

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 diagrams 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 LiZn_2 , $\alpha\text{Li}_2\text{Zn}_5$ and βLiZn_4 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 $\alpha, \beta\text{LiZn}_2$, $\alpha\text{Li}_2\text{Zn}_5$ and βLiZn_4 compounds were studied. Previous authors treated non-variant transformation near 94°C as solid state decomposition of the LiZn_2 compound. It was found, that the compound LiZn_2 has actually two modifications and polymorphic transition of LiZn_2 occurs at that temperature. The crystal structures of the αLiZn_2 , βLiZn_2 , $\alpha\text{Li}_2\text{Zn}_5$ and βLiZn_4 compounds were determined. The $\alpha\text{Li}_2\text{Zn}_5$ is the first representative of new binary structure type.

The low-temperature modification αLiZn_2 (sp. gr. P-3m1, $a=4.341(1)$ Å, $c=8.024(2)$ Å) adopts trigonal structure type $\text{Zr}_2\text{C}_{0.6}\text{H}_2$, as was determined from single crystal diffraction data. The case of βLiZn_2 is more interesting. It has cubic symmetry and two models fit well to powder XRD data - more disordered centrosymmetric with structure of BiF_3 (sp. gr. Fm-3m, $a=6.1980(3)$ Å, 250°C) or more ordered non-centrosymmetric with structure of Li_2AgSb (sp. gr. F-43m, $a=6.1763(3)$ Å, 150°C). The former slightly better describes powder pattern of LiZn_2 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 αLiZn_2 transforms into βLiZn_2 near 94°C, then βLiZn_2 undergoes gradual disordering from Li_2AgSb -type structure into BiF_3 -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 Li_2Zn_5 shows completely opposite traits. The low-temperature modification $\alpha\text{Li}_2\text{Zn}_5$ (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 $\beta\text{Li}_2\text{Zn}_5$ (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 $\alpha/\beta\text{Li}_2\text{Zn}_5$, 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 specific structural feature of the $\beta\text{Li}_2\text{Zn}_5$ is 7- and 17-member Li atom chains inside the Zn channels, while $\alpha\text{Li}_2\text{Zn}_5$ 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 $\alpha\text{Li}_2\text{Zn}_5$ and $\beta\text{Li}_2\text{Zn}_5$ 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 βLiZn_4 (sp. gr. P6₃/m, $a=19.376(4)$ Å, $c=4.386(1)$ Å) consists of the same hcp motif as both αLiZn_4 (LiZn_{4-x} , $x=0.825$ [3]) and elementary zinc. Both α and βLiZn_4 have different ordering of mixed sites, leading to very distinct unit cells. The structure of βLiZn_4 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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