Polish J. Chem., **75**, 1583–1586 (2001) **COMMUNICATION**

New $Zr_{5-x}Li_{x+y}Al_3$ and $Zr_5Zn_xAl_{3-x}$ Ternary Compounds Derived from Mn_5Si_3 Structure Type

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Alloys of the Zr–Li–Al and Zr–Zn–Al systems were prepared by arc-melting of pure metals (lithium with a purity 99.0 wt.%, zinc with a purity 99.9 wt.%, zirconium with a purity 99.98 wt.%, aluminium with a purity 99.99 wt.%) in argon atmosphere. The alloys Zr–Li–Al of ternary system were annealed at 470 K for 400 hours in tantalum containers in evacuated quartz ampoules and quenched in a cold water. Powder patterns were obtained by powder diffractometer DRON-2.0 (FeK_α-radiation, $20 \le \theta \le 100°$, 2 °/min speed of scanning). For more detailed structural investigation X-ray powder diffractometer HZG-4a with CuK_α-radiation was used. The lattice parameters and crystal structures refinement were calculated by LATCON and CSD-Universal program package for single crystal or powder structure data treatment [1].

We found at 470 K $Zr_{5-x}Li_{x+y}Al_3$ ($x = 0.2 \div 1.0$; $y = 0 \div 1$) and $Zr_5Zn_xAl_{3-x}$ ($x = 0.4 \div 0.6$) intermetallic compounds with wide homogeneity ranges. These ternary aluminides were studied by powder methods. The detailed investigation of the crystal structure $Zr_{5-x}Li_{x+y}Al_3$ has been carried out on an alloy of $Zr_{4.8}Li_{1.2}Al_3$ composition. The final crystallographic parameters are presented in Table 1. The structure was solved in space group $P6_3/mcm$ using the CSD program. The experimental X-ray diffraction pattern and the calculated and difference diffraction profiles are shown in Fig. 1, being in a very good agreement with the model based on the Ti_5Ga_4 structure type [2,3]. Atomic position parameters and interatomic distances are listed in Table 2 and 3.

The process of formation of ternary intermetallide is realized by a partial substitution of zirconium atoms in the 4(d) position by lithium atoms and insertion of lithium atoms in empty 2(b):000 position. Unit cell parameters in homogeneity range of $Zr_{5-x}Li_{x+y}Al_3$ compound change: a = 8.1336(1) ÷ 8.1757(2) Å, c = 5.7029(1) ÷ 5.6909(2) Å (Fig. 2,a).

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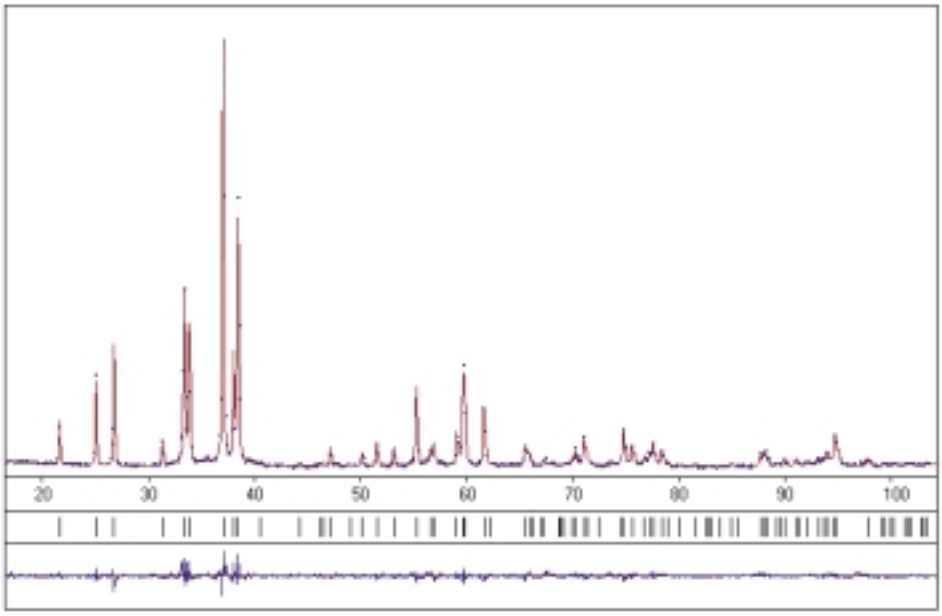


Figure 1. Experimental X-ray diffraction pattern, calculated and difference diffraction profiles for $Zr_{5-x}Li_{x+y}Al_3$ compound.

Table 1. Crystal data and structure refinement for $Zr_{5-x}Li_{x+y}Al_3$.

Space group	$P6_3/mcm$
a, (Å)	8.1757(2)
c, (Å)	5.6909(2)
Cell volume, (Å^3)	329.488(3)
F(000)	475.0
Number of atoms in cell	18.0
Calculated density, (g/cm^3)	5.3782
Absorption coefficient, (1/cm)	680.81
Radiation and wavelength	Cu 1.54178
Diffractometer	Powder
Mode of refinement	Full profile
Number of atom sites	4
Number of free parameters	14
2θ, sin(T/l) (max)	138.49 0.607
R(intensity), R(profile)	0.0749 0.1168
Scale factor	1.047(6)

Table 2. Atomic parameters of the $Zr_{5-x}Li_{x+y}Al_3$ compound.

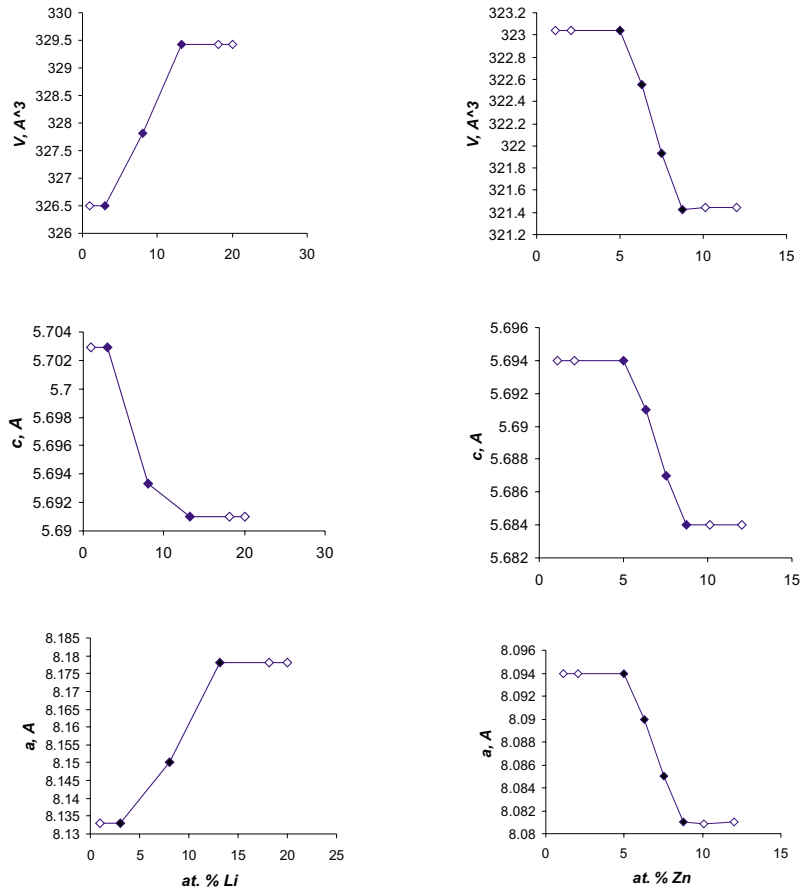
Atom	Site	*x/a*	*y/b*	*z/c*	B_{is}	G, %
Zr1	6g	0.2336 (2)	0	1/4	1.26 (6)	100
Zr2	4d	1/3	2/3	0	1.86 (7)	Zr-92, Li-8
Li	2b	0	0	0	2.9 (8)	Li-96, Zr-4
Al	6g	0.5987 (8)	0	1/4	2.3 (2)	100

Table 3. Interatomic distances and C.N. in the structure $Zr_{5-x}Li_{x+y}Al_3$.

Atoms	δ, Å	C.N.	Atoms	δ, Å	C.N.
Zr(1) – 2Li	2.3815				
– 1A1	2.8534		Al – 1Zr(1)	2.8534	
– 2A1	2.9858	15	– 4Zr(2)	2.8714	9
– 2A1	3.1582		– 2Zr(1)	2.9858	
– 4Zr(1)	3.3079		– 2Zr(1)	3.1584	
– 4Zr(2)	3.5121				
Zr(2) – 2Zr(2)	2.8454			2.3815	
– 6A1	2.8714	14	Li – 2Zr(2) – 6A1	2.8454	8
– 6Zr(1)	3.5121				

The Zr_5Al_4 binary compound (Ti_5Ga_4 structure type) [4] has not been found in Zr–Li–Al system at 470 K. It is stable between 1263 K to 1803 K. $Zr_{5-x}Li_{x+y}Al_3$ ternary compound, apparently, is remainder of high temperature substitution limited solid solution on the base Zr_5Al_4 binary compound or substitution and insertion limited solid solution on the base Zr_5Al_3 (Mn_5Si_3 structure type) [5].

New ternary $Zr_5Zn_xAl_{3-x}$ (x = 0.4÷0.6) alluminide with wide homogeneity range is formed when lithium atoms are replaced by zinc atoms in the $Zr_{5-x}Li_{x+y}Al_3$ structure. But the formation of this compound is carried out by a partial substitution of Al atoms by Zn atoms. The structure was solved in space group $P6_3/mcm$ too, but Mn_5Si_3 structure type. Change of the lattice parameters of $Zr_5Zn_xAl_{3-x}$ along of isoconcentrate 62.5 at.% of Zr is a = 8.094(3) ÷ 8.081(2) Å, c = 5.694(1) ÷ 5.684(1) Å (Fig. 2,b).



a) $Zr_{5-x}Li_{x+y}Al_3$ **b)** $Zr_5Zn_xAl_{3-x}$

Figure 2. Change of lattice parameters for the $Zr_{5-x}Li_{x+y}Al_3$ **(a)** and $Zr_5Zn_xAl_{3-x}$ **(b)**.

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