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Dieter Fischer, Martin Jansen

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Synthesis and Crystal Structure of LiZn_{13}

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Synthesis and Crystal Structure of LiZn_{13} Dieter Fischer and Martin Jansen^{*,[a]}**Keywords:** Lithium, Zinc, Structure elucidation, Thermal properties, Intermetallic phases

Abstract. By simultaneous deposition of zinc and lithium onto a cooled sapphire substrate, LiZn_{13} was obtained for the first time. It crystallizes in the NaZn_{13} structure type ($Fm\bar{3}c$, $a = 1234.92(6)$ pm, $R_p = 5.4\%$, $R_{wp} = 6.9\%$, structure analysis with the Rietveld-method). Single-phase LiZn_{13} forms from a hexagonal $\text{Li}_{0.07}\text{Zn}_{0.93}$ alloy, deposited at -196 °C, during heating up to room temperature. Above room temperature LiZn_{13} decomposes.

* Prof. Dr. M. Jansen

Fax: +49(0)711-6891502

E-mail M.Jansen@fkf.mpg.de

[a] Max-Planck-Institut für Festkörperforschung

Postfach 800665

D-70506 Stuttgart

Introduction

The cubic NaZn_{13} type of structure [1-4], which is genuinely adopted by binary alloys of alkali metals and zinc, or cadmium, of respective composition, is featuring several remarkable characteristics. Among others, the space filling tiling of three kinds of polyhedra, icosahedra, snub cube and tetrahedral star, do not show significant variations in the dimensions with the size of the alkali metal incorporated in the center of the snub cube [4]. This is e.g. reflected by the rather low increase of the lattice constant from 1379, to 1384, and to 1392 pm in the row KCd_{13} , RbCd_{13} , CsCd_{13} , respectively. From this fact one might deduce that the size of the alkali metal would not crucially determine the stability range of the structure type. Against this background,

the nonexistence of a representative of this structure type involving lithium has attracted our attention.

Since the binary system Li/Zn appears to have been extensively studied experimentally [5, 6] using the common metallurgical tools, we assume that LiZn_{13} does not exist as a thermodynamically stable compound. Recently, we have demonstrated that our low-temperature atomic beam deposition technique (LT-ABD) [7, 8] is well suited to also synthesize metastable intermetallics. Along such a procedure we have realized the metastable cubic Laves-phase $\beta\text{-CaLi}_2$ for the first time, which transforms at 150 °C to the known thermodynamic stable structure of $\alpha\text{-CaLi}_2$ (MgZn_2 -type) [9]. We have employed our preparation technique at investigating the system Li/Zn and have identified new LiZn_{13} .

Thus far, several phases have been reported to exist in the system Li/Zn, however, only LiZn (NaTl structure-type) is well documented and unambiguously confirmed [10]. For the intermetallics $\text{LiZn}_{2.5}$ and LiZn_9 (β' -phase), only the lattice parameters were given [6, 11]. The β' -phase was claimed to show a homogeneity range of up to LiZn_4 [12],

1 and to adopt a hexagonal structure (hcp) with a random
2 distribution of zinc and lithium [13]. $\text{LiZn}_{1.5}$ and LiZn_2 were
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4 observed in the course of constitutional analysis of the Li/Zn
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6 system, however, were not characterized in any respect [6,
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11 Results and Discussion

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Co-depositing zinc and lithium with a ratio of Zn:Li = 13:1 onto single-crystalline sapphire substrates at $-196\text{ }^\circ\text{C}$ results in grey-metallic samples, which show up to $-50\text{ }^\circ\text{C}$ diffraction patterns of a hexagonal-closed-packed phase with lattice constants of $a = 277.04(6)$, $c = 439.07(9)$ pm. These values are in good agreement with the lattice constants of the β' -phase $\text{Li}_{0.1}\text{Zn}_{0.9}$ reported previously with $a = 278.2$, $c = 438.5$ pm [6]. The structure refinement by the Rietveld method confirms for the here obtained alloy $\text{Li}_{0.07}\text{Zn}_{0.93}$ the same structure, with a random atomic distribution of zinc and lithium at the sites of a hcp arrangement (for details see [14]).

By subsequent warming up to room temperature, the samples transform completely into the new phase LiZn_{13} (Figure 1). The diffraction patterns of LiZn_{13} can be indexed assuming a cubic unit cell, with a refined lattice constant of $a = 1234.92(6)$ pm. The structure determined by the Rietveld method reveals LiZn_{13} to be isostructural to NaZn_{13} [4] (Figure 2). The refinements indicate a mixed occupation of zinc and lithium on the sites 8a: Li ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) and 8b: Zn (0,0,0) with an average of the Li/Zn substitution, respectively on both 8a and 8b sites, of about 25%. Table 1 shows the crystal data of the structure refinement of a texture-free X-ray pattern including interatomic distances. The crystal structure consists of a 3-dimensional zinc

network built up by corner-connected, slightly distorted stella quadrangulae (Zn2 on 96i site). This network generates Zn-icosahedra, which are centered by zinc (Zn1: 8b). Lithium is located in the centers of snub cubes formed by 24 Zn2 atoms.

The rigid zinc network of the NaZn_{13} structure type exhibits only slight response at varying the type of alkali metals incorporated. This is reflected by the small difference of 1.5 % between the lattice constants of NaZn_{13} ($a = 1227.3$) and RbZn_{13} ($a = 1245.2$) [4]. Therefore, we expected for LiZn_{13} a slightly smaller lattice constant compared to NaZn_{13} . Surprisingly the lattice constant of LiZn_{13} has been reproducibly found to be larger, ranging between the values of NaZn_{13} and KZn_{13} . We regard the mixed occupation of the center of the Zn-icosahedra with 25% of lithium the main reason for this observation. Such an explanation appears to be reasonable since the larger atom/ion radius of Li should effect an expansion of the zinc network, and thus a respective increase of the lattice constant.

LiZn_{13} decomposes irreversibly to hexagonal, metallic zinc by further heating up to $160\text{ }^\circ\text{C}$ (Figure 1). The refinement of the lattice constants has resulted in $a = 266.04(2)$ and $c = 496.06(5)$ pm (room temperature), which is in good agreement with literature data reported for elemental zinc $a = 266.5$ and $c = 494.7$ pm [15]. We were unable to trace the release of lithium by X-ray powder diffraction, obviously because of the small amounts or the fine dispersion of Li.

Samples, which were deposited in the temperature range between $-50\text{ }^\circ\text{C}$ and room temperature onto a sapphire substrate, contain mixtures of the β' -phase, LiZn_{13} and metallic zinc in different ratios, depending on the preparation conditions. Occasionally mixtures of these

phases were also found in samples deposited at $-196\text{ }^{\circ}\text{C}$. Furthermore a slow transformation of LiZn_{13} into zinc occurs already at room temperature, during several days.

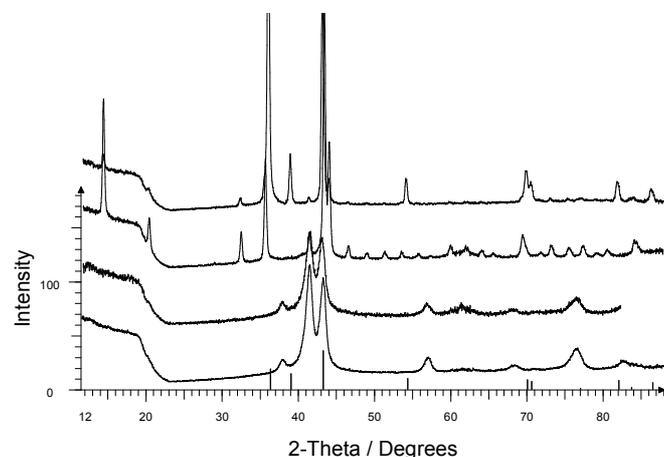


Figure 1. X-ray powder patterns of a Zn/Li co-deposition at $-196\text{ }^{\circ}\text{C}$ onto a sapphire substrate (ratio Zn:Li=13:1); scans measured at $-196\text{ }^{\circ}\text{C}$ (β' -phase), $-50\text{ }^{\circ}\text{C}$ (β' -phase), $25\text{ }^{\circ}\text{C}$ (LiZn_{13}), $160\text{ }^{\circ}\text{C}$ (Zn) from bottom to top; tick marks: metallic Zn (background s. experimental).

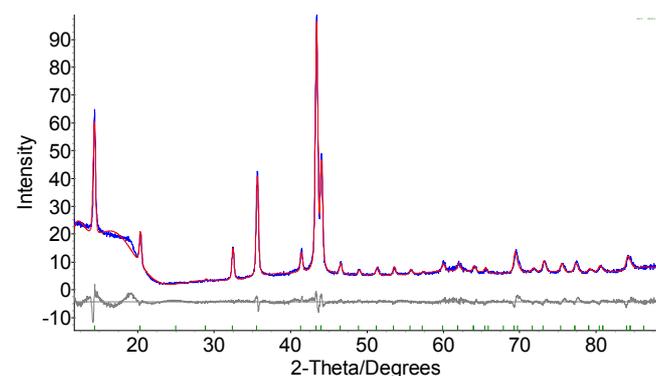


Figure 2. Rietveld refinement plot of LiZn_{13} : observed pattern (blue), fitted profile (red), difference profile (grey), tick marks: LiZn_{13} .

Table 1. Crystal data and structure refinement of LiZn_{13} [19].

Formula	LiZn_{13}
Weight (g/mol)	857.0

Temperature ($^{\circ}\text{C}$)	25
Crystal system	cubic
Space group	$Fm\bar{3}c$ (No. 226)
Lattice constant (pm)	$a = 1234.92(6)$
Formula units	8
Cell volume ($10^6 \cdot \text{pm}^3$)	1883.3
Mole volume (cm^3/mol)	141.8
X-ray density (g/cm^3)	6.1
Radiation	$\text{Cu-K}\alpha$ (1.54059, 1.54449)
Measured range (2θ)	$12 - 88^{\circ}$
Reflexes	34
Parameter	8
Crystal size (nm)	150
Atomic positions	Li: (1/4, 1/4, 1/4) Occ. Li/Zn=0.73/0.27, Zn1: (0, 0, 0) Occ. Zn/Li=0.85/0.15, Zn2: (0.1187, 0.3194(1), 0)
Isotropic thermal displacement B_{eq}	1.2(1) (Zn, Li)
R_p , R_{wp} , R_{Bragg}	5.4%, 6.9%, 1.3%
Selected interatomic distances (pm)	Zn2-Li: 359.1, Zn1-Zn2: 266.9, Zn2-Zn2: 259.4 / 269.0 / 277.6

Conclusions

The co-deposit of lithium and zinc at low temperature onto a sapphire substrate consists of the β' -phase with random Zn/Li distribution, which transforms while warming up to room temperature into LiZn_{13} . The occupation of the Zn-icosahedra in LiZn_{13} with ca. 25 % lithium results in an expansion of the zinc network and seems to be relevant for the stability of the intermetallic LiZn_{13} .

The results presented illustrate that as a particular advantage the synthesis method of LT-ABD is well suited for the synthesis of metastable solids [16, 17]. As a crucial feature of this approach the reactants are dispersed on an atomic scale. Thus, the transport distances during the subsequent solid state reactions are reduced to atomic scales allowing

1 them to be run at extremely low thermal activation.
 2
 3 Combining the deposition technique with a specially
 4
 5 adapted procedure of X-ray powder diffraction analysis
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 7 offers high potential of exploring the stability ranges of
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 9 phases, including metastable ones, in a given system.
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11 Experimental Section

12 Synthesis

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 14 Zinc (>99.9%, Fluka) and Lithium (distilled, >99.9 %, Merk) were
 15
 16 separately evaporated from a pyrolytic BN-crucible with standard
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 18 effusion cells (Dr. Eberl MBE-Komponenten GmbH), which was
 19
 20 held at a constant temperature of 220 (Zn) and 300 °C (Li) in an
 21
 22 ultra high vacuum chamber. Both metals were deposited
 23
 24 simultaneously onto sapphire substrates ((0001) orientation,
 25
 26 epitaxial polished, CrysTec GmbH) for a period of 5 to 7 hours.
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 28 Ultra high vacuum of 2 to 7×10^{-9} mbar was maintained during
 29
 30 preparation in the deposition chamber by using a turbo molecular
 31
 32 and cryo-pump system including a liquid nitrogen filled cold trap;
 33
 34 for further details of the preparation method see [7, 8]. The residual
 35
 36 gas was monitored by quadrupole mass spectrometers (QME 220,
 37
 38 Pfeiffer Vacuum GmbH; C-100M, Leybold-Inficon), and the
 39
 40 substrate temperature was controlled using a temperature sensor
 41
 42 PT-100 placed in the sample holder. The composition of the
 43
 44 obtained metallic-grey samples with a thickness of ca. 100 nm was
 45
 46 determined by ICP-OES to 93 at% Zn and 7 at% Li. The substrates
 47
 48 with the deposited samples were transferred from the deposition
 49
 50 chamber to an X-ray diffractometer, while maintaining vacuum and
 51
 52 cooling, by means of a car transfer system.

53 Structure Determination

54
 55 The powder diffraction patterns were recorded with a θ/θ X-ray
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 57 powder diffractometer (D8-Advance, Bruker AXS) with parallel
 58
 59 beam geometry (Goebel mirror, Cu-K α) in an X-ray chamber under
 60
 high vacuum (ca. 1×10^{-7} mbar) in reflection mode. Each X-ray
 pattern was measured at an angle of incidence of 10° using an area
 sensitive detector (GADDS, Bruker AXS). The corresponding

pattern was obtained by integration of the two dimensional
 diffraction cones. The background from 20° on in 2θ was reduced
 by a slit inside the vacuum chamber. For indexing and structure
 refinements (Rietveld method), the software Topas (Bruker AXS)
 was employed [18].

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16 be obtained from the Fachinformationszentrum Karlsruhe,
17
18 76344 Eggenstein-Leopoldshafen, Germany (Fax:
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20 +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de)
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