Journal of Alloys and Compounds, *186* (1992) 339–345
JALCOM 289

$Ca[(Ni_{1-x}Li_x)N]$: limited solid solutions ($0 \leqslant x \leqslant 0.58$) in the system Ca[NiN] (Y[CoC]-type structure)–Ca[LiN] (modified fluorite-type structure)

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(Received February 24, 1992)

Abstract

Solid solutions of composition $Ca[(Ni_{1-x}Li_x)N]$ ($0 \leqslant x \leqslant 0.58$) were prepared as polycrystalline materials by annealing mixtures of the ternary components Ca[NiN] and Ca[LiN]. Single crystals of the limiting composition $Ca[(Ni_{0.42}Li_{0.58})N]$ were grown from the melt (tetragonal, $P4_2/mmc$; $a = 372.3(1)$ pm, $c = 665.6(1)$ pm; $Z = 2$; $D_X = 3.03$ g cm^{-3}). The crystal structure of the mixed crystal series (Y[CoC] type) contains linear $^1_\infty[(Ni_{1-x}Li_x)N_{2/2}]$ chains with bond lengths ranging from 179.0 pm ($x = 0$) to 186.1 pm ($x = 0.58$).

1. Introduction

The quaternary systems *lithium–alkaline earth metal–transition metal–nitrogen* contain ternary and intermediate nitridometallates. Nitridoniccolates represent low valency compounds with nickel in oxidation states less than or equal to 1 and with infinite $[NiN_{2/2}]$ connections ($[(Ni_{1-x}Li_x)N_{2/2}]$ respectively) [1].

According to an early X-ray powder investigation by Sachsze and Juza [2], there is a region of solid solutions in the ternary triangle Li–Ni–N between the binary components Li_3N [3, 4] and Ni_3N [5]. The formation of mixed crystals $Li_2[Li_{1-x}Ni_x)N]$ ($0 \leqslant x \leqslant 0.63$) takes place by substitution of lithium for nickel within the $^1_\infty[LiN_{2/2}]$ chains of the Li_3N structure. This finding was also confirmed by structure determinations on single crystals of composition $Li_2[(Li_{0.66}Ni_{0.34})N]$ and $Li_2[(Li_{0.57}Ni_{0.43})N]$ [1, 6].

Besides the mixed crystal series $Li_2[(Li_{1-x}Ni_x)N]$, the following ternary and quaternary nitridoniccolates have been observed up to now.

System Li–Ba–Ni–N [1]: BaNiN [7], $Ba_8Ni_6N_7$ [8] and $Ba_2(Ni_{1-x}Li_x)Ni_2N_2$ [9] ($x = 0.43$).

System Li–Sr–Ni–N [1, 6]: $Sr_3Li_3Ni_4N_4$ [10], $Sr(Ni_{1-x}Li_x)N$ [1, 6], $Sr_2Li_4(Li_{1-x}Ni_x)N_3$ [1, 6] ($x = 0.2$) and $SrLi_3(Li_{1-x}Ni_x)N_2$ [1, 6] ($x = 0.1$).

System Li–Ca–Ni–N [1]: CaNiN [1, 11] with an extended one-phase region $Ca(Ni_{1-x}Li_x)N$ on the quasi-binary section towards CaLiN [12].

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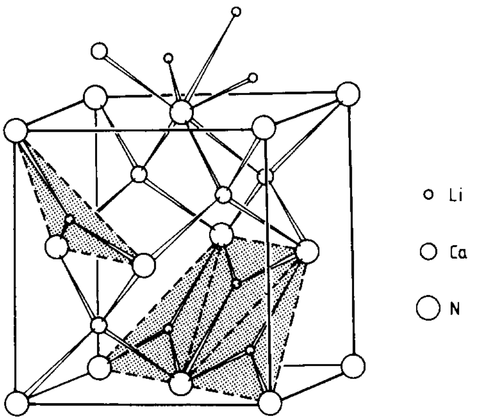

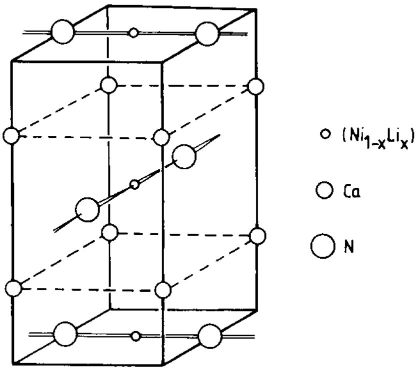

Fig. 1. Crystal structure of Ca[LiN].

Fig. 2. Crystal structure of Ca[NiN] and of the solid solution series $\mathrm{Ca}[(\mathrm{Ni}_{1-x}\mathrm{Li}_x)\mathrm{N}]$.

The present paper deals with mixed crystal phases $\mathrm{Ca}[(\mathrm{Ni}_{1-x}\mathrm{Li}_x)\mathrm{N}]$ which crystallize in the Y[CoC]-type structure [13] and which are also isotypes of Sr[LiN] [14]. The Y[CoC]-type structure can be considered in terms of a defect perovskite-type as well as a modified fluorite-type structure. Since the crystal structure of the pure lithium compound, Ca[LiN], is closely related to the fluorite type, we were interested in the formation of solid solutions in order to determine the range of solid miscibility in the quasibinary system Ca[NiN]–Ca[LiN].

The crystal structure of *Ca[LiN]* [12] (Fig. 1) has a distorted cubic close nitrogen packing with the calcium atoms in the centres of the tetrahedral holes. The lithium atoms are shifted onto the tetrahedral faces of the nitrogen tetrahedra (14 pm above the plane of nitrogen atoms). The threefold-coordinated lithium atoms are arranged in a way which causes formation of $^{1}_{\infty}[\mathrm{LiN}_{3/3}]$ ribbons as fragments of the $\mathrm{Li}_3\mathrm{N}$ structure. *Ca[NiN]* [1, 11] is an isotype of the Y[CoC] structure [13]. The metal atoms (Fig. 2) are arranged as in the known caesium chloride structure. Nitrogen occupies the centres of two opposing faces of the (compressed) Ca_8 cube. Altogether the nitrogen atoms show an arrangement of a distorted cubic close packing. Calcium occupies the centres of the tetrahedral holes; the nickel atoms are shifted onto the vertices of the nitrogen tetrahedra, thereby forming linear $^{1}_{\infty}[\mathrm{NiN}_{2/2}]$ chains which run parallel to the [100] and [010] directions.

2. Experimental details

Handling as well as preparation of the materials were carried out under dried gas (argon, nitrogen). α-$\mathrm{Ca}_3\mathrm{N}_2$ was prepared by reaction of calcium (Ventron 99.5%) with nitrogen (99.999%) in tantalum crucibles at 600 °C.

Li_3N was synthesized as described by Schönherr *et al.* [15]. The ternary compounds Ca[NiN] and Ca[LiN] were obtained by reaction of α-Ca_3N_2 with nickel powder (Ventron 99.9%, particle size 5 μm) at 1000 °C in nickel crucibles and by reaction of α-Ca_3N_2 with Li_3N (molar ratio 1:1.2) at 800 °C in tantalum crucibles respectively. The reactions were carried out under streaming nitrogen with a reaction period of 20 h. For a complete reaction of nickel with α-Ca_3N_2 the samples were re-ground after the first reaction and two more reaction cycles were carried out after mixing the powders with a 10% excess of α-Ca_3N_2. Polycrystalline samples of $Ca[(Ni_{1-x}Li_x)N]$ were prepared by solid state reaction of defined mixtures of Ca[NiN] and Ca[LiN]. The compounds were finely ground and mixed, pressed into pellets and annealed at 800 °C (20 h) in nickel crucibles under nitrogen.

Powder diffraction data were recorded on a Philips PW 1700 powder diffractometer (Cu Kα radiation quartz monochromator) as flat samples and covered with polyethylene foil to prevent the materials from hydrolysis. Using silicon as an internal standard, a correction of the d values for systematic errors was applied. Lattice parameters were refined using the programme AGL [16]. Halfwidths of the reflection profiles were found to be enlarged in some samples, thereby leading to increasing standard deviations of the cell parameters. Reactions at elevated temperatures (above 800 °C) do not give quaternary phases with a better crystallinity, but cause evaporation of lithium-containing components and the ternary compound Ca[NiN] is the only product observed.

Single crystals of $Ca[(Ni_{0.42}Li_{0.58})N]$ were obtained by reaction of nitrogen (99.999%) with a molten mixture of lithium (Ventron 99.5%, peeled under argon) and calcium (Ventron 99.5%) (molar ratio 1:1) in a nickel crucible that served as both a container and a source. After a reaction period of 15 h at 1000 °C the melt was cooled to room temperature at a rate of 20 °C h^{-1}. Tetragonal prismatic single crystals up to 0.2 mm in length were isolated from the pounded multiphase sample under dry paraffin. The crystals were fused in Lindemann capillaries. The Laue group and lattice constants of a proper crystal were determined by precession photographs. Single crystal data were recorded on a Philips PW 1100 four-circle diffractometer (Mo Kα radiation, graphite monochromator). Cell parameters were refined from the 2θ values of 25 highly indexed reflections. Three standard reflections were measured every 2 h. A total of 681 reflections (hkl and $hk\bar{l}$) were collected in the range $3° < 2\theta < 80°$; 102 unique reflections had significant intensities ($F > 4\sigma(F)$). The extinction symbol was in accordance with the space groups $P4_2mc$ (No. 105), $P\bar{4}2c$ (No. 112) and $P4_2/mmc$ (No. 131). The structure refinement was carried out using the program SHELX 76 [17]; in an advanced state a weighting scheme $1/w(hkl) = \sigma^2 F_o(hkl) + [0.001 F_o(hkl)]^2$ as well as an extinction coefficient (e.c. -0.081) were introduced. Absorption effects were taken into consideration using the program DIFABS [18]. The residual electron density after the final refinement was $\pm 0.5 \times 10^{-6}$ e pm^{-3}. Crystallographic data and atomic parameters are summarized in Table 1. Interatomic distances are given in Table 2.

TABLE 1

$Ca[(Ni_{0.42}Li_{0.58})N]$: crystallographic data and atomic parameters (for further details see text)

Crystal system	Tetragonal
Space group	$P4_2/mmc$ (No. 131)
Lattice constants (pm)	$a=372.3(1)$, $c=665.6(1)$
Z	2
μ (cm^{-1})	70.4
$D_{X\text{-ray}}$ ($g\ cm^{-3}$)	3.03
R, R_w values	0.027, 0.028

Atom	Wyckoff position	x	y	z	K	U_{eq} (pm^2)[a]
Ca	(2*e*)	0	0	$\frac{1}{4}$	1	159(2)
N	(2*c*)	0	$\frac{1}{2}$	0	1	217(13)
Li	(2*b*)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.58(.4)	161(5)
Ni	(2*b*)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.42(.4)	161(5)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	189(4)	189(4)	100(4)	0	0	0
N	205(21)	230(23)	216(21)	0	0	0
Li	175(10)	158(9)	151(6)	0	0	0
Ni	175(10)	158(9)	151(6)	0	0	0

[a] U_{eq} is defined as $\frac{1}{3}[U_{11}(a^*a)^2+U_{22}(b^*b)^2+U_{33}(c^*c)^2]$.

TABLE 2

$Ca[(Ni_{0.42}Li_{0.58})N]$: interatomic distances (pm) and bond angles (deg)

Ca–Ni	4×	249.7	(Ni, Li)–N	2×	186.1
N–Ca–N	2×	96.4			
N–Ca–N	4×	116.4			
Ca–N–Ca	2×	83.6	Ca–N–(Ni, Li)	8×	90.0
Ca–N–Ca	2×	96.4	(Ni, Li)–N–(Ni, Li)		180.0
Ca–N–Ca	2×	180.0			

3. Crystal structure of $Ca[(Ni_{0.42}Li_{0.58})N]$

$Ca[(Ni_{0.42}Li_{0.58})N]$ (Fig. 2) is an isotype of the Y[CoC]/Ca[NiN] structure [13, 11]; the chemical composition establishes the boundary of a solid solution series $Ca[(Ni_{1-x}Li_x)N]$ with $0 \leqslant x \leqslant 0.58$ (Fig. 3). The bond length $(Ni_{0.42}Li_{0.58})$–N (186.1 pm, Table 2) is longer than the Ni–N bond length in the crystal structure of Ca[NiN] (179.0 pm [11]) and is shorter than the Li–N distance (193.8(1) pm) within the infinite and linear chains of the Li_3N ($\approx Li_2[LiN]$) crystal structure [4]. The tendency of bond shortening by substitution of nickel for lithium within $^1_\infty[(Li_{1-x}Ni_x)N_{2/2}]$ chains was first

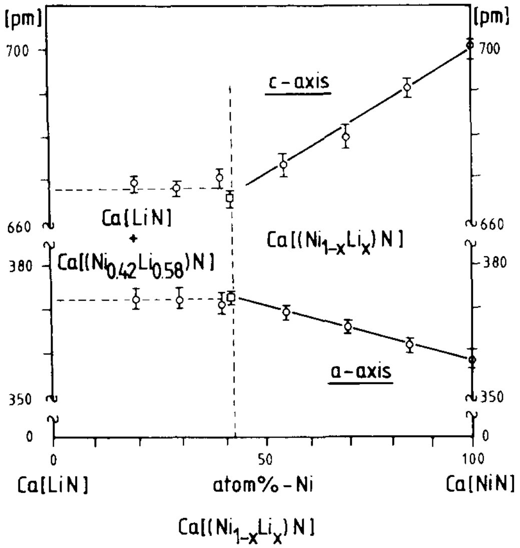

Fig. 3. Lattice parameters of the solid solution series $Ca[(Ni_{1-x}Li_x)N]$ $(0 \leqslant x \leqslant 0.58)$ in the system Ca[LiN]–Ca[NiN].

shown by Sachsze and Juza [2], who investigated the mixed crystal series $Li_2[(Li_{1-x}Ni_x)N]$ $(0 \leqslant x \leqslant 0.63)$ by X-ray powder methods; their findings were confirmed only recently [1, 6] by structure determinations of single crystals with composition $Li_2[(Li_{0.66}Ni_{0.34})N]$ $((Li_{0.66}Ni_{0.34})–N$, 185.8(1) pm) and $Li_2[(Li_{0.57}Ni_{0.43})N]$ $((Li_{0.57}Ni_{0.43})–N$, 183.8(1) pm).

The Ca–N bond lengths (249.7 pm) of the tetrahedrally coordinated Ca^{2+} ions in the crystal structure of $Ca[(Ni_{0.42}Li_{0.58})N]$ are in good agreement with the respective values in the crystal structures of Ca[NiN] (250.5 pm [11]) and Ca[LiN] (247.0 pm [12]) and they also agree very well with the sum of the effective ionic radii (248 pm) given by Baur [19].

4. Solid solution series $Ca[(Ni_{1-x}Li_x)N]$

The results of the X-ray powder investigations in the system Ca[NiN]–Ca[LiN] are summarized in Fig. 3 and Table 3. The system contains the solid solution series $Ca[(Ni_{1-x}Li_x)N]$ $(0 \leqslant x \leqslant 0.58)$ which is based on the crystal structure of Ca[NiN] [1, 11]. The *a* axis is elongated with decreasing nickel content and the *c* axis is shortened at the same time. In this way the bond lengths $(Ni_{1-x}Li_x)–N$ are increased from 179.0 pm $(x=0)$ to 186.1 pm $(x=0.58)$ whereas the Ca–N bond lengths are kept at a constant value of about 249 pm. The cell volumes of the solid solution series are enlarged with increasing lithium content and the c/a ratios decrease from 1.955 $(x=0)$ to a value of 1.787 for the limiting composition of $x=0.58$ (single-crystal data, Table 1).

TABLE 3

Lattice constants of mixed crystal phases $Ca[(Ni_{1-x}Li_x)N]$ as a function of the overall composition during preparation (for further details see text)

Overall composition during preparation	a (pm)	c (pm)	c/a	V (10^6 pm^3)^a
CaNiN	358.3(1)	700.6(3)	1.955	89.9(1)
$Ca(Ni_{0.85}Li_{0.15})N$	361.8(2)	691.5(7)	1.911	90.5(2)
$Ca(Ni_{0.70}Li_{0.30})N$	366.1(1)	680.3(3)	1.858	91.2(1)
$Ca(Ni_{0.55}Li_{0.45})N$	369.0(2)	673.6(2)	1.825	91.7(1)
$Ca(Ni_{0.40}Li_{0.60}N)^b$	370.8(1)	670.6(6)	1.808	92.2(1)
$Ca(Ni_{0.30}Li_{0.70}N)^b$	372.1(1)	668.2(9)	1.796	92.5(1)
$Ca(Ni_{0.20}Li_{0.80}N)^b$	371.7(2)	669.1(12)	1.800	92.5(2)

^{a}Volume per unit cell.
^{b}Two-phase mixtures of $Ca[(Ni_{0.42}Li_{0.58})N]$ and Ca(LiN).

5. Conclusions

In addition to the series $Li_2[(Li_{1-x}Ni_x)N]$ ($0 \leqslant x \leqslant\ = 0.63$ [2], Li_3N-type structure) the system $Ca[(Ni_{1-x}Li_x)N]$ ($0 \leqslant x \leqslant\ = 0.58$, Ca[NiN]-type structure) represents a further example of the formation and existence of solid solutions which are based on substitution of the "closed-shell" Li^+ ion for the d^9 species nickel(I) and which are extended over a broad range of composition. The common and characteristic structural feature of the mixed crystal series is the linear chains $^1_\infty[(Ni_{1-x}Li_x)-N]$ with a two-fold coordination of the substitutional position. The increase in the bond lengths $(Ni_{1-x}Li_x)-N$ in the series $Ca[(Ni_{1-x}Li_x)N]$ from 179.0 pm ($x = 0$) to 186.1 pm ($x = 0.58$) confirms that the volume increment of twofold-coordinated lithium is greater than the corresponding value of nickel(I).

Acknowledgments

We wish to acknowledge the support of this study by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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