# The reinvestigation of the Li-Zn binary system.

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Lithium alloys attract much interest due to their wide application as anodes of rechargeable batteries and ultralight materials. In spite of extensive investigation of lithium binary and multicomponent systems, our knowledge about some phase digrams and the structures of phases is far from completeness. One of them is the title Li-Zn system. The oldest investigation of this system in full concentration range in 1933[1] was surprisingly accurate. The more recent variant of the phase diagram [2] is mostly based on the previous one. However, several regions had ambiguities and the structures of LiZn2, αLi2Zn5 and βLiZn4 phases remained unknown/uncertain. In course of our reinvestigation of the title system using DTA, powder and single crystal XRD, several amendments were made. The crystal structures of the α,βLiZn2, αLi2Zn5 and βLiZn4 compounds were studied.

­Previous authors treated non-variant transformation near 94ºC as solid state decomposition of the LiZn2 compound. It was found, that the compound LiZn2 has actually two modifications and polymorphic transition of LiZn2 occurs at that temperature. The crystal structures of the αLiZn2, βLiZn2, αLi2Zn5 and βLiZn4 compounds were determined. The αLi2Zn5  is the first representative of new binary structure type.

The low-temperature modification αLiZn2 (sp. gr. P-3m1, a=4.341(1) Å, c=8.024(2) Å) adopts trigonal structure type Zr2C0.6H2, as was determined from single crystal diffraction data. The case of βLiZn2 is more interesting. It has cubic symmetry and two models fit well to powder XRD data - more disordered centrosymmetric with structure of BiF3 (sp. gr. Fm-3m, a=6.1980(3) Å, 250°C) or more ordered non-centrosymmetric with structure of Li2AgSb (sp. gr. F-43m, a=6.1763(3) Å, 150°C). The former slightly better describes powder pattern of LiZn2 alloy, annealed at 250°C, whereas the latter - for the alloy at 150°C. The pattern of the alloy at 200°C is equally well described by both models. Both models have mixed Li/Zn sites, thus the stoichiometry remains Li:Zn=1:2. While powder XRD data does not allow us to choose space group with absolute certainty, one can suppose that firstly αLiZn2 transforms into βLiZn2 near 94°C, then βLiZn2 undergoes gradual disordering from Li2AgSb-type structure into BiF3-type structure at temperatures between 150 and 250 °C. All that is in accordance with empirical rule, that temperature increase leads to increase of symmetry and degree of disorder.

Unexpectedly the compound Li2Zn5 shows completely opposite traits. The low-temperature modification αLi2Zn5 (sp. gr. P-6, a=11.5523(4) Å, c=17.606(2) Å, 136 atoms/unit cell) has hexagonal symmetry and is disordered, it has 5 disordered sites, occupied by statistical mixture of Li and Zn. In contrast to that high-temperature modification βLi2Zn5(space group P-1, 86 atoms/unit cell) has triclinic symmetry and is almost completely ordered with single partially occupied lithium position. The analysis of the electronic density maps of α/βLi2Zn5, calculated by DFT method, gives hints concerning possible mechanism of the polymorphic transformation of this compound. Both modifications share common motif despite large structural differences. It is lithium filled channels, made of zinc atoms. The 5specific structural feature of the βLi2Zn5 is 7- and 17-member Li atom chains inside the Zn channels, while αLi2Zn5 has similar 6-member Li chains and almost infinite Li chains, terminated on by Zn atoms in mixed Li25/Zn25 and Li26/Zn26 mixed sites. Both αLi2Zn5 and βLi2Zn5 have indirect contacts between Li chains through the openings in Zn channels. The suggested mechanism of polymorphic transformation, substantiated by our calculations, is the rearrangement of Li atoms inside Zn-channels leading to changes of the unit cell, symmetry and some disordering of Zn atoms, forming the walls of the channels

The high-temperature modification βLiZn4 (sp. gr. P63/m, a=19.376(4) Å, c=4.386(1) Å) consists of the same hcp motif as both αLiZn4 (LiZn4-x, x=0.825 [3]) and elementary zinc. Both α and βLiZn4 have different ordering of mixed sites, leading to very distinct unit cells. The structure of βLiZn4 is partially ordered derivative of HCP. It can be obtained by creating 7x7x1 supercell from the unit cell of zinc with subsequent partial substitution of zinc by lithium in part of positions.

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