Crystal structure of barium tetracalcium bis(dinitridocobaltate(I)), BaCa$_4$[CoN$_2$]$_2$

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Abstract

BaCa$_4$Co$_3$N$_4$, tetragonal, $P4/ncc$ (no. 130), $a = 8.3422(3)$ Å, $c = 12.2201(8)$ Å, $V = 850.4$ Å$^3$, $Z = 4$, $R_{wp}(F) = 0.026$, $wR_{wp}(F^2) = 0.048$, $T = 295$ K.

Source of material

Black single crystals of BaCa$_4$Co$_3$N$_4$ were obtained from the reaction of pellets of Ba$_2$N (by reaction of barium metal, Alfa, 99.9 % and nitrogen, Praxair, 99.999 % at 700 °C), Ca$_3$N$_2$ (by reaction of calcium metal, Alfa, 99.9 % and nitrogen, Praxair, 99.999 % at 700 °C), and Co powder (Merck, 1 μm) in the molar ratio 1:4:1. The reaction was carried out under N$_2$ at ambient pressure in Ta crucibles at 900 °C for 100 h. To prevent contamination of the products by crucible material, the sample was wrapped in Co foil. Starting materials and products are sensitive to moisture and air.

Discussion

Only few crystal structures of alkaline-earth nitridocobaltates are known up to now: LiSr$_2$[CoN$_2$]$_2$ [1], Sr$_2$Co$_2$N$_3$ [2], and Ba[CoN] [3]. Predominant structural features of these compounds are isolated dumbbells [Co$^1$N$_2$]$^{5-}$ and chains [Co$^1$N$_2$]$^{5-}$, respectively.

The crystal structure of BaCa$_4$[CoN$_2$]$_2$ is isotypic to BaCa$_4$[Cu$_2$]$_2$ [4] and Ca$_3$[Co$_2$N$_2$]$_2$ [5] and contains near-linear [Co$^1$N$_2$]$^{5-}$ anions ($d$(Co—N) = 1.805(3) Å, $\angle$N—Co—N = 177.0(2)°). Charge compensation is accomplished by Ca$^{2+}$. The isolated [Co$^1$N$_2$]$^{5-}$ ions are arranged in layers running parallel (001). The dumbbells are tilted from [001] by 11.17(1)°. The barium/calcium-nitrogen substructure is made up by double layers of edge-sharing N-centered Ba$_2$ tetragonal pyramids running parallel (001). These layers are linked via common cobalt atoms along [001], thereby completing the octahedral coordination of N(BaCa$_4$Co)$_3$. Both, Ba ($d$(Ba—N) = 2.910(3) Å) and Ca sites ($d$(Ca—N) = 2.437(3) Å—2.549(3) Å, average 2.488 Å) are fourfold coordinated by N. The interatomic distances are in good agreement with respective values in related compounds ($d$(Co—N) = 1.810 Å [1], 1.813 Å [2], 1.816 Å [3], $d$(Ba—N) = 2.860 Å [3], 2.887 Å (Ba$_2$[FeN$_3$]$_2$) [6], 2.828 Å (Ba$_2$[NN$_3$]$_2$) [7]), $d$(Ca—N) = 2.460 Å [4], 2.500 Å [5], 2.503 Å (Ca$_2$[FeN$_3$]$_2$) [8], 2.505 Å (Ca$_2$[NN$_3$]$_2$) [9]).

Table 1. Data collection and handling.

| Crystal: | black plate, size 0.10 × 0.05 × 0.03 mm |
| Wavelength: | Mo K$_\alpha$ radiation (0.71070 Å) |
| μ: | 107.75 cm$^{-1}$ |
| Diffractometer, scan mode: | Rigaku AFC7 & Mercury CCD, ϕ/ω |
| 20 max: | 62.9° |
| N(hkl)$_{measured}$, N(hkl)$_{unique}$: | 7340, 714 |
| Criterion for I$_{obs}$, N(hkl)$_{refined}$: | I$_{obs} > 2\sigma$(I$_{obs}$), 706 |
| Programs: | SHELXL-97 [10], DIAMOND [11], STRUCTURE TIDY [12] |

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

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<th>Atom</th>
<th>Site</th>
<th>x</th>
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<th>z</th>
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<td>1-x</td>
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References


