

# Phase relations in the system PbS–PbSe–PbTe

H. LIU

AND

L. L. Y. CHANG

Department of Geology, University of Maryland, College Park, Maryland 20742, U.S.A.

## Abstract

Phase relations in the system PbS–PbSe–PbTe were investigated in the temperature range between 1150 and 300°C. There is a complete solid solution series along the join PbS–PbSe, whereas miscibility gaps exist below ~350°C and 805°C along joins PbSe–PbTe and PbS–PbTe, respectively. Both gaps extend into the ternary system, and the range of the gap between PbS and PbTe reduces in size with temperature as well as Se-content.

By using the subregular model of mixing (Ganguly and Saxena, 1987), mixing energetics and activity-composition relations of PbX were derived. The temperature-dependence of the interaction parameters was calculated to be  $5057.6 - 1.7T$ ,  $9605.2 - 4.4T$ ,  $3933.2 - 3.1T$  ( $T < 500^\circ\text{C}$ ),  $6410.3 - 6.35T$  ( $T < 500^\circ\text{C}$ ),  $1649 - 0.26T$ ,  $1594.6 - 0.2T$ , and  $12906.3 - 17.3T$  for  $W_{\text{STe}}$ ,  $W_{\text{TeS}}$ ,  $W_{\text{SeTe}}$ ,  $W_{\text{TeSe}}$ ,  $W_{\text{SSe}}$ ,  $W_{\text{SeS}}$ , and  $W_{\text{SSeTe}}$ , respectively. A critical temperature along the join PbS–PbSe at ~100°C was obtained from interaction parameter calculation, which suggests the separation of the PbS–PbSe series.

Correlation of solid-solution ranges established in this study with natural occurrences was made.

**KEYWORDS:** lead chalcogenides, phase relations, thermodynamics, PbS–PbSe–PbTe system.

## Introduction

LEAD forms a single compound with each of the three chalcogen elements, and the chalcogenides, PbS, PbSe and PbTe all have the NaCl-type structure. Galena (PbS) is one of the most abundant sulphide minerals, and forms major ore deposits whereas clausthalite (PbSe) and altaite (PbTe) are relatively rare. Between galena and clausthalite, intermediate members have been prepared (Earley, 1950), and natural occurrences of the entire series are known (Coleman, 1959; Kovalenker *et al.*, 1971; Gavrilenko, 1987). The common occurrence of altaite is predominantly in association with galena, and the existence of a miscibility gap has been reported between PbS and PbTe (Darrow *et al.*, 1966). In this study, experimental determination of phase relations and of the role of selenium as an intermediary between sulphur and tellurium was made in the system PbS–PbSe–PbTe.

## Experimental procedures

Starting compositions were prepared from reagent grade lead, sulphur, selenium and tellurium; all have 99.95% purity or better. Heat treatment was made in electric furnaces in which the temperatures were controlled to within  $\pm 2^\circ\text{C}$  and the conventional technique of sealed, evacuated glass capsules (Kullerud and Yoder, 1959) was used. Generally, the duration of treatment ranged from 60 days at 500°C, 30 days at 600°C, 7 days at 700°C, and 3 days at 800°C, 1 day at 900°C to 0.25 of a day at and above 1000°C. Experimental runs at 300°C were made with chloride flux for a period of 150 days. At the end of heat treatment, the samples were quenched by compressed air. As a test of equilibrium, some samples were heated to complete melting, quenched, ground under acetone, and annealed at the desired temperatures for the same length of time as their counterparts. If the final assemblages show no differences caused

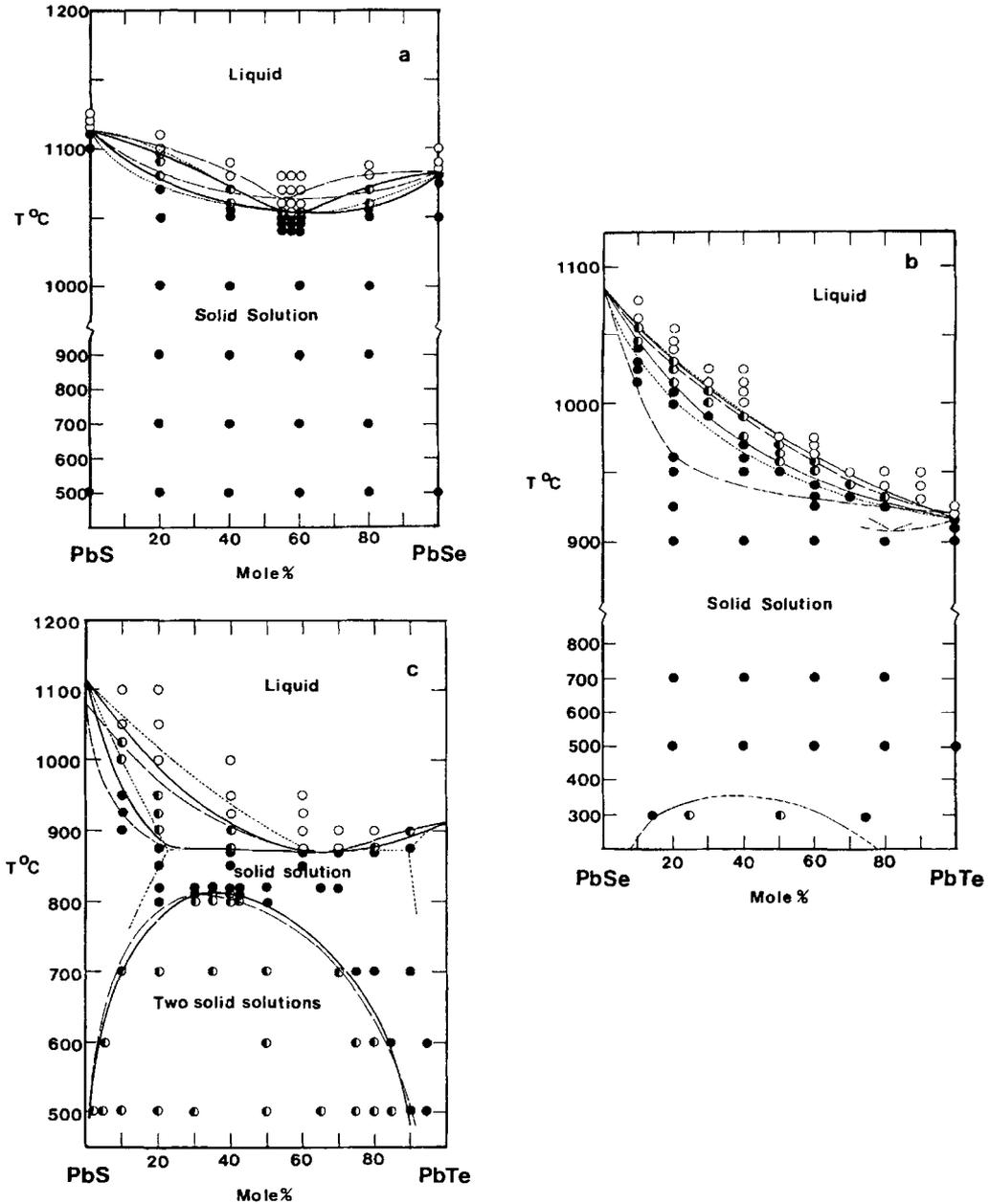


FIG. 1. Phase relations along the joins PbS-PbSe, PbSe-PbTe and PbS-PbTe with experimental data represented by open circle for liquid phase, solid circle for solid phase, and half-filled circle for two-phase assemblage. (a) The join PbS-PbSe. Two previous studies, Gromakov *et al.* (1963) and Malevskii (1963), are illustrated by broken lines and dotted lines, respectively; (b) The join PbSe-PbTe. Three previous studies, Steininger (1970), Grimes (1965), and Elagina and Abrikosov (1956), are illustrated by dotted lines, broken lines, and bar-and-dot lines, respectively; and (c) The join PbS-PbTe. Two previous studies, Gromakov (1965) and Darrow *et al.* (1966), are illustrated by dotted lines and broken lines, respectively.

by changing the procedure, equilibrium is assumed to have been attained.

X-ray powder diffraction, reflected-light microscopy and electron microprobe analysis were used for phase characterization. Cell dimensions were computed to  $\pm 0.003$  Å by using a least-squares refinement program (Benoit, 1987). Solidus and liquidus were drawn based on microscopic observations and the error is estimated to be  $< 2.5^\circ\text{C}$ . Phase boundaries in the subsolidus region were constructed mostly on the basis of cell dimensions or phase compositions; each gives a precision of 0.5 mol.%. When these data were not available, the phase disappearance method was used.

#### Phase-relations along the binary joins

The PbS–PbSe join was first studied by Earley (1950). He prepared four compositions at 20 mol.% intervals between the end members and treated them at fusion temperatures. Based upon a linear relationship between cell dimension and composition, Earley proposed a complete series of solid solutions between PbS and PbSe. The series was verified by Simpson (1961) and by Wright *et al.* (1965) with hydrothermal experiments at temperatures down to  $300^\circ\text{C}$ . Malevskii (1963) and Gromakov *et al.* (1964) presented melting relations along this join as shown in Fig. 1a with results obtained in the present study. Results from all studies correlate well, although both liquidus and solidus of the present study match the curves of Malevskii better than those of Gromakov. Simpson also determined the melting in this series. His curves have a much narrower separation within  $20^\circ\text{C}$  between  $1080^\circ$  and  $1100^\circ\text{C}$  except the melting point of PbS ( $1109^\circ\text{C}$ ). The minimum point established by the present study is at  $1053^\circ\text{C}$  and 43 mol.% PbS.

Along the PbSe–PbTe join, previous studies were restricted to temperatures greater than  $850^\circ\text{C}$ . Elagina and Abrikosov (1956) reported a complete series of solid solutions with a minimum at 18 mol.% PbSe and a temperature estimated to be  $904^\circ\text{C}$  from their diagram. Grimes (1965) and Steininger (1970) confirmed the existence of the complete series, but indicated that the temperatures of both solidus and liquidus increase with increasing Se content. Results obtained in the present study as shown in Fig. 1b agree well with Steininger's diagram. Grimes' solidus has comparatively lower temperatures. In addition, the present study extends the equilibrium relations to  $300^\circ\text{C}$  and established a miscibility gap at  $300^\circ\text{C}$ .

Phase relations along the PbS–PbTe join were studied by several investigators, but the results are in dispute. Yamamoto (1956) obtained practically no mutual solubility between PbS and PbTe, whereas Sindeyeva and Godovikov (1959) reported very limited ranges of solid solutions. Malevskii (1963) found 7 mol.% PbTe in PbS and 18 mol.% PbS in PbTe at  $886^\circ\text{C}$ . Gromakov *et al.* (1964) proposed a phase diagram for the PbS–PbTe join showing a eutectic point at  $870^\circ\text{C}$  and 36 mol.% PbS. Ranges of terminal solid solution were proposed, but only outlined with dashed lines. Darrow *et al.* (1966) found a complete series of solid solutions along the join which is stable over a narrow temperature range between  $805$  and  $871^\circ\text{C}$ . Above this range, a minimum of the solidus–liquidus exists at  $871^\circ\text{C}$  and approximately 35 mol.% PbS and below this range, the complete series decomposes to a two-phase assemblage. Romanenko and Sidorov (1975) confirmed the existence of a complete series, but at a much higher temperature of  $845^\circ\text{C}$ . Results from the present study are shown in Fig. 1c along with the data of Darrow *et al.* (1966) and Gromakov *et al.* (1964). The critical point of the immiscibility dome is at  $815^\circ\text{C}$  and 65 mol.% PbS, and both melting and subsolidus relations established match well with the data of Darrow *et al.* (1966).

#### Phase relations in the ternary system

Phase relations in the system PbS–PbSe–PbTe were studied in the temperature range  $300^\circ$  and  $1000^\circ\text{C}$ . In the subsolidus region, the miscibility gap present along the join PbS–PbTe extends into the ternary system, but decreases in size with increasing temperature and increasing amount of PbSe. At  $500^\circ\text{C}$  (Fig. 2), with 0, 20, 40, and 60 mol.% PbSe, the ranges of solid solutions at PbS- and PbTe-rich ends are 1.5 and 11.0, 4.0 and 12.0, 8.0 and 13.0, and 12.0 and 14.0 mol.% respectively. The gap disappears at the composition of 65 mol.% PbSe. When the temperature increases from  $500$  to  $600^\circ\text{C}$ , the amount of PbSe required to eliminate the gap is reduced from 65 to 26 mol.% (Fig. 3).

At  $700^\circ\text{C}$  (Fig. 3), the miscibility gap becomes distinctly asymmetrical. With 10 mol.% PbSe, the ranges of solid solution in the PbS-rich end are 17 mol.% and in the PbTe-rich end, 35 mol.%. Beyond 13 mol.% PbSe the gap disappears. At  $800^\circ\text{C}$  (Fig. 4), the gap is limited to a narrow region between 73 and 52 mol.% PbS along the join PbS–PbTe and within a maximum of 3 mol.% PbSe. A complete series of solid solution

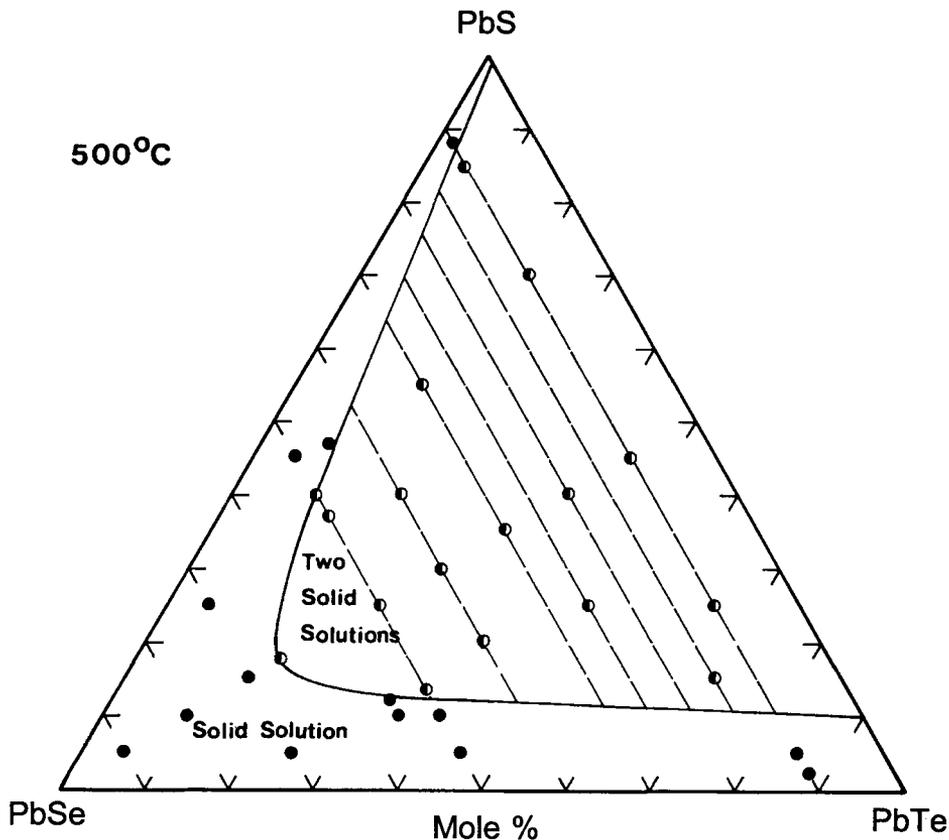


FIG. 2. Phase relations in the system PbS–PbSe–PbTe at 500°C. Solid and half-filled circles represent one- and two- phase assemblages, respectively. Tie lines are illustrated in the two-phase region by broken lines.

occupies the entire system between 815 and 870°C. Equilibria between solid and liquid phases are also shown in Fig. 4. With the increase in temperature, the liquid phase advances from a narrow, PbSe-poor strip along the join PbS–PbTe to occupy the region from 100 to about 20 mol.% PbTe.

Experimental results from flux runs made at 300°C are given in Fig. 5. The series along the join PbS–PbSe has no change in its configuration while a miscibility gap appears between PbSe and PbTe. The limits of the two terminal solid solutions determined by cell dimension measurements are at 18 and 68 mol.% PbTe.

#### Cell dimensions

All lead chalcogenides have the NaCl-type structure, and cell dimensions as a function of composition along the boundary joins and in the ternary system are shown in Figs. 6 and 7. Linear relationships exist in all of them. The linear

relation along the join PbS–PbSe confirms results established by Bethke and Barton (1961).

#### Thermodynamic consideration

From the miscibility gaps and the tie-lines obtained, mixing energetics and therefore the activity-composition relations of PbX solid solutions can be derived.

Considering the asymmetric nature of the ternary miscibility gaps, the excess free energy of mixing ( $G^{XS}$ ) of the ternary solid solutions may be described by the subregular model of mixing (Ganguly and Saxena, 1987):

$$G^{XS} = X_i X_j (W_{ij} X_j + W_{ji} X_i) \quad (1)$$

for a binary system and

$$G^{XS} = \sum_{i \neq j} (W_{ij} X_j + W_{ji} X_i) X_i X_j + X_i X_j X_k \sum_{i \neq j} (W_{ij} + W_{ji}) / 2 - X_i X_j X_k W_{ijk} \quad (2)$$

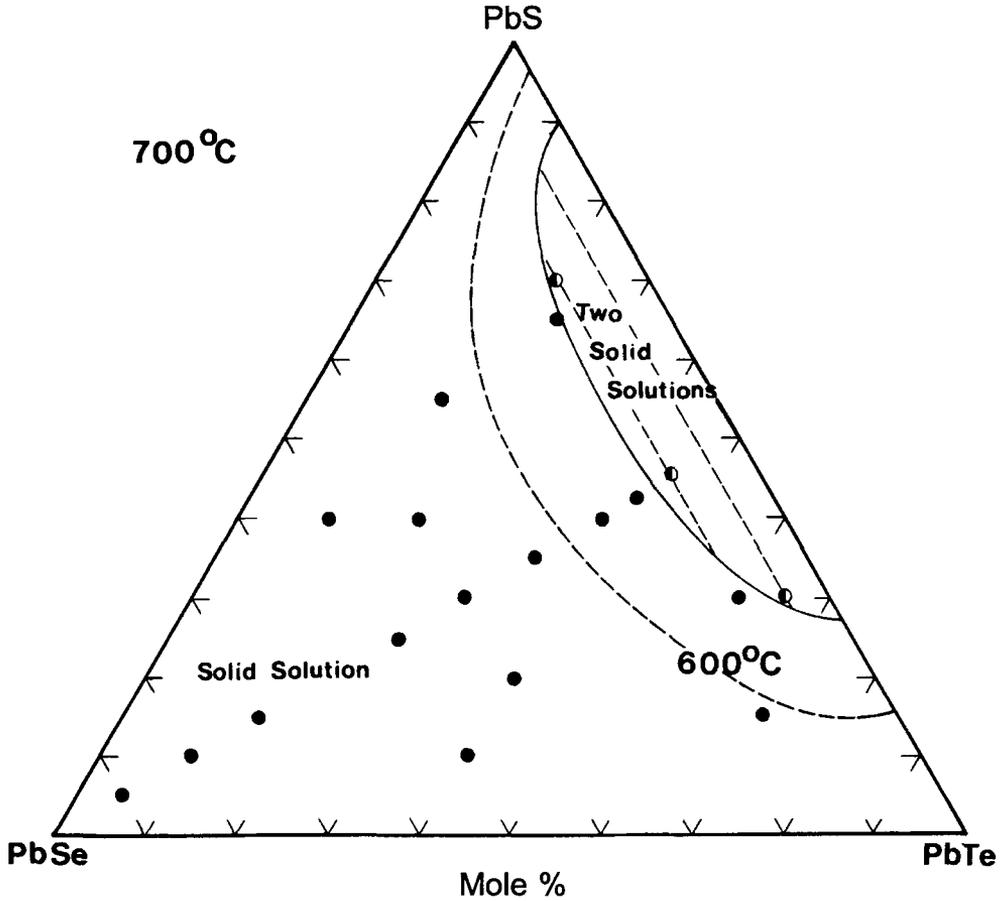


FIG. 3. Phase relations in the system PbS–PbSe–PbTe at 700°C. The boundary line between one- and two-phase assemblages at 600°C is also shown in the diagram. Experimental data are not plotted to avoid confusion with 700°C data.

for a ternary system, where  $X_i$ ,  $X_j$  and  $X_k$  are mole fractions of each component;  $W_{ij}$  and  $W_{ji}$  are binary interaction parameters in the system  $i$ – $j$ , and  $W_{ijk}$  is the ternary interaction parameter in the system  $i$ – $j$ – $k$ .

Partial derivative of  $G^{XS}$  with respect to moles of component  $i$  ( $n_i$ ,  $n_i = X_i \sum n_i$ ) in the solid solution can be used to calculate the activity coefficient of that component ( $\gamma_i$ ):

$$\partial G^{XS} / \partial n_i = RT \ln \gamma_i \quad (3)$$

where  $R$  is gas constant and  $T$  is temperature. For a binary solid solution,

$$\gamma_i = \exp\{[W_{ij}(1-2X_i) + 2W_{ji}X_i]X_j^2/RT\} \quad (4)$$

and for a ternary solid solution,

$$\begin{aligned} \gamma_i = \exp\{ & [\sum_{i \neq j} W_{ij} X_j^2 (1-2X_i) - W_{ik} X_k^2 \\ & + 2 \sum_{i \neq j} W_{ji} X_i X_j (1-X_i) - 2W_{kj} X_j X_k \\ & + \frac{1}{2} [\sum_{i \neq j} (W_{ij} + W_{ji})] (X_j X_k - 2X_i X_j X_k) \\ & - W_{ijk} (X_j X_k - 2X_i X_j X_k)] / RT \}. \end{aligned} \quad (5)$$

For a one-site mixing solid solution, the activity–composition relation of component  $i$  is represented by:

$$a_i = X_i \gamma_i \quad (6)$$

where  $a_i$  is the activity of component  $i$ . Substitute equations (4) and (5) into equation (6), the activity–composition relation of component  $i$  in PbX solid solution is established, except that all

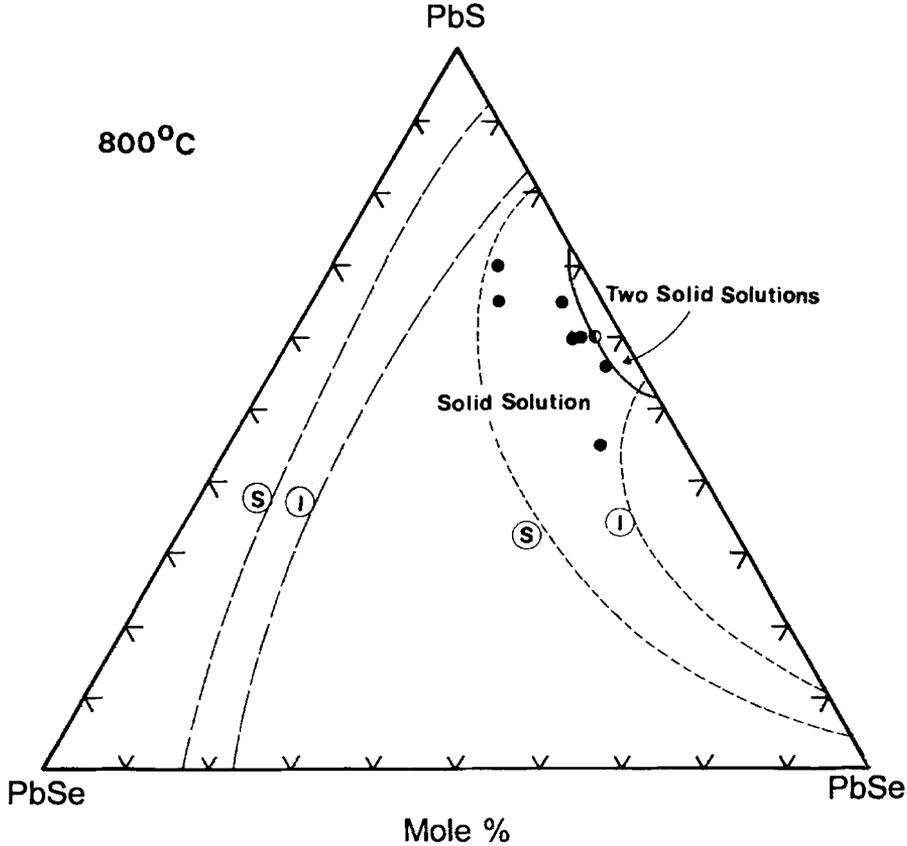


FIG. 4. Phase relations in the system PbS–PbSe–PbTe at 800°C. Liquid–solid equilibrium relations at 900° and 1000°C are represented by dashed and broken lines, respectively. ‘S’ denotes solidus and ‘I’ denotes liquidus.

the interaction parameters in equations (4) and (5) need to be determined. When two phases are in equilibrium, there is the relation:

$$RTLna_i^A = RTLna_i^B \quad (7)$$

the superscript A and B denote phases A and B.

For a binary solid solution, substitute equations (4) and (6) into equation (7) and we have:

$$RTLn(X_i^A/X_i^B) = RTLn\gamma_i^B - RTLn\gamma_i^A \\ = f(W_{ij}, W_{ji}, X_i^A, X_i^B, X_j^A, X_j^B) \quad (8)$$

in which there are two unknowns ( $W_{ij}$  and  $W_{ji}$ ) and two equations available from each tie line. Therefore, the binary interaction parameters can be calculated from this equation and the binary miscibility gaps if they exist.

The calculated  $W_{STe}$  and  $W_{TeS}$  in cal/mol. are 3169 and 4870, 3394 and 5349, 3564 and 5806, 3697 and 6193, and 4060 and 7084 at 800°, 700°, 600°, 500° and 300°C, respectively.

The calculated  $W_{SeTe}$  and  $W_{TeSe}$  at 300°C are 2130 and 2771 cal/mol., respectively. There is no miscibility gap along the join PbSe–PbTe above 500°C, but a value of 1500 cal/mol. for both  $W_{SeTe}$  and  $W_{TeSe}$  was obtained from Dombrugov and Zhovnir’s work (1986). Dombrugov and Zhovnir calculated  $W_{SeTe}$  (or  $W_{TeSe}$ ) at 500°C based on the coexisting liquid and solid compositions in the system Pb–PbSe–PbTe by using a simple regular solution model, which can be considered as equivalent to the present subregular treatment if the solution is symmetric and so the  $W_{SeTe}$  and  $W_{TeSe}$  values are identical. Although the miscibility gap along the PbSe–PbTe join at 300°C is somewhat asymmetric, as the temperature increases, especially above the critical point, the lattice characteristics of the two end members are closely alike, and so  $W_{SeTe}$  and  $W_{TeSe}$  tend to be close in value and the symmetric treatment of the mixing can be considered a reasonable approach.

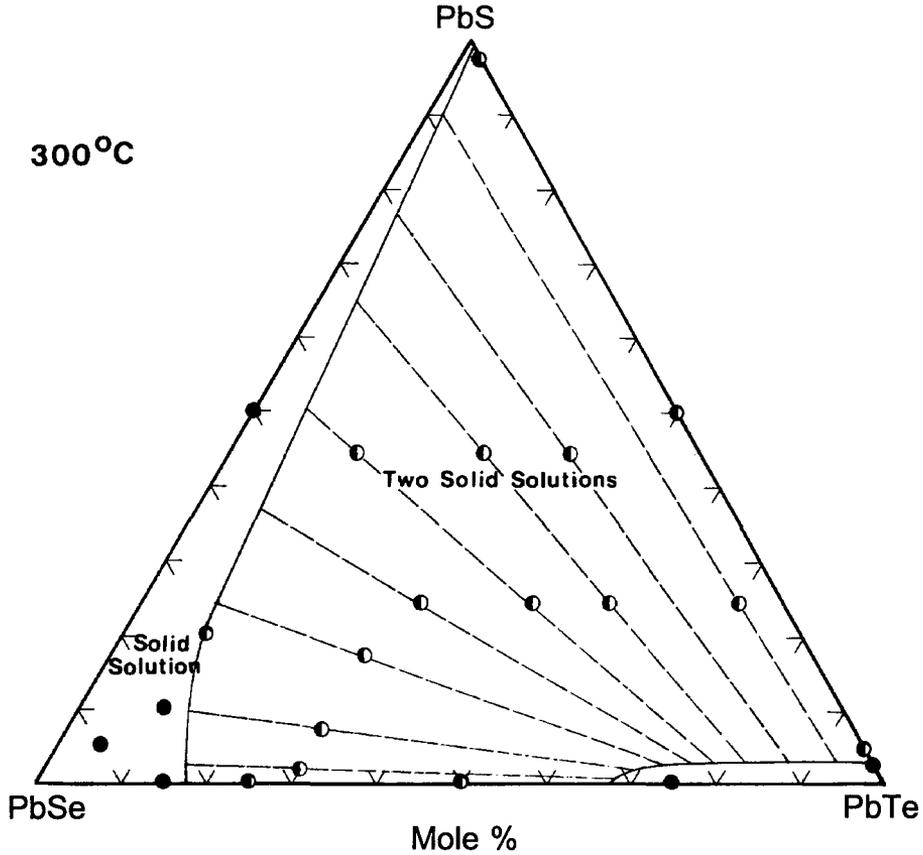


FIG. 5. Phase relations in the system PbS–PbSe–PbTe at 300°C from chloride flux experiments.

The remaining three undetermined interaction parameters in equation (5),  $W_{Sse}$ ,  $W_{SeS}$  and  $W_{SSeTe}$ , can be calculated by using the tie lines in the ternary miscibility gaps. Substituting equations (5) and (6) into equation (7), we have

$$\begin{aligned}
 RT \ln(X_i^A/X_i^B) &= RT \ln \gamma_i^B - RT \ln \gamma_i^A \\
 &= f(W_{STe}, W_{TeS}, W_{SSe}, W_{SeS}, W_{SeTe}, W_{TeSe}, \\
 &\quad W_{SSeTe}, X_i^A, X_i^B, X_j^A, X_j^B), \quad (9)
 \end{aligned}$$

in which only  $W_{Sse}$ ,  $W_{SeS}$  and  $W_{SSeTe}$  are unknown variables. Gathering the known quantities on the left hand side of the equation, we obtain expressions of the form:

$$K_i = M_i W_{Sse} + N_i W_{SeS} + P_i W_{SSeTe} \quad (10)$$

for each of the  $i$  components. The  $K_i$ ,  $M_i$ ,  $N_i$  and  $P_i$  are functions of the coexisting phases only at each temperature. From  $n$  tie-lines, we can obtain  $3n$  statements of equation (10). By least-squares

refinement of these equations,  $W_{Sse}$ ,  $W_{SeS}$  and  $W_{SSeTe}$  can be calculated. Results in the order of  $W_{Sse}$ ,  $W_{SeS}$  and  $W_{SSeTe}$  and in cal/mol. are 1448(150), 1440(150), and  $-428(200)$  at 500°C with a standard error of 0.2 and  $R^2$  of 0.97 and 1500(600), 1490(550), and 12906.3(1100) at 300°C with a standard error of 0.4 and  $R^2$  of 0.8.

Substituting all the interaction parameters into equation (5), the activity–composition relations for PbX ternary solid solutions can be calculated at constant temperatures. The  $a$ – $X$  relations of PbS–PbSe solid solutions at 500° and 300°C are shown in Fig. 8, in which  $\gamma_i$  was calculated from equation (4).

The temperature-dependence of the  $W$ 's was calculated to be  $5057.6 - 1.7T$ ,  $9605.2 - 4.4T$ ,  $3933.2 - 3.1T$  ( $T < 500^\circ$ ), and  $6410.3 - 6.35T$  ( $< 500^\circ$ ) for  $W_{STe}$ ,  $W_{TeS}$ ,  $W_{SeTe}$  and  $W_{TeSe}$ , respectively. For  $W_{Sse}$ ,  $W_{SeS}$  and  $W_{SSeTe}$ , they are  $1649 - 0.26T$ ,  $1594.6 - 0.2T$ , and  $12906.3 - 17.3T$  ( $T < 500^\circ$ ), respectively. The variation in the

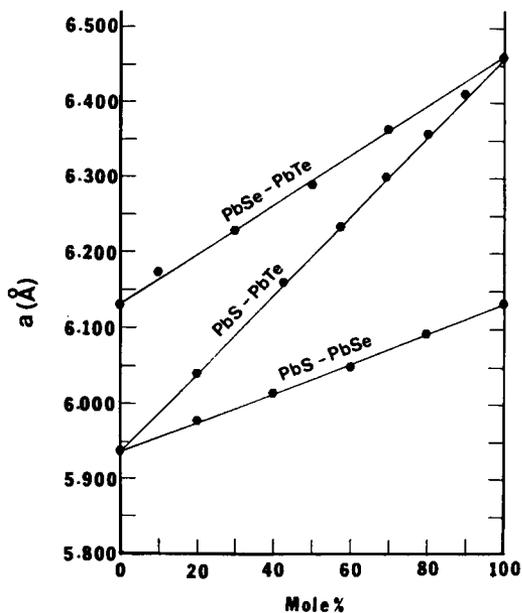


FIG. 6. Variation of cell dimension 'a' with composition along the joins PbS-PbSe, PbSe-PbTe and PbS-PbTe.

$W$ 's of the join PbS-PbSe with temperature is shown to be small, probably because it is in the temperature range above the critical point and far below the melting point. It is thus reasonable to extend the  $T$ -dependence equations for this system to temperatures above  $500^{\circ}\text{C}$ . In addition, the  $W$ 's of this system suggest that the system has a symmetric mixing character ( $W_{\text{SSe}} \approx W_{\text{SeS}}$ ) in this temperature range and thus can also be described by a symmetric regular model in which  $G^{\text{xs}} = WX_1X_2$  and  $W$  does not change much with temperature if there is any. As a consequence, the critical temperature ( $T_c$ ) in this system can be approximated from the equation (Saxena, 1973):

$$2RT_c = W$$

The resultant  $T_c$  is about  $100^{\circ}\text{C}$ . In other words, the complete series of galena-clausthalite solid solution dissociates below  $100^{\circ}\text{C}$ .

The  $T$ -dependence equations obtained for the  $W$ 's in the system PbSe-PbTe may only be suitable for the temperature range below  $500^{\circ}\text{C}$ . Above  $500^{\circ}\text{C}$ , the  $W$ 's may not change as much as that at lower temperatures because of the disappearance of the miscibility gap. In addition,

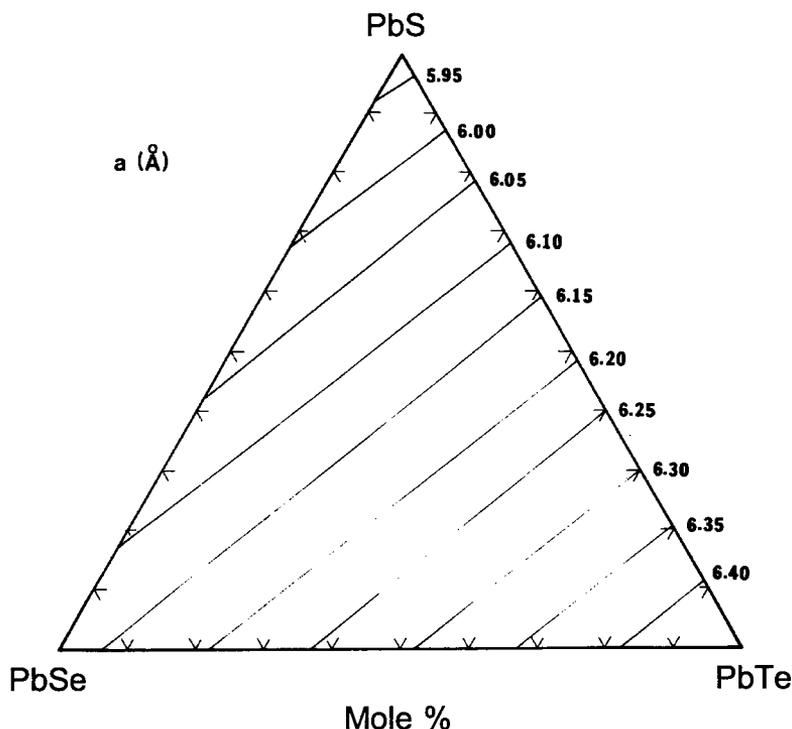


FIG. 7. Variation of cell dimension 'a' with composition in the system PbS-PbSe-PbTe.

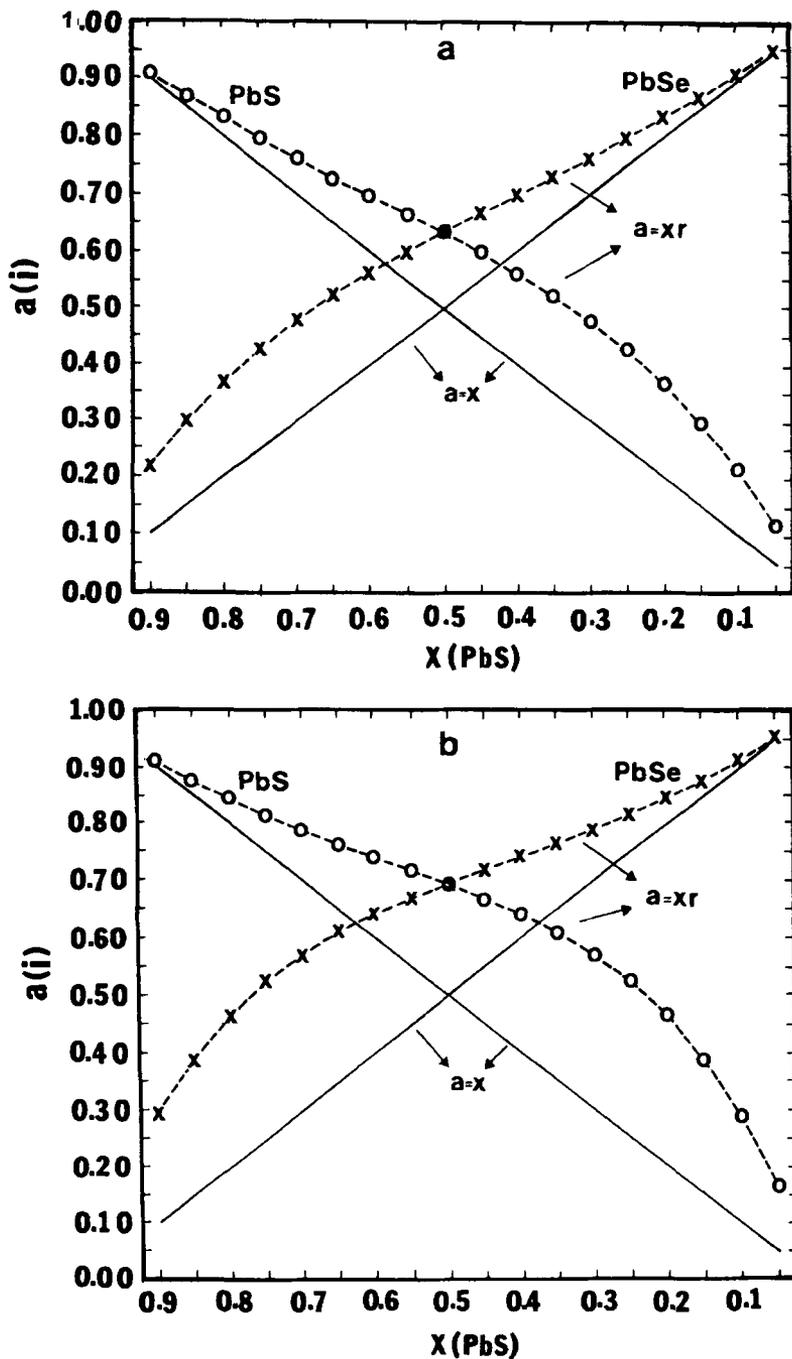


FIG. 8.  $a_i$ - $X_i$  relations of PbS-PbSe binary solid solutions at (a) 500°C and (b) 300°C. Solid lines are activities of ideal solid solutions. The deviation of  $a_{\text{PbS}}$  from ideality decreases as temperature increases.

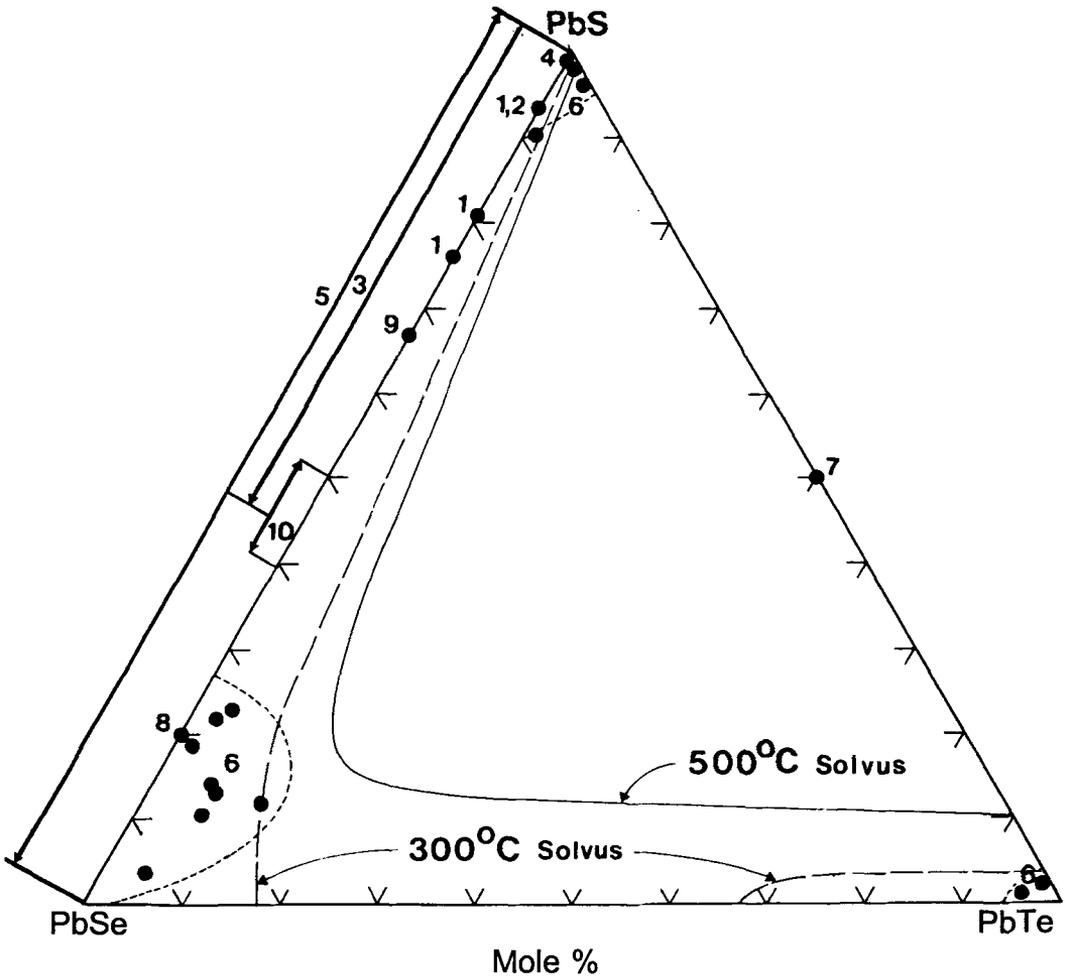


FIG. 9. Reported occurrences of Pb(S,Se,Te) solid solutions: (1) Vikre (1985); (2) Izawa *et al.* (1990); (3) Kovlenker *et al.* (1971); (4) Spiridonov *et al.* (1986); (5) Coleman (1959); (6) Gavrilenko (1987); (7) Filimonova *et al.* (1986); (8) Threadgold (1960); (9) Yushkin and Parlov (1983); and (10) Johan *et al.* (1987).

with  $W_{\text{SSe}}$  and  $W_{\text{SeS}}$  extrapolated from low-temperature data,  $W_{\text{SeTe}}$  and  $W_{\text{TeSe}}$  at 600 and 700°C can be calculated from the established corresponding ternary miscibility gaps. Results show that the slopes of their  $T$ -dependence equations are similar to those of  $W_{\text{SSe}}$  and  $W_{\text{SeS}}$ .  $W_{\text{SSeTe}}$  can also be calculated, giving a value of 1600 cal/mol. between 600 and 700°C.

In theory, the interaction parameters calculated can be used to extrapolate the phase relations to the temperatures which are not covered by experimental data. Substituting the  $T$ -dependence equations into equation (9), the formation temperature can be calculated if there is a pair of PbS-rich and PbTe-rich ternary solid solutions with known compositions coexisting in equi-

ilibrium. However, because the  $T$ -dependence equations for interaction parameters are based on a relatively small database, a diagrammatic geothermometer as shown in Figs. 2,3,4 and 5 is preferred whenever possible.

#### Geological considerations

Some of the naturally occurring PbX solid solutions are shown in Fig. 9. In the study of sulphides associated with the uranium–vanadium deposits of the Colorado Plateau, Coleman (1959) found members of the galena–clausthalite series with compositions covering the entire series, even in a single ore body. If the minerals reported all

formed in the same time as the ore minerals, this complete series may indicate a temperature of formation above 100°C, which supports a hydrothermal origin rather than a sedimentary origin of the Colorado uranium deposits (Guilbert and Park, 1986). On the other hand, the compositions of graphitic galena–clausthalite solid solution in Trout Lake massive sulphide ores, Flin Flon, Manitoba (Healy and Petruk, 1992), reflect a miscibility gap along the join and may indicate a temperature of formation lower than 100°C. Threadgold (1960) reported galena, clausthalite and a member of the series,  $\text{Pb}(\text{S}_{0.20}\text{Se}_{0.80})$  with  $a = 6.10 \text{ \AA}$ , that co-exist in uranium-bearing shale, sandstone and chert. The relatively large scattering in mineral composition may reflect a miscibility gap or that the mineral did not form at the same time. Kovalenker *et al.* (1971) found minerals with compositions ranging from 42 to 99.9 mol.% PbS of the galena–clausthalite series in sulphide ores of millerite, chalcopyrite, bornite and pentlandite, which may also reflect a temperature of formation greater than 100°C, consistent with coexisting mineral data. In quartz–sulphide veins in limestone at Novaya Zemlya, Russia, minerals of compositions close to  $\text{PbS}_{0.67}\text{Se}_{0.33}$  exist in association with tetrahedrite, pyrite and chalcopyrite, and the temperature of formation of this sulphide mineral assemblage was estimated to be between 180 and 250°C (Yushkin and Parlov, 1983). In the National District, Humboldt, Nevada (Vikre, 1985), minerals of compositions  $\text{Pb}_{0.98}(\text{S}_{0.76}\text{Se}_{0.24})$  and  $\text{Pb}_{1.28}(\text{S}_{0.81}\text{Se}_{0.19})$  were reported with other sulphides and sulphosalts disseminated uniformly along interfaces between silicate bands. Temperature of formation was estimated to be between 100 and 250°C. All the findings, as shown in Fig. 9, correlate well with the experimental results that illustrate the existence of a complete solid-solution series.

Along the join PbSe–PbTe, no natural occurrence of lead selenide–tellurides was reported to date. Such an absence seems to indicate that the miscibility gap established at 300°C widens its range at lower temperatures and limits the lead chalcogenides close to end members. The reported  $\text{Pb}_2\text{STe}$  by Filimonova *et al.* (1986) from a porphyry copper deposit may indicate the presence of an ordered phase in the system PbS–PbTe at low temperatures, at least below 300°C (Fig. 1c). Gavrilenko (1987) examined the sulphide–selenide–telluride mineral assemblages in the Kola Peninsula and offered twelve chemical analyses. Except the one at the PbS-rich corner with approximately 3 mol.% PbTe, all fall into the solid-solution region at 300°C established in this study (Fig. 9).

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