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Lead and bismuth chalcogenide systems

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ABSTRACT

Phase relations in the systems of lead and bismuth chalcogenides were examined in the temperature range of 500–900 °C. In the system PbS-PbSe-Bi_2S_3-Bi_2Se_3, a complete series of solid solutions exists between $Pb_9Bi_4S_{15}$ (heyrovskyite) and $Pb_9Bi_4Se_{15}$, whereas along the join from $Pb_8Bi_6S_{17}$ (lillanite) to $Pb_8Bi_6Se_{17}$ there are two terminal solid solutions. The join $PbBi_2S_4$-$PbBi_2Se_4$ is characterized by an extensive solid solution based on weibullite. Six extensive ranges of solid solution exist in the system PbSe-PbTe-Bi_2Se_3-Bi_2Te_3, and their compositions fall along the joins in Pb(Se,Te):Bi_2(Se,Te)$_3$ ratios of 1:0, 2.7:1, 2:1, 1:1, 1:2, and 0:1.

New phases and solid solutions in the systems of lead and bismuth sulfide and telluride and selenide and telluride are all structurally related, and their structures are based on stacked layers of PbTe (two layers) and Bi_2Te_3 (five layers). The total number of layers (N) in the unit cell of a phase, $m\text{PbTe}\cdot n\text{Bi}_2\text{Te}_3$, is expressed by the equation $N = Z(2m + 5n)$, where Z is the number of formula units in the unit cell and can only be derived from experimental data. For the four phases along the galena-tetradymite join in the PbS-PbTe-Bi_2S_3-Bi_2Te_3 system, $Pb_2Bi_2S_3Te_2$, $Pb_3Bi_4S_5Te_4$, $PbBi_2S_2Te_2$, and $PbBi_4S_3Te_4$ have N, Z, a, and c, respectively: 9, 1, 4.23 Å, and 16.71 Å; 32, 2, 4.23 Å, and 60.00 Å; 21, 3, 4.23 Å, and 39.83 Å; and 12, 1, 4.24 Å, and 23.12 Å.

INTRODUCTION

Lead and bismuth chalcogenides are of interest because of the large number of minerals reported in the group. The atomic structures of Pb and Bi differ by a single 6p electron, and their crystallochemical behaviors show many similarities, which are well illustrated in their sulfides. The BiS_6 polyhedron has bond lengths and bond angles very similar to those of the PbS_6 octahedron. Consequently, various galena-like structural units can be formed by combining Pb and Bi polyhedra (Makovicky, 1981). However, no significant solid solutions were found between their respective chalcogenides. The purpose of this study is to examine the distinctions and similarities in the Pb- and Bi-containing systems sulfide and selenide, selenide and telluride, and sulfide and telluride.

Phase relations among lead sulfbismuthinides were studied by Van Hook (1960) and Craig (1967). There are four lead sulfbismuthinides stable along the join PbS-Bi_2S_3: $Pb_9Bi_4S_{15}$, $Pb_8Bi_6S_{17}$, $PbBi_2S_4$, and $PbBi_4S_7$. The first three phases have been shown to be analogous to heyrovskyite, lillianite, and galenobismutite, respectively. $PbBi_4S_7$ is a high-temperature phase stable between 680 and 725 °C.

Along the join PbSe-Bi_2-Se_3, Elagina (1961) reported three intermediate phases, $Pb_3Bi_4Se_9$, $PbBi_2Se_4$, and $PbBi_4Se_7$, and a wide range of PbSe-type solid solution extending to 20 mol% Bi_2Se_3 at 720 °C. Godovikov et al. (1967) reported two phases, $PbBi_2Se_4$ and $PbBi_4Se_7$, and a small range of solid solution, represented by $Pb_2Bi_2Se_5$ at 500 °C.

Phase relations along the join PbTe-Bi_2Te_3 have been the subject of several studies. Elagina and Abrikosov (1959) and Golovanova and Zlomanov (1983) reported a single intermediate phase, $PbBi_4Te_7$, stable along the join. Hirai et al. (1967) also reported a single intermediate phase, but with a composition of $Pb_3Bi_4Te_9$. Zhukova and Zaslavskii (1976) and Skoropanov et al. (1985) observed the formation of $Pb_2Bi_2Te_5$, $PbBi_2Te_4$, and $PbBi_4Te_7$. Chami et al. (1983) and Dumas et al. (1985) proposed a join containing two intermediate phases, $PbBi_2Te_4$ and $PbBi_4Te_7$.

EXPERIMENTAL PROCEDURES

Reagent-grade Pb, Bi, S, Se, and Te, all with 99.99% purity, were used in the preparation of starting compositions. Heat treatment was performed in electric furnaces in which the temperature was controlled to within ±2 °C, and the conventional technique of sealed, evacuated silica glass capsules (Kullerud and Yoder, 1959) was used. Generally, the duration of the treatment ranged from 60 d at 500 °C to 1 d at 900 °C. At the end of the heat treatment, the samples were quenched to room temperature by compressed air to preserve phase assemblages synthesized at high temperatures. Test experiments demonstrated that the quenching procedure is capable of lowering the temperature from the 500–900 °C range to 100

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°C in 2–3 s. Visual examination of reaction between sample and capsule glass was made, and any experiment with evidence of reaction was discarded. 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 showed no differences caused by changing the procedure, equilibrium was assumed to have been attained.

X-ray powder diffraction, reflected-light microscopy, and electron microprobe analysis were used for phase characterization. No high-temperature X-ray diffraction was performed to examine phase assemblages at experimental temperatures. Cell dimensions were computed using a least-squares refinement program (Benoit, 1987). For the determination of melting, the quenched samples were made into polished sections and examined microscopically for the presence of liquid textures. Phase boundaries in the subsolidus region were constructed by both parametric and phase-disappearance methods.

EXPERIMENTAL RESULTS

The binary joins

Phase relations along the join PbSe-Bi_2Se_3 established in the present study are shown in Figure 1a. Three intermediate phases were found: $Pb_9Bi_4Se_{15}$ (phase U), $Pb_8Bi_6Se_{17}$ (phase V), and a $PbBi_2Se_4$-based solid solution (phase W). The first two are Se analogues to heyrovskyite and lillianite, respectively. The $PbBi_2Se_4$-based solid solution (weibullite) has a range of 47–57 mol% Bi_2Se_3 at 500 °C and 47–53 mol% Bi_2Se_3 at 400 °C. All lead bismuth selenides melted congruently, and the melting points determined are 560 ± 3 °C for $Pb_9Bi_4Se_{15}$, 575 ± 3 °C for $Pb_8Bi_6Se_{17}$, and 655 ± 3 °C for $PbBi_2Se_4$. Among the reported phases, only $PbBi_2Se_4$ was confirmed in this study.

Along the join PbTe-Bi_2Te_3, results obtained in the present study are shown in Figure 1b. There are two lead bismuth tellurides: $PbBi_2Te_4$ (phase A) and $PbBi_4Te_7$ (phase M). $PbBi_2Te_4$ melted incongruently at 585 ± 3 °C, and $PbBi_4Te_7$ melted congruently at 570 ± 3 °C.

The lead and bismuth chalcogenides

Phase relations in the system PbS-PbSe-Bi_2S_3-Bi_2Se_3 at 500 °C are shown in Figure 2a. Heyrovskyite and the selenian analogue of heyrovskyite form a complete series of solid solution, whereas, between lillianite and the selenian analogue of lillianite, two terminal solid solutions exist. Cell dimensions determined are listed in Table 1. The cell dimensions of heyrovskyite obtained are com-

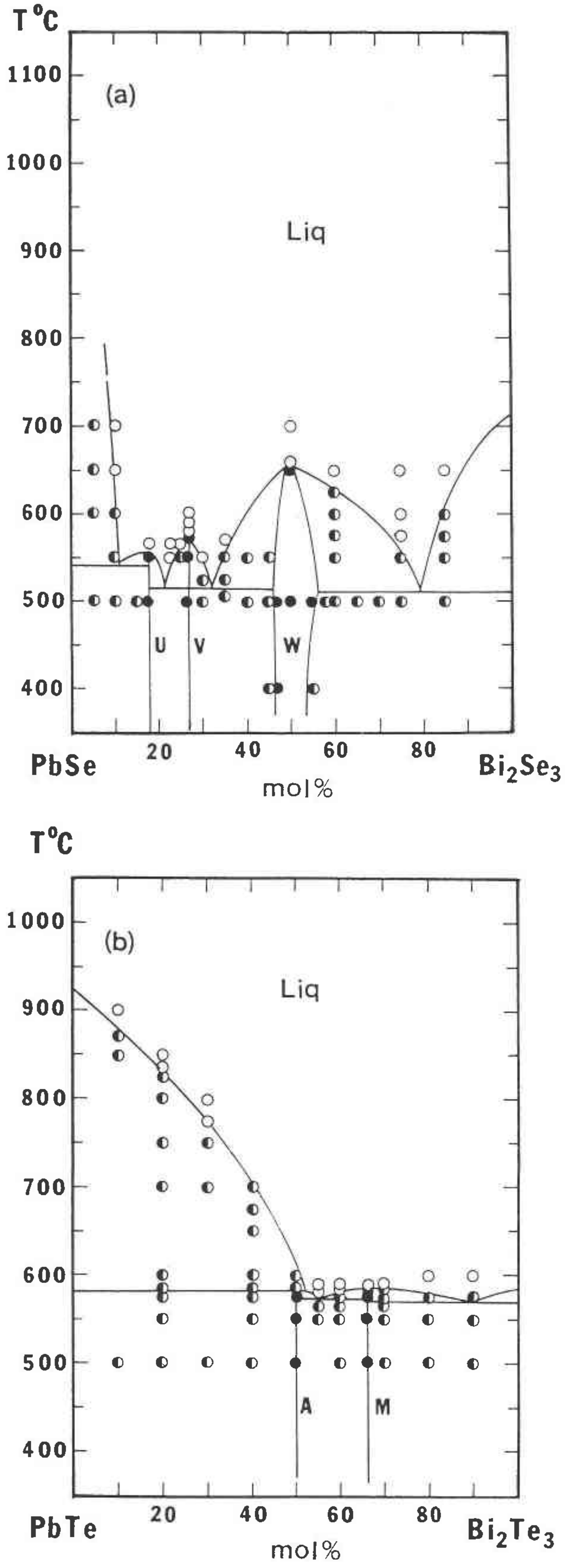

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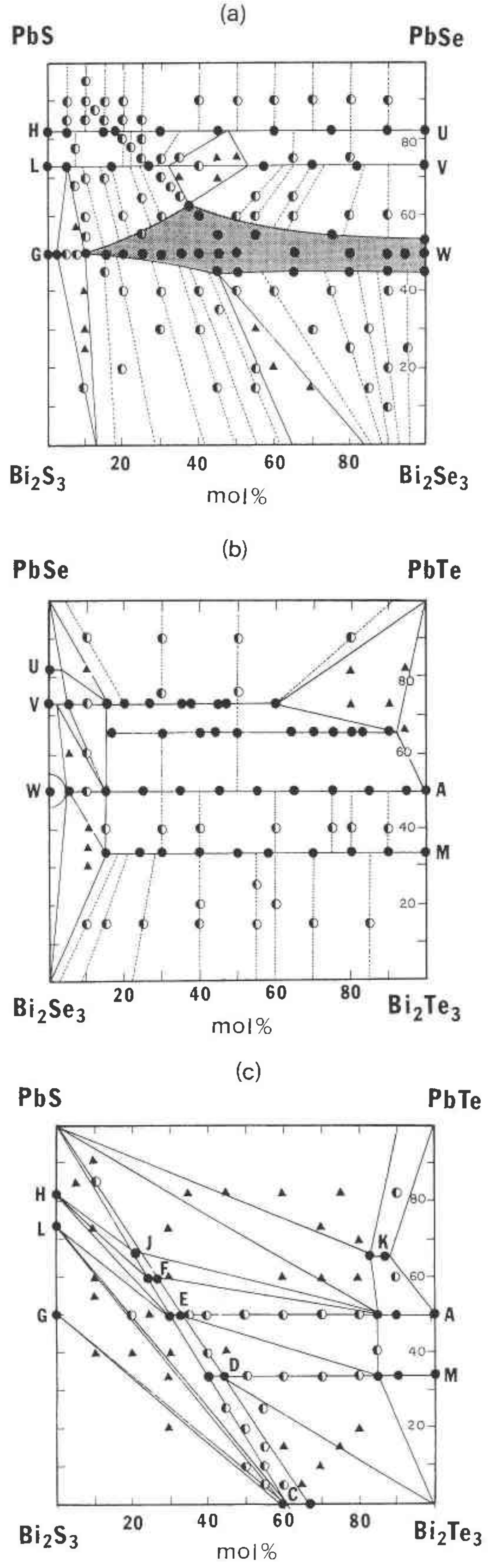
Fig. 1. Phase relations along the joins (**a**) PbSe-Bi_2Se_3 and (**b**) PbTe-Bi_2Te_3. Open circles, solid circles, and half-solid circles represent liquid, solid, and two-phase assemblages, respectively. Letters denote single phases.



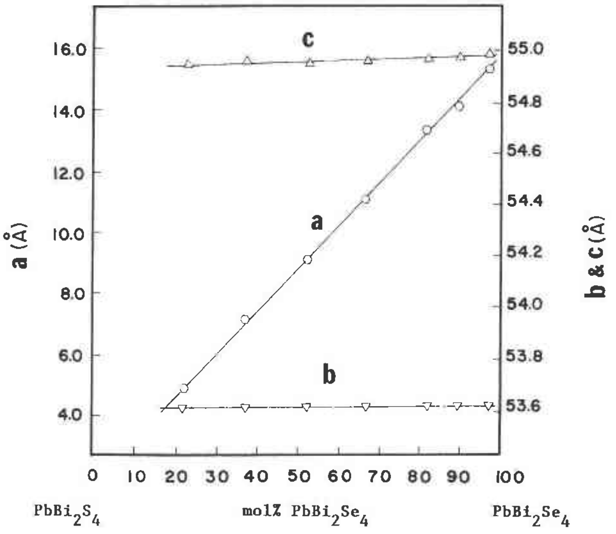


Fig. 3. Variation of cell dimensions with composition for the PbBi$_2$(S,Se)$_4$ (phase W) solid solution synthesized at 500 °C.

parable with those reported by Klominsky et al. (1971), although the naturally occurring heyrovskyite from its type locality contains Ag.

The most distinct feature in the system is the extensive region of solid solution based on weibullite [$Pb_{1+x}Bi_{2+y}(S,Se)_{4+x+1.5y}$], which ranges from PbBi$_2$Se$_4$ to 90 mol% PbBi$_2$S$_4$ at x and $y = 0$. Along the PbS-Bi$_2$Se$_3$ join, the series extends to the compositions that include the Pb-Bi ratio of wittite (Johansson, 1924). Powder X-ray diffraction data of synthetic weibullite match those from the weibullite obtained by Mumme (1980), and variations of cell dimensions with compositions along the PbBi$_2$(S,Se)$_4$ join are shown in Figure 3. The changes reflect the size difference between S and Se. The miscibility gap along the Bi$_2$S$_3$-Bi$_2$Se$_3$ join forms a three-phase assemblage with the weibullite solid solution.

Phase relations in the PbSe-PbTe-Bi$_2$Se$_3$-Bi$_2$Te$_3$ system at 500 °C are shown in Figure 2b. Because of the binary phases along the PbTe-Bi$_2$Te$_3$ join, phase A and phase M form two extensive ranges of solid solutions by substitution of Se for Te. Phase A extends from PbBi$_2$Te$_4$ to PbBi$_2$(Se$_{0.78}$Te$_{0.22}$)$_4$ and phase M from PbBi$_4$Te$_7$ to PbBi$_4$(Se$_{0.75}$Te$_{0.25}$)$_7$. A 2:1 type solid solution is stable in the system between Pb$_2$Bi$_2$(Se$_{0.06}$Te$_{0.94}$)$_5$ and Pb$_2$Bi$_2$(Se$_{0.75}$Te$_{0.25}$)$_5$. Despite the small range of solid solution of Se analogue of lillianite and the absence of a 8:3 phase (heyrovskyite-type)

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Fig. 2. Phase relations at 500 °C in the systems (**a**) PbS-PbSe-Bi$_2$S$_3$-Bi$_2$Se$_3$, (**b**) PbSe-PbTe-Bi$_2$Se$_3$-Bi$_2$Te$_3$, and (**c**) PbS-PbTe-Bi$_2$S$_3$-Bi$_2$Te$_3$. Solid circles, half-solid circles, and triangles represent one-, two-, and three-phase assemblages. Letters denote a single phase. Shaded area in **a** represents weibullite solid solution.

TABLE 1. Cell dimensions of the phases synthesized in the system PbS-PbSe-Bi_2S_3-Bi_2Se_3

Phase	Chemical composition (mol%)				Cell dimension (Å)		
	PbS	PbSe	Bi_2S_3	Bi_2Se_3	*a*	*b*	*c*
Heyrovskyite	82	0	18	0	13.68(1)	32.57(2)	4.23(1)
Heyrovskyite solid solution	55	27	18	0	13.90(1)	32.75(1)	4.23(1)
Heyrovskyite solid solution	40	42	18	0	13.96(1)	32.90(1)	4.23(1)
Lillianite	73	0	27	0	13.51(1)	20.56(1)	4.10(1)
Lillianite solid solution	73	0	22	5	13.62(1)	20.67(1)	4.11(1)
Lillianite solid solution	73	0	10	17	13.74(1)	20.85(1)	4.15(1)
Lillianite solid solution	73	0	0	27	13.83(1)	21.03(1)	4.17(1)
Galenobismutite	50	0	50	0	11.81(1)	14.59(1)	4.08(1)
Weibullite	60	0	0	40	54.39(1)	4.20(1)	15.79(1)
Weibullite	45	0	0	55	54.21(1)	4.19(1)	15.73(1)
Weibullite	5	45	0	50	54.92(1)	4.24(1)	15.77(8)
Weibullite	20	30	0	50	54.78(2)	4.23(1)	15.71(4)
Weibullite	35	15	0	50	54.70(3)	4.22(1)	15.65(5)
Weibullite	50	0	5	45	54.42(1)	4.20(1)	15.60(1)
Weibullite	50	0	15	35	54.18(1)	4.18(1)	15.54(1)
Weibullite	50	0	25	25	53.96(3)	4.15(1)	15.51(4)
Weibullite	50	0	35	15	53.69(1)	4.12(2)	15.46(1)

Note: standard deviations are in parentheses. All phases listed are orthorhombic.

along the PbTe-Bi_2Te_3 join, a series of solid solutions with compositions Pb_8Bi_6 $(Se,Te)_{17}$ is stable in the system from $Pb_8Bi_6(Se_{0.26}Te_{0.74})_{17}$ to $Pb_8Bi_6(Se_{0.72}Te_{0.24})_{17}$. Variations of cell dimensions with composition in the system are shown in Figure 4.

Phase relations in the system PbS-PbTe-Bi_2S_3-Bi_2Te_3 at 500 °C are shown in Figure 2c. Both phase A and phase M of the binary join PbTe-Bi_2Te_3 have ranges of solid solution by S substitution. The A series extends from $PbBi_2Te_4$ to $PbBi_2(Te_{3.65}S_{0.35})$ and the M series from $PbBi_4Te_7$ to $PbBi_4(Te_{6.475}S_{0.525})$. In addition to tetradymite along the Bi_2S_3-Bi_2Te_3 join, five lead bismuth sulfide telluride phases are stable in the system. They are designated as phase K with compositions between $Pb_2Bi_2(Te_{4.5}S_{0.5})$ and $Pb_2Bi_2(Te_{4.7}S_{0.3})$, phase D with compositions between $PbBi_4(Te_{3.94}S_{3.06})$ and $PbBi_4(Te_{3.68}S_{3.32})$, phase E with compositions between $PbBi_2(Te_{1.8}S_{2.2})$ and $PbBi_2(Te_2S_2)$, phase F with compositions between $Pb_3Bi_4(S_5Te_4)$ and $Pb_3Bi_4(S_{5.4}Te_{3.6})$, and phase J with compositions between $Pb_2Bi_2(S_{3.2}Te_{1.8})$ and $Pb_2Bi_2(S_3Te)$. Powder X-ray diffraction data and determined and calculated cell dimensions are listed in Tables 2 and 3, respectively.

DISCUSSION

The structure of heyrovskyite is considered to contain slabs of PbS units connected by a twin operation on one set of the $(113)_{PbS}$ planes, and its ideal chemical formula should be $Pb_6Bi_2S_9$ (Otto and Strunz, 1968). The sample with such a composition gave a two-phase assemblage in this experimental study, whereas the synthetic composi-

TABLE 2. X-ray powder diffraction data for phases D, E, F, and J in the system PbS-PbTe-Bi_2S_3-Bi_2Te_3

Phase D				Phase E				Phase F				Phase J			
I	d_{obs}	d_{calc}	*hkl*	*I*	d_{obs}	d_{calc}	*hkl*	*I*	d_{obs}	d_{calc}	*hkl*	*I*	d_{obs}	d_{calc}	*hkl*
16	4.6134	4.6242	005	17	4.4210	4.4235	009	53	4.6115	4.6156	0.0.13	16	5.5760	5.5711	003
12	3.6273	3.6299	101	18	3.6027	3.6044	102	36	3.5280	3.5296	0.0.17	13	4.1720	4.1783	004
21	3.2981	3.3030	007	6	3.4361	3.4392	104	83	3.3689	3.3674	107	22	3.5783	3.5795	101
100	3.1016	3.1016	104	26	3.3230	3.3176	0.0.12	100	3.0385	3.0403	1.0.11	25	3.3420	3.3427	005
10	3.6567	2.6597	106	100	3.0796	3.0807	107	74	2.3225	2.3207	1.0.20	100	3.0585	3.0615	103
6	2.5655	2.5690	009	4	2.9491	2.9511	108	84	2.1890	2.1873	1.0.22	34	2.2162	2.2176	106
4	2.4541	2.4568	107	13	2.6945	2.6963	1.0.10	35	2.1410	2.1429	0.0.28	23	2.1161	2.1157	110
6	2.3088	2.3121	0.0.10	9	2.5630	2.6541	0.0.15	74	2.1159	2.1141	110	18	2.0899	2.0892	008
39	2.2781	2.2719	108	10	2.5744	2.5752	1.0.11	49	2.1003	2.1024	113	35	2.0020	2.0005	107
44	2.1211	2.1221	110	6	2.3483	2.3500	1.0.13	45	2.0333	2.0348	118	35	1.8151	1.8149	108
23	1.9544	1.9571	1.0.10	51	2.2464	2.2467	1.0.14	78	1.9699	1.9712	1.1.11	19	1.7911	1.7898	202
16	1.9282	1.9286	115	9	2.2112	2.2117	0.0.18	69	1.8179	1.8183	0.0.33	20	1.7413	1.7405	103
8	1.8268	1.8246	1.0.11	49	2.1160	2.1160	110	51	1.7909	1.7905	207				
12	1.7847	1.7854	117	8	2.0585	2.0586	1.0.16	52	1.7291	1.7282	1.1.20				
25	1.7519	1.7514	204	28	1.9733	1.9734	1.0.17								
				10	1.9093	1.9088	119								
				10	1.8956	1.8958	0.0.21								
				11	1.8195	1.8190	1.0.19								
				16	1.7849	1.7840	1.1.12								
				30	1.7447	1.7442	207								

Note: diffraction conditions: *K*α, λ = 1.5418 Å, Ni filter, peak height intensities, W metal (99.9999%) as internal standard, with (110) at 40.26°, cutoff 10° 2*θ*.

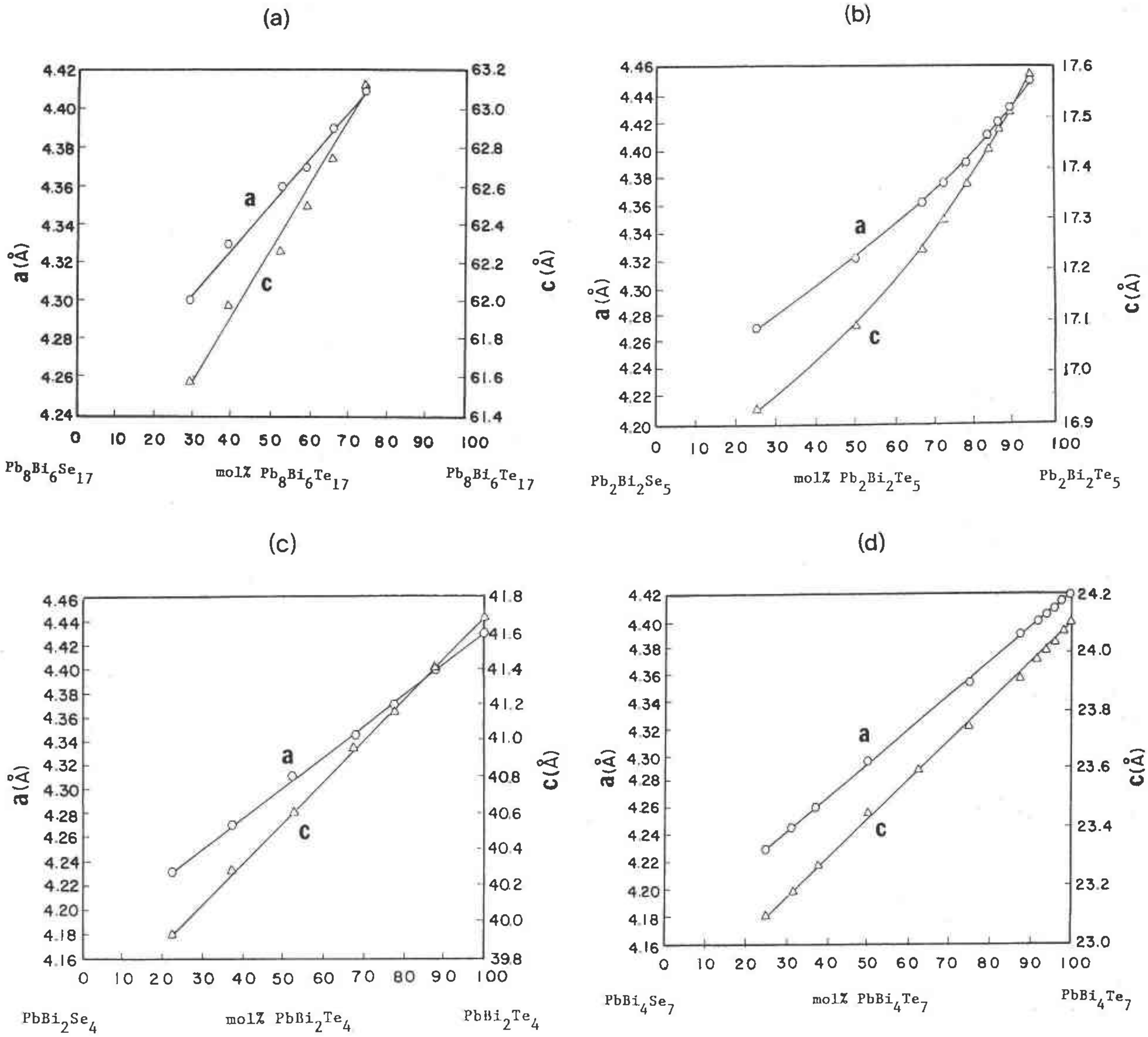

Fig. 4. Variations of cell dimensions with composition for (**a**) $Pb_8Bi_6(Te,Se)_{17}$ solid solution, (**b**) $Pb_2Bi_2(Te,Se)_5$ solid solution, (**c**) $PbBi_2(Te,Se)_4$ solid solution, and (**d**) $PbBi_4(Te,Se)_7$ solid solution, synthesized at 500 °C.

tion of $Pb_{5.4}Bi_{2.4}S_9$ indicates a structural formula of $(Pb_{5.4}Bi_{0.4})Bi_2S_9$, in which 0.6Pb atoms are replaced by 0.4Bi, relative to nine S atoms. The natural heyrovskyite has compositions ranging from $[Pb_{4.98}Bi_{0.60}(Ag,Cu)_{0.42}]Bi_2S_9$ to $[Pb_{5.52}Bi_{0.30}(Ag,Cu)_{0.18}]Bi_2S_9$, in which the coupled substitution of Bi + (Ag,Cu) → 2Pb is used to satisfy the structural requirement. The mineral with the ideal heyrovskyite formula ($Pb_6Bi_2S_9$) and monoclinic symmetry, which was named aschamalmite (Mumme et al., 1983), is not a stable phase in the system at 500 °C. For lillianite, the ideal formula is $Pb_3Bi_2S_6$ (Otto and Strunz, 1968), which produced a two-phase assemblage in the system at 500 °C. The synthetic composition of $Pb_{2.82}Bi_{2.12}S_6$ shows a substitution of 0.12Bi for 0.18Pb in terms of the structure formula. Xilingolite (Hong et al., 1982), with the formula of $Pb_{3+x}Bi_{2-2/3x}S_6$ (or $Pb_{3.18}Bi_{1.81}S_6$), has a monoclinic symmetry and is not a dimorph of lillianite. No stability field of xilingolite was found in this system. The above results show that in these slab-twinning structures of lead and bismuth sulfosalts a certain amount of Bi is required to fill in the Pb sites to stabilize the structures.

With the substitution of S and Se, weibullite has an extensive range of solid solution in the system PbS-PbSe-Bi_2S_3-Bi_2Se_3. The extent and limit of the solid solution may be structurally controlled. The crystal structure of weibullite comprises two elongated blocks (Mumme, 1980). One block has an octahedral galena-like structure, and the other block contains Pb and Bi atoms in irregular coordinations. Both blocks elongate along (001) and are in alternating sequence. The octahedral block has the

Table 3. Experimentally determined and calculated cell dimensions of the phases in the lead and bismuth chalcogenide systems

Phase	Composition	PbX-Bi_2X_3 ratio	Layers in unit cell	Cell dimension (Å)					
				a_{exp}	c_{exp}	a_{calc}	c_{calc}	$\lvert\Delta a\rvert$	$\lvert\Delta c\rvert$
				PbS-$PbTe$-Bi_2S_3-Bi_2Te_3					
K	$Pb_2Bi_2(Te_{0.91}S_{0.09})_5$	1:1	9	4.44(1)	17.54(1)	4.47	17.61	0.03	0.07
J	$Pb_2Bi_2(S_3Te_2)$	2:1	9	4.23(1)	16.71(1)	4.21	16.71	0.02	0.00
D	$PbBi_4(Te_4S_3)$	1:2	12	4.24(1)	23.12(1)	4.21	23.14	0.03	0.02
M	$PbBi_4Te_7$*	1:2	12	4.42(1)	24.10(2)	4.47	24.06	0.05	0.04
M	$PbBi_4(Te_{0.94}S_{0.06})_7$	1:2	12	4.42(1)	24.07(1)				
E	$PbBi_2(S_2Te_2)$	1:1	21	4.23(1)	39.83(1)	4.21	39.85	0.02	0.02
A	$PbBi_2Te_4$*	1:1	21	4.44(1)	41.70(2)	4.47	41.67	0.03	0.03
A	$PbBi_2(Te_{0.95}S_{0.05})_4$	1:1	21	4.42(1)	41.54(2)				
A	$PbBi_2(Te_{0.925}S_{0.075})_4$	1:1	21	4.40(1)	41.32(5)				
F	$Pb_3Bi_4(S_5Te_4)$	3:2	32	4.23(1)	60.00(2)	4.21	59.99	0.02	0.01
				$PbSe$-$PbTe$-Bi_2Se_3-Bi_2Te_3					
K	$Pb_2Bi_2(Te_{0.94}Se_{0.06})_5$	2:1	9	4.45(1)	17.59(1)	4.46	17.57	0.01	0.02
K	$Pb_2Bi_2(Se_{0.73}Te_{0.27})_5$	2:1	9	4.27(1)	16.93(1)	4.26	16.96	0.01	0.03
V	$Pb_8Bi_6(Se_{0.61}Te_{0.39})_{17}$	8:3	31	4.33(1)	62.2(1)	4.33	58.5	0.0	3.7
V	$Pb_8Bi_6(Te_{0.66}Se_{0.34})_{17}$	8:3	31	4.38(1)	62.8(0)	4.4	59.4	0.02	3.4

Note: standard deviations are in parentheses.

* Confirmed by structural determination (Imamov and Semiletov, 1970; Petrov and Imamov, 1969).

overall composition $(Pb,Bi)_{14}(S,Se)_{24}$, and the other block has the composition $(Pb,Bi)_{14}(S,Se)_{34}$, with 22 of the (S,Se) atoms in common between them. Such an arrangement allows extensive substitution between S and Se. In galenobismutite, on the other hand, the Pb atom is coordinated by eight S atoms (Iitaka and Nowacki, 1962), and any substitution of Se for S increases the size of the coordinated anions, which is not favored by the eightfold-coordinated galenobismutite structure.

In lead and bismuth tellurides, the subunits of PbTe (two layers) and Bi_2Te_3 (five layers) are simply stacked together to form the structure of the complex compounds, each subunit keeping its own structural characteristics (bond length, bond angle, coordination configuration). The resulting structures are all hexagonal in symmetry, similar to Bi_2Te_3. The number of layers in the complex compounds depends on the chemical composition (Imamov and Semiletov, 1970; Imamov et al., 1970). If the formulas of the compounds are expressed as $m\mathrm{PbTe}\cdot n\mathrm{Bi_2Te_3}$, the number of layers ($L$) in the unit stack of the structure is $(2m + 5n)$, and the total number of layers (N) in the cell can be expressed by the equation $N = Z(2m + 5n)$, where Z is the number of formula units in the unit cell and can only be determined experimentally. Cell dimensions of the compounds can be predicted by the equation

$$a_{\mathrm{hex}} = \tfrac{1}{2}(a'_{\mathrm{hex}} + a'_{\mathrm{c}}/2^{1/2});\ c_{\mathrm{hex}} = (Z/3)(ma'_{\mathrm{c}}3^{1/2} + nc'_{\mathrm{hex}})$$

where a'_{hex} and c'_{hex} are cell dimensions of Bi_2Te_3, and a'_{c} is the cubic cell dimension of PbTe.

Experimental data from this study show that structures and cell dimensions of lead and bismuth tellurides and of Se-Te solid solutions follow exactly the scheme described above, although pure lead and bismuth selenides from this study cannot be indexed on the basis of hexagonal symmetry. Table 3 lists four phases established in the system $PbSe$-$PbTe$-Bi_2Se_3-Bi_2Te_3 with their composition types, number of layers in the unit cell, and cell dimensions. As derived from anionic distribution in $Bi_2(Te,Se)_3$ (Nakajima, 1963), it can be predicted that Se first fills the inner layers of the unit stacks in Pb-Bi-(Te,Se) solid solutions.

In the system PbS-$PbTe$-Bi_2S_3-Bi_2Te_3, both layer-stacking sequences and anionic substitution patterns of the structures can be derived from experimentally determined cell dimensions and the scheme of layer stacking described above. Phases K, A, and M contain <10 mol% S of the total anion and have nine, seven, and 12 layers in their unit stacks, respectively, as calculated from the equation $L = 2m + 5n$. When one considers that Pb should be in the regular octahedral position as in PbX (X = S, Se, Te), and when one also refers to the structures of $PbBi_2Te_4$ and $PbBi_4Te_7$ determined by Petrov and Imamov (1969) and Imamov et al. (1970), the Te end-members of the phases K, A, and M are predicted to have layer sequences of TeBiTePbTePbTeBiTe, TeBiTePbTeBiTe, and TeBiTePbTeBiTe TeBiTeBiTe in their unit stacks, respectively. The substitution of S for Te suggests that S occupies the inner 3, 2, and 3 anionic layers of the unit stacks in phases K, A, and M, respectively, when one considers that the inner positions of the stack exhibit bonding more ionic in nature, as suggested by Nakajima (1963) for Bi_2STe_2 and Bi_2SeTe_2, in which S and Se occupy the inner sites. The resulting anionic substitution pattern for phases K, A, and M is one in which the inner anionic layers accommodate up to 16.7, 17.5, and 17.5 mol% S in their structures, respectively. These are relatively large amounts when one considers that PbTe can accommodate only 10 mol% PbS in its structure at 500 °C. On the other hand, the random substitution of S in all the anionic layers limits the substitution to <10 mol%.

Phase E has 50–55 mol% S of the total anion and seven layers in the unit stack, as calculated. Compared with the structure of $PbBi_2Te_4$ (Imamov and Semiletov, 1970) and Bi_2STe_2 (Harker, 1934), the atomic arrangement in phase

E may be TeBiSPbSBiTe for 50 mol% S ($PbBi_2S_2Te_2$). For 55 mol% S ($PbBi_2S_{2.2}Te_{1.8}$), the two Te layers must accommodate 10 mol% S, which is consistent with the solid-solution range and the resulting anionic substitution pattern of phase C (tetradymite, Bi_2STe_2-$Bi_2S_{1.2}Te_{1.8}$).

Phase D has 43–48 mol% S of the total anion and 12 layers in the unit stack, as calculated. By analogy with the structure of $PbBi_4Te_7$ (Petrov and Imamov, 1969), the layer sequence of the unit stack may be TeBiSPbSBiTe TeBiSBiTe, which is actually a seven-layer phase E (rucklidgeite) unit stack with an additional five-layer phase C (tetradymite) unit stack. If the substitution data obtained from these structures were used, the four Te layers in the phase E and phase C unit stacks could accommodate up to 10 mol% S, and the amount of S in phase D would be in the range of 43–49 mol% of the total anion, which is in good agreement with the experimental data obtained. The result also confirms the atomic arrangement proposed for phase E.

Phase F has a PbX-Bi_2X_3 ratio of 3:2, with 56–60 mol% S of the total anion. Its calculated unit stack has 16 layers. The layer sequence may be arranged as TeBiSPbSPbSBiTe TeBiSPbSBiTe, in which the amount of S is 56 mol% of the total anion. By using the anionic distribution data of phases C, D, and E, in which the outer Te layers accommodate up to 10 mol% S, the resulting amount of S (predicted) in phase F would just be in the range of 56–60 mol% of the total anion. Phase J has a composition range of 60–64 mol% S of the total anion. Its calculated unit stack has nine layers, with a sequence of TeBiSPbSPbSBiTe, and the outer two Te layers may also accommodate 0–10 mol% S.

In summary, the ternary compounds and solid solutions formed in the system PbS-$PbTe$-Bi_2S_3-Bi_2Te_3 are actually composed of several basic structures, such as five-layer (phase C, tetradymite), seven-layer (phase E, rucklidgeite), and nine-layer (phase J), and their combinations, such as phase D (five and seven layers) and phase F (seven and nine layers). Phases K, A, and M may be considered as binary solid solutions in which small amounts of S are randomly distributed in the Te layers.

Combining experimental results established in the lead and bismuth chalcogenide systems with the structural features of the end-members, the composite layer-type structures should also have the following characteristics: (1) PbX layers form the central parts of the unit stacks. (2) As in PbX compounds, the PbX_6 polyhedra should be regular, and so the two X layers above and below the Pb layer should be the same in composition. (3) On the basis of the structure of tetradymite, if two or more chalcogen elements are present, the smaller one should occupy the inner layers of the unit stacks. (4) The degree of substitution among the chalcogen elements in each X layer should be similar to that in their end-members.

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ERRATUM

An improved method for algebraic analysis of metamorphic mineral assemblages, by George W. Fisher (v. 78, p. 1257–1261). Tim Fagan of the University of California, Davis, has pointed out that Equations 19 and 20 are incorrect. They should read as follows:

$$(\mathbf{D}\cdot\mathbf{A}^{t})\cdot(\mathbf{D}\cdot\mathbf{B}) = \mathbf{C} \tag{19}$$

$$\mathbf{B}_{ls} = (\mathbf{D}\cdot\mathbf{A}^{t})\backslash(\mathbf{D}\cdot\mathbf{C}). \tag{20}$$