NEW VARIANT OF THE STRUCTURE OF THE $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ INTERMETALLIC COMPOUND

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Abstract

Existence of compound with wide homogeneity range along isoconcentrate of 0.33 atomic part of Li $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ have been confirmed and composition and lattice periods have been determined by powder diffraction (powder diffractometer DRON-2.0, FeKα-radiation): a = 1.4017(3) ÷ 1.3904(3) n; increasing of lattice period with changing x from 0 to 0.06 part of lithium is 0.0023 nm.

The crystal structure of LiZnAl have been solved by the single-crystal X-ray analysis (KM-4 automatic diffractometer, MoKα-radiation with graphite monochromator, ω/θ scan mode, 4° ≤ 27° ≤ 70°, number of unique (hkl) - 434, R = 0.044). This compound crystalized in LiCuSi structure type, space group $Im\overline{3}$.

For statistical mixture of Zn and Al in general characteristic icosahedral coordination of polyhedrons (coordinating numbers 11 for M3, 12 for M2 and M4 and 14 for M1). For Li atoms characteristic more complicated polyhedrons with coordinating numbers 15 for Li1 and 16 for Li2 and Li3.

1. Introduction

First information about the existence of the compound with a wide homogeneity range along the isoconcentrate of 33.3 at.% of Li in the Li-Zn-Al system was presented in [1]. The $Mg_{32}(Zn,Al)_{49}$ structure type for this compound with approximate composition $LiZn_{0.5-1.3}Al_{1.5-0.7}$ was proposed in [2].

We have investigated Li-Zn-Al system in whole concentration range at 470 K and confirmed existence of this compound. Results of our research elaborated the homogeneity range for this compound: $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$. We have also refined its crystal structure in LiCuSi structure type by the X-ray single crystal method.

2. Experimental

Alloys of the Li-Zn-Al system were prepared by arc-melting pieces of the pure metals (lithium with a purity 98.2 wt.%, zinc with a purity 99.98 wt.%, aluminium with a purity 99.99 wt.%) in the argon atmosphere. The alloys were annealed at 470 K for 400 hours in a tantalum containers in an evacuated quartz ampoules and quenched in a cold water.

Powder patterns were obtained by powder diffractometer DRON-2.0 (FeKα-radiation, 20° ≤ θ ≤ 100°, 2°/min speed of scanning). Lattice parameters were calculated using LATCON program.

The X-ray intensities data were collected by a Kuma-Diffraction KM-4 four-circle single crystal diffractometer using graphite-monochromatized MoKα radiation (ω/θ scan mode, 4° ≤ 2θ ≤ 70°, 0.03-0.1° /min speed of scanning). Structure was solved by the direct method and refined by the full-matrix least squares method using the SHELXL program [3].

3. Results and Discussion

The main reason of the present investigation was the conclusion of author [2] on the belonging of the crystal structure of the $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ compound to the $Mg_{32}(Zn,Al)_{49}$ structure type which was based only on the comparison of Debye-Scherrer photographs (camera RKD-57.3) of compounds with composition from concentration interval $LiZn_{0.5-1.3}Al_{1.5-0.7}$ with photograph of early investigated compound Li_3CuAl_5, without refinement of the structure. Boundaries of homogeneity range and change of lattice parameters in it we calculated using powder patterns. Change of the lattice parameters a of $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ along the isoconcentrate 33.3 at.% of Li is 1.4017(3)1.3904(3) nm and the increase of lattice parameters a with change of x from 0 to 0.06 is 0.0023 nm.

For the refinement of crystal structure of $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ compound we investigated single crystal, obtained from alloy with composition LiZnAl, by the Kuma-Diffraction KM-4 four-circle single crystal diffractometer. Structure was solved in $Im\overline{3}$ space group, but as LiCuSi structure type in contrast to $Mg_{32}(Zn,Al)_{49}$ structure type proposed by [2]. Our model of crystal structure of the $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ compound differs from the model [2] by two aspects: first, the site 2(a) is vacant (in

Table 1. Atomic parameters of the LiZnAl compound

Atom	Site	x	y	z	B_{eq}
M1(13%Zn+87%Al)	12(e)	1/2	0.096(1)	0	0.375
M2(89%Zn+11%Al)	24(g)	0	0.312(2)	0.177(2)	0.460
M3(58%Zn+42%Al)	24(g)	0.154(1)	0.094(2)	0	0.407
M4(31%Zn+69%Al)	48(h)	0.406(2)	0.191(2)	0.158(2)	0.420
Li1	12(e)	1/2	0	0.196(1)	0.489
Li2	16(f)	0.187(1)	0.187(1)	0.187(1)	0.489
Li3	24(g)	0	0.118(2)	0.302(2)	0.450

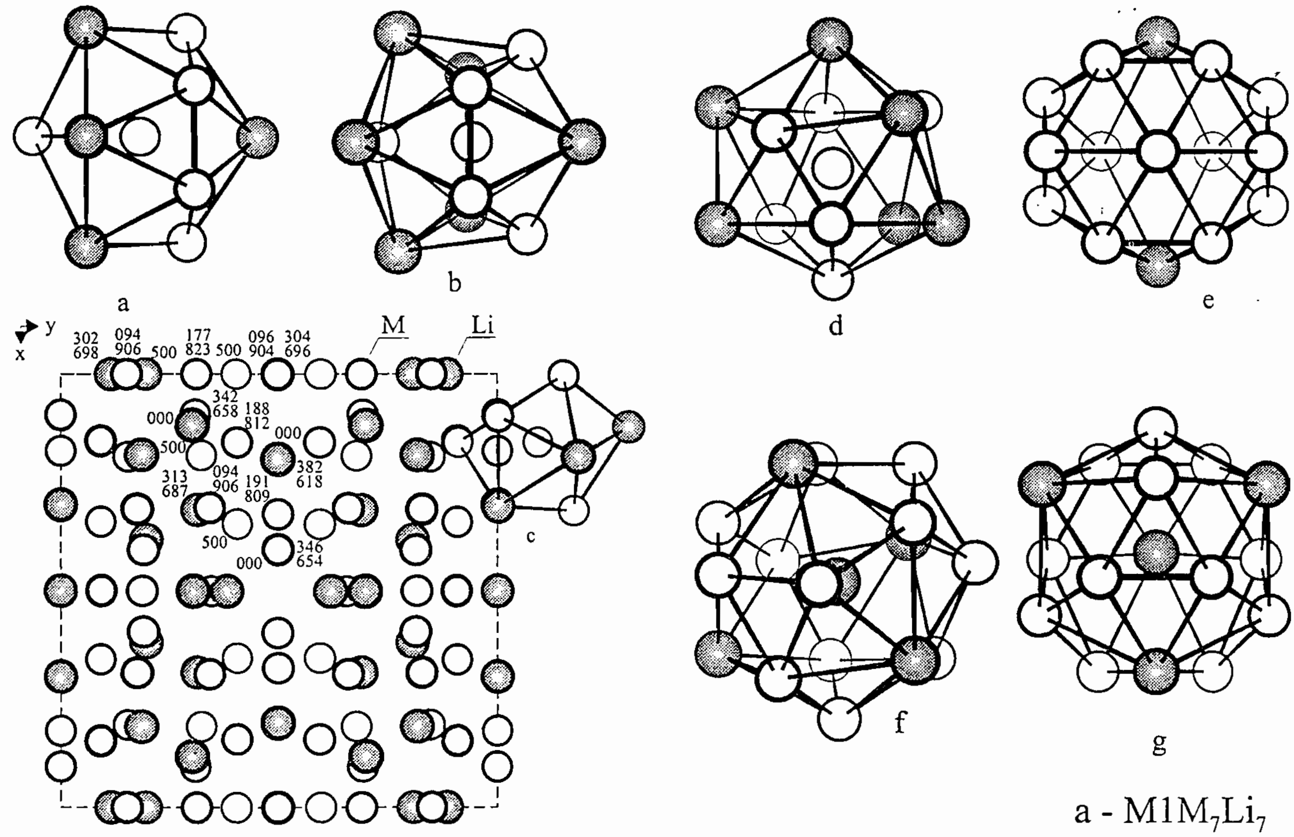

Fig.1 The projection of the unit cell of the $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ compound on the X-Y plane and the coordination polyhedra of the atoms.

a - $M1M_7Li_7$

b - $M2M_6Li_6$

c - $M3M_6Li_5$

d - $M4M_6Li_6$

e - $Li1M_{13}Li_2$

f - $Li2M_{12}Li_4$

g - $Li3M_{12}Li_4$

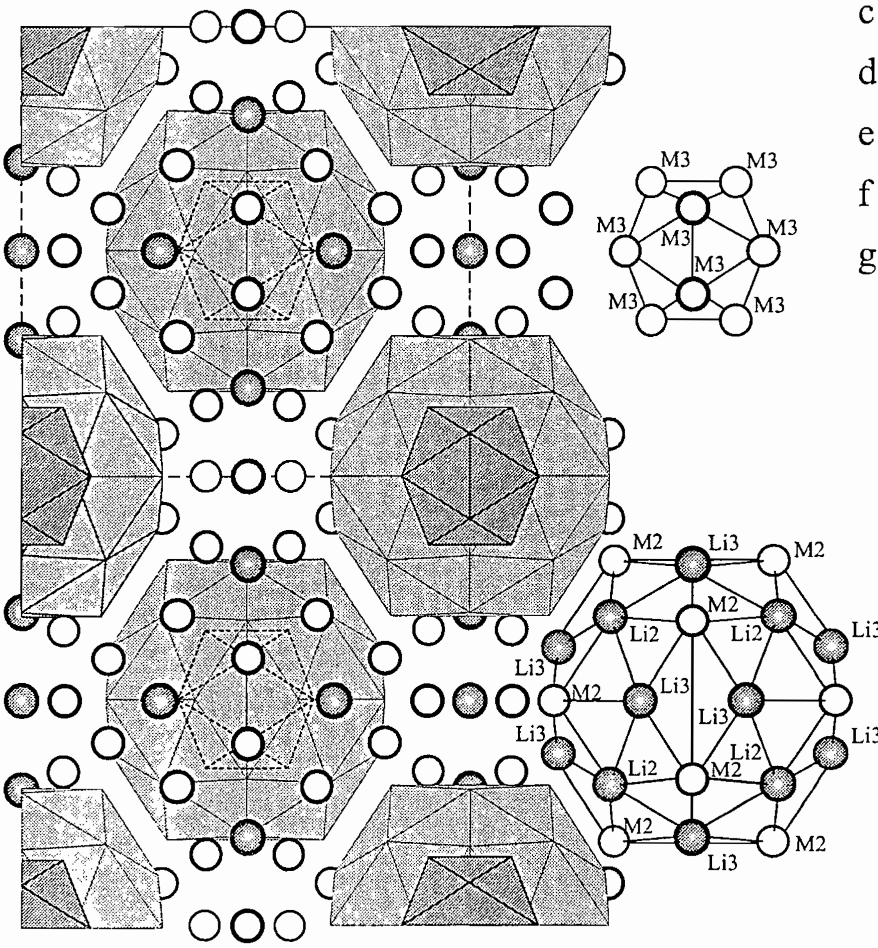

Fig.2. Packing of 32-vertices polyhedron complexes formed from M2, M3, Li2 and Li3 atoms around vacancies in 0 0 0 and ½ ½ ½ positions in the structure of the $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ compound.

Table 2. Interatomic distances and C.N. in the LiZnAl structure

Atoms		d, nm	C.N	Atoms		d, nm	C.N.
M1-	M1	0.2678		M2-	M3	0.249	
	2M2	0.2856			2M4	0.2572	
	4M4	0.2887	14		2M4	0.2649	
	2Li1	0.2902			M1	0.2856	12
	Li1	0.3045			2Li3	0.2971	
	4Li3	0.3483			2Li2	0.3141	
M3-	M2	0.2490			Li1	0.3165	
	M3	0.2623			Li3	0.3219	
	4M3	0.2652	11	M4-	M2	0.2572	
	Li3	0.2945			M4	0.2623	
	2Li3	0.2948			M2	0.2649	
	2Li2	0.2950			2M4	0.2658	
Li1-	M1	0.2902			M1	0.2887	
	2Li3	0.3000			Li1	0.3010	12
	4M4	0.3010	15		Li1	0.3017	
	4M4	0.3017			Li3	0.3022	
	2M1	0.3045			Li2	0.3042	
	2M2	0.3165			Li2	0.3082	
Li3-	M3	0.2945			Li3	0.3085	
	2M3	0.2948		Li2-	3M3	0.2950	
	2M2	0.2971			3M4	0.3042	
	Li1	0.3000			2Li2	0.3044	
	2M4	0.3022	16		3M4	0.3082	
	2M4	0.3085			2M2	0.3141	
	2Li2	0.3210			3Li3	0.3210	
	M1	0.3219					
	Li3	0.3292					
	2M1	0.3483					

model [2] this site is occupied by Al atoms); second, one of the sites 12(e) is occupied by Li atoms (in model [2] both sites 12(e) are occupied by mixtures of Zn and Al atoms statistically). Finally crystal structure is refined in isotropic approximation with $F(hkl) > 3\sigma(F)$ to $R = 0.044$ (number of unique (hkl) - 434). Atomic parameters obtained after refining are presented in the Table 1. Atomic coordinates are transformed in standard setting according to [4] (Table 1). Interatomic distances and coordination numbers (C.N.) in the structure of LiZnAl compound are presented in the Table 2.

The projection of the unit cell on the X-Y plane and the coordination polyhedra of the atoms are shown in Fig 1. Statistical mixture of Zn and Al atoms (atoms with minimal size in this structure) are characterized by icosahedral coordination. The coordination polyhedra of M2 and M4 are distorted icosahedra $[M2M_6Li_6]$ and $[M4M_6Li_6]$, the coordination polyhedron of M3 is defected icosahedron $[M3M_6Li_5]$ (vacancy in 2(a) site in icosahedron sphere). The coordination polyhedron of M1 has 14 vertices - $[M1M_7Li_7]$. There are three complicated coordination polyhedra of lithium atoms: one with 15-vertices $[Li1M_{13}Li_2]$ and two with 16-vertices: $[Li2M_{12}Li_4]$ and $[Li3M_{12}Li_4]$.

The crystal structure of $Li_{1+x}Zn_{0.5-1.5}Al_{1.5-0.5}$ compound can be described as a packing of 32-vertices polyhedron complexes formed from M2, M3, Li2 and Li3 atoms around vacancies in 0 0 0 and ½ ½ ½ positions and surrounded by the net from the M1, M4 and Li1 atoms (Fig. 2). The regular icosahedron from M3 atoms is in the a center of the complex. Li3 atoms are situated in opposite to every from 12 icosahedron edges which is in the form of isosceles triangles, Li2 atoms are situated in opposite to every from 8 icosahedron edges which is in the form of equilateral triangles, M2 atoms are situated in opposite to icosahedron vertices.

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