Preparation and Crystal Structure of $Na_7Ba_{14}CaN_6$: A New Subnitride in the $Na_xBa_{14}CaN_6$ Series

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Dedicated to Professor Kurt Dehnicke on the occasion of his 70th birthday

Keywords: Barium / Calcium / Sodium / Nitrides / Cluster compounds / Subvalent compounds / Structure elucidation

The crystal structure of a new subnitride, $Na_7Ba_{14}CaN_6$, could be solved and refined based on single crystal and powder X-ray diffraction data. The compound contains $Ba_{14}CaN_6$ clusters, which are arranged in a Na matrix as in the other subnitrides of the $Na_xBa_{14}CaN_6$ (x = 8, 14, 17, 21, 22) series. The $Ba_{14}CaN_6$ clusters form a slightly distorted ccp arrangement, with octahedral holes filled by Na_7 units and with tetrahedral holes remaining empty. Details of the crystal structure, such as packing and occurrence of voids, are compared to these in closely related $Na_8Ba_{14}CaN_6$. Preparations of samples composed mostly of $Na_7Ba_{14}CaN_6$ and intergrown crystals of $Na_7Ba_{14}CaN_6$ and $Na_8Ba_{14}CaN_6$ are described.

Introduction

In a recent publication[1] the crystal structure and preparation of a new member of the $Na_xBa_{14}CaN_6$ series with x = 8 was reported. This compound joined the family of the previously known $Na_{14}Ba_{14}CaN_6$,[2,3] $Na_{17}Ba_{14}CaN_6$,[3] $Na_{21}Ba_{14}CaN_6$,[3] and $Na_{22}Ba_{14}CaN_6$.[3,4] All of these compounds feature $Ba_{14}CaN_6$ clusters, which are bonded ionically in their interior and bonded metallically to Na atoms between the clusters.

While probing various synthetic routes leading to $Na_8Ba_{14}CaN_6$, X-ray powder diffraction patterns, presumably belonging to further phases in the $Na_xBa_{14}CaN_6$ series, were observed.[1] One of these phases could be identified as $Na_7Ba_{14}CaN_6$. Below we report the preparation and crystal structure of this new subnitride.

Results and Discussion

The crystal structure of the new phase $Na_7Ba_{14}CaN_6$ is closely related to that of the recently reported $Na_8Ba_{14}CaN_6$.[1] Both structures are built from nearly identical hexagonal layers of $Ba_{14}CaN_6$ clusters separated by sodium atoms, as shown in Figure 1 and 2. This specific type of cluster is a condensate of six face-sharing Ba_5CaN octahedra, as described earlier.[2,3] While in the case of $Na_8Ba_{14}CaN_6$ these clusters stack on top of each other (Figure 2), rhombohedral stacking, a distorted variant of ccp arrangement, is observed in $Na_7Ba_{14}CaN_6$ (Figure 1); because of this, the sodium chains filling the available channels between the clusters in $Na_8Ba_{14}CaN_6$ are interrupted with a formal loss of one sodium atom per cluster. The sodium atoms in $Na_7Ba_{14}CaN_6$ can be viewed as clustered in Na_7 units (Figure 3), although this viewpoint is purely formal. This provides, however, a different approach to describe the structure of the subnitride. If one considers the centers of mass of the Na_7 and $Ba_{14}CaN_6$ blocks in $Na_7Ba_{14}CaN_6$, the trigonally distorted NaCl structure type emerges: while the $Ba_{14}CaN_6$ clusters are arranged in a

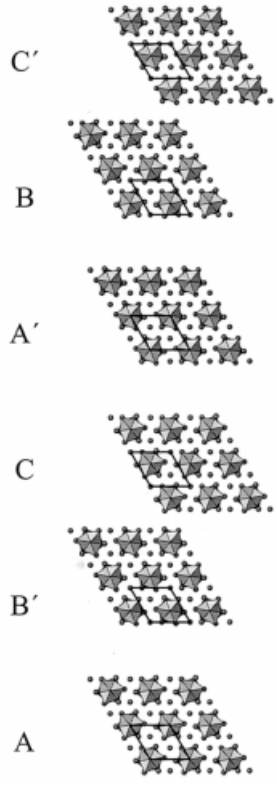

Figure 1. Six layers of $Ba_{14}CaN_6$ clusters with sodium atoms in between comprising a repeat unit of $Na_7Ba_{14}CaN_6$ in the [001] direction viewed along the c-axis; the unit cell is outlined; the nearly ccp arrangement of the clusters is indicated by the AB′CA′BC′ labelling, where the primed and unprimed layers differ in the cluster orientation; this layer representation is purely formal, it does not imply strong anisotropy in bonding

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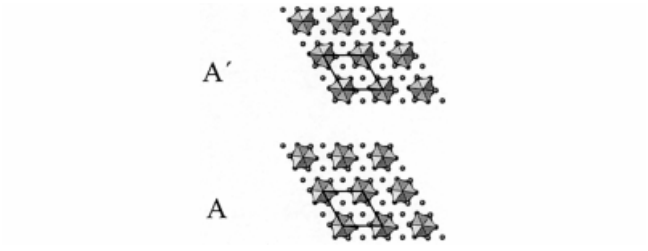

Figure 2. Two layers of $Ba_{14}CaN_6$ clusters with sodium atoms in between comprising a repeat unit of $Na_8Ba_{14}CaN_6$ in the [001] direction viewed along the *c*-axis; the unit cell is outlined; the simple hexagonal packing of the clusters is indicated by the AA′ labelling, where the primed and unprimed layers differ in the cluster orientation (using the same symbols A and A′ in Figures 1 and 2 ignores the slightly different cluster orientation: while the A′ layers are practically identical in both figures, the A layers differ)

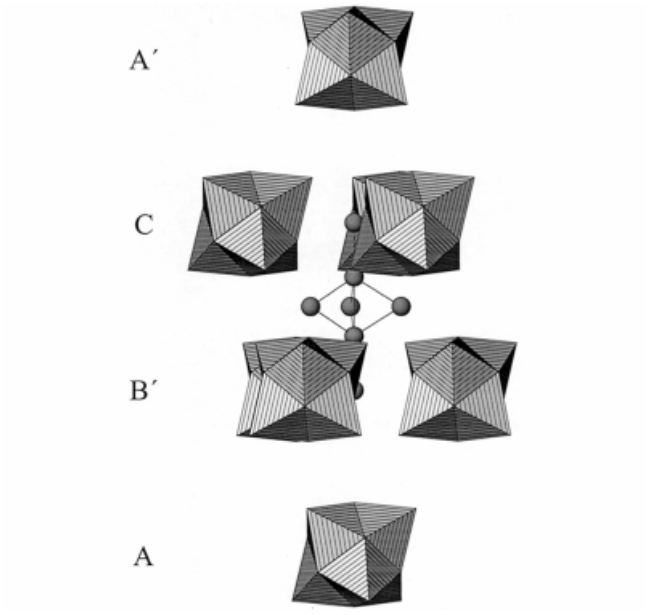

Figure 3. An Na_7 unit in an octahedral hole of the nearly ccp arrangement of $Ba_{14}CaN_6$ clusters in $Na_7Ba_{14}CaN_6$ (the *c*-axis is vertical); the labelling of the cluster layers is the same as in Figure 1

nearly ccp fashion as mentioned above, with the effective *c*/*a* ratio only 13% greater than that of the ideal cubic lattice, the Na_7 units occupy all octahedral holes.

Details of the crystallographic data for $Na_7Ba_{14}CaN_6$ can be found in Table 1. All interatomic distances (see Table 2) in $Na_7Ba_{14}CaN_6$ are similar to these in the other $Na_xBa_{14}CaN_6$ compounds. The intracluster distances are compared to those of $Na_8Ba_{14}CaN_6$ in Table 2; these are characteristic of ionic bonding.[2] The Na−Na (3.44, 3.77, and 3.80 Å) and Na−Ba (4.01−4.51 Å) distances are also in the range of the values observed in the other subnitrides of the series and are indicative of metallic bonding.[2] The intercluster Ba−Ba (4.767 and 4.781 Å) contacts are almost identical to those in $Na_8Ba_{14}CaN_6$.

The displacement factors for the sodium atoms (Table 3 and 4) are relatively large, which also has been linked to the metallic nature of the Na−Na and Na−Ba bonding.[1] In addition, two sodium positions feature strongly elongated thermal ellipsoids (split position refinement was unsuccessful). This, however, could be due to the chemical environment of these sodium atoms: thermal motion along the *c*-direction is much easier, as for the similar positions in $Na_8Ba_{14}CaN_6$, where thermal ellipsoids elongated parallel to the *c*-axis are also observed for the sodium atoms in the channels between $Ba_{14}CaN_6$ clusters.

A strong anisotropy of the Na thermal ellipsoids could also be caused by the presence of voids in the crystal structure of $Na_7Ba_{14}CaN_6$, which are similar to those found in the other compounds of the $Na_xBa_{14}CaN_6$ series. In an earlier investigation[3] it was definitely ruled out that these voids are due to the presence of contaminants, in particular hydrogen. We therefore anticipate that the voids in the structure of $Na_7Ba_{14}CaN_6$ are empty, too, in spite of the presence of hydrogen in the investigated sample as indicated by the contamination by Ba_2NH. The largest void in $Na_7Ba_{14}CaN_6$, located at (0,0,0.1106), is surrounded by a distorted cube of four Na and four Ba atoms (Figure 4). The distances from these atoms to the center of the void are 3.16 Å [Ba(3), 3×], 3.47 Å [Na(1), 1×], 3.66 Å [Ba(1), 1×], and 4.40 Å [Na(3),

Table 1. Details of the single crystal and powder diffraction investigations on $Na_7Ba_{14}CaN_6$

	Single crystal data	Powder data
Radiation, wavelength	Mo-K_α, 0.71073 Å	Cu-$K_{\alpha1}$, 1.54051 Å
Crystal system, space group	Rhombohedral, $R\bar{3}c$ (No. 167), $Z = 6$	
Unit cell dimensions	a = 11.35(1) Å [a]	a = 11.360(1) Å
	c = 62.85(5) Å [a]	c = 63.061(7) Å
Unit cell volume, d_{calc}	7009(11) Å^3 [a]	7048(2) Å^3, 3.121(1) g/cm^3
Refinement method	Full-matrix least-squares	Full profile
2θ and index ranges	3.88°−56.68°	7°−35°
	$-14 \le h,k \le 14$, $-83 \le l \le 83$	$-4 \le h,k \le 4$, $-22 \le l \le 22$
Reflections measured/unique	19286/1931 ($R_{internal}$ = 8.6%)	70
Data/restraints/parameters	1931/0/44	1401/5/18
Final R values	$R1(2\sigma)$ = 13.1%	R(intensity) = 4.8%
	$R1$(all) = 13.5%	R(profile) = 12.8%
	$wR2$(all) = 34.8%	
Largest diff. peak and hole	8.98 and −2.80 Å^{-3}	

[a] The unit cell constants for two investigated crystals differed [a = 11.335(1) Å and c = 62.89(1) Å for one, a = 11.361(1) Å and c = 62.80(1) Å for the other]; the values given in the table are averages of the two data sets. The structure solution and refinement were carried out using the data collected on the first crystal.

Table 2. Bond lengths within the $Ba_{14}CaN_6$ cluster in $Na_7Ba_{14}CaN_6$; the corresponding values for $Na_8Ba_{14}CaN_6$ are given in the rightmost column for comparison; the site symmetry of the cluster is S_6 ($\bar{3}$) in both compounds

Distance (labels of $Na_7Ba_{14}CaN_6$)	Multiplicity (per $Ba_{14}CaN_6$ cluster)	$Na_7Ba_{14}CaN_6$	$Na_8Ba_{14}CaN_6$[1]
Ca(1)−N(1)	6×	2.59(3)	2.560(3)
Ba(1)−N(1)	6×	2.79(3)	2.742(3)
Ba(2)−N(1)	6×	2.71(3)	2.747(3)
	6×	2.77(3)	2.765(4)
	6×	2.84(3)	2.802(4)
Ba(3)−N(1)	6×	2.43(3)	2.463(3)
Ba(1)−Ca(1)	2×	3.318(3)	3.2540(5)
Ba(2)−Ca(1)	6×	3.287(2)	3.2968(3)
Ba(1)−Ba(2)	6×	3.821(3)	3.8091(4)
Ba(2)−Ba(2)	6×	3.788(3)	3.7799(4)
Ba(1)−Ba(3)	6×	4.102(2)	4.0588(4)
Ba(2)−Ba(3)	6×	4.098(3)	4.1262(5)
	6×	4.137(3)	4.1442(6)
	6×	4.158(3)	4.1481(5)

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Na_7Ba_{14}CaN_6$; U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	Position	x	y	z	U_{eq}
Ba(1)	12c	0	0	0.0526(1)	0.029(1)
Ba(2)	36f	0.2935(2)	0.0471(2)	0.0172(1)	0.032(1)
Ba(3)	36f	0.3213(2)	0.3880(2)	0.0465(1)	0.041(1)
Ca(1)	6b	0	0	0	0.021(2)
Na(1)	12c	0	0	0.1656(7)	0.067(10)
Na(2)	12c	0	0	0.2201(6)	0.060(9)
Na(3)	18e	0.709(2)	0	1/4	0.051(6)
N(1)	36f	0.164(3)	0.203(3)	0.0238(4)	0.031(6)

Table 4. Anisotropic displacement parameters (Å^2) for $Na_7Ba_{14}CaN_6$; the anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2(a^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	0.031(1)	U_{11}	0.027(1)	0	0	$U_{11}/2$
Ba(2)	0.026(1)	0.037(1)	0.033(1)	0.001(1)	−0.004(1)	0.016(1)
Ba(3)	0.035(1)	0.033(1)	0.040(1)	−0.009(1)	−0.006(1)	0.006(1)
Ca(1)	0.020(4)	U_{11}	0.023(6)	0	0	$U_{11}/2$
Na(1)	0.029(8)	U_{11}	0.14(3)	0	0	$U_{11}/2$
Na(2)	0.021(7)	U_{11}	0.14(3)	0	0	$U_{11}/2$
Na(3)	0.063(15)	0.061(11)	0.030(10)	0.008(5)	0.015(10)	0.031(7)
N(1)	0.027(13)	0.035(14)	0.032(13)	−0.006(11)	0.000(10)	0.015(12)

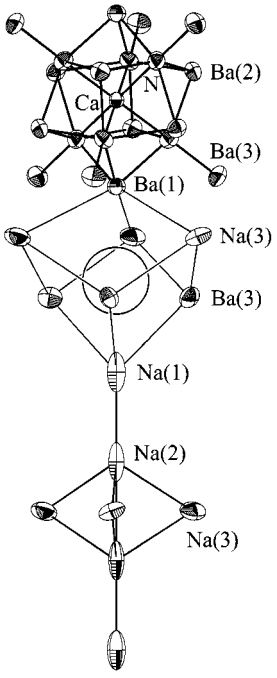

Figure 4. A fragment of the $Na_7Ba_{14}CaN_6$ structure with a $Ba_{14}CaN_6$ cluster (top), a Na_7 fragment (bottom), and the largest void (middle); the rather cube-like surrounding of the void is emphasized; the thermal ellipsoids are drawn for all atoms, the c-axis is vertical

3×]. The strongly anisotropic thermal ellipsoids of the sodium atoms may be considered a consequence of the preferred thermal motion in the direction of the void. We also note that these voids represent the tetrahedral holes in the ccp arrangement of the $Ba_{14}CaN_6$ clusters.

Experimental Section

Preparations: Due to the extreme sensitivity to air and moisture of all substances involved, these were handled either under high vacuum (10^{-6}−10^{-5} mbar) or under purified argon. Preparation of distilled metallic Ba, filtered metallic K, Na−K alloy, and the mixed subnitride $Ba_{1.83}Ca_{0.17}N$ have been described in detail previously. All syntheses mentioned below were carried out, unless stated otherwise, in cleaned Ta containers sealed under argon; these containers were themselves also sealed under argon in Duran glass ampoules. For details of these procedures refer to ref.[1]

$Na_{14}Ba_{14}CaN_6$ was prepared from metallic Ba (291.4 mg, 2.12 mmol), $Ba_{1.83}Ca_{0.17}N$ (1156 mg, 4.24 mmol), and Na-rich Na−K alloy (1300 mg; 31 mmol Na and 15 mmol K). The reagents with the overall stoichiometry $K_{21}Na_{45}Ba_{14}CaN_6$ were mixed and heated to 120 °C, then held at this temperature for a year. During the course of the reaction the ampoule was taken out four times for a short time and gently shaken. The solid reaction product was separated from excess alloy in a press. The product is $Na_{14}Ba_{14}CaN_6$ (the observed reflections matched the expected pattern of the cubic structure with a = 17.895 Å as reported in ref.[2]) with about 10 wt.% of a $NaBa_3N$ impurity (hexagonal with a = 8.4414 Å and c = 6.9817 Å[5]) according to X-ray diffraction. NaBa

was prepared as described in ref.[6] Equimolar amounts of Na and Ba were mixed in a Duran glass container and heated under argon at 140°C for two days. The resulting diffraction pattern matched that of the cubic structure with a = 17.027 Å.[7]

Single crystals of $Na_7Ba_{14}CaN_6$ were obtained in the following way. In sample A, $Ba_{1.83}Ca_{0.17}N$ (687.9 mg, 2.50 mmol), NaBa (203.4 mg, 1.27 mmol), and Na (49.4 mg, 2.2 mmol) with an approximate $Na_8Ba_{14}CaN_6$ overall stoichiometry were mixed, pressed into a pellet, and heated to 192 °C for 10 days, then held at 220 °C for 52 days and at 250 °C for 42 days with intermediate grindings of the pellet. This product (635.4 mg, 0.285 mmol "$Na_8Ba_{14}CaN_6$") was then mixed with K-rich Na−K alloy (206.0 mg; 0.96 mmol Na and 4.7 mmol K), yielding a $K_{17}Na_{11}Ba_{14}CaN_6$ overall stoichiometry. The mixture was heated to 350 °C and held at this temperature for 20 days, then cooled at 0.5°C/hour to 220 °C, held at 220 °C for 24 days, and finally cooled to room temperature by switching off the furnace. Crystals were manually selected from the resulting alloy-solid mixture and sealed under argon in glass capillaries.

A sample composed mostly of $Na_7Ba_{14}CaN_6$ was obtained by extracting sodium from $Na_{14}Ba_{14}CaN_6$ with metallic potassium. In sample B, $Na_{14}Ba_{14}CaN_6$ (217.8 mg, 0.091 mmol) was mixed with potassium (109.2 mg, 2.80 mmol), the resulting molar ratio being K:$Na_{14}Ba_{14}CaN_6$ = 31:1. The mixture was heated to 250 °C for 10 days, cooled at 0.2 °C/hour to 150 °C, and then finally cooled at 0.5 °C/hour to room temperature. Na−K alloy formed in the course of the reaction; the solid residue was separated from the alloy in a press. A portion of the solid product was ground together with glass powder and sealed in a 0.3 mm glass capillary for powder X-ray diffraction analysis.

Crystal Structure Investigations: Crystals obtained from sample A were first tested on a precession camera. Already at this stage it was apparent that most crystals were either pure $Na_8Ba_{14}CaN_6$ (hexagonal with a = 11.419 Å and c = 21.543 Å[1]) or intergrown with crystals of another phase, which is rhombohedral with the a-axis being practically the same as that of the $Na_8Ba_{14}CaN_6$ phase and the c-axis approximately three times that of the $Na_8Ba_{14}CaN_6$ phase, suggesting a structural similarity between the two phases. Two crystals featuring the largest fraction of the new phase (about 50%) were further investigated on a STOE image-plate diffractometer (IPDS). It was possible to separate the reflections belonging to the new phase from those belonging to $Na_8Ba_{14}CaN_6$; the poor quality of the obtained reflection data also introduced some ambiguity in finding the correct space group (see above). The initial measurement of the lattice parameters for the crystals yielded a = 11.35(1) Å and c = 62.85(5) Å (see footnote to Table 1). Using the linear V/Z vs. x correlation in the $Na_xBa_{14}CaN_6$ series,[1] the approximate x value of 6.7 could be obtained, suggesting that the new phase might have the stoichiometry $Na_7Ba_{14}CaN_6$.

Crystal structure solution was attempted based on the data collected at room temperature on one of the two crystals using direct methods (SHELXS-97), followed by full-matrix least-squares structure refinement (SHELXL-97).[8] The structure could be solved in space groups $R\bar{3}$ (No.148), $R32$ (No. 155), and $R3c$ (No. 161); their common subgroup $R3$ (No. 146) could, of course, also be used. A closer inspection of the structures obtained in these space groups revealed their mutual similarity, hence a refinement in the common supergroup $R\bar{3}c$ (No. 167) was attempted. All atoms could be refined anisotropically yielding indeed the stoichiometry $Na_7Ba_{14}CaN_6$ and chemically reasonable distances and displacement factors. The final R value of 13.1% was, however, a cause for concern. Closer inspection of the data set revealed that this relatively high value was mainly due to the inconsistency of equivalent reflections as indicated by the $R_{internal}$ value of 8.6%. This could have been caused by incomplete separation of reflections of $Na_7Ba_{14}CaN_6$ and $Na_8Ba_{14}CaN_6$. The large final R value is also manifested by substantial peaks in the Fourier difference map, the largest of which lie within 1.2 Å of the Ba(3) position.

In order to support the structural solution obtained from the single crystal diffraction data, a Rietveld refinement of the powder diffraction data, which were collected with sample B on a STADI-P STOE diffractometer with Cu-$K_{\alpha 1}$ radiation at room temperature, was attempted using the CSD package.[9] Before the refinement, the impurity reflections belonging to Ba_2NH (≈10 wt.%), $Na_8Ba_{14}CaN_6$ (≈5 wt.%), and $NaBa_3N$ (≈5 wt.%) were removed from the pattern (Figure 5). The refinement was carried out in the 2θ range from 7° to 35°. While the isotropic displacement factors for the barium atoms could be refined, those for all other atoms had to be fixed at the values obtained in the refinement of the single crystal diffraction data. The positions of the atoms obtained in the Rietveld refinement were less accurate than those deduced from the single crystal diffraction data, though both sets were within error bars from each other. The Rietveld refinement resulted in more accurate unit cell parameters: a = 11.360(1) Å and c = 63.061(7) Å. The corresponding unit cell volume leads to the improved x value of 6.9 in $Na_xBa_{14}CaN_6$, if the linear V/Z vs. x correlation[1] is employed.

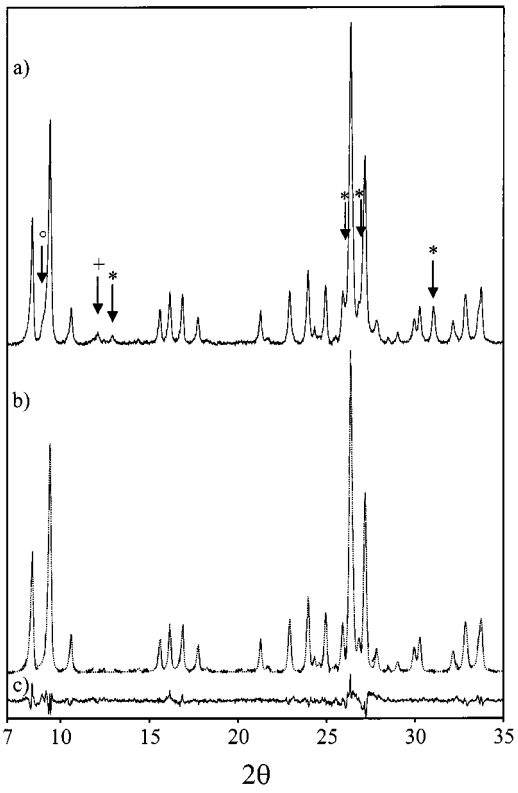

Figure 5. Measured X-ray diffraction pattern of $Na_7Ba_{14}CaN_6$: (a) strong reflections of impurity phases are indicated with arrows: $Na_8Ba_{14}CaN_6$ (°), $NaBa_3N$ (+), and Ba_2NH (*); these impurity reflections were removed from the pattern before Rietveld refinement was carried out; (b) the solid line represents the measured data and the dotted line shows the calculated curve; the difference between the two lines is plotted below (c)

Refinement of Guinier diffraction data (23 reflections) leads to similar lattice constants: a = 11.368(4) Å and c = 63.094(14) Å. In

addition, decomposition of $Na_7Ba_{14}CaN_6$ at ≈272 °C could be observed in a temperature-dependent Guinier measurement. The strongest reflections of the resulting diffraction pattern belong to $Na_8Ba_{14}CaN_6$.

The results of the single crystal and powder diffraction investigations are combined as follows. The unit cell parameters are taken from the Rietveld refinement (see Table 1 for refinement details), but the atomic positions (Table 3) and the anisotropic displacement factors (Table 4) are taken from the refinement of the single crystal diffraction data (see also Table 1 for details).

Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-411488.

Acknowledgments

The authors thank Dr. O. Oeckler for collecting and help with analyzing the single crystal diffraction data, Dr. J. Köhler for providing programs to analyze crystal structures for voids and for help with Rietveld refinement, and W. Röthenbach for temperature-dependent Guinier measurements. Thanks are also due to the Max Planck Society and the Alexander von Humboldt Foundation for providing G.V.V. with financial support during this study.

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Received September 27, 2000
[I00369]