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Homogeneity range of the NaTl-type Zintl phase in the ternary system Li–In–Ag

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Abstract

The remarkably broad homogeneity range of the NaTl-type Zintl phase in the ternary phase diagram Li–In–Ag at room temperature was determined by structure evaluation using X-ray powder diffraction. The colours of the investigated Zintl phases correlate with the valence electron concentration (VEC) as already established for the quasibinary cut $Li_{0.5}(In_xAg_{1-x})_{0.5}$ with $0.47 \leqslant x \leqslant 1.00$, i.e. with decreasing VECs the colour changes from grey over reddish to bright yellow. All compounds in the new quasibinary cut $Li_x(In_{0.5}Ag_{0.5})_{1-x}$ with $0.47 \leqslant x \leqslant 0.60$ appear free from vacancies in the Li-sublattice, even for Li-deficient compositions. The partial occupation of Li-sites by excess Ag and In instead is in full agreement with the behaviour of the binary NaTl-type Zintl phases Li_xZn_{1-x} and Li_xCd_{1-x} ($0.47 \leqslant x \leqslant 0.54$) with a low VEC about 1.5.

Keywords: Phase diagram; Valence electron concentration; Zintl; B32 structure type

1. Introduction

For the exploration of the necessary and sufficient criteria for the existence of NaTl-type Zintl phases the investigation of their homogeneity ranges in respective ternary systems will provide more information than the binary systems, because the third component opens an additional degree of freedom for the variation of important parameters like the valence electron concentration (VEC) and the averaged radii of involved randomly mixed atomic sets. The Li–In–Ag system is appropriate for a first comprehensive investigation of the full homogeneity range and boarderlines of the NaTl-type Zintl phase in this ternary system, because the yet known binary and quasibinary cuts—Li_xIn_{1-x} [1,2] and $Li_{0.5}(In_xAg_{1-x})_{0.5}$ [3,4], point to an extended stability region.

The nature of NaTl-type Zintl phases is often and sometimes controversly discussed in the literature. It seems that depending on the investigation method the bonding character of these alloys is described rather as heteropolar, homoeopolar, metallic or as a combination of them [5–16].

Binary NaTl-type Zintl phases are extremely rare—at ambient conditions only seven have been found, namely LiZn, LiCd, LiAl, LiGa, LiIn, NaIn, and NaTl. The majority of them have a VEC of 2.0, only LiZn and LiCd have a VEC of 1.5.

E. Zintl et al. [17]—who first found and investigated these alloys—described them correctly as f.c.c. (space-group *Fd*-3*m*) in which the tri- or di-valent atoms and the monovalent alkali atoms each form diamond-like sublattices which are situated into each other, shifted along the diagonal of the conventional F-centered cell. These authors proposed a heteropolar and homoeopolar bonding character especially for the alloys with a VEC = 2.0: The trivalent atoms Al, Ga, In, Tl take an

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electron from the alkaline atom becoming isoelectronic with carbon in the diamond lattice, and form a three-dimensional anionic sublattice of homoeopolar character with the largest interstitials occupied by the alkaline cations like heteropolarly bonded ions in a salt. This description, however, does not explain the existence of the same structure type for LiZn and LiCd with a VEC $= 1.5$, because an analogues three-dimensional anionic sublattice of homoeopolar character would lack one bonding electron. Sometimes the distinctive colours of LiZn and LiCd (in contrast to the grey VEC $= 2.0-$Zintl phases) were assigned to the electronic imperfectness of the anion sublattice (lacking one electron as a chromophor) characterizing these 2 compounds as especially exotic within the NaTl-type Zintl phases.

Lateron, a lot of ternary NaTl-type Zintl phases with the composition Li_2EX ($E =$ Cu,Ag,Au, $X =$ Al,Ga, In,Tl,Si,Ge,Sn,Pb,Sb,Bi) were found [3]. Only five of them belong to the VEC $= 2.0$ case, eight of them have VECs of 1.75, and seven of them VECs of 1.5. These findings reverse the situation found within the binary group of Zintl phases (in which group the alloys with VEC's < 2.0 represent the minority). The ternary NaTl-type Zintl phases are also grey for a VEC $= 2.0$, but coloured for VECs $= 1.75$ or 1.5, respectively, like the binary ones. This correlation between VEC and colour also holds for the quasibinary cut $Li_{0.5}(In_xAg_{1-x})_{0.5}$ with VECs from 1.47 to 2.00, where the colour changes from golden yellow through red violet, greenish blue, blueish green to grey [3,4]. This yet known extended homogeneity range of the NaTl-type Zintl phase in the ternary Li–In–Ag-system and the interplay between VEC and colour initiated a much broader investigation of the respective phase diagram. In this report we focus on the homogeneity range and the boarderlines of the NaTl-type Zintl phase.

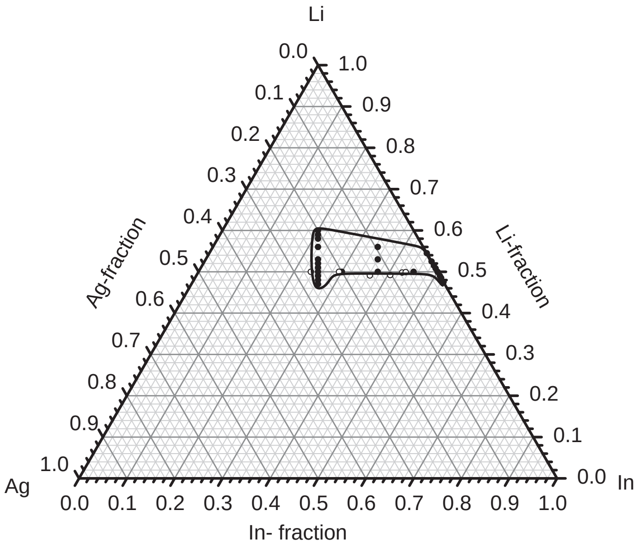

Fig. 1. Field of homogeneous NaTl-type Zintl phases in the Li–In–Ag system and the proposed boarderline, (a) for the complete phase diagram. Full circles (●) mark alloys which were evaluated as homogenious single phases, empty circles (○) mark alloys which were evaluated from heterogeneous 2-phase fields.

2. Experimental

All investigated samples were prepared from the following elements: lithium (rods, 99.9 at%), indium (ingots, 99.999 at%) and silver (wire 99.999 at%). Lithium and lithium-containing compounds were handled in a glovebox under dry argon atmosphere.

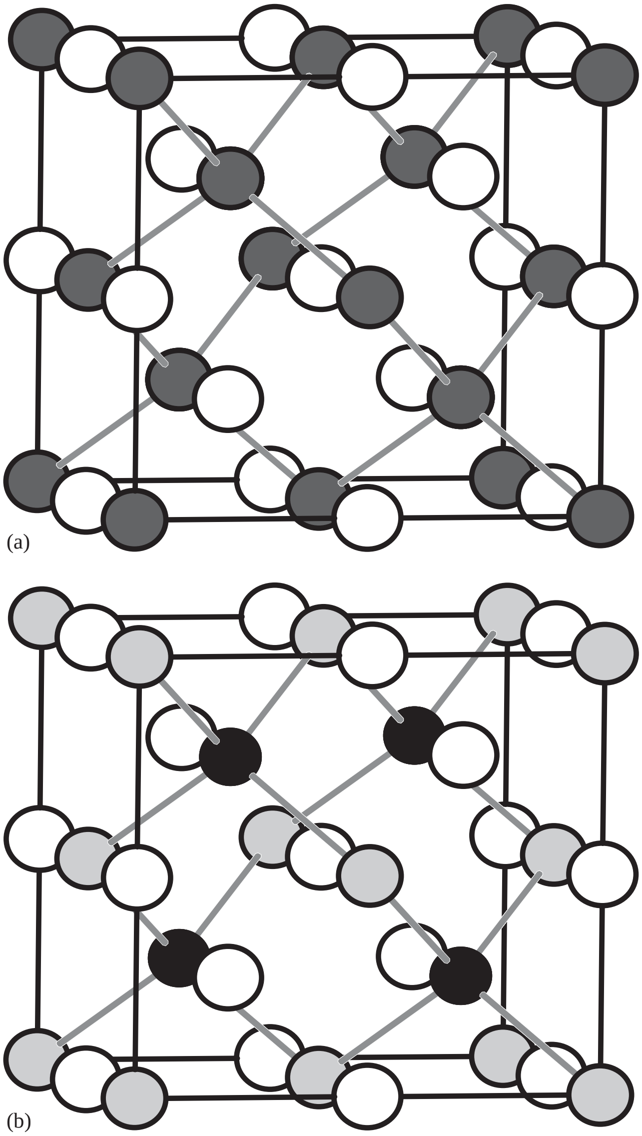

Fig. 2. Atom distribution in (a) the statistical Zintl phase (B32A [3]) and (b) the ordered Zintl phase (XA [3]). White circles refer to Li atoms, light grey to In, black to Ag and dark grey to a statistically mixed occupation with In and Ag.

For the determination of the homogeneity range of the NaTl-type Zintl phase in the Li–In–Ag system more compositions in addition to the known binary cut $\mathrm{Li}_x\mathrm{In}_{1-x}$ with $0.47 \leqslant x \leqslant 0.55$ [1,2] and the quasibinary cut $\mathrm{Li}_{0.5}(\mathrm{In}_x\mathrm{Ag}_{1-x})_{0.5}$ with $0.47 \leqslant x \leqslant 1.00$ [3,4] had to be prepared and analysed. The two quasibinary cuts $\mathrm{Li}_x(\mathrm{Ag}_{0.5}\mathrm{In}_{0.5})_{1-x}$ with $0.44 \leqslant x \leqslant 0.62$ and the adjacent parallel cut with approximated composition $\mathrm{Li}_x(\mathrm{Ag}_{\approx 0.25}\mathrm{In}_{\approx 0.75})_{1-x}$ with $0.49 \leqslant x \leqslant 0.58$ have been selected, because they are expected to provide most significant information on the phase boundaries.

According to the aimed stoichiometry appropriate amounts of the elements were filled into unalloyed steel crucibles. These were closed by welding, placed into a perpendicular furnace which was preheated to 1100 °C. When the temperature of the crucible reached approximately 1000 °C it was taken out of the furnace and heavily shaked to mix the molten reactants properly. After a twofold or threefold repetition of the heating and shaking procedure the crucible was cooled down to room temperature in ambient conditions, so that all products can be considered to result from quenching. The walls of the crucibles were thinned down on a lathe from 2 mm to approximately 0.2 mm and then mechanically opened in the glove box.

X-ray powder diffraction patterns were collected in steps of 0.02° for 2θ from 8° to 55° on a STOE STADI P ($\mathrm{Mo}K\alpha_1$ radiation) in Debye-Scherrer mode. Glass capillaries of 0.3 mm diameter were filled with ground powder and sealed. All diffraction patterns have been analysed by full-profile Rietveld refinements, using the software package WinPLOTR [18].

Table 1
Interesting properties of the (binary and) ternary Li–In–Ag alloys in the homogeneity field of the NaTl-type Zintl phases

Cut no.	Composition	In/Ag ratio	Lattice constants [a/Å]	Valence electron concentration [(VEC)]	Colour
1	$\mathrm{Li_{47.0}In_{26.5}Ag_{26.5}}$	1.00	6.580(5)	1.53	↑ Gradually increasing tendency from golden-yellow towards reddish-violet
	$\mathrm{Li_{48.0}In_{26.0}Ag_{26.0}}$		6.587(5)	1.52	
	$\mathrm{Li_{49.0}In_{25.5}Ag_{25.5}}$		6.582(5)	1.51	
	$\mathrm{Li_{50.0}In_{25.0}Ag^{a}_{25.0}}$		6.579(5)	1.50	
	$\mathrm{Li_{51.0}In_{24.5}Ag_{24.5}}$		6.576(5)	1.49	Gradually increasing tendency from golden-yellow towards pure yellow
	$\mathrm{Li_{52.0}In_{24.0}Ag_{24.0}}$		6.575(5)	1.48	
	$\mathrm{Li_{53.0}In_{23.5}Ag_{23.5}}$		6.579(5)	1.47	
	$\mathrm{Li_{56.0}In_{22.0}Ag_{22.0}}$		6.582(5)	1.44	
	$\mathrm{Li_{59.0}In_{20.5}Ag_{20.5}}$		6.582(6)	1.41	
	$\mathrm{Li_{60.0}In_{20.0}Ag_{20.0}}$		6.575(6)	1.40	↓
2	$\mathrm{Li_{50.0}In_{37.5}Ag^{b}_{12.5}}$	3.00	6.684(3)	1.75	Greenish-blueish
	$\mathrm{Li_{53.0}In_{36.0}Ag_{11.0}}$	3.27	6.679(3)	1.72	
	$\mathrm{Li_{56.0}In_{34.5}Ag_{9.5}}$	3.63	6.676(3)	1.69	
3	$\mathrm{Li_{47.5}In_{52.5}}$	∞	6.7724(6)	2.05	Grey
	$\mathrm{Li_{48.5}In_{51.5}}$		6.7817(7)	2.03	Grey
	$\mathrm{Li_{49.0}In_{51.0}}$		6.7839(8)	2.02	Grey
	$\mathrm{Li_{49.5}In_{50.5}}$		6.7913(8)	2.01	Grey
	$\mathrm{Li_{50.0}In^{c}_{50.0}}$		6.7920(6)	2.00	Grey
	$\mathrm{Li_{51.5}In_{48.5}}$		6.7897(7)	1.97	Grey
	$\mathrm{Li_{52.5}In_{47.5}}$		6.7887(10)	1.95	Grey
	$\mathrm{Li_{54.5}In_{45.5}}$		6.7807(14)	1.91	Grey
4	$\mathrm{Li_{50.0}In^{c}_{50.0}}$	∞	6.792(1)	2.00	Grey
	$\mathrm{Li_{50.0}In_{45.0}Ag_{5.0}}$	9.00	6.744(1)	1.90	Faint blueish-greenish
	$\mathrm{Li_{50.0}In_{37.5}Ag_{12.5}}$	3.00	6.684(3)	1.75	Greenish-blueish
	$\mathrm{Li_{50.0}In_{30.0}Ag_{20.0}}$	1.50	6.618(4)	1.60	Reddish-violet
	$\mathrm{Li_{50.0}In_{25.0}Ag^{a}_{25.0}}$	1.00	6.572(5)	1.50	Golden-yellow
	$\mathrm{Li_{50.0}In_{23.5}Ag_{26.5}}$	0.89	6.560(5)	1.47	Towards pure-yellow

The half-widths and thus the estimated standard deviations increase significantly with increasing silver contents of the alloys.

Cut no. 1 and cut no. 2 (except $\mathrm{Li_{50.0}In_{37.5}Ag_{12.5}}$) are new data. Standard deviations (σ) are estimated to give a 95% probability within the $\pm 2\sigma$ interval in agreement with Refs. [3,4].

Cut no. 3: The compositions and the lattice parameters are taken from Table 1 in paper [2].

Cut no. 4: All data are taken from the papers [3] and [4].

(b) The same data for the alloy $\mathrm{Li_{50.0}In_{37.5}Ag_{12.5}}$ appear twice in cuts 2 and 4 for better comparability.

Lattice constants for two different alloys with the same aimed composition have been determined independently, and the agreement is very good in case of (c), fairly good in case of (a).

All specifications about alloy compositions and corresponding VECs are nominal values, calculated from the ratio of the used educts. Li-losses are expected to be lower than or equal to 1%, based on earlier systematic investigations with comprehensive chemical analyses [3].

3. Results and discussion

The homogeneity range of the NaTl-type structure within the overall ternary phase diagram is shown in Fig. 1, together with all investigated compositions within this homogeneity range. It is distinguished whether these compositions were evaluated from single-phase products (filled circles) or found as one phase in a heterogeneous mixture (open circles). Based on these findings, the boarderline, which separates the homogeneous single-phase region from heterogeneous multi-phase regions, is proposed and shown as a drawn line. Accordingly, the stability range of the NaTl-type Zintl phase becomes broader with increasing Ag-content, especially for Li-rich compositions whereas the stability range of the Li-poorer compositions is somewhat squeezed over a wide part by the respective boarderline. Note that the boarderline at the Li-rich end of the quasibinary cut $Li_x(Ag_{0.5}In_{0.5})_{1-x}$ is only poorly defined: the transition from unambiguously homogeneous samples to unambiguously heterogeneous multiphase samples is proceeding gradually, most clearly reflected in differences between the profile shapes of reflections (*hkl*) with *h*, *k*, and *l* even in comparison to those Bragg reflections with *h*, *k*, and *l* odd. We propose an increasing amount of antiphase boundaries in this transition region. The domain sizes between antiphase boundaries become smaller, resulting in a size-dependent broadening of the reflections with *h*, *k*, and *l* odd, while those reflections with *h*, *k*, and *l* even are not affected. This model is supported by the significantly improved agreement between calculated and experimental diffraction patterns in Rietveld refinements, when this effect is taken into account. For higher Li-content, starting from $x > 0.60$, the reaction products along the quasibinary cut $Li_x(In_{0.5}Ag_{0.5})_{1-x}$ are mixtures of at least two phases.

The crystal structures within the stability range of the NaTl-type Zintl phase can be described in the following way: 16 atoms in the conventional F-centered unit cell are distributed on the fully occupied Wyckoff-sites (8a) and (8b) in space group Fd-3m, see Fig. 2a. The site-specific occupations depend on composition, and one site is mainly (in case of less than 50% Li fully) occupied by the heavy atoms In and Ag, the other site mainly (in case of more than 50% Li exclusively) by Li-atoms. Due to the very similar atomic form amplitudes of In and Ag the random distribution of In and Ag on one site can hardly be proven by X-ray diffraction, but has earlier been confirmed for selected ternary compositions. The most convincing evidence (of randomly distributed In- and Ag-atoms) is based on neutron diffraction at the ILL in Grenoble on $Li_{0.50}In_{0.25}Ag_{0.25}$, $Li_{0.508}In_{0.246}Ag_{0.246}$, and $Li_{0.5}In_{0.375}Ag_{0.125}$. Not any indication for a Bragg reflection (*hkl*) from an ordered superstructure, i.e. with $h^2 + k^2 + l^2 = 8n + 4$, could be detected for these compounds [19]. However, such a tendency for Ag- and In-ordering on different sites in the region of lower Li-content is supported by neutron diffraction on $Li_{0.492}In_{0.254}Ag_{0.254}$ where the Bragg reflections (200) and (222) could clearly be identified. (In that publication the ordering tendencies in the alloy $Li_{0.492}In_{0.254}Ag_{0.254}$ have not yet been mentioned.) In this case the symmetry is reduced to spacegroup F-43m, with In and Ag atoms on separate sites, see Fig. 2b. Such an ordered Zintl phase structure has earlier been denoted as XA structure type [3] and is considered as part of the homogeneity region. The increase of this degree of order is expected to proceed smoothly, so that the corresponding boundary between purely random distribution and the onset of order cannot be resolved. The composition $Li_{0.44}In_{0.28}Ag_{0.28}$ reveals a two-phase mixture and is clearly outside the homogeneity range of the NaTl-type Zintl phase. At the first glance also the alloy $Li_{0.44}In_{0.28}Ag_{0.28}$ looks like a high Li-deficient homogeneous NaTl-type Zintl phase, but a more precise analysis reveals that it consists of two face-centered cubic phases instead. The very similar lattice constants of both phases conceal the heterogeneous character of this composition. Therefore, the alloy with this composition was not included into the homogeneity region shown in Fig. 1.

The cell parameter is a more-dimensional function of the content of all components. However, there is a

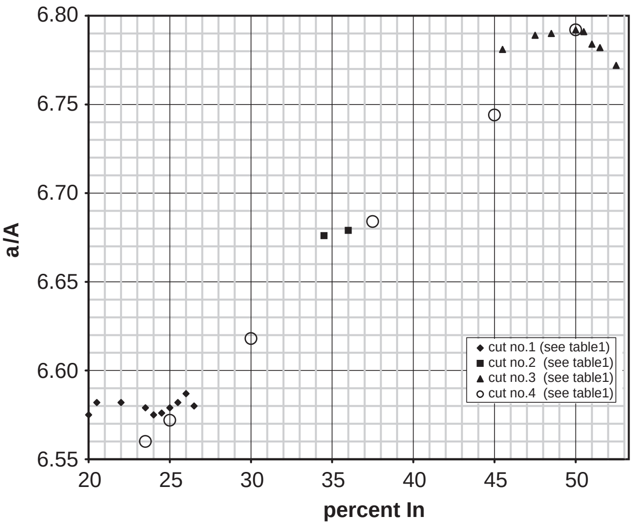

Fig. 3. Lattice parameters versus the In- content of the (binary and) ternary Li–In–Ag alloys in the homogeneity field of the NaTl-type Zintl phases.

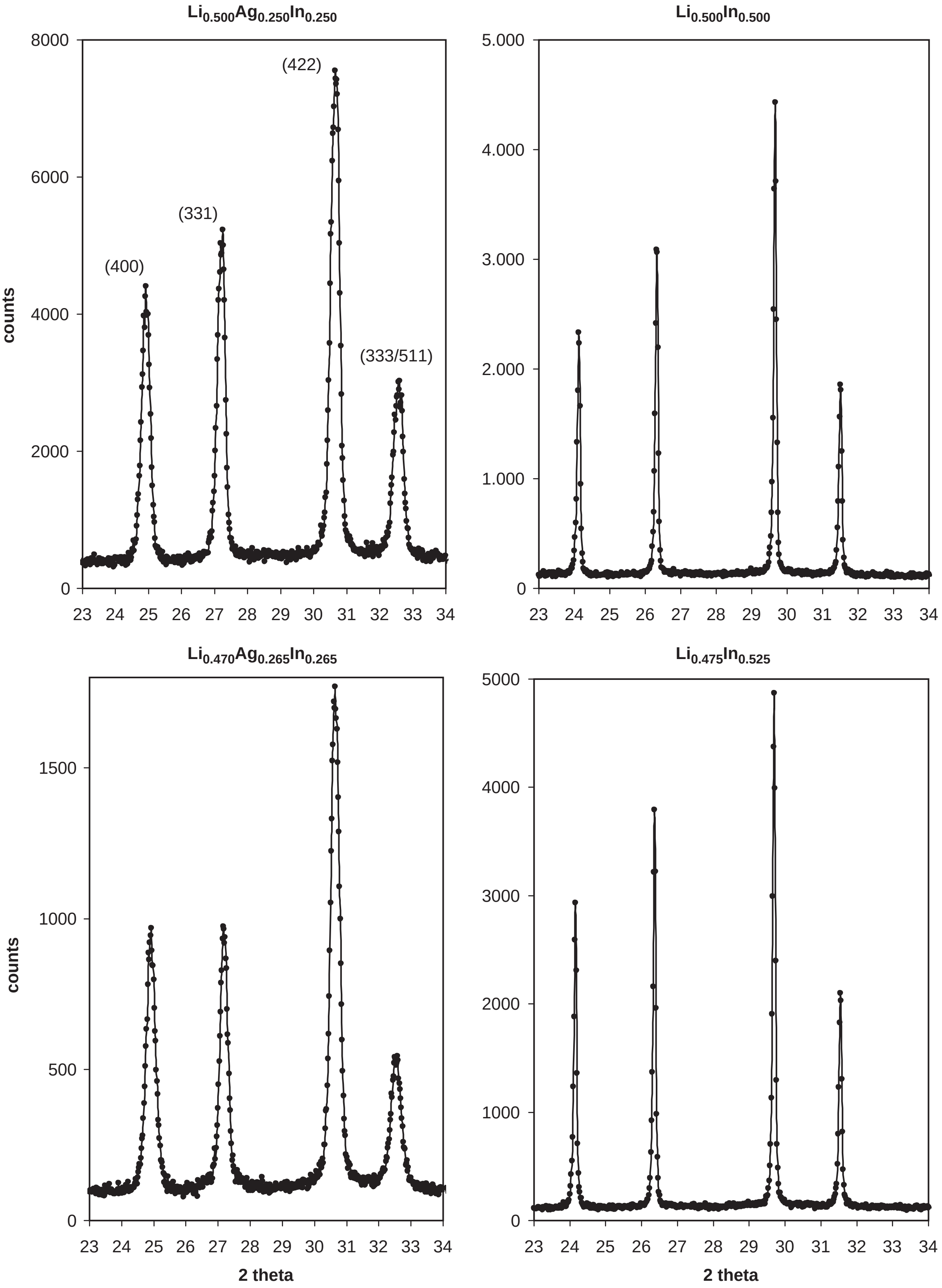

Fig. 4. Selected X-ray patterns from the quasibinary cut $Li_x(In_{0.50}Ag_{0.50})_{1-x}$ and from the binary cut Li_xIn_{1-x}, both with $x \leqslant 0.50$. In the quasibinary cut the intensity ratios of the odd to even Bragg-reflexes is decreasing with decreasing x-values (no vacancies in the Li-sublattice) whereas in the binary cut the respective intensity ratios stay constant (increasing amounts of vacancies in the Li-sublattice). [Intensity ratios deduced from lower indexed Bragg reflexes like (111), (220), and (311) could be considered as less confident due to the much stronger influence of angle dependent parameters, especially absorption. Thus they are omitted here.]

strong evidence for a more pronounced dependence on the Ag:In ratio for fixed Li-content than on Li-content for fixed Ag:In ratio, see Table 1 and Fig. 3. The correlation between lattice parameters and Ag:In ratios supports an early concept of Zintl [20]: accordingly, large rigid In-atoms and similar rigid but smaller Ag-atoms are together forming a diamond lattice, and the largest interstitials are occupied by the rather soft and compressible Li-atoms. This size-disorder on one site (the Ag/In site) results in a significant broadening of reflections in comparison with binary Li–In compounds, see the two diffraction patterns on the left- and right-hand side in Fig. 4, respectively [Note: such a size disorder should not result in a broadening—only in the case of non-random clustering!]. The rather compressible and thus adaptable Li-atoms are inbedded in the largest holes of this diamond lattice. (As K. Kuriyama [1] and T.S. Huang and J.O. Brittain [2] showed the lattice constants in the binary cut Li_xIn_{1-x} pass even through a flat maximum, see Fig. 3 and the third cut in Table 1).

Vacancies in the Li-sublattice are known for Li-deficient members along the binary cut Li_xIn_{1-x}, i.e. for $x<0.5$ [2]. Such vacancies, however, are unprobable for the ternary Li–In–Ag-Zintl phases, even in case of Li-deficient compositions. This conclusion is based on the intensity ratios between odd- and even-indexed Bragg-reflections: If the decreasing Li-content results in a partial occupation of the Li-site by heavier excess elements, the odd-indexed reflection intensities will drop with respect to the intensities of even-indexed reflections. This can be seen in Fig. 4 for selected X-ray patterns from the quasibinary cut $\{Li_x(In_{0.50}Ag_{0.50})_{1-x}\}$ in comparison with each other. The selected Bragg reflections (400) to (331) and (422) to (333/511) in the samples with 50% and 47% Li confirm the described change in intensity ratios due to the onset of partial Ag and In occupation on the Li-site. The situation is essentially different along the binary cut Li_xIn_{1-x}, where the intensity ratios remain virtually constant for decreasing Li-content as expected for the formation of vacancies in the Li-sublattices and Ag and In only on the other site. The lack of Li-vacancies in the Li-deficient ternary phases with VECs < 2.0 fits well with the likewise lack of vacancies for Li-deficient binary Zintl phases LiZn and LiCd [21,22]. In the binary and in the ternary low VEC-alloys the deficient Lithium atoms are exclusively replaced by the heavy excess atoms in the Lithium sublattice, in contrast to the binary high VEC Li_xIn_{1-x} compounds in which the deficient Lithium atoms are exclusively replaced by vacancies on the Li-sublattice [1,2] (see also Fig. 4). This behaviour is probably not restricted to the quasibinary cut $\{Li_x(Ag_{0.50}In_{0.50})_{1-x}\}$ but proposed as a general feature within the homogeneous stability range of the NaTl-type Zintl phase. The only exception is the binary cut $\{Li_xIn_{1-x}\}$ and the very close adjacent compositions—the Li-deficient ternary alloys (Li-content lower than 50%) do not induce vacancies in the Li-sublattice because the VECs become smaller than 2.0. This suggestion is strongly supported by the investigations of K. Kishio and J.O. Brittain who doped LiAl (isostructural with LiIn) with small amounts of Ag and registered promptly the decreasing and vanishing of the vacancies [23].

The colours of all investigated compositions correlate directly with the VECs, see Table 1. The optical properties of the quasibinary cuts in the analogue systems LiZn-LiIn and LiCd-LiIn with solid solutions of the NaTl-type Zintl phase and VECs also changing from 1.5 to 2.0 were experimentally and theoretically investigated by M. Zwilling et al. [24]. NaTl-type Zintl phases with different composition but very similar or identical VECs appear generally in the same colour. This observation is highly reproducable if samples of the same composition are prepared for several times, supporting the correlation between colour and VEC. An impurity effect or the influence of defects should be less reproducable and, therefore, appears very unprobable.

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