ADVANCED FUNCTIONAL MATERIALS

# Supporting Information

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## Achieving zT > 1 in Inexpensive Zintl Phase $Ca_9Zn_{4+x}Sb_9$ by Phase Boundary Mapping

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## Achieving $zT > 1$ in inexpensive Zintl phase $Ca_9Zn_{4+x}Sb_9$ by phase boundary mapping

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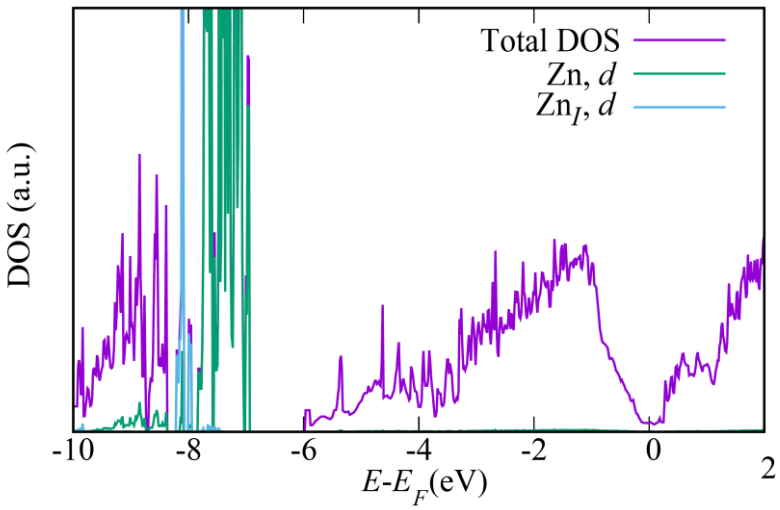


**Figure S1** The calculated DOS plot of the relaxed $Ca_{18}Zn_9Sb_{18}$-cell, showing that the *d*-states of the interstitial Zn atom ($Zn_I$) is far below the Fermi level (about -7 eV). The green line is the sum of all *d*-character states of all 8 "non-interstitial" Zn atoms, and the blue line is the *d*-state of $Zn_I$.

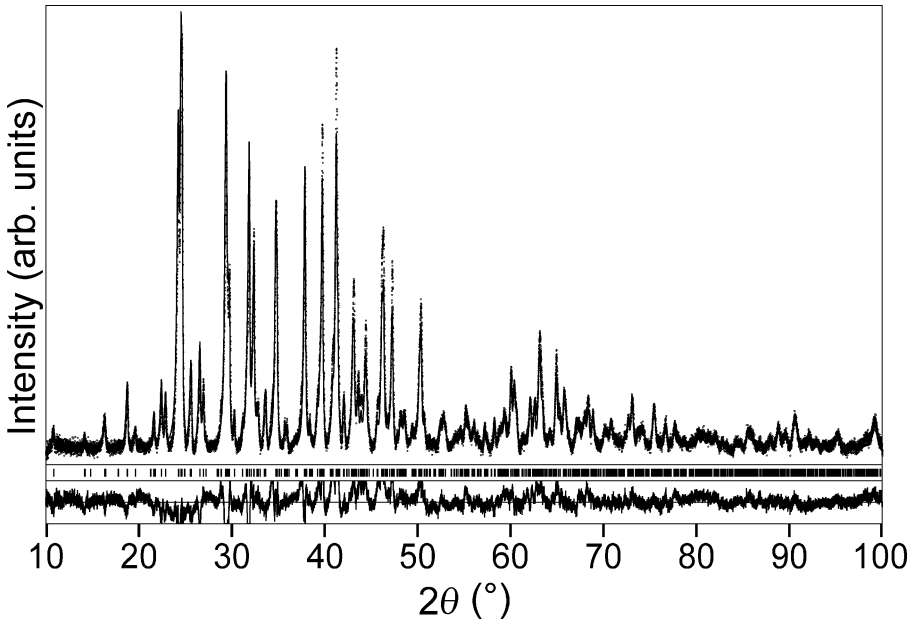


**Figure S2** Rietveld fit of $Ca_9Zn_{4.3}Sb_9$ (Cu-$K_{\alpha 1}$ radiation). Ticks mark the calculated reflection positions of the target phase while the baseline corresponds to the residuals of a Rietveld refinement ($R_i$ = 0.09, $R_p$ = 0.20, $R_{wp}$ = 0.20) based on the reported crystal structure. In the crystal structure of

$Ca_9Zn_{4+x}Sb_9$ (space group: *Pbam*), there are five Ca (1×2*b*, 3×4*g*, 1×4*h*) and Sb (1×2*d*, 2×4*g*, 2×4*h*), and three Zn (2×4h, 1×4*g*) Wyckoff sites. Based on the reported single crystal data, apart from the Zn3 position at the 4*g* site, which is partially occupied (23.9(4) %), all other sites are fully occupied. We identified the partial occupancy at the Zn3 site to be close to 24.5(5) %, corresponding to the composition of $Ca_9Zn_{4.49(1)}Sb_9$ which is reasonable considering $\boldsymbol{\delta}$ calculated in this work (Table 1).The lattice parameters of this sample were found to be $a$ = 21.8525(5) Å, $b$ = 12.5305(3) Å, $c$ = 4.5427(1) Å.

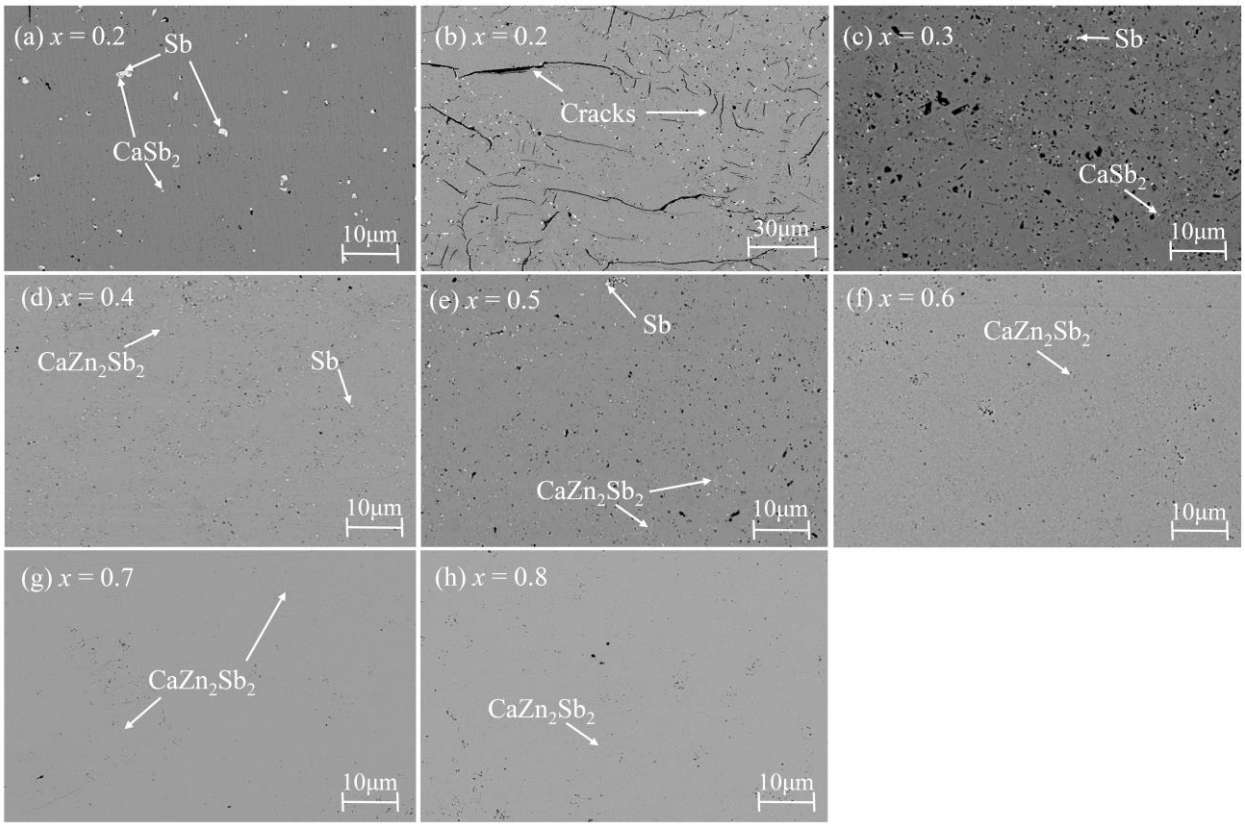


**Figure S3** SEM results of $Ca_9Zn_{4+x}Sb_9$ ($x$ = 0.2-0.8) samples. (b) Lower magnification of $x$ = 0.2 microstructure to visualize micro cracks on the sample surface.

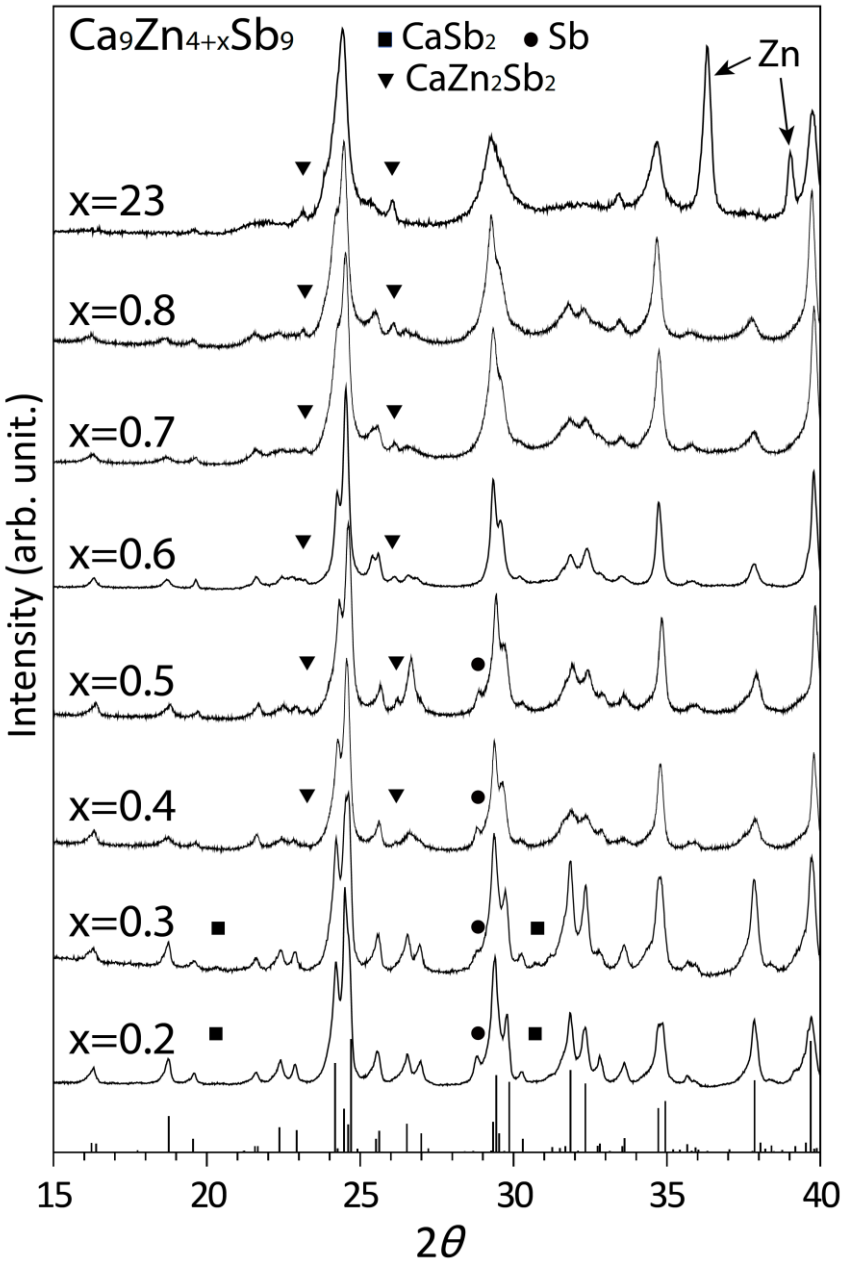


**Figure S4** XRD results of $Ca_9Zn_{4+x}Sb_9$ ($0.2 \leq x \leq 0.8, x = 23$). Bottom bars indicate the peak positions of $Ca_9Zn_{4.478}Sb_9$ acquired by single crystal XRD. Different secondary phases were observed for different samples, which were used to determine the phase regions of each sample.

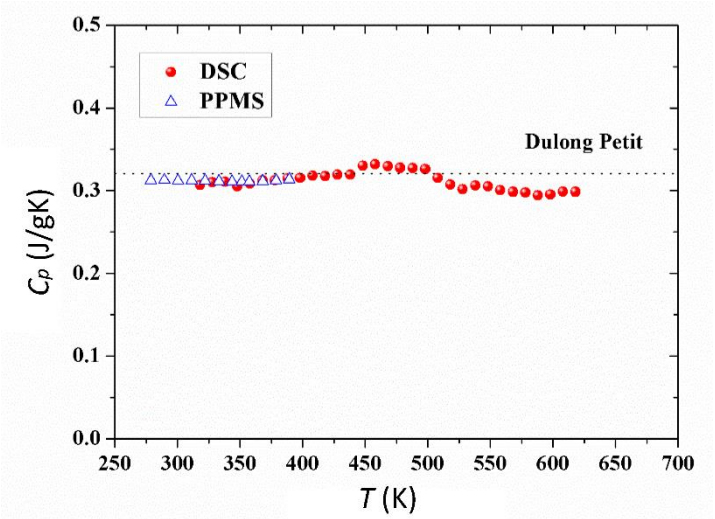


**Figure S5** Heat Capacity ($C_p$) measurement result as a function of temperature by PPMS and DSC. Both data sets overlap at around room temperature and measured values are very similar to the Dulong Petit value.

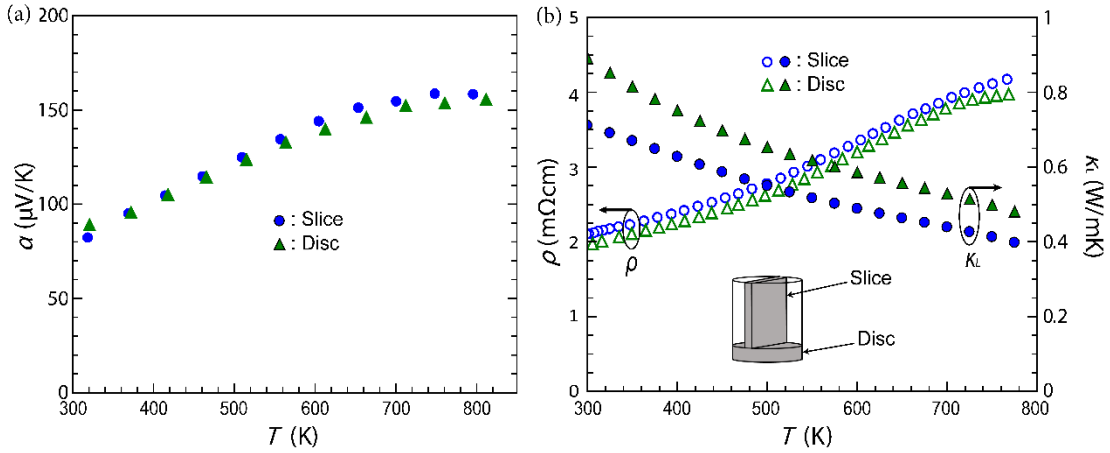


**Figure S6** Isotropic electronic properties of $Ca_9Zn_{4.5}Sb_9$. Temperature dependent Seebeck coefficient (a), resistivity, and lattice thermal conductivity (b) in the directions parallel (blue/circle) and perpendicular (green/triangle) to that of the pressure applied during the hot press. Thermal conductivity indicates some anisotropy, in which the difference is almost the same as the values between $x = 0.4$ and 0.5 samples in Fig. 5. Thus further investigation is required to identify the origin of small difference in thermal conductivity.

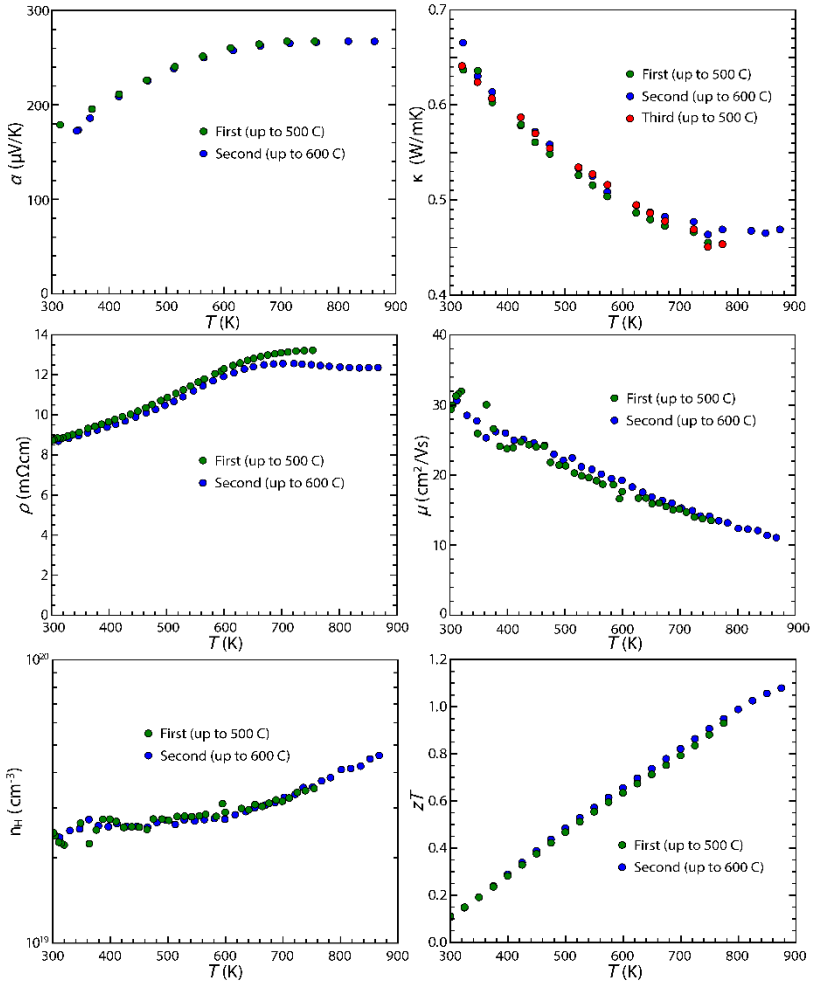


**Figure S7** Reproducibility of thermoelectric properties of $Ca_9Zn_{4.6}Sb_9$. Transport properties were measured at least twice to verify the results. First and second measurement were carried out up to 500 °C and 600 °C, respectively. All of the measurement results show almost identical properties.

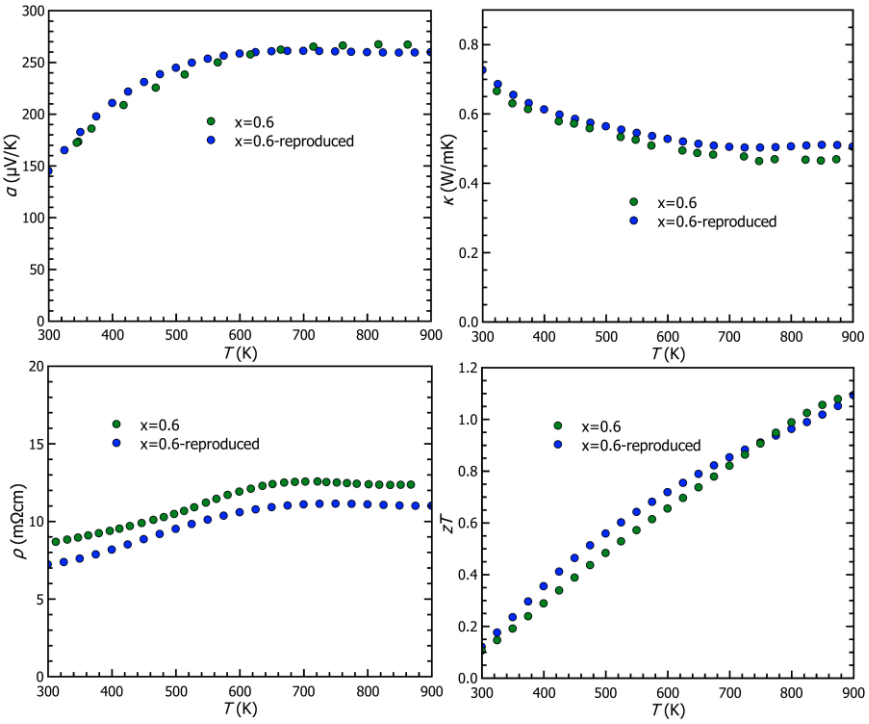


**Figure S8** Sample reproducibility of $Ca_9Zn_{4.6}Sb_9$ ($x$ = 0.6). The reproduced sample was synthesized at NASA/JPL for testing this material to be used in a future thermoelectric generator. 50 g of powder was pressed to acquire sample pellet with a diameter of three inches. The reproduced sample displays almost identical transport behaviour with very similar $zT$ up to 875 K.

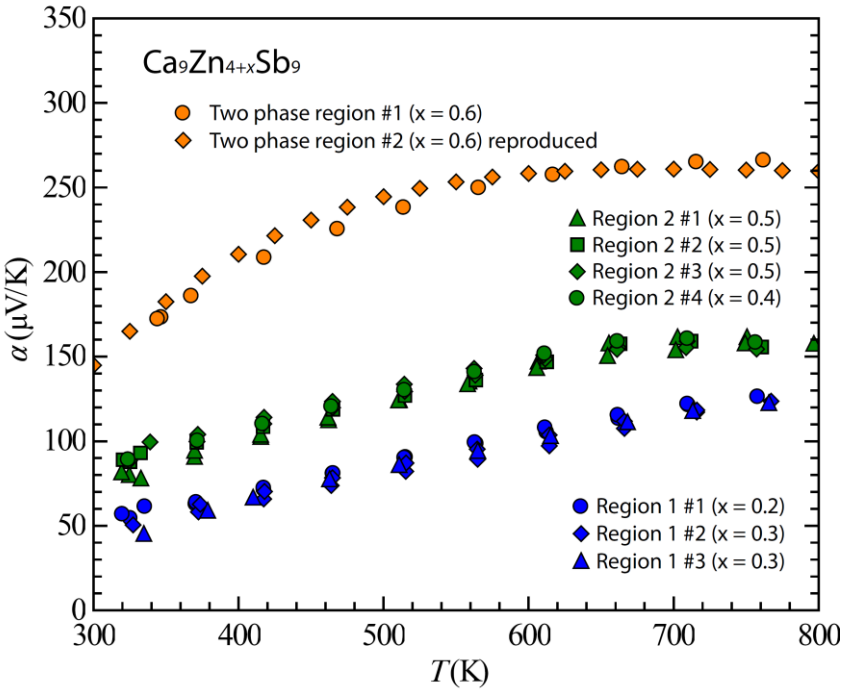


**Figure S9** Reproducibility of the samples in different phase regions. The samples of $x$ = 0.3 and 0.5 are reproduced and their Seebeck coefficients are measured. The symbols with the same color show the data from the samples in the same three-phase regions. The result shows that we can acquire almost identical samples repeatedly from the same phase region. The three-phase region numbers are shown in Figure 4 in the main text with the same colors: $x$ = 0.2 and 0.3 belong to region 1 (blue), $x$ = 0.4 and 0.5 are in region 2 (green), and $x$ = 0.6 sample exists in the two phase region between region 2 and 3 (orange).

**Table. S1** The relaxed atomic positions, used for electronic structure calculations of $Ca_9Zn_4Sb_9$.

| **Atom** | **Site** | ***x*** | ***y*** | ***z*** |
|---|---|---|---|---|
| Ca1 | 2*b* | 0.00000 | 0.00000 | 0.50000 |
| Ca2 | 4*g* | 0.13668 | 0.13106 | 0.00000 |
| Ca3 | 4*g* | 0.09049 | 0.43244 | 0.00000 |
| Ca4 | 4*g* | 0.26378 | 0.37404 | 0.00000 |
| Ca5 | 4*h* | 0.39771 | 0.20844 | 0.50000 |

| | | | | |
|---|---|---|---|---|
| Sb1 | 2*d* | 0.00000 | 0.50000 | 0.50000 |
| Sb2 | 4*g* | 0.49299 | 0.30683 | 0.00000 |
| Sb3 | 4*g* | 0.30490 | 0.11584 | 0.00000 |
| Sb4 | 4*h* | 0.35391 | 0.45580 | 0.50000 |
| Sb5 | 4*h* | 0.16831 | 0.30594 | 0.50000 |
| Zn1 | 4*h* | 0.04581 | 0.27471 | 0.50000 |
| Zn2 | 4*h* | 0.23671 | 0.11227 | 0.50000 |