mm in thickness is cleaved from this bowl. This specimen is argon sealed into a quartz tube and heat treated under a specified partial pressure of selenium. The partial pressure of selenium is controlled by regulating the temperature of selenium which is sealed in the same quartz tube at separate position. Temperatures are controlled with the accuracy of $\pm 3^\circ\text{C}$, corresponding variation in selenium pressure reaches as high as $\pm 20\%$ at lower pressure. After being kept at a given temperature for a given duration, the specimen as sealed in quartz tube is water quenched and its thermoelectric power is measured at room temperature in the air. The *i* boundary by which *n*-type with excess lead is separated from *p*-type with excess selenium can be determined through a series of such measurements.

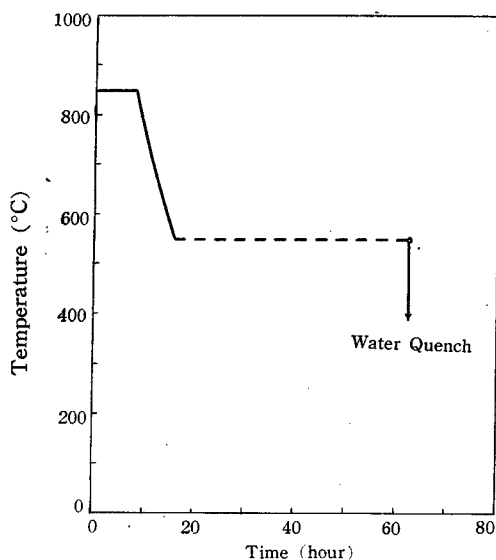


Fig. 1 Typical example of cooling along *i* boundary and heat treatment for the purpose to obtain low carrier concentration.

solid line — along *i* boundary

broken line — small deviation from *i* boundary

Specimen for Hall effect and conductivity measurements (*ca.* $5 \times 1.5 \times 1.5$ mm) is heat treated similarly in a specified selenium pressure. In order to get an uniform specimen with lower carrier concentration, it is found to be efficacious to cool it along this *i* boundary and then to treat at a lower temperature. Unless it may result into a non-uniform material or it may take much longer time to attain equilibrium. Typical example of such a treatment is shown in Fig. 1. After the heat treatment specimen is water quenched and Hall effect and conductivity measurements are made by conventional *d-c* method over a temperature range from 77°K to room temperature. As contact leads 0.075 mm ϕ Pt wires are used and welded to the specimen by condenser discharge in argon atmosphere.

Thermal analysis of the freezing process under a specified selenium pressure is performed on the similar principle as above, using a set up shown in Fig. 2. Melt composition does depend not only on selenium pressure but also on the temperature at which melt has been kept. But when this temperature is too close to the freezing temperature, resolution of thermal analysis curve is too low to give a clear freezing temperature. Usually melt is kept at about 10°C above its freezing temperature, in order to have not too much supercooling and sufficiently high resolution on thermal analysis. Supercooling is not larger than 3°C and freezing temperature can be determined in the error within $\pm 2^\circ\text{C}$.

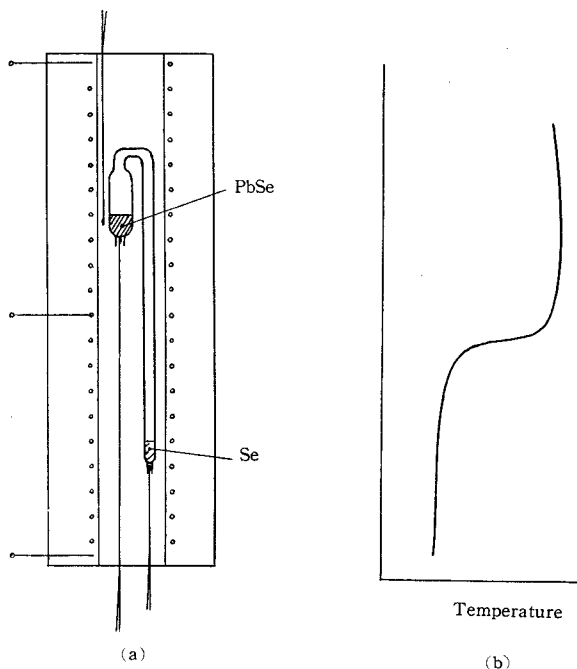


Fig. 2 Set up used for thermal analysis of freezing process under a specified selenium pressure (a) and an example of the temperature profile (b).

3. Results

(a) *i* boundary There is no available data on the *p-n* transition *i* boundary for PbSe.

In this work i boundary for PbSe is determined from the measurement of thermoelectric power of quenched specimen. Thermoelectric power is shown as a function of selenium pressure in Fig. 3. Specimen which is equilibrated at 1230°K to a selenium pressure higher than 0.7 mmHg is shown to be p -type and which is equilibrated to a lower pressure is n -type. Selenium pressure corresponding to this i boundary P_{Se}^i is determined from a series of these measurements and can be expressed in the following equation for the temperature range from 800°K to 1230°K.

$$\log P_{Se}^i = -9500/T + 7.4 \quad (\text{in mmHg})$$

where T is temperature at which specimen is equilibrated to selenium pressure.

This boundary is shown as line FG on P-T-x diagram Fig. 6.

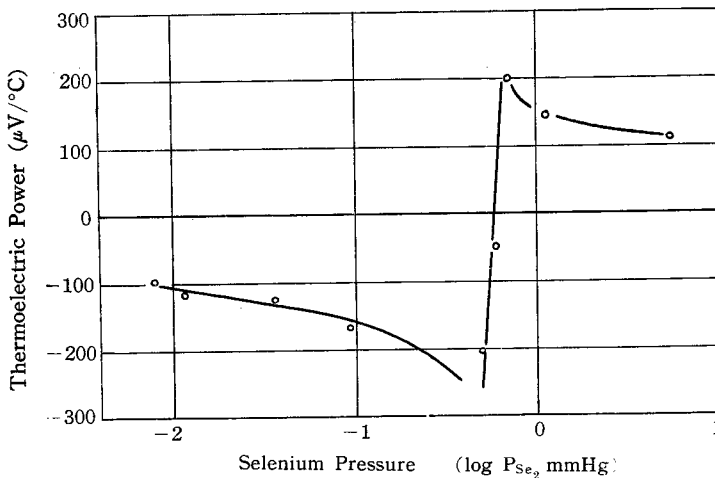


Fig. 3 Thermoelectric power as a function of selenium pressure. Specimen is water quenched from 1230°K, after equilibrating to various Se pressure.

(b) **Carrier concentration** Information on the carrier concentration is obtained from Hall coefficient R at the exhaustion range. For most specimen Hall coefficient is nearly constant for the entire temperature range, but estimation of carrier concentration only from the knowledge at room temperature may lead to a wrong conclusion because room temperature can not be always in the exhaustion range. Specimen with low carrier concentration, for example less than $5 \times 10^{16} \text{ cm}^{-3}$, shows rather prominent decrease in Hall coefficient with the increase of temperature above 200°K, possibly due to the occurrence of intrinsic conduction. Carrier concentration is extending over a wide range from 10^{16} to 10^{19} cm^{-3} , and it is rather inadequate to draw a clear border line between Maxwell-Boltzmann and Fermi-Dirac statistics. Therefore in this report carrier concentration n is estimated from the following relation, tentatively assuming classical statistics, and single type of carrier, $n=1/Re$, where e is charge of electron. Carrier concentration as a function of selenium pressure is shown in Fig. 4, temperature at which specimen is brought into equilibrium is shown as a parameter. Similar results for other temperatures

make possible to draw equi-concentration curves on P-T-x diagram, as shown in Fig. 6. Relation between carrier concentration and composition is referred by R. F. Brebrick *et al.*¹⁰⁾ for this group of semiconductors, equi-concentration curves can be safely regarded as equivalent to equi-composition curves. Lack of data for low selenium pressure is caused from the fact that a state for total pressure minimum may predominate for such a low pressure and PbSe condenses at the tube wall of cooler portion. Equilibrium state to such a low pressure can not be obtained in this experiment using closed vessel.

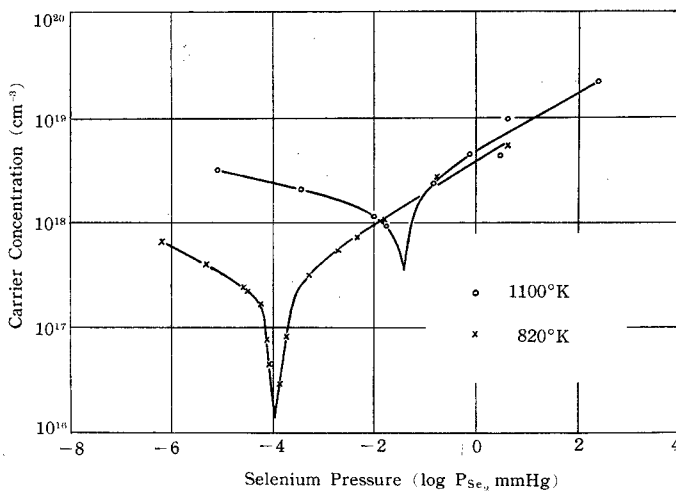


Fig. 4 Carrier concentration as a function of selenium pressure. Temperature at which specimen is brought into equilibrium is shown as parameter.

(c) **Melting point of PbSe with deviation from stoichiometry** Cooling curves are read on K-type potentiometer for the freezing process of PbSe under a specified selenium pressure. Some representative curves are shown in Fig. 5. It is rather seldom to observe a clear temperature plateau, but peak temperature after supercooling can not differ from its melting point more than 2°C. With the decreasing selenium pressure melting point increases and passing a maximum then begins to decrease. The highest melting point obtained in this experiment is 1351°K and agrees quite well with the available data.^{11)~12)} These melting points are plotted as border line ACD on P-T-x diagram (Fig. 6). From the same reason mentioned in the previous section (b), data for low selenium pressure is not obtained in this experiment. Broken line portion on CD line should be accepted with large ambiguity.

(d) **Stability limit of PbSe** From the phase diagram of Pb-Se system^{11)~12)} it is known that the solid phase PbSe may coexist with pure component element at the lower temperature than 950°K. As the first approximation, stability limit of PbSe is worked out assuming that PbSe can coexist with pure component element. Anyhow it is true that stable range of PbSe can not extend over these limits.

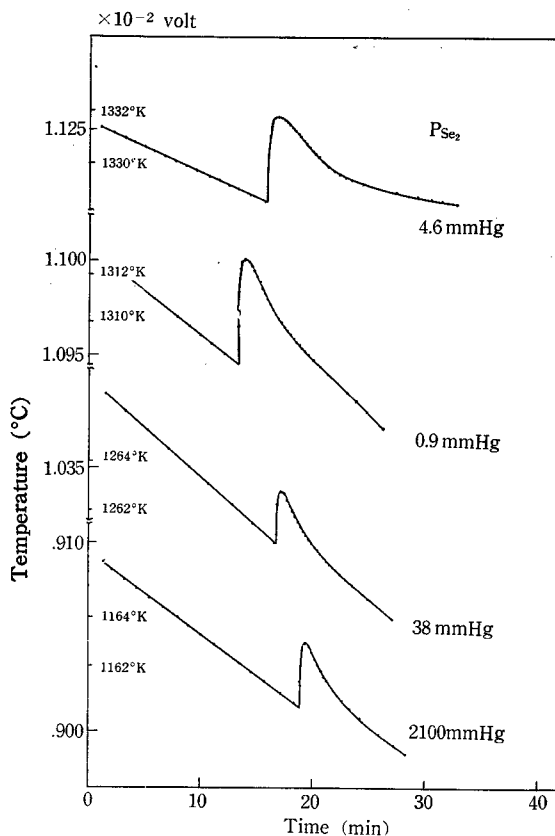


Fig. 5 Thermal analysis of freezing process under a specified selenium pressure. Selenium pressure is shown as parameter.

Upper line AB in P-T-x diagram (Fig. 6) is the pressure of pure selenium, and is easily obtained from the table of physical and chemical constants.¹⁵⁾ Lower line DE is the selenium pressure corresponding to the pressure of pure lead. Procedures to determine this line DE will be given in the following. If dissociation constant of PbSe is determined from the knowledge of the standard free energy of formation, the selenium pressure corresponding to the pressure of pure lead will be easily obtained. The standard free energy of formation of PbSe is obtained by C. B. Finch *et al.*¹³⁾ from the electromotive force measurements, and is expressed in the following equation.

$$\Delta G_T^0(1) = -23,352 + 3.8 \times (T - 523) \text{ cal.} \quad (\text{A})$$

This equation is for the reaction



and is valid for the temperature range T: 490°–573°K. Starting from this relation, estimation is made on the standard free energy of formation, valid to higher temperature and to gas phase reaction, using the thermal data of component elements and some probable assumptions.

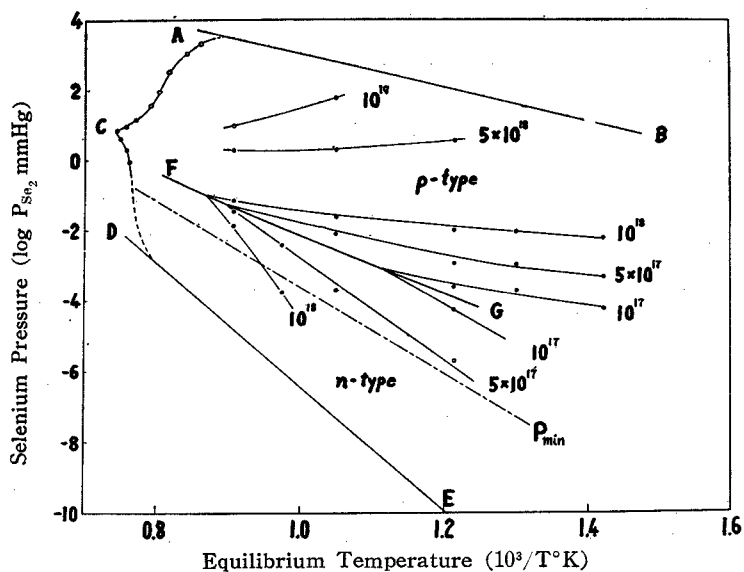


Fig. 6 P-T-x diagram of PbSe.

AB — pressure of pure selenium

C — highest melting point

DE — selenium pressure corresponding to the pressure of pure lead

 FG — *i* boundary

Consider the following change,



latent heat of fusion and specific heat of liquid and solid lead are available,¹⁵⁾ therefore standard way of calculation gives the free energy change for this change

$$\Delta G_T^0(2) = -420 + 2.11T \ln T - 1.515 \times 10^{-3}T^2 - 12.05T \quad (B)$$

Similarly for the change



$$\Delta G_T^0(3) = -46,627 - 2.78T \ln T + 0.365 \times 10^{-3}T^2 + 43.48T \quad (C)$$

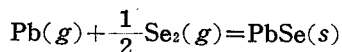
But for the change



there is no available data for the specific heat of Se₂(*g*). For these diatomic molecule gases the difference in the specific heat is mainly due to the difference in the characteristic temperature for vibration θ_v . Using the analogy of the dependence of θ_v on the atomic weight for several series of similar elements with the same configuration of outer shell electrons, θ_v for Se₂ gas is estimated to be 750°K. Further taking into consideration C_p for S₂(*g*) and Te₂(*g*), $C_p\left[\frac{1}{2}\text{Se}_2(g)\right]$ is assumed to be 4.385. Then the free energy change for the change (4) is given as

$$\Delta G_T^0(4) = -16,885 - 2.615T \ln T + 34.945T \quad (D)$$

Accordingly, for the reaction (1)+(2)+(3)+(4), that is,



the standard free energy of formation is obtained as (A)+(B)+(C)+(D), and is expressed in the following equation

$$\Delta G_T^0 = -89,271 - 3.285T \ln T - 1.15 \times 10^{-3}T^2 + 70.175T$$

Assuming only ideal gases to be involved, reaction isotherm becomes $-\Delta G_T^0 = NkT \ln K$ where Nk is gas constant, K is equilibrium constant for gaseous system and $1/K$ is equal to $P_{\text{Pb}} \times (P_{\text{Se}_2})^{1/2}$ in atm. From this relation, selenium pressure corresponding to the pressure of pure lead is calculated as is shown in Table 1. These values are plotted on P-T-x diagram (Fig. 6) as line DE. At a fixed temperature $P_{\text{Pb}} \times (P_{\text{Se}_2})^{1/2}$ is constant, therefore it is easily shown that total pressure $P_{\text{Tot}} = P_{\text{Pb}} + P_{\text{Se}_2}$ becomes minimum for

$$P_{\text{Se}_2} = \frac{1}{2} P_{\text{Pb}} = (2)^{-2/3} K^{-2/3}. \quad (\text{in atm.})$$

Selenium pressure corresponding to the minimum total pressure is shown as P_{min} in Fig. 6. In the above treatment, the contribution from the partial pressure of PbSe is neglected, but this pressure may reach to a comparable order of magnitude with that of the component elements and PbSe is known to evaporate in molecular form of PbSe.¹⁴⁾ However there is no available thermal data on liquid or gaseous PbSe, therefore this contribution can not be estimated. Also, effects caused by the deviation from stoichiometry are not taken into consideration. It must be admitted that the border line DE corresponding to the equilibrium with excess lead has its significance as the first approximation.

Table 1. Calculation of the selenium pressure corresponding to the pressure of pure lead.

Temp. (°K)	ΔG_T^0 (cal)	$-\log_{10}K$	P_{Pb} (mmHg)	P_{Se_2} (mmHg)
700	-55,779	-17.417	1.6×10^{-5}	2.5×10^{-17}
900	-47,160	-11.453	1.26×10^{-3}	3.42×10^{-9}
1100	-38,780	-7.706	9.7×10^{-2}	1.83×10^{-5}
1300	-30,666	-5.156	2.05	5.08×10^{-3}

4. Consideration

Deviation from stoichiometry in PbSe can be controlled by the proper heat treatment under a regulated selenium pressure. The best procedure to obtain an uniform specimen with a specified carrier concentration is to cool the specimen along the corresponding

equi-concentration curve. In order to obtain low carrier concentration it is recommended to cool along i boundary at the higher temperature range and then along the equi-concentration curve corresponding to the expected carrier concentration. Careful consideration must be taken to obtain a uniform specimen, because the improper heat treatment may give rise to a non-uniform specimen. In such a case, properties of the surface regions and the inner regions may differ significantly and anomalous effects may be observed on Hall measurements even to cause an apparent change of its sign.

The lowest carrier concentration obtained in our laboratory is $2.9 \times 10^{16} \text{ cm}^{-3}$ for p -type, this value is lower than any one previously reported including for natural or vapor growth crystals. The highest mobility obtained is $4.3 \times 10^4 \text{ cm}^2/\text{V}\cdot\text{sec}$ at 77°K for holes and is higher than any one previously reported. From this fact it is known that the specimen prepared in this laboratory is of sufficient high purity and the contamination effects from the heat treatment are not serious.

Electrical properties on the specimen with the controlled deviation from stoichiometry will be reported in other papers.

Some informations obtained from P-T-x diagram will be raised in the following.

(i) The aspect of P-T-x diagram of PbSe is quite similar to that of PbS, except that the composition with highest melting point is in the p -type region.

(ii) The best control of the freezing process itself would not give a specimen with carrier concentration less than 10^{18} cm^{-3} . Heat treatment at the lower temperature under a specified selenium pressure is indispensable to obtain uniform low carrier concentration.

(iii) The reason why natural single crystal or vapor growth crystal often shows lower carrier concentration than that of the crystal grown from its melt, is easily understandable from the aspect of P-T-x diagram. Vapor growth technique still leaves some difficulties unresolved, such as to control the nucleation site or growth orientation, but it may be one of the most promising techniques for obtaining uniform specimen with controlled deviation from stoichiometry.

Deviation from stoichiometric composition is one of the most important problems in the field of semiconducting intermetallic compounds, serious effects from this deviation are clearly observed for PbSe and the necessary procedures to obtain a uniform specimen with a specified carrier concentration are described.

Stable range of PbSe is obtained as a function of selenium pressure and temperature, P-T-x diagram for PbSe is established including the equi-concentration curves in it.

5. Acknowledgement

The authors wish to acknowledge gratefully the cooperation of Mr. T. Shimada, Mr. H. Tanaka and Mr. T. Uyeda during the course of this study. Thanks are also due to the Hayakawa Electric Corporation for the loan of some experimental facilities.

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