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Intermetallic lithium compounds have found a wide range of applications owing to their light mass and desirable electronic and mechanical properties. Here, by compressing pure lithium and zinc mixtures in a diamond-anvil cell, we observe a direct reaction forming the stoichiometric compound LiZn, at pressures below 1 GPa. On further compression above 10 GPa, we observe the formation of Li₂Zn, which is the highest lithium content compound to be discovered in the Li–Zn system. Our results constrain the structures of these compounds and their evolution with pressure, furthering our understanding of potentially useful light volume-efficient energy storage materials. *Published by AIP Publishing.* https://doi.org/10.1063/1.5035454

I. INTRODUCTION

The immense development of portable electronics and its market since the 1980s has warranted a vast research effort into battery design to further drive down manufacturing costs, promote their capacity, and increase portability. Li-ion batteries (LIBs) are arguably the most prolific energy-storage technology currently available, finding widespread applications in automotive, telecommunication, and national grid energy management.

Currently, there is interest to improve LIB performance by the generation of new higher capacity anode materials¹ resulting in lighter more powerful battery technology. Stoichiometric Li intermetallic compounds have significantly greater Li-content when compared with conventional intercalationtype carbon anodes, offering an intriguing solution to increasing LIB energy density.² The Li–Zn system, in particular, is a promising candidate, with Zn being a historically important³ and prolific battery material primarily due to its low cost and natural abundance, exemplified by Zn–MnO₂, Zn-carbon, and Zn-air being currently the most economically competitive batteries in the market.

The Li–Zn system has been extensively studied at ambient pressures, with typical synthesis techniques that involve alloying of the pure elements at high temperatures.⁴ Although successful in revealing an exceedingly rich binary phase diagram, including the phases LiZn₁₃,⁵ LiZn₄,⁶ Li₂Zn₅,⁷ Li₂Zn₃,⁸ and LiZn,⁹ no phase exhibits a desirable molar ratio of Li to Zn greater than unity.

High pressure is an indispensable tool to further explore exotic chemistry and novel materials not observed under ambient conditions. Recent theoretical investigations on Li-rich regimes at pressure have proposed a wealth of stable stoichiometric Li_xZn intermetallic compounds with 1 < x < 4,¹⁰ ultimately finding the equiatomic phase LiZn to be the most

energetically favourable composition up to 100 GPa. Due to the continual demand for cheaper, lighter, and better performing energy storage materials, specifically for LIB batteries, it is essential to experimentally explore the synthesis of Li-rich Li–Zn compounds and to have a more complete description of lithium chemistry.

In this work, through the application of pressure, we experimentally investigated the desirable Li-rich regime of the binary Li–Zn system up to 20 GPa at room temperature. We found that at remarkably low pressures (<1 GPa) a direct reaction between the pure elements forms the LiZn intermetallic. Upon compression above 10 GPa, Li₂Zn was synthesised, an experimentally novel intermetallic with the highest Li content in the Li–Zn system.

II. EXPERIMENTAL METHODS

High-pressure measurements were conducted in a symmetric-type diamond-anvil cell (DAC) with typical diamond culets varying from 200 to 300 μ m in diameter. Samples were loaded in a laser-milled Re-foil gasket chamber with initial dimensions of 20-30 μ m in thickness and approximately half the culet size in diameter. No pressures higher than 20 GPa were probed, due to the known pressure-enhanced diffusivity of Li into the diamond anvils leading to their premature mechanical failure.^{11,12} Pressures during the experiments were determined by using the equation of state of pure Li,¹¹ and the excess reactant was detectable in all measurements, as seen in Fig. 1.

High-purity Li (Alfa Aesar 99.9%) and Zn (Alfa Aesar 99.9%) samples were loaded under an argon-protected environment within a glove box. All samples were loaded such that the chambers in the Re-foil were first completely occupied by Li and then grains of zinc, <10 μ m in diameter, were



FIG. 1. Representative Rietveld refinements at 13 GPa (top panel, $wR_p = 1.13\%$, $wR_{all,Li_2Zn} = 6.86\%$, $wR_{all,Li_Zn} = 5.05\%$) and 3 GPa (bottom panel, $wR_p = 1.20\%$, $wR_{all,LiZn} = 10.11\%$) on compression. After synthesis of Li₂Zn on compression, trace diffraction of LiZn is observed to the highest studied pressures.

embedded. This ensured an excess of Li (estimated 1%-2% Zn by volume) to encourage the exploration of the Li-rich part of the Li–Zn system, whilst also providing semi-hydrostatic conditions for synthesised samples.

Powder X-ray diffraction data were collected at the BL10XU beamline at SPring-8, Japan. The diffraction from 0.4136 Å wavelength X-rays was recorded using a digital flat-panel detector, after which it was integrated using the DIOPTAS¹³ software to a two-dimensional data set. The data were subsequently indexed using GSAS-II.¹⁴ Le Bail¹⁵ refinement and Rietveld¹⁶ refinement were carried out in *Jana2006*.¹⁷

III. RESULTS AND DISCUSSION

Through the application of high pressures, we have explored the Li-rich Li–Zn system to 20 GPa at room temperature. Two intermetallics are reported, LiZn and Li₂Zn, stressing the importance of high pressure as a useful tool in exploring Li-chemistry, whereas only previous high-temperature alloying⁴ or sophisticated synthesis techniques, such as molecular beam epitaxy,⁵ have proven successful. By analysis of the adopted high-pressure Li–Zn phases via X-ray diffraction (Fig. 1), we have identified the adopted structures (Fig. 2) and their pressure-evolution at room temperature (Fig. 3). These results give us insight into their mechanical and electrical properties, which we compare to the metrics used in choosing appropriate candidate energy-storage materials.

At remarkably low pressures, <1 GPa, we found for the first time via a direct reaction the formation of a LiZn intermetallic at room temperature, identified from the highquality powder diffraction data (Fig. 1, top panel). The LiZn crystal structure was identified to be of the NaTl-type (space



FIG. 2. Crystal structures observed in the Li–Zn system at high pressures, and Li atoms are in red, whilst Zn atoms are in blue. (a) The equiatomic LiZn intermetallic, a NaTl-type structure $(Fd\bar{3}m)$ with interlocking Li and Zn diamond sublattices. (b) Li₂Zn (*P6/mmn*) formed on compression above 10 GPa, where Zn atoms are encapsulated in a hexagonal prism composed of 12 Li atoms.



FIG. 3. (a) Volume per formula unit curves of LiZn (purple circles) and Li_2Zn (green circles), plotted alongside the known volume curves of Li + Zn (black line) and 2Li + Zn (gray line). (b) The normalised lattice parameters *a* (blue circles) and *c* (red circles) of the Li₂Zn structure with pressure. (c) Volume per formula unit curves of the non-stoichiometric alloy ($Li_{1-x}Zn_x$), observed as volume-expanded *fcc*-Li peaks in the integrated patterns (Fig. 1, top panel), alongside Li (red), Zn (blue), and Li + 0.06Zn (gray). In all figures, data on compression and decompression are shown as filled and empty symbols, respectively.

group— $Fd\bar{3}m$) (see Fig. 2 and the bottom panel in Fig. 1). This structure is in agreement with the well-established experimental measurements on LiZn produced by a more common metallurgical tool, high-temperature alloying, in 1933.⁹ The intermetallic was stable at all pressures studied, with detectable trace diffraction detected even after the synthesis of the high-pressure Li₂Zn phase (Fig. 1, top panel), which is discussed later. The highly accessible pressure regimes required to manipulate the alloying between these two species may be suitable for new mechanical energy harvesting analogous to piezoelectric devices¹⁸ and has already been ingeniously applied in the Li-Si system.¹⁹ The stability is in accordance with the previous numerical calculations,¹⁰ which suggested LiZn to be the most energetically competitive phase up to 100 GPa. Calculations also indicate two possible pressureinduced structural transitions, first through an intermediate Imma phase (45-53 GPa), before finally adopting a $Pm\bar{3}m$ structure.¹⁰ Here, in agreement with the theory, no structural modification of the equiatomic LiZn was detected up to 20 GPa.

Upon compression above 10 GPa, we observe the formation of a novel Li_2Zn phase, appearing as a fine powder in our

X-ray diffraction patterns (Fig. 1, top panel). This compound persists as the dominant phase to 20 GPa, the highest pressure reached in this study, and decomposes on decompression to LiZn at 7.4 GPa. Li₂Zn was found to adopt a hexagonal structure of the AlB₂-type (space group—P6/mmm), seen in Fig. 2, with lattice parameters a = 4.3685 Å and c = 2.5509 Å at 7.4 GPa. This structure, which is prolific in intermetallic binary and ternary systems,²⁰ was found to have one Znatom occupying the 1a Wyckoff site (0, 0, 0), whilst the Li-atoms occupy the 2d Wyckoff site $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. The structure is analogous to the binary lithium intermetallics produced with the Pt-group, Li_2M (where M = Pd, Pt),^{21,22} where the transition metal atoms are contained between graphene-like sheets of lithium (see Fig. 2). The Li₂Zn phase reported here has also been observed in previous numerical calculations,¹⁰ and it is suggested to undergo a structural change to another orthorhombic phase (also space group symmetry Imma) above 80 GPa, a pressure which was out of the scope of this study. Recent calculations have reported the thermodynamic stability of Li:Zn with stoichiometry 1:1 and 2:1,¹⁰ albeit finding the 1:1 ratio to be the most stable up to 100 GPa. Here, Li2Zn was observed and found to be the dominant phase above

pressures of 7.4 GPa (see Fig. 1, top panel). We therefore find that the relative abundance of the coexisting phases are primarily driven by the initial concentration of the constituent elements.

As mentioned previously, in both the high-pressure intermetallic compounds, LiZn and Li₂Zn, the Li atoms are constrained by symmetry to special positions within their respective structures. Therefore, despite the weak scattering of lithium, it is still possible to extract Li–Zn bond distances which are summarised in Fig. 4. It is found that in LiZn, the Zn is encapsulated by a total of 10 Li atoms: 4 nearest neighbours and 6 next-nearest neighbours [NNNs are represented in Fig. 4(a) as the face-centred Li atoms], measured to be 2.470(2) Å and 2.852(2) Å, respectively, at 19.3 GPa, whilst the Zn atoms in Li₂Zn are found to lie within hexagonal cages consisting of 12 equally spaced Li atoms varying from



FIG. 4. (a) Structural model of the unit cell of LiZn omitting all atoms apart from a reference Zn atom and its nearest and next nearest neighbouring Li atoms, coloured black, blue, and red, respectively. (b) Distances between Zn and its neighbouring Li atoms in their respective structures: LiZn—nearest (blue) and next nearest (red) and Li₂Zn—nearest (green). The gray dashed line represents the average Zn–Li distance of the LiZn intermetallic. Data on compression and decompression are shown as filled and empty symbols, respectively.

distances of 2.825(4) Å to 2.633(3) Å in the pressure range covered, 7.4–19.3 GPa.

Interestingly, Li_2Zn is found to have comparable Zn–Li distances to the average distances reported in the LiZn compound, despite being the higher pressure phase, seen in Fig. 4(b). In fact, the values are found to exactly match at the Li₂Zn formation pressure, 2.825(4) Å at 7.4 GPa. The similarity of these values is a demonstration of the pressure-distance paradox,²³ i.e., an increase in co-ordination of the Zn atoms, rather than a continual reduction in Zn–Li separation over the pressure regime studied.

In addition to the previously mentioned stoichiometric phases, a non-stoichiometric Zn-alloyed lithium phase $(Li_{1-x}Zn_x)$ was also observed [see Fig. 1, top panel, and Fig. 3(c)]. The signature of the alloying can be readily seen above 10 GPa, where Bragg peaks of Li were shadowed by an identical set of reflections shifted to slightly lower 2θ , seen in Fig. 1, top panel. These diffraction rings could only be observed in regions containing LiZn/Li2Zn and were not observed in the surrounding excess Li. The marginal volume expansion of the Li is attributed to Zn partially dissolved in Li [see Fig. 3(c)], slightly expanding the Li lattice. The percentage of alloying was estimated via a volume analysis of the pure species,^{11,24} where no interspecies charge transfer is assumed. It is found to be at a maximum of 6% at 9.9 GPa [shown in Fig. 3(c)], diminishing almost linearly with pressure to 2%. The expulsion/inclusion of Zn in the host Li accounts for the seemingly large compressibility of this alloy when compared with pure Li, seen in Fig. 3(c). The solubility of Zn was observed to be independent on the pressure path as seen by being reversible on decompression. The effect of Zn-alloying on the rich phase diagram of Li could have implications for its low-temperature superconductivity,²⁵ cold melting,¹² and exotic higher pressure phases.¹²

Complete understanding of the mechanical properties of materials is a key metric in battery design. This is especially the case for LIBs, whereby the process of (de)lithiation can result in significant volume changes;² for example, Li₁₅Si₄ reports a 280% expansion,²⁶ which therefore needs to be accommodated in the battery architecture. We find that Zn has a typical expansion of 98% at 0.7 GPa when forming the LiZn intermetallic, in good agreement with the previous results^{2,9} and roughly a tenfold increase when compared with conventional intercalation-graphite anodes used in current LIBs.² The relative expansion is found to be weakly pressure independent falling by 13% over the entire pressure regime studied. Consequently, Li₂Zn shows a significant 205% volume increase at 7.4 GPa when compared to unlithiated Zn; unsurprisingly, it is approximately a two-fold increase when compared with the volume expansion of the equiatomic Li-Zn phase for the same pressure.

The bulk and linear moduli of LiZn and Li₂Zn as a function of pressure were calculated, using procedures in EoSfit7,²⁷ and are summarised in Table I. The fitted lattice parameters of the unit cells and their respective volumes were found to be well described by the 3rd order Birch-Murnaghan relation.²⁸ The Li₂Zn structure was found to exhibit moderate anisotropic compressibility, with a two-fold greater linear compressibility along the *a*, *b*-axis when compared to the *c*-axis; see Table I.

TABLE I. Refined parameters of 3rd order Birch-Murnaghan equation-of-state fits for LiZn and Li₂Zn, plotted in Fig. 3. The zero-pressure structural parameters of LiZn and Li₂Zn are given: volume—V₀ and lattice constants— a_0 and c_0 . The bulk (B₀) and linear (M₀) moduli with their respective pressure derivatives at zero pressure, *B'* and *M'*, are also included.

	Space group	$V_0(\text{\AA}^3)$	Lattice parameter (Å)	B ₀ (GPa)	B′	M ₀ (GPa)	Μ′
LiZn	Fd3m	249(7)	$a_0 = 6.29(2)$	42(13)	3.1(11)	127(14)	9.3(12)
Li ₂ Zn	P6/mmm	53(3)	$a_0 = 4.75(8)$	22(8)	3.5(6)	61(19)	9.3(11)
			$c_0 = 2.7623(6)$			32(3)	30(4)

Intuitively, this can be seen as the hexagonal planes of Li being more susceptible to compression, opposed to the linear chains of Zn atoms which lie in parallel to the *c*-axis, seen in Fig. 2 and quantified in Fig. 3(b). The measured volume of Li₂Zn was found to be completely reversible on decompression, although found to be stable to lower pressures than when originally synthesised, 7.4 GPa, seen in Fig. 1. By contrast, however, a small but notable deviation of unit cell volume and pressure path for LiZn was observed. An effect can be readily seen in the experimental data provided, see Fig. 3(a), with the unit cell of LiZn found to be 0.8 Å³ smaller on compression up to 10 GPa with respect to values measured on decompression. The deviation is attributed to the sample not in a fully equilibrated state, whereby insufficient time has been given during the course of the compression for the complete lithiation of Zn, consequently resulting in a reduced unit-cell volume. In both intermetallics, LiZn and Li2Zn, the evolution of the unit cell volume corresponds well with that of the relative equations of state for the formula units of the pure species (Li + Zn for LiZn and 2Li + Zn for Li_2Zn), seen in Fig. 3(a), further establishing the correct stoichiometry. Small reductions in volumes were found, for example, at 14 GPa 1.3 Å³ for LiZn and 1.7 Å³ for Li₂Zn relative to the equation of state (EoS) of the pure species formula units, indicative of charge transfer inherent to intermetallic compounds and in agreement with the previous Bader charge analysis of Li–Zn compounds.¹⁰

Finally, theoretical capacities (Q_T) were calculated using Faraday's law of electrolysis, where n_{Li} is the number of Li ions involved in the (de)lithiation process, F is Faraday's constant, and M_w is the molar weight,

$$Q_T[mAhg^{-1}] = \frac{n_{Li}F}{36M_w}.$$
 (1)

Therefore, assuming that complete charge/discharge of zinc can be exploited, the realization of the Li₂Zn means that a potential capacity of 676 mAh g⁻¹ is available in the Li–Zn system which is found to be greater than a twofold increase, when compared with conventionally used carbon anodes, 372 mAh g⁻¹.²⁹ Intriguingly, this result could also explain anomalously large discharges reported in previous Zn-anode Li-ion battery studies,³⁰ suggesting that although Li₂Zn is not found to be quenchable to ambient pressures, there might be a possibility to stabilise it electrochemomechanically.

IV. CONCLUSIONS

In summary, using high-pressure powder X-ray diffraction, we have explored the Li-rich Li–Zn system up to 20 GPa at room temperature. We have verified the synthesis of both LiZn and Li₂Zn upon compression, the latter possessing the highest Li-molar content in the respective binary system. We report that the synthesised LiZn intermetallic to be the previously well-established NaTl-type structure⁹ and was present at all pressures studied. Additionally, Li₂Zn was synthesised on compression above 10 GPa, adopting a hexagonal structure in agreement with recent theoretical calculations,¹⁰ as well as analogous to other previously reported binary Li-intermetallics.²¹ These results are important in the quest for new higher capacity Li-bearing materials and could find applicability in future battery design.

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