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TERNARY AND QUATERNARY METAL-NITRIDES IN THE Li-Sr-Ni-N-SYSTEM*

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SUMMARY

Single crystals of ternary and quaternary phases of the Li-Sr-Ni-N-system were grown from the melt under nitrogen and were investigated by X-ray diffraction methods. The crystal structures are classified into the following groups: i. solid solutions (substitutional type) of the Li_3N-structure ($Li_{1-x}Ni_x[Li_2N]$), ii. structures containing fragments of the Li_3N-structure (Li_4SrN_2, LiSrN and $Li_4Sr_2(Li_{0.8}Ni_{0.2})N_3$ and iii. structures which can be derived from interstitial binary metal nitrides of the first transition series ($Li_3Sr_3Ni_4N_4$). The crystal structure of SrNiN is not quite clear at present, but shows close relations to the crystal structure of BaNiN ($Sr(Ni_{1-x}Li_x)N$, resp.).

INTRODUCTION

According to an early work of Juza et al. (ref. 1) there is a small region of solid solutions between the binary nitrides Li_3N (refs. 2,3) and Ni_3N (ref. 4). The formation of mixed crystals takes place by substitution of lithium atoms between the Li_2N-layers of the Li_3N ($=Li[Li_2N]$)-structure. The limiting formula is given by $Li_{1-x}Ni_x[Li_2N]$ with $0 \leq x \leq 0.63$. The easy formation of the ternary mixed crystal series is undoubtedly remarkable because the enthalpy of formation of pure binary Ni_3N merely is -0.84 kJ/mole (ref. 5).

A much more recent finding refers to an intermediate phase with 1:1:1-composition in the ternary system Li-Sr-N. The compound LiSrN (ref. 6) is an isotype of the YCoC-structure (ref. 7).

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Lithium and nitrogen atoms are arranged together to form infinite linear chains (-Li-N-Li-N-Li-) which are also present in the Li_3N crystal structure. Along the c-axis direction each chain is turned 90° with respect to the other. Strontium atoms (tetrahedral coordination by nitrogen atoms) are connecting these chains in a mode which causes orthorhombic bipyramidal coordination of the nitrogen atoms. The three-dimensional structure is formed by corner and edge sharing orthorhombic bipyramids, $NLi_{2/2}Sr_{4/4}$. This very simple structural type is also realized in the quaternary compound $(Li_{0.5}Ni_{0.5})CaN$ with the crystallographic data: tetr., $P4_2/mmc$, a = 371.1(2) pm, b = 663.4(2) pm, Z = 2 (ref. 8).

The interesting facts given in the ternary systems Li-Ni-N and Li-Sr-N induced us to extend the investigations to the quaternary Li-Ni-Sr-N-system.

PREPARATION OF INTERMEDIATE PHASES

Intermediate phases in the quaternary system which were identified up to now are shown in Fig. 1. Single crystals were grown from the melt under nitrogen. Compounds containing nickel were obtained by using nickel cruicibles as both a container and a source. The phases 2, 4, 5 and ss (see Fig. 1) were prepared by reaction of the metallic elements with nitrogen (1 atm) at elevated temperatures up to 1100°C, followed by cooling from the

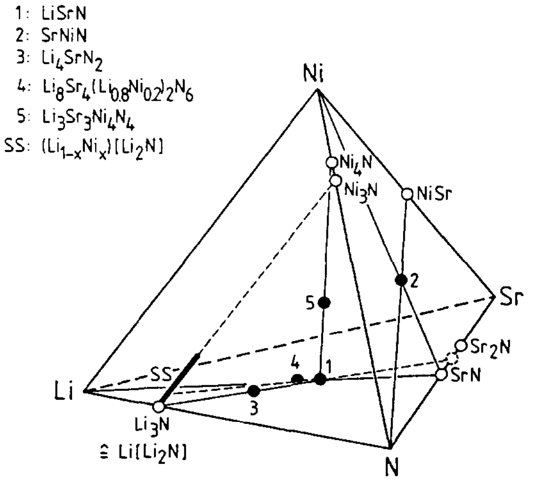

Fig. 1. Ternary and quaternary phases in the Li-Sr-Ni-N-system.

melt at a rate of 20°C/h. Compounds 1 and 3 (s. Fig. 1) were obtained from the reaction of lithium nitride with strontium (stoichiometric molar ratios Li:Sr) under nitrogen atmosphere (1 atm) in tantalum cruicibles at 700°C; the melts were cooled to room temperature over a period of 12 hours.

The crystalline reaction products show a dark-metallic lustre. To avoid spontaneous reaction with moisture the samples were handled under inert gas and under dry paraffin. Single crystals for structural investigations were mounted in Lindemann capillaries.

CRYSTALLOGRAPHIC DATA AND CRYSTAL STRUCTURES

Crystallographic data of the ternary and quaternary phases in the Li-Sr-Ni-N-system are listed in Table 1. The crystal structures of the intermediate phases can be classified into three groups:

i. solid solutions (substitutional type) of the Li_3N-structure

ii. structures containing fragments of the Li_3N-structure

iii. structures which can be derived from interstitial binary metal nitrides of the first transition series.

As it was already mentioned in the introduction, the formation of solid solutions of the Li_3N-structure (group i.) takes place by substitution of the lithium atoms between the Li_2N-layers, a

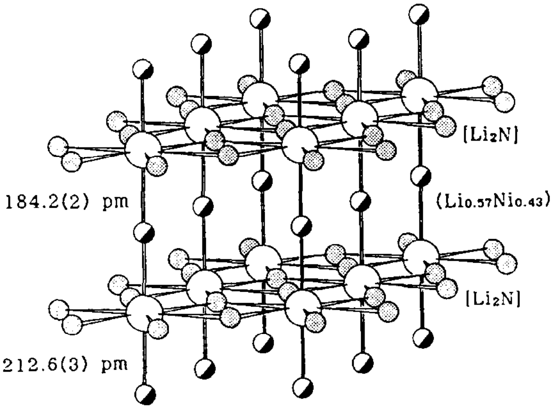

Fig. 2. The crystal structure of $Li_{1-x}Ni_x[Li_2N]$; x = 0.43.

TABLE 1
Crystallographic data of ternary and quaternary phases in the Li-Sr-Ni-N-system (Numbers are consistent with Fig.1)

ss:	$Li_{1-x}Ni_x[Li_2N]$	x = 0.43, hex.,	P6/mmm,	a = 369.3(2) pm, c = 368.4(2) pm	Z = 1
1:	LiSrN (ref. 6)	tetr.,	$P4_2/mmc$,	a = 392.4(3) pm, c = 708.5(4) pm	Z = 2
2:	SrNiN	(hex./orth.), close relations to the crystal structure of BaNiN (ref. 8)			
3:	Li_4SrN_2 (ref. 9)	tetr.,	$I4_1/amd$,	a = 382.2(2) pm, c = 2704.2(9) pm	Z = 4
4:	$Li_4Sr_2(Li_{0.8}Ni_{0.2})N_3$	orth.,	Cmmm,	a = 376.7(1) pm, b = 2073.9(3) pm c = 391.6(1) pm	Z = 2
5:	$Li_3Sr_3Ni_4N_4$	orth.,	Immm,	a = 401.1(1) pm, b = 709.8(2) pm c = 1665.4(3) pm	Z = 2

finding (ref. 1) which was confirmed by our single crystal investigation in a member of the mixed crystal series $Li_{1-x}Ni_x[Li_2N]$ with x = 0.43 (see Fig. 2). Compared with pure Li_3N (ref. 3) the bond lengths $(Li_{0.57}Ni_{0.43})$-N are significantly shortened (184.2(2) pm; 193.8(1) pm in Li_3N). Li-N-distances within the Li_2N-layers remain nearly unchanged (213.0(1) pm in Li_3N, 212.6(3) pm in the mixed crystal).

A schematic representation of the crystal structures which contain fragments of the Li_3N-structure (group ii.) is given in Fig. 3.

Large fragments of the Li_3N-structure with two-dimensional expansion are present in the crystal structure of Li_4SrN_2 (ref. 9). The sections are formed by replacing three of the six lithium atoms within the equatorial plane of the hexagonal bipyramidal coordination around the nitrogen atoms in Li_3N by two strontium atoms. The graduation of bond lengths Li_{ax}-N and Li_{eq}-N in the crystal structure of Li_3N (193.8(1) pm and 213.0(1) pm) remains nearly unchanged in the Li_2N-fragment of the crystal structure of Li_4SrN_2 (191.3(2) pm and 211.2(2) - 214.9(2) pm). The Li_2N double-layers are connected by strontium atoms which are tetrahedrally coordinated by nitrogen atoms of adjacent layers. This mode of connection causes 90°-turning of the double-layers along the crystallographic c-axis direction. Li_4SrN_2 is a lithium-ion conductor, but with a conductivity which is much lower compared to

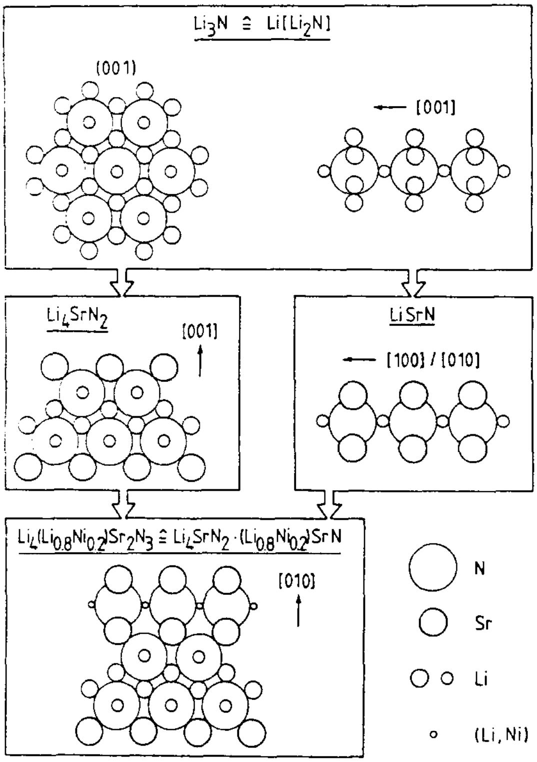

Fig. 3. Schematic representation of the Li_3N structure and the crystal structures of phases which contain fragments of the Li_3N-structure.

that of pure Li_3N (ref. 10).

The crystal structure of LiSrN (ref. 6) has already been described in the introduction. The bond lengths Li-N within the infinite linear chains (196.2(2) pm) are comparable with Li_{ax}-N-distances in the crystal structure of Li_3N (193.8(1) pm).

The structural units of the crystal structures of Li_4SrN_2 and LiSrN are joined together in the crystal structure of $Li_4Sr_2(Li_{0.8}Ni_{0.2})N_3$. Along the b-axis direction Li_2N slabs alternate with single-layers which consist of linear LiN-chains in parallel orientation. These fragments of the Li_3N-structure are interconnected by strontium atoms which are tetrahedrally coordinated by nitrogen atoms of adjacent structural units. Li-N-distances along the chains in LiSrN (196.2(2) pm) are shortened (188.4(1) pm) by partial substitution of lithium atoms by nickel atoms ($Li_{0.8}Ni_{0.2}$), an observation, which is consistent with the respective tendencies in $Li_{1-x}Ni_x$ [Li_2N] (see Fig. 2).

By changing the position within the quaternary system (Fig. 1) from the Li_3N-rich region to the section LiSrN-Ni_4N, a quaternary phase of stoichiometric composition $Li_3Sr_3Ni_4N_4$ (group iii.) occurs, whose crystal structure is related to some extent to the perovskite-type (interstitial) nitride Ni_4N (ref. 4). Fig 4

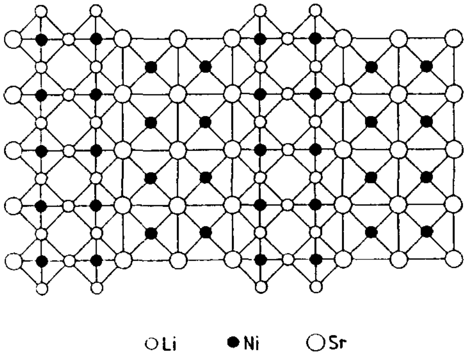

Fig. 4. The crystal structure of $Li_3Sr_3Ni_4N_4$. Polyhedral representation along [010]. The centres of the distorted octahedra are occupied by nitrogen atoms.

shows a projection on one octahedral layer of the crystal structure of $Li_3Sr_3Ni_4N_4$. Nitrogen atoms are in distorted [2+4]-coordinations. Along [010] the nickel atoms occupy opposite apices of the octahedra and interconnect adjacent layers to give a three-dimensional octahedral structure with alternating $N(Ni_{2/2}Sr_{2/3}Sr_{2/4})$- and $N(Ni_{2/2}Li_{3/2}Sr_{1/3})$-octahedra sharing common Ni-apices. As can be seen from Fig. 4, the structure contains domains of octahedral connections which can be described in terms of one-dimensional fragments of the ReO_3 structure type. Bond lengths within the infinite Ni-N-chains along [010] amount to 177.6(3) pm. By taking into consideration only those nitride-crystal structures which exclusively contain the nitrogen atoms in [2+4]-coordination, a nearly linear dependence is identified concerning the bond lengths $(Li_{1-x}Ni_x)$-N and the degree of substitution (x): $x = 0$ (SiSrN, ref. 6) 196.2(2) pm; $x = 0.5$ ($(Li_{0.5}Ni_{0.5})CaN$, ref. 8) 186.2(2) pm; $x = 1$ ($Li_3Sr_3Ni_4N_4$) 177.6(3) pm.

Crystals of SrNiN are affected with twinning. Though the structure is not completely clear at present, symmetry (orth./hex.) and cell parameters indicate a close similarity to the crystal structure of BaNiN (orth., Pnma, a = 962.8(3) pm, b = 1364.5(4) pm, c = 541.7(3) pm, Z = 12; ref. 8). This assumption is also supported by the very recent observation of a limited region of solid solutions between the ternary nitrides LiSrN and SrNiN (connecting line between the phases 1 and 2 in Fig. 1). The crystal structure of a member of this mixed crystal series $Sr(Ni_{1-x}Li_x)N$ with $x = 0.45$ (orth., Pnma, a = 899.8(3) pm, b = 1311.7(7) pm, c = 543.1(2) pm, Z = 12) was determined to be an isotype of the BaNiN-structure and which contains infinite and planar zig-zag chains $(-(Ni_{0.55}Li_{0.45})-N)_\infty$.

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