# Crystal structure of tetra(calcium/strontium) cyanamide dinitride, $Ca_{4-x}Sr_x[CN_2]N_2$ ($x$ = 0.80)

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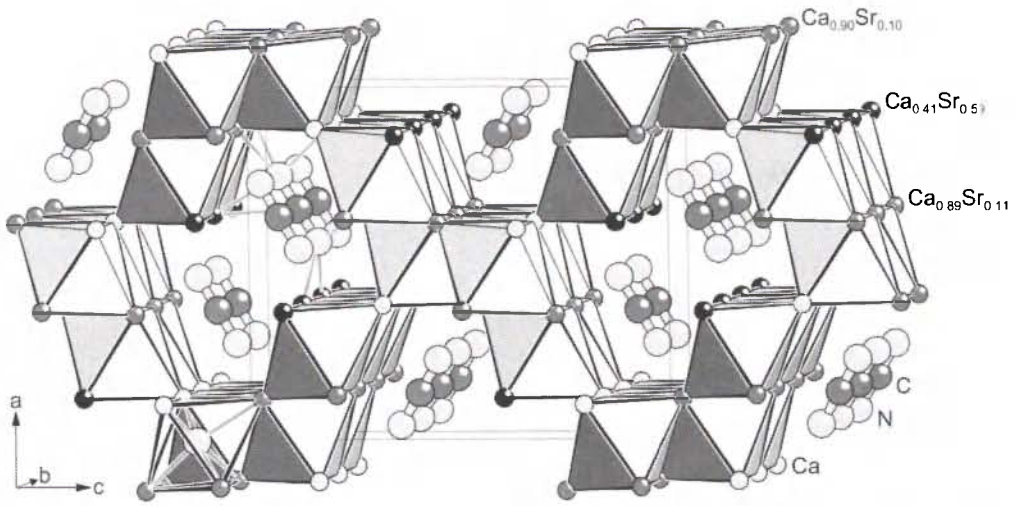


**Abstract**

$CCa_{3.20}N_4Sr_{0.80}$, orthorhombic, *Pnma* (No. 62), $a$ = 11.677(1) Å, $b$ = 3.6470(4) Å, $c$ = 13.911(1) Å, $V$ = 592.4 Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.057, $T$ = 293 K.

**Source of material**

Yellow-green single crystals of $Ca_{4-x}Sr_x[CN_2]N_2$ ($x$ = 0.80(1)) were obtained as a minor phase by reaction of $Ca_3N_2$ (from Ca and $N_2$ at 1123 K), $Sr_2N$ (from Sr and $N_2$ at 1123 K), Li and Fe in iron crucibles under $N_2$. Carbon was probably introduced either by leaching out of the iron crucible or due to impurities on the surface of Ca- or Sr-pieces. The mixtures were heated to 1123 K (100 K/h), annealed for 36 h, and cooled down (50 K/h) to ambient temperature. Direct synthesis of single phase powder samples was possible by annealing stoichiometric mixtures of $Ca_3N_2$, $Sr_2N$ and C at a temperature of 1123 K.

**Discussion**

In an early investigation on the system Ca-N a high temperature phase γ-$Ca_3N_2$ was reported [1]. It has been shown recently [2, 3], that this phase has to be regarded as $Ca_4[CN_2]N_2$. Here we report on a strontium substituted phase. The structure is built up by a framework of corner and edge sharing $(Ca/Sr)_6N$ octahedra; the cyanamide ions are stacked within channels of the framework. The average bond lenghts in the cyanamide ions (1.226 Å) are similar to those reported for $Ca_4[CN_2]N_2$ (1.234 Å) [2] and $Ca[CN_2]$ (1.224 Å) [4]. The extent of substitution of Ca by Sr depends on the location of the cations in the framework; average distances $d$(Ca/Sr—N) (2.416 Å, 100% Ca – 2.603 Å, 41% Ca) increase with increasing Sr content and are in the range observed in the binary nitrides ($Ca_3N_2$: 2.465 Å [5], $Sr_2N$: 2.612 Å [6]).

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | yellow-green, irregular, size 0.1 × 0.1 × 0.1 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71070 Å) |
| μ: | 99.78 cm$^{-1}$ |
| Diffractometer, scan mode: | Siemens P4, ω/2θ |
| $2\theta_{max}$: | 59.98° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 2643, 987 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 861 |
| $N(param)_{refined}$: | 60 |
| Programs: | SHELXS-97 [7], SHELXL-97 [7], DIAMOND [8] |

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**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | Occ. | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sr(1) | 4c | 0.587(3) | 0.38560(4) | 1/4 | 0.10800(4) | 0.0144(2) | 0.0147(2) | 0.0172(3) | 0 | –0.0013(2) | 0 |
| Sr(3) | 4c | 0.110(3) | 0.37968(6) | 1/4 | 0.53740(5) | 0.0139(4) | 0.0132(4) | 0.0140(4) | 0 | –0.0006(2) | 0 |
| Sr(4) | 4c | 0.102(2) | 0.14778(6) | 1/4 | 0.23978(5) | 0.0122(3) | 0.0140(4) | 0.0178(4) | 0 | –0.0009(3) | 0 |
| Ca(1) | 4c | 0.413 | 0.38560 | 1/4 | 0.10800 | 0.0144 | 0.0147 | 0.0172 | 0 | –0.0013 | 0 |
| Ca(2) | 4c | | 0.10587(7) | 1/4 | 0.82415(6) | 0.0152(4) | 0.0134(4) | 0.0160(4) | 0 | 0.0037(3) | 0 |
| Ca(3) | 4c | 0.890 | 0.37968 | 1/4 | 0.53740 | 0.0139 | 0.0132 | 0.0140 | 0 | –0.0006 | 0 |
| Ca(4) | 4c | 0.898 | 0.14778 | 1/4 | 0.23978 | 0.0122 | 0.0140 | 0.0178 | 0 | –0.0009 | 0 |
| N(1) | 4c | | 0.0028(3) | 1/4 | 0.1184(3) | 0.014(2) | 0.013(2) | 0.022(2) | 0 | –0.000(1) | 0 |
| N(2) | 4c | | 0.2279(3) | 1/4 | 0.6830(3) | 0.014(1) | 0.016(2) | 0.017(2) | 0 | –0.001(1) | 0 |
| N(3) | 4c | | 0.4449(3) | 1/4 | 0.8707(3) | 0.019(2) | 0.035(2) | 0.045(3) | 0 | 0.002(2) | 0 |
| N(4) | 4c | | 0.2585(3) | 1/4 | 0.9517(3) | 0.024(2) | 0.032(2) | 0.024(2) | 0 | –0.001(2) | 0 |
| C(1) | 4c | | 0.3508(4) | 1/4 | 0.9094(3) | 0.027(2) | 0.019(2) | 0.013(2) | 0 | –0.007(2) | 0 |

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