Ba₁₁Cd₈Bi₁₄: Bismuth Zigzag Chains in a Ternary Alkaline-Earth Transition-Metal Zintl Phase

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SUPPORTING INFORMATION

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Disorder Modeling

As already discussed in the text, the systematic absence of reflections with indexes hkl , $hk0$: $h + k \neq 2n$; $h0l$, $h00$: $h \neq 2n$, and $0kl$, $0k0$: $k \neq 2n$, confirmed the C -centering of the cell. The β angle is very close to 90° , however data integration in orthorhombic symmetry proved that the lattice is indeed monoclinic. The reflection conditions suggested three possible space groups: $C2$ (No. 5), Cm (No. 8), and $C2/m$ (No. 12), and the intensity statistics was consistent with a centro-symmetric space group. The structure was successfully solved in $C2/m$ by direct methods, however, during the subsequent structure refinements, a problem with the temperature parameters for Cd1 and Bi7 became apparent – their shapes were abnormally elongated in direction almost parallel to the Cd–Bi bond. Additionally, a peak of $ca.$ $10 \text{ e}/\text{\AA}^3$ in height, $1.4 \text{ \AA}$ away from both Bi7 and $1.7 \text{ \AA}$ away Cd1 was left in the difference Fourier map (Figure S3). These distances are evidently abnormally short even for Bi–O or Cd–O interactions, which rules out the possibility for an interstitial oxygen or another light atom in that position. In the next refinements cycles, partially occupied Cd was refined in the position of the “Q”, which resulted in an occupation factor of less than 10%. In these refinements, the difference Fourier map is flat with deepest hole/highest peak in the order of $3 \text{ e}/\text{\AA}^3$. This, together with the fact that when Bi7 and Cd1 were refined with freed occupation factors, there was virtually no improvement of their displacement parameters means that both sites are statistically disordered. All attempts to find an ordered structure in lower symmetry (in both Cm and $C2$ and even in $P1$) did not provide evidence for the existence of a long-range ordering. Additionally, no supercell reflections were observed to indicate that a cell with doubled parameters might exist. All other sites (6 Ba’s, 3 more Cd’s and

6 more Bi's) refine without any problems. Structure refinements of data collected on crystals from different reaction batches indicated similar problems.

A possible explanation of the disorder of Bi7 and Cd1 can be derived from the difference Fourier map, when Cd1 and Bi7 are refined with isotropic displacement parameters (Figure S4). The map suggests that these sites could be split on two partially occupied pairs named by Cd1A/Cd1B and Bi7A/Bi7B, respectively. Refinements in $C2/m$ employing split Cd1A/Cd1B and Bi7A/Bi7B resulted in featureless difference Fourier map and temperature parameters that are not as large as when the atoms are refined as Bi7 and Cd1. The site occupancies are *ca.* 40% for the A-pair and *ca.* 60% for the B-pair, which implies purely statistical distribution. The relative atomic distances are 2.939(8) Å for Cd1A-Bi7A, 3.108(6) for Cd1B-Bi7B, and 3.023(7) for Bi7A-Bi7B respectively. This is schematically illustrated in Figure S5. The split is very small and the distances between the A and B counterparts are very short, 0.454 and 0.303 Å for Cd1A-Cd1B and Bi7A-Bi7B, respectively. Evidently the Bi-Bi zigzag chain does not have the full symmetry of the average structure and the Bi-atoms, most likely are not equidistant. This, in turn results in large displacement for the next nearest cadmium, Cd1, which is evident for the elongation of the anisotropic parameter almost in the same direction of the Cd-Bi bonding. The high residual density is thus an artifact stemming from the positional disorder of two heavy atoms, and not an indication of wrong choice of space group. Thus, in this paper, for the sake of simplicity and clarity of the presentation, we confined the discussion on the averaged, non-disordered model.

Figure S1. A view of the crystal structure of $\text{Ba}_{11}\text{Cd}_8\text{Bi}_{14}$ projected approximately along the direction of the b -axis. Thermal ellipsoids are drawn at the 95% probability level. Color code: Bi – yellow crossed ellipsoids, Cd – green full ellipsoids, Ba – blue open ellipsoids.

Figure S2. Coordination polyhedra around the Ba atoms in the structure of $\text{Ba}_{11}\text{Cd}_8\text{Bi}_{14}$. The atoms are labeled accordingly. Relevant distances are given in Table 3 (see text).

Figure S3. Plots of the Fourier (a) and difference Fourier map (b), showing the locations of the highest residual peaks. The atoms are labeled accordingly. Viewing direction shown in the inset.

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Figure S5. A close-up view of the disordered Cd1A/Cd1B and Bi7A/Bi7B sites in the structure of $\text{Ba}_{11}\text{Cd}_8\text{Bi}_{14}$. The projection is the same as in Figure 3 in the text.

Table S1. –ICOHP of different atomic interactions.

Bonds	Atomic distances (Å)	Average –ICOHP (eV/cell)
Ba1-Bi3	3.574	0.775
Ba1-Bi4	3.654	0.604
Ba1-Bi6	3.789	0.393
Ba2-Bi1	3.543	0.568
Ba2-Bi3	3.601	0.561
Ba3-Bi1	3.682	0.426
Ba3-Bi3	3.557	0.650
Ba3-Bi5	3.426	0.624
Ba3-Bi6	3.591	0.445
Ba4-Bi1	3.641	0.495
Ba4-Bi2	3.677	0.559
Ba4-Bi2	3.781	0.488
Ba4-Bi5	3.606	0.563
Ba5-Bi2	3.451	0.643
Ba5-Bi4	3.440	0.594
Ba5-Bi5	3.913	0.101
Ba5-Bi7	3.561	0.358
Ba5-Bi7	3.611	0.296
Ba6-Bi4	3.732	0.420
Ba6-Bi5	3.476	0.628
Ba6-Bi6	3.906	0.227
Ba6-Bi7	3.742	0.319
Ba6-Bi7	4.126	0.123
Bi1-Cd2	2.960	1.229
Bi1-Cd4	3.014	1.089
Bi2-Cd1	2.947	1.263
Bi2-Cd4	2.972	1.363
Bi3-Cd2	3.010	1.287
Bi3-Cd3	3.084	1.400
Bi4-Cd4	3.017	1.217
Bi4-Cd2	3.079	0.925
Bi5-Cd1	2.838	1.442
Bi6-Cd3	2.978	1.264
Bi6-Cd3	3.098	0.897
Bi7-Cd1	3.041	0.713
Bi2-Bi2	3.406	0.132
Bi7-Bi7	3.055	1.223