Thermochimica Acta, 32 (1979) 57–62
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PHASE DIAGRAM OF THE SYSTEM A(I)–B(V)–C(VI). II. TERNARY SYSTEM Na–Sb–Se

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(Received 31 August 1978)

ABSTRACT

The ternary system Na–Sb–Se has been studied by DTA and X-ray diffraction methods in the ranges NaSb–Se, Na_2Se_4–Sb and $Na_{0.22}Se_{0.78}Sb$ (the Na_2Se–Sb_2Se_3 range has already been investigated by the authors). From the data, the liquid surface of the Na–Sb–Se ternary system was constructed. The largest primary crystallization field belongs to the $NaSbSe_2$ compound. There is a large immiscibility region with boundaries about 44–82 at. % Sb. X-Ray data for two forms of $NaSbSe_2$ are also given.

INTRODUCTION

The Na–Sb–S ternary system was the first one investigated[1, 2] in the series A(I)–B(V)–C(VI). In the Na–Sb–Se system, only the binary systems Na–Sb (ref. 3), Na–Se (ref. 3), Sb–Se (ref. 4) and Na_2Se–Sb_2Se_3 (ref. 5), have been studied earlier.

In the present paper, we describe the results of our investigation of the Na–Sb–Se ternary system by DTA and X-Ray diffraction methods.

EXPERIMENTAL

The starting materials used in this study were Sb metal (99.9 %), selenium (99.99 %) and the $NaSbSe_4$ compound which has been synthesized from the elements.

DTA heating and cooling curves were recorded on an NTR-64 thermal analysis apparatus in evacuated and sealed silica tubes. The heating rate was 8–10 deg min^{-1}. Temperature was measured with a Pt/10 % Rh–Pt thermocouple with an accuracy to ±5 °C. X-Ray data were obtained on a DRON-1,5 diffractometer with unfiltered Fe radiation. X-Ray examination of all samples was carried out in air.

The alloys prepared were heated for 300–500 h at 300–400 °C to assure complete homogeneity (on X-ray data). Specimens from the NaSb–Se_2 region were quenched from a temperature above 480 °C in order to make the NaSbSe a more homogeneous region. The samples on the NaSb–Se region were heated until they were in equilibrium and after this they were quenched from 500–600 °C to room temperature.

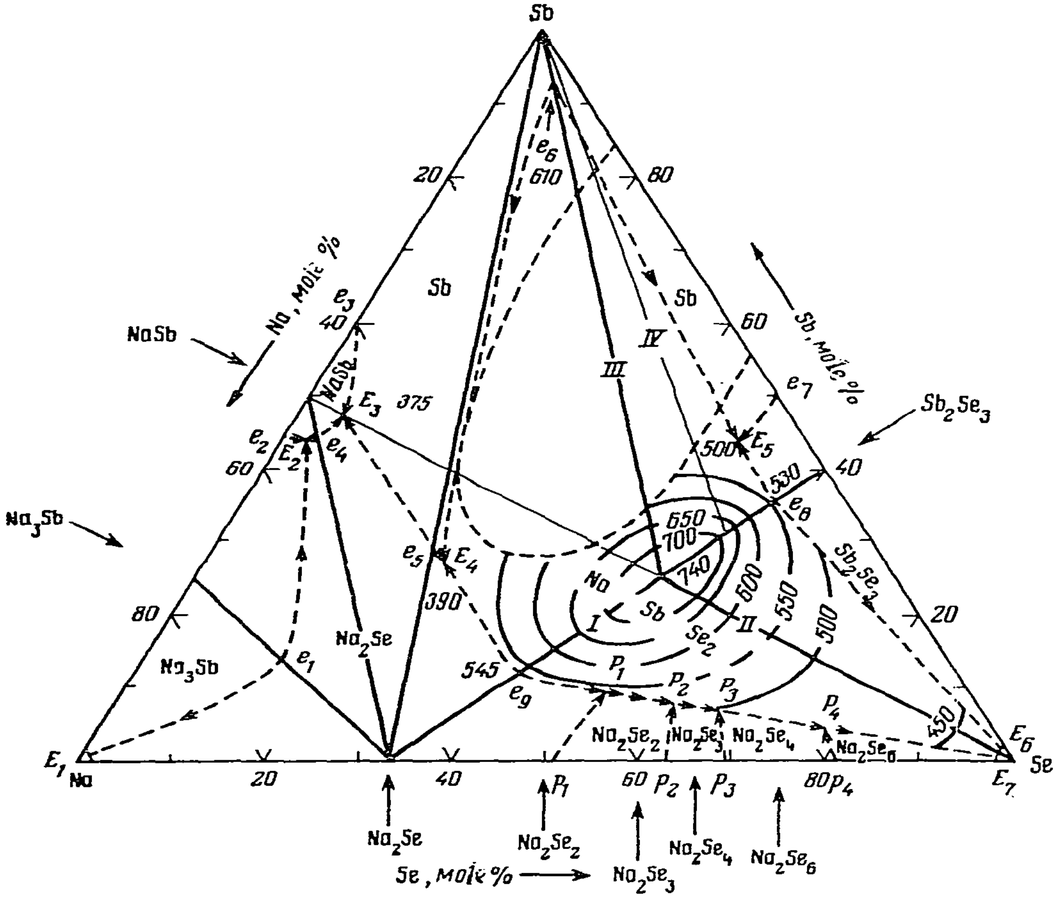

Fig. 1. Liquidus surface of the Na–Sb–Se system.

RESULTS

Four regions Na_2Se–Sb_2Se_3 (see ref. 3), Se–NaSb, $Na_{0.33}Se_{0.67}$–Sb and $Na_{0.22}Se_{0.78}$–Sb have been investigated to construct the phase diagram. The liquidus surface of the ternary system is given in Fig. 1 (triangulating sections are shown by the heavy lines) given in our earlier paper[6]. For the phase diagram construction, there were taken into account the data of Na_3Sb and NaSb alloys in Na–Sb binary systems[3] (melting point 856 and 465 °C, respectively), Na_2Se in the Na–Se binary system[3] (m.p. 875 °C) and the other four compounds in the system with decomposition points at 435, 313, 290 and 258 °C, and also the Sb_2Se_3 compound in the Sb–Se binary system[4] which melts congruently from the study at 621 ± 3 °C.

It has been found that from above four regions that the region Na_2Se–Sb_2Se_3 is quasibinary and in this region the only ternary compound $NaSbSe_2$ crystallizes[5]. This compound has two modifications with a transition point at 480 ± 5 °C. The high-temperature form crystallizes in the cubic system with a cell parameter $a = 5.965 \pm 0.001$ Å, NaCl type structure, space group *Fm*3*m*. Powder diffraction data and indexation are given in Table 1.

TABLE 1

POWDER DIFFRACTION DATA OF HIGH-TEMPERATURE $NaSbSe_2$

h	*k*	*l*	d_{obs} (*Å*)	d_{calc} (*Å*)	*I*
1	1	1		3.444	
2	0	0	2.980	2.983	100
2	2	0	2.106	2.110	43
3	1	1	1.783	1.799	2
2	2	2	1.719	1.724	24
4	0	0	1.492	1.493	18
3	3	1		1.3686	
4	2	0	1.3336	1.3343	38
4	2	2	1.2168	1.2166	33
5	1	1	1.1480	1.1485	3
4	4	0	1.0572	1.0568	7

$a = 5.965 \pm 0.001$ Å, S.G. $Fm3m$ (NaCl type)

The $NaSbSe_2$ low-temperature form crystallizes as an orthorhombic system. The cell parameters were calculated on an M-222 computer using a special program[7]. The powder spectrum for the $NaSbSe_2$ low-temperature form was fully indexed on the basis of an orthorhombic unit cell of dimensions $a = 10.69$ Å, $b = 9.37$ Å and $c = 10.93$ Å. This cell may be related with the high-temperature cubic lattice by the relationships $a_{orth} \sim a_{cub}\sqrt{3}$; $b_{orth} \sim a_{cub}\sqrt{2}$; $c_{orth} \sim a_{cub}\sqrt{3}$.

The theoretical density for ten formula units in the cell is 4.60 g cm^{-3}. Pycnometric measurements on the finely powdered material in dry toluene give the average value 4.52 g cm^{-3}. Theoretical and pycnometric densities of the cubic $NaSbSe_2$ were 4.74 and 4.68 g cm^{-3}, respectively.

Table 2 gives the fully indexed X-ray powder pattern for the low-temperature $NaSbSe_2$. Systematic absences were observed for $h \neq 2n$ in $h00$ reflections and for $k \neq 2n$ in $0k0$ reflections, $l \neq 2n$ in $00l$ reflections, also for $h + l \neq 2n$ in $h0l$ reflections and for $k + l \neq 2n$ in $0kl$ reflections. The possible space groups are then $Pnn2$-C_{2v}^{10} or $Pnnm$-D_{2h}^{12}.

The NaSb–Se region consists of two parts: NaSb–NaSbSe (the first part and the non-quasibinary subregion) and the $NaSbSe_2$–Se (the quasibinary subregion) which shows a degenerated eutectic at 220 °C. At the $Na_{0.33}Se_{0.67}$–Sb quasibinary region, a eutectic is located at 610 °C; a large immiscibility region stretches from ~33.3 to ~78 Sb at. % and the monotectic temperature is 720 °C. The $Na_{0.22}Se_{0.78}$–Sb is a non-quasibinary region possessing a large immiscibility region which has boundaries at ~44–83 Sb at. % and the monotectic temperature is located between 685 and 700 °C. The total list of equilibrium equations is given in Table 3.

TABLE 2

POWDER DIFFRACTION DATA OF LOW-TEMPERATURE $NaSbSe_2$

I	d_{obs}	d_{calc}	h	k	l
11	5.96	5.92	1	1	1
66	5.43	5.46	0	0	2
16	5.29	5.34	2	0	0
5	4.74	4.680	0	2	0
14	4.29	4.32	1	1	2
		4.29	1	2	0
		4.27	2	1	1
4	4.02	3.99	1	2	1
2	3.60	3.56	0	2	2
100	2.998	3.000	0	3	1
98	2.986	2.988	1	3	0
5	2.775	2.780	3	2	0
9	2.631	2.628	1	3	2
9	2.620	2.620	2	3	1
4	2.479	2.500	4	1	1
8	2.459	2.458	3	1	3
12	2.368	2.370	0	3	3
5	2.308	2.305	1	3	3
9	2.295	2.296	3	3	1
		2.290	1	4	0
10	2.240	2.240	1	4	1
		2.238	3	2	3
36	2.147	2.145	0	4	2
		2.143	2	4	0
21	2.098	2.100	4	1	3
		2.098	5	0	1
28	2.086	2.088	1	1	5
		2.084	5	1	0
7	1.982	1.978	2	1	5
7	1.909	1.915	5	2	1
		1.911	4	0	4
3	1.848	1.847	0	5	1
		1.846	1	5	0
5	1.762	1.766	1	3	5
		1.764	5	3	0
		1.762	4	4	0
7	1.750	1.750	6	1	0
8	1.741	1.742	5	3	1
2	1.667	1.666	0	5	3
		1.665	6	2	0
3	1.626	1.630	3	5	1
8	1.5001	1.5018	0	6	2
		1.4990	2	6	0
8	1.3218	1.3213	3	5	5

$a = 10.69 \pm 0.02$ Å; $b = 9.37 \pm 0.02$ Å; $c = 10.93 \pm 0.02$ Å; S.G. $Pnn2$ or $Pnnm$.

TABLE 3

INVARIANT POINTS AND EQUILIBRIUM EQUATIONS IN THE Na–Sb–Se TERNARY SYSTEM

Invariant point	*T (°C)*	*Equilibrium equation*
E_1	97	$L \rightleftarrows Na_3Sb + Na_2Se + Na$
E_2		$L \rightleftarrows Na_3Sb + Na_2Se + NaSb$
E_3	475	$L \rightleftarrows Na_2Se + NaSb + Sb$
E_4		$L \rightleftarrows Na_2Se + \alpha\text{-}NaSbSe_2 + Sb$
E_5	500	$L \rightleftarrows \alpha\text{-}NaSbSe_2 + Sb_2Se_3 + Sb$
E_6	220	$L \rightleftarrows \alpha\text{-}NaSbSe_2 + Sb_2Se_3 + Se$
E_7	220	$L \rightleftarrows \alpha\text{-}NaSbSe_2 + Na_2Se_6 + Se$
e_1		$L \rightleftarrows Na_3Sb + Na_2Se$
e_2	435	$L \rightleftarrows Na_3Sb + NaSb$
e_3	400	$L \rightleftarrows NaSb + Sb$
e_4		$L \rightleftarrows NaSb + Na_2Se$
e_5		$L \rightleftarrows Na_2Se + Sb$
e_6	610	$L \rightleftarrows \alpha\text{-}NaSbSe_2 + Sb$
e_7	530	$L \rightleftarrows Sb_2Se_3 + Sb$
e_8	530	$L \rightleftarrows \alpha\text{-}NaSbSe_2 + Sb_2Se_3$
e_9	545	$L \rightleftarrows \alpha\text{-}NaSbSe_2 + Na_2Se$
P_1		$L + Na_2Se \rightleftarrows \alpha\text{-}NaSbSe_2 + Na_2Se_2$
P_2		$L + Na_2Se_2 \rightleftarrows \alpha\text{-}NaSbSe_2 + Na_2Se_3$
P_3		$L + Na_2Se_3 \rightleftarrows \alpha\text{-}NaSbSe_2 + Na_2Se_4$
P_4		$L + Na_2Se_4 \rightleftarrows \alpha\text{-}NaSbSe_2 + Na_2Se_6$
p_1	495	$L + Na_2Se \rightleftarrows Na_2Se_2$
p_2	313	$L + Na_2Se_2 \rightleftarrows Na_2Se_3$
p_3	290	$L + Na_2Se_3 \rightleftarrows Na_2Se_4$
p_4	258	$L + Na_2Se_4 \rightleftarrows Na_2Se_6$

DISCUSSION

From these studies, taking into account the earlier study, the liquidus surface of the Na–Sb–Se ternary system was constructed (see Fig. 1). On the basis of the phase diagram, the compound $NaSbSe_2$ was found to be the only ternary phase present in the system. It melts congruently at 740 ± 5 °C and has a reversible phase transition at 480 °C. The high-temperature (β) modification has a face-centered cubic unit cell and crystallizes in the NaCl type structure[8].

Miller's indexes in Table 1 with $h + k + l \neq 2n$ are very weak and its intensities are near a background. Such a ratio of intensities for $h + k + l = 2n$ and $h + k + l \neq 2n$ indexes supposes an NaCl structure with statistically distributed sodium and antimony atoms in (4a) sites with (0,0,0) and (0,1/2,1/2, ↴) positions. Se atoms are located in (4b) sites with (1/2,1/2,1/2) and (0,0,1/2, ↵) positions. The crystal structure of β-$NaSbSe_2$ one can derive by octahedrally coordinated anions and mixed cations (Na + Sb) which are links in a three-dimensional framework with edge-sharing octahedra. The observed distortion of the cubic lattice causes a change of both octahedron types.

$NaSbSe_2$ possesses the biggest primary crystallization field. Another large primary crystallization field belongs to the Na_2Se compound. There are also primary crystallization fields of NaSb, Na_3Sb, Na_2Se_n (n = 2,3,4,6) and Sb_2Se_3 phases, a large one of Sb metal and degenerated primary crystallization fields of sodium and selenium. There is a broad immiscibility region in the Na–Sb–Se system (dotted line in Fig. 1).

Boundary lines of monovariant equilibria cross over seven ternary eutectic points, four ternary peritectic points (so-called points of double ascent), nine binary eutectic points (six of which are saddle points) and four binary peritectic points. The boundaries of the primary crystallization fields in the figure are drawn with dotted lines and are extrapolated on the basis of triangulating sections.

We would like to emphasize the fact of the existence of a high-temperature form of NaSbSe in the homogeneity region along the NaSb–Se region to 54–55 Se at.%. Observed distortion of cubic structure on cooling may be connected with decreasing selenium solubility and changing stabilization factors and lattice energy.

From a comparison of the Na–Sb–Se ternary system phase diagram (from refs. 1 and 2) with this system, the followed conclusions may be drawn.

(1) In a system with heavier chalcogen the number of ternary compounds decreases from four to one.

(2) There is no immiscibility region in a chalcogenic field in the Na–Sb–Se system compared with the Na–Sb–S system.

(3) Both in the Na–Sb–S system and in the Na–Sb–Se system, the ternary compounds $NaSbX_2$ (X = S,Se) possess the largest primary crystallization fields.

(4) The Na_2X–Sb_2X_3 regions are quasibinary in both the ternary systems.

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