Polish J. Chem., **77**, 1027–1031 (2003)

Interaction of the Components in Li–V–Sn System at 470 K

by O. Azarska* and V. Pavlyuk

Ivan Franko L'viv National University, Department of Inorganic Chemistry, Kyryl and Mefodiy str. 6, 79005, L'viv, Ukraine
e-mail: Azarska@ukr.net

(Received February 7th, 2003; revised manuscript May 5th, 2003)

The isothermal section of the Li–V–Sn system at 470 K has been investigated by X-ray phase analysis. There is an unmixing region, which extends at ternary system to about 12 at. % of Sn. Two ternary phases $Li_{11}V_3Sn_4$ and ~LiV_2Sn and solid solutions based on the binary compounds were obtained. Crystal structures were determined for both ternary phases: $Li_{11}V_3Sn_4$ is a superstructure to $Li_{13}Sn_5$ binary compound, and LiV_2Sn crystallizes in a BiF_3 structure type. The solubility of the third component in the binary compounds is less than 10 at. %.

Key words: phase diagram intermetallic compound, X-ray diffraction

The ternary systems of the Li–T–X group (where T = transition metal, X = 4p-element) have not yet been thoroughly studied, that is why isothermal sections have been constructed only for 21, while more than 100 ternary systems of lithium with d-metals have already been researched partially or completely [1].

Phases Li_2TX, LiT_2X and $LiTX_2$, crystallizing in Heusler type (BiF_3 structure type with statistical distribution of positions, $MnCu_2Al$ and $CuHg_2Ti$ with ordered distribution of atoms), are the most common ternary compounds of Li–T–X group.

The interaction of lithium with vanadium and tin over the whole range of concentrations has not yet been studied. Therefore, the side systems Li–V, Li–Sn and V–Sn have been widely studied, including the phase diagrams over the whole concentration range [1,2]. Both compounds in the V–Sn system have a homogeneity range. The V_3Sn (structure type Cr_3Si) binary compound contains near 20–21 at. % Sn and V_2Sn_3 (structure type $CuMg_2$) binary compound contains near 60–62 at. % Sn. The metastable phase V_3Sn (structure type Ni_3Sn) [3] was not observed.

In this paper we present results on the isothermal section of the Li–V–Sn system at 470 K and data on the new ternary phases and solid solutions based on the binary compounds.

*Corresponding author.

EXPERIMENTAL

Isothermal section of the Li–V–Sn system has been investigated by X-ray phase analysis of 60 ternary and 5 binary alloys. The samples were prepared by reaction of the pure elements. High purity metals (Li – 99.96; V – 99.999; Sn – 99.997) were used. Alloys have been prepared by arc melting under argon atmosphere (with Ti as a getter), using nonconsumable tungsten electrode. During arc melting the weight losses were less than 2%. The alloys were annealed in quartz ampoules in vacuum at 470 K for 400 h.

Powder patterns for the phase analysis were obtained on powder diffractometers DRON-2.0 (FeKα-radiation) and HZG-4a (CuKα-radiation). The unit cell and structure parameters have been refined using the LATCON and RIETWELD ANALYSES programs [4].

The isothermal section of the Li–V–Sn system at 470 K has been constructed by comparing and analysis of the X-ray diffraction patterns of the alloys and identification of the phases in each sample.

RESULTS AND DISCUSSION

The interaction of lithium with vanadium and tin has not yet been studied. Isothermal section of the Li–V–Sn system has been constructed over the whole concentration range (Fig. 1). This system is characterized by the presence of field of unmixing Li and V, which reaches approximately up to 12 at. % of Sn in the ternary area.

Limited solid solutions based on binary compounds of Li–Sn and Sn–V systems were observed. $Li_{17}Sn_4$ binary compound dissolves up to 10 at. % V (Fig. 2); LiSn, $Li_{13}Sn_5$

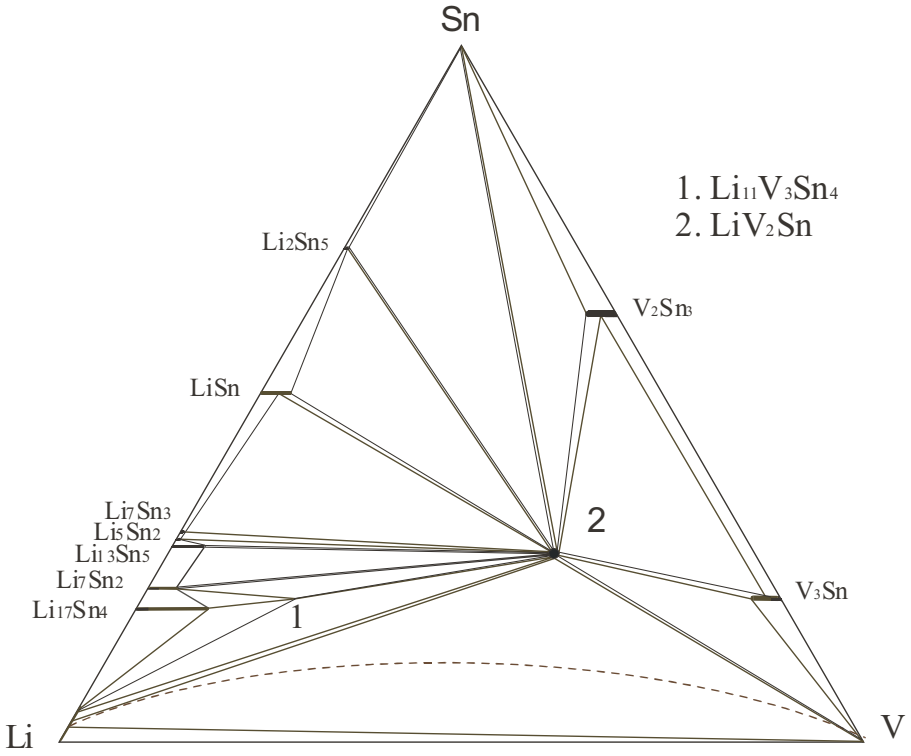

Figure 1. Isothermal section of the Li–V–Sn system at 470 K.

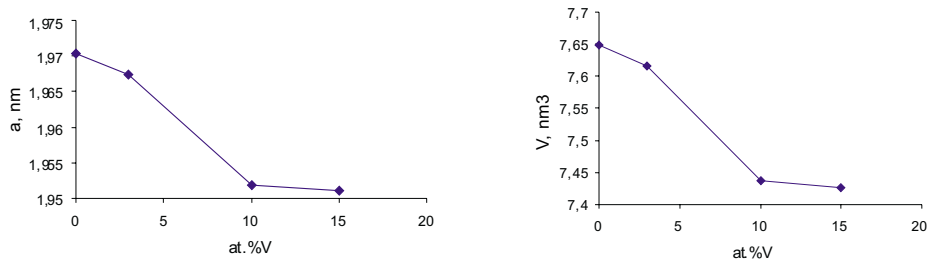

Figure 2. Change of lattice parameters for the solid solution based on the $Li_{17}Sn_4$ binary compound.

and Li_7Sn_2 binary compounds dissolve up to 5 at. % V; Sn_3V_2 and SnV_3 binary compounds dissolve up to 5 at. % Li. Change of the lattice parameters of the solid solutions are given in Table 1.

Two ternary phases were found in this system at 470 K. The phase $Li_{11}V_3Sn_4$ is a superstructure to $Li_{13}Sn_5$ binary compound (a = 0.47082(1) nm, c = 1.71004(2) nm, R_p = 8.04). This superstructure has a $Li_{13-x}V_{x+y}Sn_{5-y}$ general formula. Ternary phase LiV_2Sn has a BiF_3 structure type (a = 0.621292(1) nm, R_p = 5.29). The atomic coordinates for LiV_2Sn are given in Table 2. The atomic coordinates for $Li_{11}V_3Sn_4$ are given in Table 3.

The comparison of Li–V–Sn system with earlier studied systems Li–T–X (where T = transition metal, X = p-element) shows a single resemblance – a forming a small number of ternary compounds, some of them crystallizing in Heusler type.

The comparison of Li–V–Sn and Li–{Ti,V}–{Ge,Si} ternary systems shows that there exist: a field of unmixing of Li and Ti, Li and V; forming solid solutions on the base of binary phases; and a small quantity of ternary compounds [5,6].

Table 1. Change of the lattice parameters of the solid solutions based on the $Li_{17}Sn_4$, LiSn, $Li_{13}Sn_5$, Li_7Sn_2, Sn_3V_2 and SnV_3 binary compounds.

Compound	At. % V (Li)	Lattice parameters			Volume, nm^3
		a, nm	b, nm	c, nm	
$Li_{17}Sn_4$	0	1.9703			7.6492
	5	1.9643			7.575
	10	1.9519			7.437
	15	1.9511			7.427
LiSn	0	0.37907	0.3182	1.2035	0.14288
	5	0.3677	0.3031	1.1261	0.1238
	10	0.3676	0.3029	1.126	0.1237
$Li_{13}Sn_5$	0	0.4703		1.71301	0.3281
	5	0.4677		1.7002	0.3221
	10	0.4676		1.7	0.322

Table 1 (continuation)

Li_7Sn_2	0	0.9801	1.3809	0.475	0.6437
	5	0.9719	1.367	0.4715	0.626
	10	0.9717	1.367	0.4712	0.625
Sn_3V_2	0	0.9076	0.5287	1.826	0.8762
	5	0.90844	0.51752	1.77598	0.83495
	10	0.9085	0.5175	1.7759	0.8345
SnV_3	0	0.5289		0.4245	0.10286
	5	0.53981		0.4329	0.10926
	10	0.5398		0.433	0.1101

Table 2. The atomic coordinates for LiV_2Sn ternary phase.

Atom	Wyckoff positions	x/a	y/b	z/c
M1	8c	0.25	0.25	0.25
M2	4b	0.5	0.5	0.5
M3	4a	0	0	0

M1 = 45.4% Li + 54.6% Sn
M2 = 2.6% Li + 97.4% V
M3 = 8.6% Li + 91.4% V

Table 3. The atomic coordinates for $Li_{11}V_3Sn_4$ ternary phase.

Atom	Wyckoff position	x/a	y/b	z/c	B_i
Li1	1b	0	0	0.5	3.8
Li2	2c	0	0	0.65(2)	3.8
Li3	2c	0	0	0.83(2)	3.8
Li4	2d	0.3333	0.6667	0.96(2)	3.8
Li5	2d	0.3333	0.6667	0.28(2)	3.8
Li6	2d	0.3333	0.6667	0.12(1)	3.8
V	2d	0.3333	0.6667	0.438(2)	2.6(8)
Sn1	1a	0	0	0	2.9(8)
Sn2	2d	0.3333	0.6667	0.610(1)	2.9(4)
M	2d	0.3333	0.6667	0.779(2)	2.4(4)

M (2d) = 0.4(1) Sn + 1.6(1) V (20% Sn + 80% V).

REFERENCES

1. Ternary Alloys: binary alloys, quaternary alloys; Evaluated constitutional data, phase diagrams, crystal structures and applications of lithium alloy system, Eds: G. Effenberg, F. Aldinger, O. Bodak, Assoc. Ed. W. Pavlyuk, VCH Verlagsgesellschaft mbH, D-69469 Weinheim, 1995, V. 14–15, 906 p.
2. Massalski T.B., Binary Alloys Phase Diagrams, Am. Soc. Met., 1986, **1–2**, 2223 p.
3. Basile F., *Ann. Chim*., **6**, 241 (1971).
4. Wiles D.B., Sakthivel A. and Young R.A., Program DBW 3.2S for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns, Atlanta, Georgia Institute of Technology, 1988, 11 p.
5. Kevorkov D.G., Pavlyuk V.V. and Stepien-Damm I., Isothermal Sections of the Li–Ti–{Si,Ge} Phase Diagrams at 470 K. The 5 International School "Phase Diagram in Material Science", Katsyvely, 23–29 September 1996, p. 63–64.
6. Lozova O.A., Zatorska G.M., Kevorkov D.G. and Pavlyuk V.V., *Ukr. Chim. J*., **67** (5), 27 (2001).