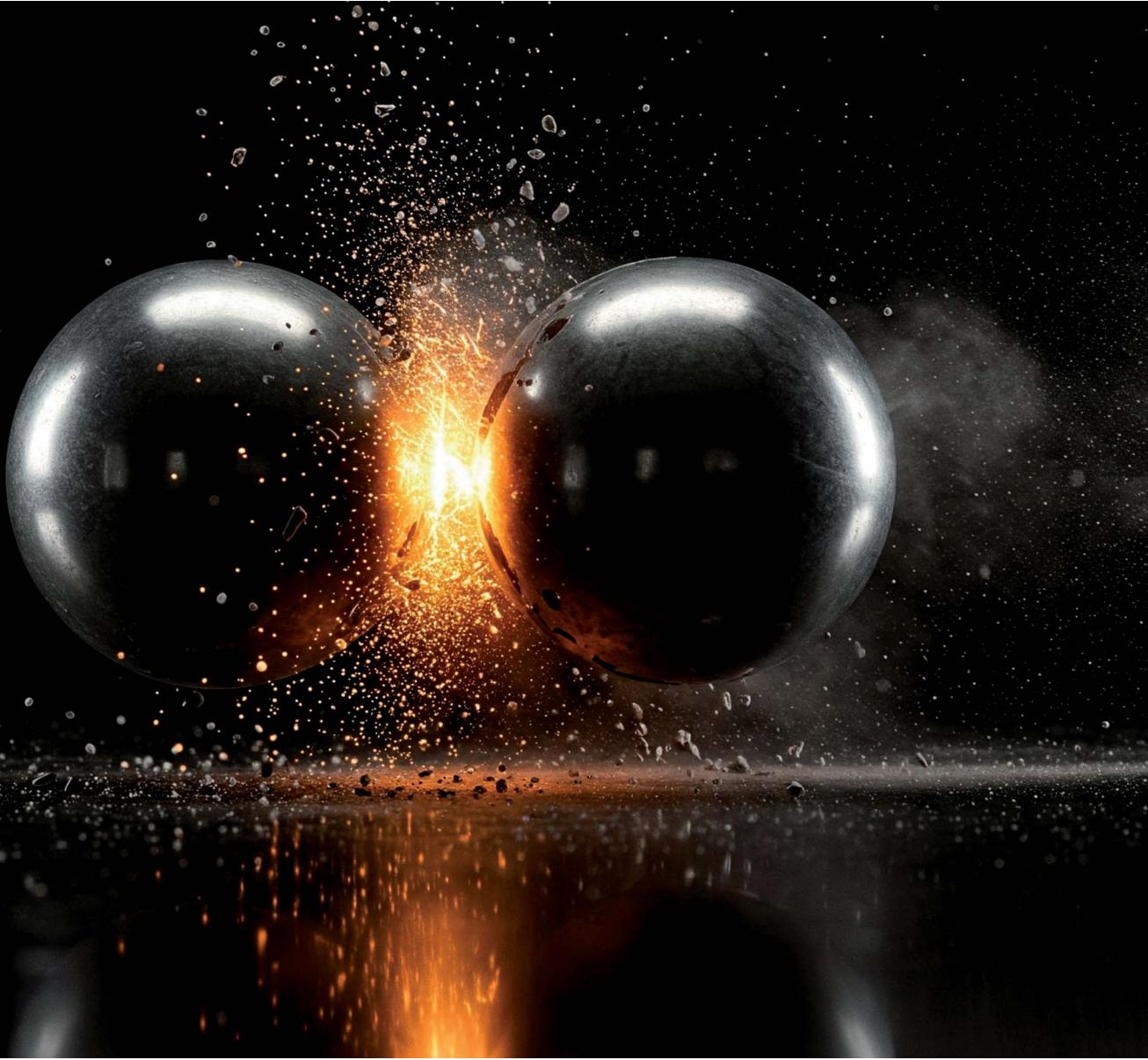


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## The cubic structure of $\text{Li}_3\text{As}$ stabilized by pressure or configurational entropy *via* the solid solution $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$ †‡

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The hexagonal to cubic phase transition of  $\text{Li}_3\text{As}$  was investigated at high pressure and temperature, revealing a cubic high-pressure polymorph in the  $\text{Li}_3\text{Bi}$  structure type. This cubic structure type is preserved in the solid solution of  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  synthesized *via* mechanochemical ball milling. The solid solutions were investigated *via* X-ray powder diffraction, showing a linear dependency of the lattice parameter  $a$  on the mole fraction of the boundary phases  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$ , according to Vegard's law. Configurational entropy is generated by mixed anion lattice occupation between arsenide and selenide and therefore stabilizes the cubic structure of the solid solution. At elevated temperatures, the solid solution of  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  reveals an exsolution process by forming the boundary phases  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$ , proving the metastable character of the system. Impedance spectroscopy was used to determine the lithium-ion conductivities in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system, showing significantly higher conductivity values ( $\sim 10^{-4}$  to  $10^{-6}$  S cm $^{-1}$  at 50 °C) compared to the pure end members  $\text{Li}_3\text{As}$  ( $\sim 10^{-7}$  S cm $^{-1}$  at 50 °C) and  $\text{Li}_2\text{Se}$  ( $\sim 10^{-7}$  S cm $^{-1}$  at 175 °C).

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## Introduction

For all binary lithium pnictogenides  $\text{Li}_3\text{Pn}$  ( $\text{Pn} = \text{N, P, As, Sb, Bi}$ ), a cubic modification in the  $\text{Li}_3\text{Bi}$  structure type is mentioned in the literature; however, to the best of our knowledge, for the cubic modification of  $\text{Li}_3\text{As}$ , no experimental data are available in scientific publications.<sup>1,2</sup> In 2022, we reported lithium-ion mobility in  $\text{Li}_3\text{As}$  and calculated the phase stability of the cubic high-pressure modification *via* DFT (density functional theory).<sup>3</sup> Herein, we report experimental results on the cubic polymorph of  $\text{Li}_3\text{As}$ , *i.e.*, X-ray powder diffraction (XRPD) of a quenched sample obtained from high-pressure and high temperature conditions in a belt press. Thus, this missing part in the puzzle for  $\text{Li}_3\text{Pn}$  ( $\text{Pn} = \text{N, P, As, Sb, Bi}$ ) is available now.

We further show that the pressure induced cubic structure of  $\text{Li}_3\text{As}$  can also be stabilized by the formation of a solid solution in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system. Two examples for solid solutions between binary lithium chalcogenides and lithium pnictogenides are known in the literature. Restle *et al.* reported a solid solution of  $\text{Li}_3\text{N}$  and  $\text{Li}_2\text{O}$  in a rigid open framework boron structure ( $\text{Li}_6\text{B}_{18}(\text{Li}_3\text{N})_{1-x}(\text{Li}_2\text{O})_x$ ,  $0 \leq x \leq 1$ ), since the authors claim that pristine  $\text{Li}_3\text{N}$  and  $\text{Li}_2\text{O}$  are not miscible in the solid

state.<sup>4,5</sup> The second example for solid solutions of binary lithium chalcogenides and lithium pnictogenides was reported by Szczyka *et al.* in the  $\text{Li}_3\text{P}-\text{Li}_2\text{S}$  system, showing miscibility between the two phases in the range of  $0.39 \leq x \leq 0.75$  ( $x\text{Li}_3\text{P}-(1-x)\text{Li}_2\text{S}$ ).<sup>6</sup> The two boundary phases  $\text{Li}_2\text{S}$  and  $\text{Li}_3\text{P}$  crystallize in the cubic antifluorite structure type and the hexagonal  $\text{Na}_3\text{As}$  structure type, respectively. Despite the significant structural difference between  $\text{Li}_2\text{S}$  and  $\text{Li}_3\text{P}$  under ambient conditions, a solid solution in the antifluorite structure type is formed. The authors explain the miscibility by the fact that under pressure (4 GPa)  $\text{Li}_3\text{P}$  undergoes a hexagonal to cubic phase transition. Since the synthesis of the solid solution is carried out by high-energy ball milling of mixtures of  $\text{Li}_3\text{P}$  and  $\text{Li}_2\text{S}$ , the phase transition of  $\text{Li}_3\text{P}$  could be induced mechanochemically to form a cubic structure which is compatible with the cubic structure of  $\text{Li}_2\text{S}$ .<sup>6</sup> High temperature experiments reveal the decomposition of the solid solution into  $\text{Li}_3\text{P}$  and  $\text{Li}_2\text{S}$  at elevated temperatures (400–500 °C) indicating thermal stability of the solid solution only at lower temperatures.<sup>6</sup> Investigations on lithium-ion mobility show that the samples of the mixtures exhibit significantly higher lithium-ion mobility ( $\sim 10^{-4}$  to  $10^{-5}$  S cm $^{-1}$ ) than the boundary phases ( $\text{Li}_2\text{S}$ :  $10^{-14}$  to  $10^{-10}$  S cm $^{-1}$ ,  $\text{Li}_3\text{P}$ :  $10^{-7}$  S cm $^{-1}$ ).<sup>6-8</sup>

$\text{Li}_3\text{Pn}$  ( $\text{Pn} = \text{N, P, As, Sb, Bi}$ ) compounds that adopt the cubic structure type under less extreme conditions are  $\text{Li}_3\text{Sb}$  and  $\text{Li}_3\text{Bi}$ .  $\text{Li}_3\text{Bi}$  indeed crystallizes in the cubic structure type under ambient conditions. In a detailed computational study, Hautier *et al.* discussed the potential application of  $\text{Li}_3\text{Sb}$  as a high-mobility p-type transparent conductor.<sup>9</sup> Furthermore,  $\text{Li}_3\text{Sb}$

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† Dedicated to Prof. Hans Jörg Deiseroth on the occasion of his 80th birthday.

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and  $\text{Li}_3\text{Bi}$  have been theoretically predicted to be above-average thermoelectric materials.<sup>10,11</sup> The improved thermoelectric performance of  $\text{Li}_3\text{Sb}$  samples that transform to the cubic polymorph *via* ball milling was demonstrated by Snyder and Aldemir *et al.*<sup>12</sup>

In this work, we show that the system with the higher homologues ( $\text{Li}_3\text{As}$ – $\text{Li}_2\text{Se}$ ) has similar properties to the solid solution of  $\text{Li}_3\text{P}$ – $\text{Li}_2\text{S}$ . X-ray powder diffraction data of ball milled samples with the stoichiometry of  $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$  ( $0.2 \leq x \leq 1$ ) confirm the formation of a solid solution in a cubic structure. Analogous to the  $\text{Li}_3\text{P}$ – $\text{Li}_2\text{S}$  system, the formation of the solid solution in the  $\text{Li}_3\text{As}$ – $\text{Li}_2\text{Se}$  system can be rationalized by the accessibility of the high-pressure modification of  $\text{Li}_3\text{As}$  *via* mechanochemical synthesis since high local temperature and pressure are involved during ball milling. Configurational entropy introduced by the cubic mixed anion lattice ( $\text{As}^{3-}$  and  $\text{Se}^{2-}$ ) in the solid solution could stabilize its cubic structure. Enhancing phase stability by introducing high configurational entropy to a structure is well known for cations in high entropy oxides which have gained significant interest over the recent decade.<sup>13–15</sup> However, stabilizing entropic contributions from anions are rarely mentioned in the literature. With the multi-anionic and -cationic oxofluoride  $\text{Li}_x(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{OF}_x$ , Wang *et al.* showed the stabilizing entropic effect originating from the mixed anion lattice ( $\text{O}^{2-}/\text{F}^-$ ) revealing promising properties for use as a cathode material in lithium-ion batteries.<sup>16</sup>

## Results and discussion

### The cubic high-pressure modification of $\text{Li}_3\text{As}$

For the cubic to hexagonal phase transition of  $\text{Li}_3\text{As}$ , Beister *et al.* reported a pressure of 4.5 GPa, but apart from the conversion pressure, no further information or experimental data was published.<sup>2</sup>

In this work we present the synthesis of the cubic structure of  $\text{Li}_3\text{As}$  by applying high-pressure (3.6 GPa) and high temperature (1350 °C) on a phase pure sample of hexagonal  $\text{Li}_3\text{As}$  ( $\text{Na}_3\text{As}$  structure type) using a belt press. XRPD was performed on a quenched sample. The powder diffraction pattern in Fig. 1 reveals high intensities of the cubic phase of  $\text{Li}_3\text{As}$ , which was indexed and refined (see the ESI†) with a profile function, leading to the lattice parameter  $a = 6.214(1)$  Å. Indexing and refinement of the cubic phase was performed based on the  $\text{Li}_3\text{Bi}$  structure type with the space group  $Fm\bar{3}m$  (no. 225). The corresponding calculated diffraction profile of the cubic structure model shows perfect agreement with the measured diffraction pattern (Fig. 1). Previous DFT modelling by our group on the phase stability of  $\text{Li}_3\text{As}$  under high-pressure conditions predicted the cubic phase of  $\text{Li}_3\text{As}$  in the  $\text{Li}_3\text{Bi}$  structure type with the lattice parameter  $a = 6.1909$  Å which differs only by 0.4% from the experimental data.<sup>3</sup> These findings confirm a hexagonal to cubic phase transition ( $\alpha\text{-Li}_3\text{As} \rightarrow \beta\text{-Li}_3\text{As}$ ) at high pressure and high temperature for the compound under study (Fig. 2). The still pronounced reflections of hexagonal  $\alpha\text{-Li}_3\text{As}$  (36%) prove that the hexagonal to cubic phase transition is not completed under the applied conditions. The cubic modification of  $\text{Li}_3\text{As}$  could be stabilized after quenching the sample from high pressure and high temperature to ambient

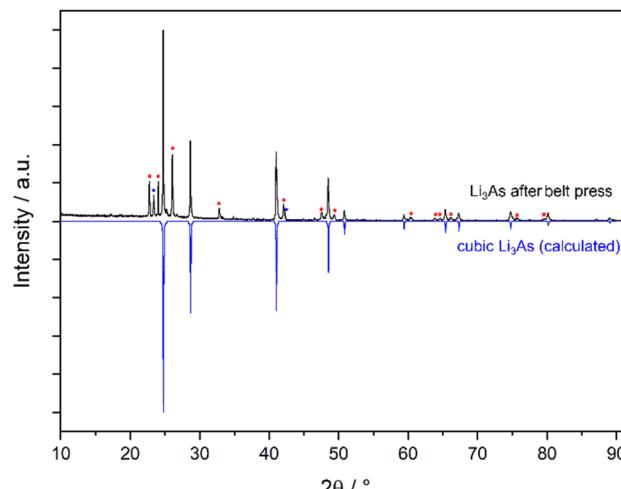


Fig. 1 Powder diffractogram of  $\text{Li}_3\text{As}$  after quenching from high-pressure and temperature to ambient conditions (black). Intensities marked with red stars can be assigned to hexagonal  $\text{Li}_3\text{As}$  ( $\sim 36\%$ ). The intensity marked in blue cannot be assigned to any phase. Negative intensities show the calculated cubic  $\text{Li}_3\text{As}$  modification in the space group  $Fm\bar{3}m$  (no. 225) with lattice parameters determined from the measured diffractogram.

conditions. Quenching is crucial to prevent the reverse cubic to hexagonal phase transition, which is observed during slow pressure and temperature reduction to ambient conditions. A similar behavior was found for the related compound  $\text{Li}_3\text{P}$  by Leonova *et al.*<sup>17</sup> *In situ* XRPD measurements under decreasing pressure from high to ambient pressure reveal the reverse cubic to hexagonal phase transition for  $\text{Li}_3\text{P}$ .<sup>17</sup> The heavier homologue  $\text{Li}_3\text{Sb}$  also behaves similarly, although the cubic structure is

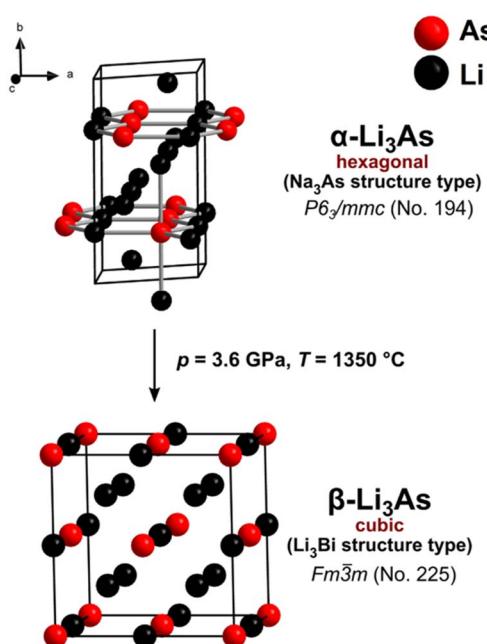


Fig. 2 Scheme of the hexagonal to cubic phase transition of  $\text{Li}_3\text{As}$  at 3.6 GPa and 1350 °C.



adopted after ball-milling, independent of the starting material (from the elements or transformation from hexagonal  $\text{Li}_3\text{Sb}$ ). Thus, the application of high pressure forces the phase transformation of  $\text{Li}_3\text{Sb}$  at ambient temperature,<sup>12</sup> while additional high temperature is necessary for  $\text{Li}_3\text{As}$ . A minimal amount of the cubic polymorph already forms at 700 °C (Fig. S4†). Furthermore, the metastable nature of the cubic polymorph of  $\text{Li}_3\text{Sb}$  was proven by annealing the cubic samples, which then transformed to the hexagonal phase.<sup>12</sup>

### The solid solution in the $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$ system

In the ternary  $\text{Li}-\text{As}-\text{Se}$  system, the phases  $\text{Li}_2\text{Se}$ ,<sup>18</sup>  $\text{LiAs}$ ,<sup>19</sup>  $\text{Li}_3\text{As}$ ,<sup>20</sup>  $\text{Li}_3\text{As}_7$ ,<sup>21</sup>  $\text{As}_4\text{Se}_3$ ,<sup>22</sup>  $\text{As}_4\text{Se}_4$ ,<sup>23</sup>  $\text{As}_2\text{Se}_3$ ,<sup>24</sup>  $\text{AsSe}_2$ ,<sup>25</sup> and  $\text{LiAsSe}_2$ <sup>26</sup> are known (Fig. 3). The solid solution  $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$  ( $0.2 \leq x \leq 1$ ) is highlighted in red in Fig. 3 between the two binary phases  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$ .

### Synthesis and structure

Since the solid solution in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system was not accessible *via* classical solid-state reaction, it was realized by mechanochemical synthesis of the corresponding elements *via* ball milling. Ten samples in steps of  $x = 0.1$  between  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$  ( $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$ ) were synthesized. To obtain phase pure samples, the number of ball milling cycles (5 minutes of milling followed by 4 minutes of sample equilibration) was adjusted in the range of 12 to 36, since higher proportions of  $\text{Li}_3\text{As}$  need more mechanochemical treatment (higher energy input) to form a solid solution with  $\text{Li}_2\text{Se}$ . In Fig. 4 all powder diffractograms of the prepared samples are shown depending on their composition. Since samples with a stoichiometric ratio of 1 : 9 for  $\text{Li}_3\text{As} : \text{Li}_2\text{Se}$  (equivalent to  $x = 0.1$ ) show no significant formation of the cubic phase after several ball milling cycles, it is concluded that a miscibility gap is present near  $\text{Li}_3\text{As}$  in the solid solution with  $\text{Li}_2\text{Se}$ . Nevertheless, in the range of  $0.2 \leq x \leq 1$  ( $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$ ), all samples show XRPD pattern profiles originating from  $\text{Li}_2\text{Se}$ , which shift to lower  $2\theta$  values with

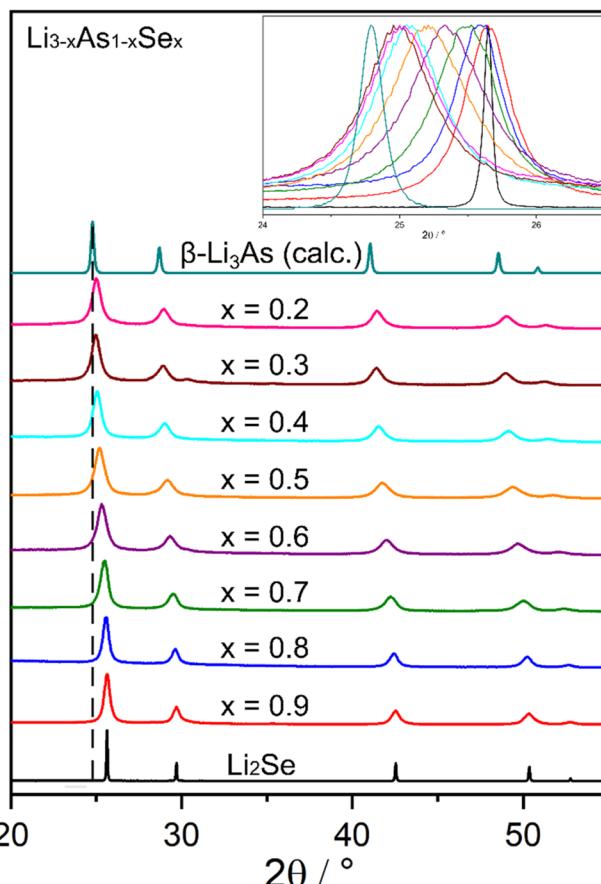


Fig. 4 Powder diffractograms of the solid solution  $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$  ( $0.2 \leq x \leq 1$ ). The powder diffractogram of  $\beta\text{-Li}_3\text{As}$  was calculated.

increasing mole fractions of  $\text{Li}_3\text{As}$ . The cubic lattice parameter  $a$  of all samples including pure  $\text{Li}_2\text{Se}$  and the cubic modification of  $\text{Li}_3\text{As}$  was obtained from the corresponding diffraction patterns (Table S1†) and plotted against the mole fraction  $x$ , as shown in Fig. 5. The lattice parameters of the solid solution show a Vegard-like trend, since the experimentally determined

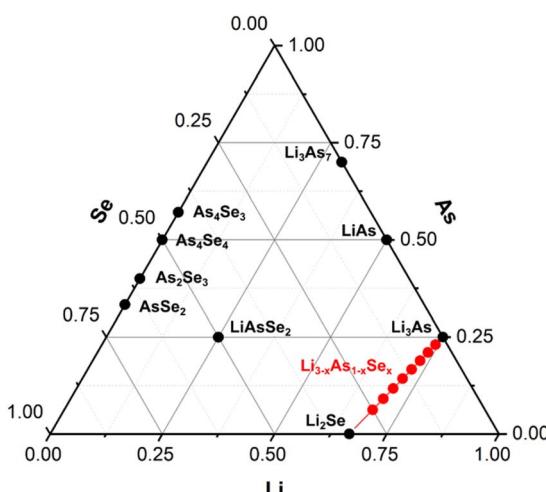


Fig. 3 Ternary phase diagram of the  $\text{Li}-\text{As}-\text{Se}$  system. The solid solution  $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$  ( $0.2 \leq x \leq 1$ ) is displayed in red.

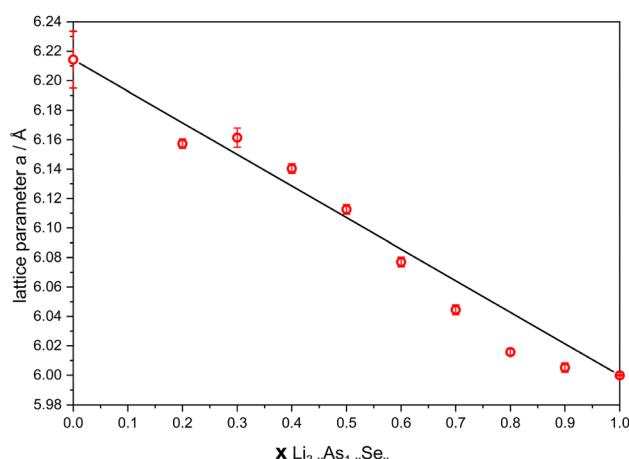


Fig. 5 Lattice parameter  $a$  plotted against the mole fraction  $x$  of the solid solution  $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$  ( $0.2 \leq x \leq 1$ ).



values exhibit deviations of less than 0.5% from the arithmetic mean of the lattice parameters from  $\beta$ -Li<sub>3</sub>As and Li<sub>2</sub>Se.<sup>27</sup> The small deviations, however, can be attributed to minimal amounts of oxygen in the samples, incomplete reactions or reactions with the container material, although these cannot be quantified.

Therefore, the stoichiometric compositions of the samples correspond with the lattice parameter  $a$  and the structure of the solid solution can be described as a cubic closed packing of arsenide and selenide ions forming a mixed occupancy site (Fig. 6). The tetrahedral voids are fully occupied with lithium cations and the octahedral voids are partly filled with lithium cations depending on the arsenide : selenide ratio of the anions, since the arsenic anions carry a higher negative charge.

Since Li<sub>3</sub>As (hexagonal) and Li<sub>2</sub>Se (cubic) differ in their crystal systems under ambient conditions, complete miscibility of both phases should not be possible in the solid state. Nevertheless, a solid solution is formed and a similar behavior has been reported for the lighter homologues in the Li<sub>3</sub>P (hexagonal) and Li<sub>2</sub>S (cubic) systems.<sup>6</sup> This can be rationalized by the fact that Li<sub>3</sub>As and Li<sub>3</sub>P possess a cubic high-pressure modification, which may become accessible during the ball milling process. In the presence of Li<sub>2</sub>Se a metastable solid solution with the cubic high-pressure modification of Li<sub>3</sub>As is formed. The formation of a solid solution series under the applied conditions (mechnochemical synthesis) can be rationalized by the smaller unit cell volume of the solid solution compared to the smaller combined unit cell volumes of the boundary phases Li<sub>2</sub>Se and  $\alpha$ -Li<sub>3</sub>As as well as the gain in configurational entropy, which is generated by introducing selenide to the anion lattice of arsenide (Fig. 6). The free mixing energy ( $\Delta G_{\text{mix}}$ ) for a solid solution is defined as the sum of the mixing enthalpy ( $\Delta H_{\text{mix}}$ ) and the mixing configurational entropy ( $\Delta S_{\text{mix}}$ ).<sup>28</sup> The mixing enthalpy ( $\Delta H_{\text{mix}}$ ) can be further described as the sum of the inner energy ( $\Delta U_{\text{mix}}$ ) and the product of the applied pressure ( $p$ ) and the change in the volume ( $\Delta V_{\text{mix}}$ ):

$$\Delta G_{\text{mix}} = \Delta U_{\text{mix}} + p\Delta V_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

$\Delta V_{\text{mix}}$  is negative because the unit cell volume of the solid solution is smaller than the combined unit cell volumes of the boundary phases Li<sub>2</sub>Se and Li<sub>3</sub>As. This is because the cubic modification of Li<sub>3</sub>As in the solid solution has a smaller unit cell volume than its hexagonal polymorph. Additional local high-

pressure applied *via* mechanochemical synthesis results in an increased negative contribution to  $\Delta G_{\text{mix}}$  and therefore favors the formation of the cubic solid solution. Secondly, elevated temperatures in the mechanochemical synthesis favor the presence of configurational entropy ( $\Delta S_{\text{mix}}$ ), which can be calculated by taking the mole fractions of arsenide ( $x_{\text{As}}$ ) and selenide ( $x_{\text{Se}}$ ) into account:<sup>28</sup>

$$\Delta S_{\text{mix}} = -R(x_{\text{As}} \ln x_{\text{As}} + x_{\text{Se}} \ln x_{\text{Se}}), \quad (2)$$

where  $R$  (J K<sup>-1</sup> mol<sup>-1</sup>) is the gas constant.

This gain in entropy leads to a higher free energy (negative  $\Delta G_{\text{mix}}$ ) for the solid solution of Li<sub>3</sub>As–Li<sub>2</sub>Se compared to the pristine compounds Li<sub>3</sub>As and Li<sub>2</sub>Se and stabilizes the cubic phase. Hence the cubic structure of Li<sub>3</sub>As can be stabilized by a sufficient degree of heterovalent substitution in the anion lattice.

### Thermodynamic stability of the solid solution

Thermal properties of the Li<sub>3</sub>As–Li<sub>2</sub>Se system were investigated by annealing Li<sub>2.6</sub>As<sub>0.6</sub>Se<sub>0.4</sub> samples to temperatures ranging from 200 °C to 700 °C for one week. Fig. 7 shows no change in the reflection profile up to a temperature of 300 °C, indicating phase stability. At 400 °C, the powder diffractogram shows complete decomposition (exsolution) of the solid solution into hexagonal Li<sub>3</sub>As and Li<sub>2</sub>Se revealing the metastable character of the solid solution. Similar findings have been reported for the Li<sub>3</sub>P–Li<sub>2</sub>S system, where powder diffraction data display the exsolution of the solid solution into Li<sub>3</sub>P and Li<sub>2</sub>S in the temperature range of 400 °C to 500 °C.<sup>6</sup> The thermodynamic instability of the solid solution at elevated temperatures indicates that the phases synthesized through mechanochemical methods are only kinetically stable under ambient conditions and decompose when energy (heat) is introduced to the system. This confirms the assumption that the synthesis conditions during the ball milling process must exceed ambient pressure and temperature since the solid solution is not accessible *via* classical solid state synthesis at elevated temperatures. At 700 °C, the two most intense reflections of Li<sub>2</sub>Se broaden and shift to lower 2 $\theta$  values accompanied by an intensity decrease of Li<sub>3</sub>As compared to the XRPD data at 600 °C. These two observations suggest that after annealing the sample to 700 °C, some quantities of Li<sub>3</sub>As remain incorporated in a solid solution with Li<sub>2</sub>Se, indicating an increase in the phase stability of the solid

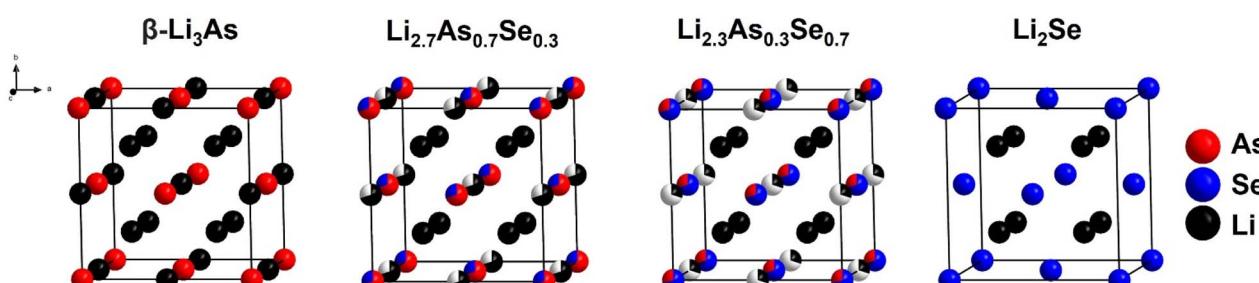


Fig. 6 Structural progression of the solid solution in the system Li<sub>3-x</sub>As<sub>1-x</sub>Se<sub>x</sub> (0.2 ≤ x ≤ 1) with the parent compounds  $\beta$ -Li<sub>3</sub>As and Li<sub>2</sub>Se.



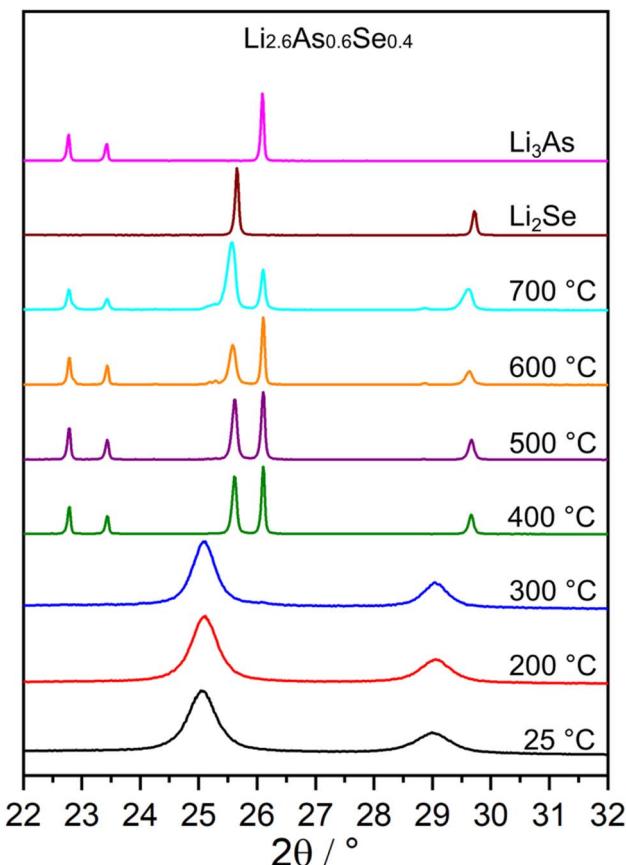


Fig. 7 Powder diffractograms of the  $\text{Li}_{2.6}\text{As}_{0.6}\text{Se}_{0.4}$  compound after annealing to the displayed temperatures for one week and powder diffractograms of the end members  $\text{Li}_3\text{As}$  (hexagonal) and  $\text{Li}_2\text{Se}$ .

solution. This finding may be thermodynamically explained since the free mixing energy of solid solutions at high temperatures and constant pressure is predominantly determined by the additional configurational entropy ( $\Delta G_{\text{mix}} = \Delta U_{\text{mix}} + p\Delta V_{\text{mix}} - T\Delta S_{\text{mix}}$ ) of the arsenide/selenide lattice and therefore phase stability of the solid solution at temperatures above 700 °C might be possible. However, further investigations at higher temperatures were not performed, because the quartz tubes were already severely damaged after heat treatment at 700 °C. DTA of  $\text{Li}_{2.6}\text{As}_{0.6}\text{Se}_{0.4}$  (Fig. S2‡) shows one endothermic peak in the two heating cycles (478 °C and 486 °C) and one exothermal peak in the two cooling cycles (469 °C and 470 °C), which can be assigned to melting and recrystallisation processes, since the formation of a regulus was observed. Additionally, XRPD of the analyzed sample reveals the presence of  $\text{Li}_3\text{As}$  and  $\text{LiAs}$  after DTA and the XRPD pattern of the cubic solid solution is shifted to higher  $2\theta$  values, indicating a lower mole fraction of  $\text{Li}_3\text{As}$  in the solid solution after DTA (Fig. S3‡). Both findings combined indicate a partial decomposition process of the solid solution during the DTA into hexagonal  $\text{Li}_3\text{As}$  and  $\text{LiAs}$ , forming a  $\text{Li}_2\text{Se}$ -richer solid solution. The annealed samples, as shown in Fig. 7, confirm the thermal instability of the solid solution above 400 °C. Additionally, since the cubic structure of  $\text{Li}_3\text{As}$  is not stable under these conditions, the exsolution of arsenide anions from the solid solution is plausible.

## Impedance spectroscopy

AC impedance spectroscopy with ion blocking electrodes (indium) was performed to investigate the lithium-ion mobility in the solid solution in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system. For the phases  $\text{Li}_{2.2}\text{As}_{0.2}\text{Se}_{0.8}$ ,  $\text{Li}_{2.4}\text{As}_{0.4}\text{Se}_{0.6}$ ,  $\text{Li}_{2.6}\text{As}_{0.6}\text{Se}_{0.4}$  and  $\text{Li}_{2.8}\text{As}_{0.8}\text{Se}_{0.2}$  Nyquist plots (Fig. S5‡) were recorded in the temperature range from 50 to 100 °C in steps of 10 °C. Impedance spectra were fitted with an equivalent circuit (Table S4‡) and the resulting resistance values were used to calculate the specific ion conductivities of the samples (Table S2‡). In Fig. 8 the specific ion conductivities of the homogeneous solid solutions in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system are displayed in an Arrhenius plot. Activation energies ( $E_a$ ) are given in Table S5.‡ Higher lithium-ion conductivities are observed with increasing content of As in the samples. Conductivity values at 50 °C of the solid solution range from  $10^{-6} \text{ S cm}^{-1}$  for  $\text{Li}_{2.2}\text{As}_{0.2}\text{Se}_{0.8}$  to  $10^{-4} \text{ S cm}^{-1}$  for  $\text{Li}_{2.8}\text{As}_{0.8}\text{Se}_{0.2}$  with an activation energy of approximately 0.45 eV (Table S2‡). This two-order-of-magnitude difference in lithium-ion conductivities can be explained by the increasing lithium-ion content in the octahedral voids along with the increasing As content. The higher charge carrier concentration in the octahedral voids therefore correlates with a higher overall lithium-ion conductivity. All measured ion conductivities in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system show significantly better lithium-ion mobility than the parent compounds  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$ . Our group previously reported a lithium-ion conductivity of about  $10^{-7} \text{ S cm}^{-1}$  for  $\text{Li}_3\text{As}$  (gold blocking electrodes) at 50 °C and herein we observed lithium-ion conductivities of about  $10^{-7}$  to  $10^{-5} \text{ S cm}^{-1}$  (gold blocking electrodes) for  $\text{Li}_2\text{Se}$  in the temperature range of 175 to 300 °C (Fig. S5 and Table S3‡).<sup>3</sup> At lower temperatures, the lithium-ion conductivities of  $\text{Li}_2\text{Se}$  were not measured because the impedance exceeded the range of our setup. Nevertheless,  $\text{Li}_2\text{Se}$  exhibits significantly lower lithium-ion conductivity values compared to the corresponding solid

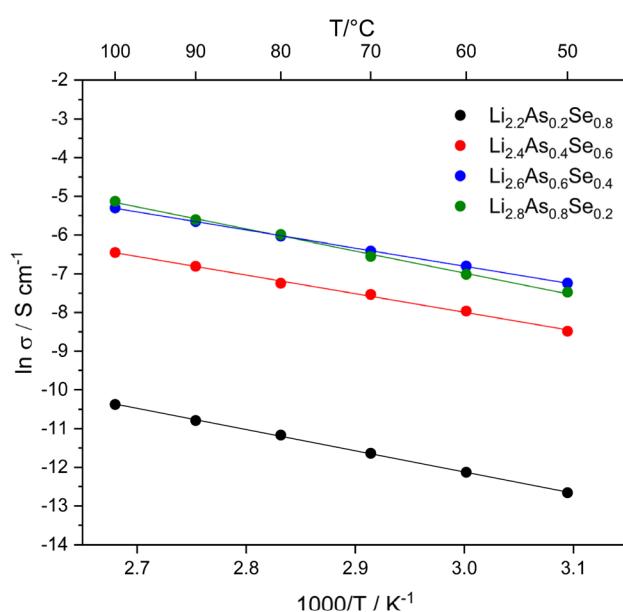


Fig. 8 Arrhenius plot of the solid solution  $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$  ( $0.2 \leq x \leq 1$ ).



solution. Similar findings have been reported for the closely related solid solution in the  $\text{Li}_3\text{P}-\text{Li}_2\text{S}$  system. For this system, impedance spectroscopy (lithium blocking electrodes) shows lithium-ion conductivities of  $10^{-5}$  to  $10^{-4}$   $\text{S cm}^{-1}$  at room temperature, increasing with the P content, and these values are significantly higher compared to the binary phases  $\text{Li}_2\text{S}$  ( $10^{-14}$  to  $10^{-10}$   $\text{S cm}^{-1}$ )<sup>7,8</sup> and  $\text{Li}_3\text{P}$  ( $10^{-7}$   $\text{S cm}^{-1}$ ).<sup>6</sup> However, the best Li ion conductors to date like  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  achieve conductivities up to  $10^{-2}$   $\text{S cm}^{-1}$ ,<sup>29</sup> which is not reached within the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system.

## Experimental

Because of the high air- and moisture-sensitivity of the compounds under discussion all manipulations were carried out in an argon-filled glovebox (M Braun) with oxygen and moisture levels less than 0.5 ppm. The materials must be handled with extreme caution, since the investigated compounds are highly toxic and reach high vapor pressures upon heating.

### High-pressure synthesis

High-pressure experiments were performed in a belt apparatus according to the method described by *Range* and *Leeb* by using BN crucibles.<sup>30</sup> Samples of hexagonal  $\text{Li}_3\text{As}$  were pressed for 3 days at a temperature of 1350 °C and 3.6 GPa and were subsequently quenched to ambient conditions.

### Synthesis

The samples in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system were prepared *via* ball milling (FRITSCH Pulverisette 7 premium line, 10 zirconia grinding balls ( $\varnothing = 10$  mm), and 25 mL zirconia grinding bowls). Stoichiometric amounts (batch size: 2 g) of the elements Li (Merck, 99%), As (Chempur, sublimed) and Se (99.99%). 12 to 36 milling cycles (5 minutes of milling followed by 4 minutes of sample equilibration) at a rotation speed of 600 rotations per minute were performed to synthesize the compounds.

### Powder diffraction

The powders of the samples were finely ground in an agate mortar, filled in quartz capillaries ( $\varnothing = 0.3$  mm) and were subsequently flame sealed. The capillaries were placed on a STOE STADI P diffractometer (Stoe & Cie) equipped with a spinner, and a Mythen 1 K detector, using  $\text{CuK}\alpha_1$ -radiation ( $\lambda = 1.5406$  Å). Raw data were handled with the WinXPOW software package (Stoe & Cie).<sup>31</sup>

### Differential thermal analysis (DTA)

Flame-sealed quartz tubes ( $\varnothing = 2$  mm) filled with the reacted samples were measured using a SETARAM TG-DTA 92.16.18. Thermal analysis was carried out in the temperature range of 25 to 800 °C at a heating/cooling rate of 10 °C min<sup>-1</sup>.

### Impedance spectroscopy

AC impedance conductivity measurements were performed using a Zahner Zennium impedance analyzer. Temperature was controlled using an Eurotherm heating device. The whole setup was placed in a glovebox (M Braun) under an argon atmosphere. Impedance data were recorded in steps of 10 °C from 50–100 °C for frequencies of 1 MHz to 100 mHz. Active cooling is not possible with the setup in the argon-filled glovebox. Therefore, the temperature dependent series were started at 50 °C. The samples were cold pressed to pellets ( $\varnothing = 8$  mm) and placed between pieces of indium foil which were in contact with platinum electrodes. The processing and fitting of the data were performed using the Zahner Analysis software package.<sup>32</sup>

## Conclusions

We report the synthesis and characterization of the hexagonal ( $\text{Na}_3\text{As}$  structure type) to cubic ( $\text{Li}_3\text{Bi}$  structure type) phase transition of  $\text{Li}_3\text{As}$  at high temperature and high pressure. The cubic polymorph of  $\text{Li}_3\text{As}$  was obtained through heat and pressure treatment in a belt press followed by quenching to ambient conditions and characterization *via* XRPD.

Furthermore, we investigated the solid solution in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system stabilizing the cubic modification of  $\text{Li}_3\text{As}$  *via* configurational entropy by heterovalent substitution of the arsenide ions with selenide ions. The samples in the  $\text{Li}_3\text{As}-\text{Li}_2\text{Se}$  system were synthesized *via* ball milling of stoichiometric amounts of the corresponding elements. Powder diffraction data of the ball milled samples show miscibility of  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$  in the range of  $0.2 \leq x < 1$  ( $\text{Li}_{3-x}\text{As}_{1-x}\text{Se}_x$ ). The cubic lattice parameter of these samples follow Vegard's law.<sup>27</sup> The structure of the solid solution series can be described as a filled anti-fluorite structure type or alternatively as a deficient  $\text{Li}_3\text{Bi}$  structure type, *i.e.* arsenide and selenide ions occupy the anion positions of a fcc lattice. The tetrahedral voids therein are fully occupied by lithium cations. The octahedral voids are partly filled with the remaining lithium cations, as determined from the arsenide:selenide ratio. Despite the different crystal systems of  $\text{Li}_3\text{As}$  (hexagonal) and  $\text{Li}_2\text{Se}$  (cubic) under ambient conditions a solid solution is formed after mechanochemical synthesis. Since we have evidence for the cubic high-pressure modification of  $\text{Li}_3\text{As}$ , it is plausible to claim that cubic  $\text{Li}_3\text{As}$  is accessible *via* mechanochemical synthesis. We propose the formation of the solid solution during the ball milling process. The gain in configurational entropy ( $\Delta S_{\text{mix}}$ ) from mixing arsenide and selenide in the anion lattice along with the smaller volume ( $\Delta V_{\text{mix}}$ ) of the solid solution compared to the boundary phases can be regarded as the driving force for the formation of the cubic solid solution. Elevated local pressure and temperature in the mechanochemical synthesis amplify both influences on the free mixing energy ( $\Delta G_{\text{mix}} = \Delta U_{\text{mix}} + p\Delta V_{\text{mix}} - T\Delta S_{\text{mix}}$ ), thus leading to the stabilization of the solid solution. The exsolution process of the solid solution at 400 °C into the boundary phases  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$  reveals the metastable character of the solid solution at elevated temperatures. Impedance spectroscopy shows high lithium-ion conductivity for  $\text{Li}_3\text{As}$ .



$\text{Li}_2\text{Se}$ , ranging from about  $10^{-4}$  to  $10^{-6} \text{ S cm}^{-1}$  at  $50^\circ\text{C}$ , which is significantly higher than the conductivities of the parent compounds  $\text{Li}_3\text{As}$  and  $\text{Li}_2\text{Se}$ .<sup>3</sup>

## Data availability

All data, *i.e.*, X-ray powder data, thermal analyses and impedance measurements are available from the authors on request.

## Conflicts of interest

There are no conflicts to declare.

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