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The crystal and electronic structures of the $Li_{2-x}Ag_{1+x}In_3$ ($x=0.05$) indide

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ABSTRACT

The crystal structure of $Li_{2-x}Ag_{1+x}In_3$ ($x=0.05$) has been determined on a single crystal synthesized from the elements in a tantalum crucible. The compound crystallizes in orthorhombic space group Pmma ($a=9.325$ (3) Å, $b=3.198$ (1) Å, $c=8.043$ (3) Å at 296 K) with 12 atoms per unit cell and represents a new structure type. The structure of $Li_{2-x}Ag_{1+x}In_3$ is closely related to the $LaCoAl_4$ structure and belongs to the structural family, the representative members of which may be derived from the hexagonal AlB_2 structure type by a combination of internal deformation and substitution. The strong In–In interaction and close to zero electrons concentration around Li and Ag atoms, calculated by LTMO, allow to suggest high mobility of lithium atoms located within the channels formed by the strongly waved [–In–In–] polyanionic chains.

1. Introduction

With regard to high theoretical capacities, chemical and thermal stability, intermetallic materials have been investigated as possible anode materials for lithium-ion batteries [1,2]. Some studies in this field, focused on the ternary systems with lithium and *p*- and *d*-elements, have yet been done, including synthesis of new intermetallic compounds, and studies of their crystal structures and properties [3–10].

During the X-ray powder investigation of the In-rich corner in the ternary Li–Ag–In system a new phase of first unknown structure became noticeable mixed with two to even five other yet known phases like ternary Zintl- or Heusler phases [3,4], hexagonal Ag_3In- phase (ζ- phase) [11,12], $AgIn_2$- phase [11,13], and eventually In- phase, depending from the composition of the educts and the thermal treatment after the manufacturing at high temperatures (quenching or annealing at different temperatures and times). Interestingly this new phase was also detected during the electrochemical lithium extraction starting from the lithium rich $Li_{278}Ag_{40}In_{114}$- compound as anode. (The results of this electrochemical investigation will be separately published.)

In this paper a detailed analysis of the crystal structure of the new ternary phase $Li_{2-x}Ag_{1+x}In_3$ is given by a single crystal X- ray structure analysis, along with calculations of its electronic structure.

2. Experimental details

An alloy with the composition $Li_{30}Ag_{20}In_{50}$ was prepared from lithium rod (99.9%, Alfa Aesar), indium shot (99.999%, Alfa Aesar) and silver granules 2–8 mm (99.99%, Chempur) in a welded tantalum crucible. All preparation steps were performed in a glove box under dried argon atmosphere. The reaction between the metals was carried out in an induction furnace at 1100 °C. After 15 min, the sample was rapidly cooled down to room temperature by removing the crucible from the furnace. For equilibration the alloy was then annealed at 150 °C for 1 month. After this treatment, the sample could easily be separated from the tantalum container. No side-reaction of the alloy with the crucible was detected. The brittle dark-gray metallic alloy is very sensitive to the humidity in air.

The amount of Li-loss during sample preparation in hermetically closed crucibles can be estimated, based on previous studies with successive detailed chemical analyses of similar systems [14–16]. Accordingly, a lithium loss up to 1% versus the nominal composition can be expected.

Initial sample characterization was performed by X-ray powder diffraction in Debye-Scherrer mode using a STOE STADI/P powder diffractometer (Mo–Kα_1 radiation). Structure refinement was performed by the Rietveld method using the Winplotr

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software package [17]. The phase analysis revealed that the alloy was not fully homogeneous, i.e. besides of the title compound as the main phase three additional well-known phases could be identified (see next section). Therefore a chemical analysis of the heterogeneous bulk material was not useful, and thus was not carried out.

Table 1
Crystal data and structure refinement for $Li_{2-x}Ag_{1+x}In_3$ (x=0.05).

Empirical formula	$Li_{2-x}Ag_{1+x}In_3$ (x=0.05)	
Diffractometer/ radiation	Bruker Kappa APEXII/ Mo-Kα	
Symmetry, space group	orthorhombic, *Pmma*	
Structure type	own	
Pearson symbol	*oP12*	
Temperature, *K*	296 (2)	150 (2)
Unit cell dimensions:		
a, Å	9.325 (3)	9.289 (3)
b, Å	3.198 (1)	3.1726 (9)
c, Å	8.043 (3)	7.996 (2)
V, $Å^3$	239.9 (1)	235.6 (1)
Z	2	2
Calculated density, g/sm^3	6.531	6.649
Absorption coefficient, mm^{-1}	18.272	18.602
θ range for data collection	2.53÷26.37	2.55÷24.45
F (000)	405	405
Reflections collected/ unique	2475/307	1629/242
Data/ restraints/ parameters	307/0/23	242/0/19
Goodness-of-fit on F^2	1.142	1.138
R indices [$I > 2\sigma(I)$]	$R1$=0.0289 $wR2$=0.0613	$R1$=0.0276 $wR2$=0.0509
R indices (all data)	$R1$=0.0406 $wR2$=0.0523	$R1$=0.0350 $wR2$=0.0653
Largest diff. peak and hole, e/$Å^{-3}$	1.912 and −1.655	1.494 and −1.201

The single crystal was selected under dried paraffin and sealed in a glass capillary. The single crystal data were collected on a Bruker Kappa APEXII CCD area detector diffractometer at 296 K and 150 K.

The electronic structure of the title compound was calculated using the tight-binding, linear muffin-tin orbital method in the atomic spheres approximation (TB–LMTO–ASA) [18–21]. The exchange and correlation were interpreted in the local density approximation [22].

3. Results and discussion

3.1. Crystal structure

A good quality single crystal was isolated by mechanical fragmentation from the alloy $Li_{30}Ag_{20}In_{50}$ annealed at 150 °C. The structure solution by direct methods and subsequent structure refinement was performed using the Shelx97 software package [23]. The structure was solved after the analytical absorption correction. In the first stage of the structure solution the positions of In and Ag atoms were obtained accurately by direct methods. After the refinement of In and Ag atoms the residual factor $R1$ was equal to 0.0512 and the most pronounced difference peak − 11.586 e/$Å^{-3}$. The remaining Li atoms were located in subsequent difference Fourier syntheses and after refinement of their parameters the residual factor was reduced to $R1$=0.0335, and the highest difference peak was decreased to

Table 2
Atomic coordinates and displacement parameters ($Å^2 \times 10^3$) for $Li_{2-x}Ag_{1+x}In$ (x=0.05).

Atom	Site	x/a	y/b	z/c	U_{iso}/U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
296 K											
Ag	*2e*	1/4	0	0.1809 (2)	19 (1)	8 (1)	29 (1)	21 (1)	0	0	0
In1	*4j*	0.0223 (1)	1/2	0.3204 (1)	17 (1)	12 (1)	19 (1)	19 (1)	0	0 (1)	0
In2	*2f*	1/4	1/2	0.8727 (2)	16 (1)	8 (1)	19 (1)	21 (1)	0	0	0
(Li,Ag)	*2a*	0	0	0	25 (4)	21 (8)	26 (9)	27 (9)	0	−7 (7)	0
Li	*2e*	1/4	0	0.537 (4)	28 (8)	–	–	–	–	–	–
(Li, Ag)=0.95 (1) Li+0.05 (1) Ag											
150 K											
Ag	*2e*	1/4	0	0.1810 (2)	12 (1)	5 (1)	18 (1)	14 (1)	0	0	0
In1	*4j*	0.0222 (1)	1/2	0.3201 (1)	11 (1)	7 (1)	13 (1)	12 (1)	0	1 (1)	0
In2	*2f*	1/4	1/2	0.8729 (2)	11 (1)	5 (1)	14 (1)	13 (1)	0	0	0
(Li, Ag)	*2a*	0	0	0	16 (4)	–	–	–	–	–	–
Li	*2e*	1/4	0	0.533 (4)	17 (8)	–	–	–	–	–	–
(Li, Ag)=0.95 (1) Li+0.05 (1) Ag											

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

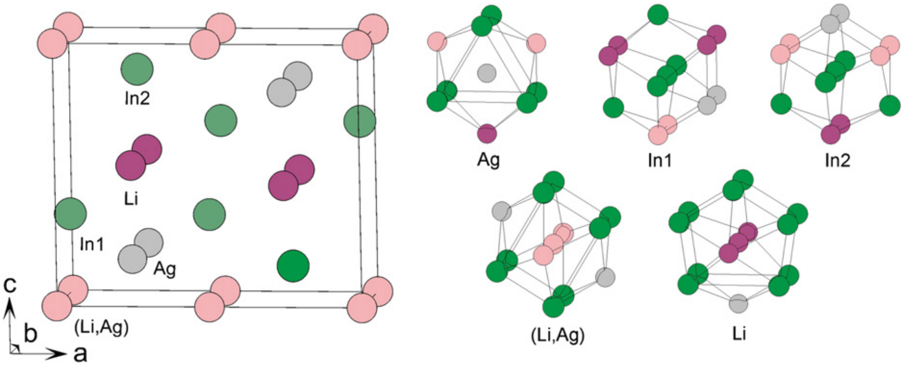

Fig. 1. The unit cell and the coordination polyhedra of the atoms in the structure of $Li_{2-x}Ag_{1+x}In_3$ (x=0.05).