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Remarkable multimember-ring configurations in new family of $Na_7 M^{II}Sb_5S_{12}$

(M^{II} = Zn, Cd, Hg) exhibiting various three-dimensional tunnel structures

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1. Synthesis of Title Compounds

High-purity chemicals including the Na block (99%), ZnS powder (99.9%), CdS (99.9%), HgS powder (99.9%), Sb₂S₃ powder (99.9%), and S powder (99.99%) were used as purchased from Shanghai Aladdin Biochemistry Technology Co., Ltd. To better ensure the reliability of raw material ratio, vacuum glove box was chosen to complete the preparation process and avoid the effect of air oxidation. Raw mixtures with stoichiometric proportion including Na (7 mmol; 0.161 g), ZnS/CdS/HgS (1 mmol; 0.097, 0.144, 0.232 g), Sb₂S₃ (2.5 mmol, 0.848 g), and S (3.5 mmol, 0.112 g) were firstly loaded into the graphite crucibles and then put them into silica tubes. Using the flame gun and air extractor, silica tubes were carefully vacuum-sealed with the internal vacuum degree (~ 10^{-3} Pa) in ampoules. Muffle furnace was used to complete the crystallization reaction and the setting temperature process was shown as following: firstly heated to 300 °C in 10 h and left at this temperature for 20 h to make the partial S participate into the reaction, further heated up to 850 °C to ensure the mixture melt completely and kept at this temperature within 4 days, then slowly cooled down to 300 °C in 100 h, finally quickly down to the room temperature in one day. Fortunately, many air-stable red crystals were found under the optical microscope.

2. Structural Refinement and Crystal Data

Selected high-quality crystals were used for data collections on a Bruker SMART APEX II 4K CCD diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) at 296 K. The crystal structures were solved by direct method and refined using the SHELXTL program package.^[1] Multi-scan method was used for absorption correction.^[2] Taking Na₇ZnSb₅S₁₂ as the example, while the Sb atom was completely occupied on one site, the unreasonable anisotropy parameters (0.052) and unbalanced formula (Na₇Sb₆S₁₂) appeared after the initial structure refinement. In order to verify the existence of the Zn element in the structure, EDX equipped Hitachi S-4800 SEM was used to determine the element contents in title compounds. The measured results on single crystals of Na₇ZnSb₅S₁₂ confirmed the Na/Zn/Sb/S molar ratio of 7.18:1:4.82:12.30. Similarly, the EDS elemental analyses on single crystals of Na₇CdSb₅S₁₂ and

 $Na_7HgSb_5S_{12}$ confirmed the Na/Cd(Hg)/Sb/S molar ratio of 6.83:1.05:5.19:11.81 and 7.13:1.15:4.89:12.26, respectively, which are also in good agreement with the stoichiometric proportions. Based on the measured results, we have attempted to constrain the Zn and Sb atoms sharing the same crystallographic site and the ratio is Zn : Sb = 0.13: 0.87 after the random refinement. To maintain the charge balance, the occupation factor of refined site is set to be 1:5 for Zn:Sb using "*exyz*" and "*eadp*" commands. The refinement result has converged to be the suitable anisotropy parameter and $Na_7ZnSb_5S_{12}$ formula was finally determined. Besides, the refinement processes of other two compounds are similar to that of $Na_7ZnSb_5S_{12}$, thus, the final $Na_7M^{II}Sb_5S_{12}$ (M^{II} = Zn, Cd, Hg) have been obtained for title compounds. PLATON was also used to check the final structures and no other symmetries were found.^[3]

3. Property Characterization

3.1 Powder X-ray Diffraction

Powder X-ray diffraction (XRD) patterns of title compounds were collected on a Bruker D2 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) at room temperature. The 2θ range was 10-70° with a step size of 0.02° and a fixed counting time of 1s/step.

3.2 UV-Vis-Near-IR (NIR) Diffuse-Reflectance

Diffuse-reflectance spectra were measured by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 200–2600 nm at room temperature. The absorption spectra were converted from the reflection spectra via the Kubelka–Munk function.^[4]

3.3 Raman Spectroscopy

Hand-picked crystals were firstly put on an object slide, and then a LABRAM HR Evolution spectrometer equipped with a CCD detector by a 532 nm laser was used to record the Raman spectra. The integration time was set to be 5 s.

3.4 Computational Description

In order to further investigate the relationship of structure-property, the electronic structures of title compounds were studied by density functional theory (DFT) based

on ab initio calculations.^[5] The exchange-correlation potential was calculated using Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme.^[6] The following orbital electrons were treated as valence electrons, Na: $2s^2 2p^6 3s^1$, Zn: $3d^{10} 4s^2$, Cd: $4d^{10} 5s^2$, Hg: $5d^{10} 6s^2$, Sb: $5s^2 5p^3$, S: $3s^2 3p^4$. To achieve energy convergence, a plane-wave basis set energy cutoff was 700 eV within normal-conserving pseudo-potential (NCP),^[7] and the Monkhorst–Pack scheme was $2 \times 2 \times 2$ in the Brillouin Zone (BZ) of the primitive cell are chosen.

4. Figures and Tables

Table S1. Crystal data and structure refinement for $Na_7M^{II}Sb_5S_{12}$ ($M^{II} = Zn, Cd, Hg$).

Table S2. Positional coordinates and equivalent isotropic displacement parameters for title compounds.

Table S3 Comparison on the selected compounds with positional disorder of M^{II}/M^{III} sites ($M^{II} = Zn$, Cd, Hg; $M^{III} = Ga$, In) and title compounds.

Table S4. Bond lengths of (M^{II}/Sb) -S and Na-S $(M^{II} = Zn, Cd, Hg)$ in title compounds.

Table S5. Structural comparisons on series of quaternary Na-based thioantimonates and title compounds.

Fig. S1 The whole crystal structures of (a) Na₆MnS₄ and (b) Na₂BaGeS₄.

Fig. S2 (a) isolated $(Sb_3S_7)_n$ chains and (SbS_3) units; (b) crystal structure of Na₉Gd₅Sb₈S₂₆; (c) 3D network composed of NaS_n units.

Fig. S3 (a) crystal structure of α - NaSbP₂S₆; (b) isolated (SbS₄)_{*n*} chains; (c) edges and corners-sharing (NaS₆)_{*n*} layers.

Fig. S4 (a) crystal structure of β - NaSbP₂S₆; (b) isolated (SbS₄)_n chain; (c) cornerssharing (NaS₅)_n layer.

Fig. S5 (a) isolated (SbS₃) unit; (b) crystal structure of Na₂CuSbS₃; (c) corners and edges sharing (NaS₆)_n layer.

Fig. S6 NaCdSbS₃: (a) isolated (SbS₃) unit; (b) corners and edges sharing $(NaS_6)_n$ layer.

Fig. S7 Band structures of (a) Na₇ZnSb₅S₁₂, (b) Na₇CdSb₅S₁₂, and (c) Na₇HgSb₅S₁₂, respectively.

Fig. S8 The partial density states (PDOS) of (a) Na₇ZnSb₅S₁₂, (b) Na₇CdSb₅S₁₂, and (c) Na₇HgSb₅S₁₂, respectively.

Fig. S9 The calculated electron density difference (EDD) and electron localization function (ELF) of $Na_7CdSb_5S_{12}$ (top panels) and $Na_7CdSb_5S_{12}$ (bottom panels), respectively.

Fig. S10 The calculation of spin-orbit coupling for Na₇HgSb₅S₁₂.

Empirical formula	$Na_7ZnSb_5S_{12}$	$Na_7CdSb_5S_{12}$	$Na_7HgSb_5S_{12}$
Formula weight	1219.77	1266.80	1354.99
Crystal system		Trigonal	
Space group		$R\overline{3}$	
Empirical formulaFormula weightCrystal systemSpace groupUnit cell dimensions Z, V Density (calculated)Completeness to theta = 27.28Goodness-of-fit on F^2 Final R indices $[F_0^2 > 2\sigma(F_0^2)]^{[a]}$ R indices (all data) $[a]$ Extinction coefficientLargest diff. peak and hole	a = 14.4964(12) Å	a = 14.517(2) Å	a = 14.537(9) Å
Unit cell dimensions	c = 9.8156(17) Å	c = 9.835(3) Å	c =9.815(13) Å
Ζ, <i>V</i>	3, 1786.4(4) Å ³	3, 1795.0(6) Å ³	3, 1796(3) Å ³
Density (calculated)	3.402 g/cm ³	3.505 g/cm ³	3.758 g/cm ³
Completeness to theta $= 27.28$	100.0%	100.0 %	99.9 %
Goodness-of-fit on F^2	1.152	1.074	1.123
Final <i>P</i> indians $[F^2 > 2 - (F^2)]^{[a]}$	$R_1 = 0.0233$	$R_1 = 0.0276$	$R_1 = 0.0355$
$\Gamma \text{ indices } [\Gamma_0^- > 20(\Gamma_0^-)]^{1/3}$	$wR_2 = 0.0432$	$wR_2 = 0.0577$	$wR_2 = 0.0849$
D indiana (all data) [1]	$R_1 = 0.0265$	$R_1 = 0.0364$	$R_1 = 0.0408$
K mulees (an data)	$wR_2 = 0.0442$	$wR_2 = 0.0619$	$wR_2 = 0.0882$
Extinction coefficient	0.00061(2)	0.00025(3)	0.00048(6)
Largest diff. peak and hole	1.230 and -0.736 e $\rm \AA^{-3}$	1.310 and –0.791 e Å $^{-3}$	1.919 and -1.848 e $\rm \AA^{-3}$

 Table S1. Crystal data and structure refinement for title compounds.

^[a] $R_1 = F_o - F_c / F_o$ and $wR_2 = [w (F_o^2 - F_c^2)^2 / wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma (F_o^2)$

Although M^{II} (Zn or Cd) atoms usually exhibit the regular tetrahedral coordination with S atoms, they can still form the highly-distorted $M^{II}S_4$ tetrahedra with large S–Cd–S angles. For example, the S–Cd–S angles ranging from 95.34(7) to 165.8(2)° indicate a severe distortion of the tetrahedral coordination geometry in the reported

NaCdSbS₃, which is similar to that $(\angle S-Cd/Sb-S = 83.10(2) -172.2(1)^{\circ})$ in Na₇CdSb₅S₁₂.

In addition, many compounds with the mixed occupancy of M^{II}/M^{III} sites ($M^{II} = Zn$, Cd, Hg; $M^{III} = Ga$, In) have been discovered, such as previously reported 1-4-5-12 family $AM^{II}_4M^{III}_5Q_{12}$ (A = K, Rb, Cs; $M^{II} = Mn$, Zn, Cd; $M^{III} = Ga$, In; Q = S, Se, Te) and KHg₄Ga₅Se₁₂. Note that they are isostructural and M^{II} and M^{III} atoms occupy the same crystallographic sites.

In this work, we have also discovered four new compounds with positional disorder, such as Na₇HgIn₅S₁₂ (unreported in this work) and Na₇M^{II}Sb₅S₁₂ (M^{II} = Zn, Cd, Hg). As for the structure of Na₇HgIn₅S₁₂, Hg and In atoms occupy the same crystallographic site (Hg/In = 1:5), which is reasonable and similar to the known compounds, such as KHg₄Ga₅Se₁₂ (Hg/Ga = 4:5). Remarkably, In view of their same space group (R_{3}) and similar cell parameters, Na₇M^{II}Sb₅S₁₂ and Na₇HgIn₅S₁₂ can be acceptable in view of the disordered Hg/In site. Note that the detailed structural refinement process has been shown in the 2. Structural Refinement and Crystal Data section in the ESI. Moreover, the low occupancy (~16.7%) of M^{II} atom in Sb site is not affect the asymmetric environment for Sb atoms. Thus, based on the above consideration, we think that the structural refinement for the mixed occupancy of M^{II}/Sb site in title compounds is reasonable.

title compounds.							
Site	x	У	Ζ	Ueq (Å ²)	Occupancy		
	$Na_7ZnSb_5S_{12}$						
Sb(1)	5477(1)	1562(1)	43(1)	25(1)	0.833		
Zn(1)	5477(1)	1562(1)	43(1)	25(1)	0.167		
Na(1)	6667	3333	3333	19(1)	1		
Na(2)	3622(1)	1055(1)	3390(2)	25(1)	1		
S (1)	4297(1)	84(1)	1447(1)	22(1)	1		
S(2)	4985(1)	2861(1)	1390(1)	19(1)	1		
		Na ₇ 0	$CdSb_5S_{12}$				
Sb(1)	5476(1)	1562(1)	42(1)	24(1)	0.833		
Cd(1)	5476(1)	1562(1)	42(1)	24(1)	0.167		
Na(1)	6667	3333	3333	19(1)	1		
Na(2)	3622(2)	1052(2)	3391(2)	23(1)	1		
S (1)	4296(1)	81(1)	1446(1)	21(1)	1		
S(2)	4986(1)	2863(1)	1387(1)	18(1)	1		
	Na ₇ HgSb ₅ S ₁₂						
Sb(1)	8811(1)	583(1)	1710(1)	24(1)	0.833		
Hg(1)	8811(1)	583(1)	1710(1)	24(1)	0.167		
Na(1)	10000	0	5000	8(1)	1		
Na(2)	11059(2)	3632(2)	1609(3)	19(1)	1		
S (1)	10470(1)	1677(1)	3047(2)	12(1)	1		
S(2)	7634(1)	876(1)	3107(2)	13(1)	1		

 Table S2. Positional coordinates and equivalent isotropic displacement parameters for

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Compounds	Space group	mixed occupancy	Ref.
$AZn_4Ga_5S_{12} (A = K - Cs)$	<i>R</i> 3	Zn/Ga = 4:5	S8
$ACd_4Ga_5S_{12}$ (A = K-Cs)	<i>R</i> 3	Cd/Ga = 4:5	S9
$AX^{II}_{4}X^{III}_{5}Se_{12}$ (A = K–Cs; X ^{II} = Mn,	<i>R</i> 3	$X^{II}/X^{III} = 4:5$	S10
Cd; $X^{III} = Ga^{3+}, In^{3+})$			
$AZn_4In_5Se_{12}$ (A = Rb, Cs)	<i>R</i> 3	Zn/In = 4:5	S11
$C_{s}X^{II}_{4}In_{5}Te_{12} (X^{II} = Mn, Zn, Cd)$	<i>R</i> 3	$X^{II}/In = 4:5$	S12
KHg ₄ Ga ₅ Se ₁₂	<i>R</i> 3	Hg/Ga = 4:5	S13
Na ₇ HgIn ₅ S ₁₂	$R\bar{3}$	Hg/In = 1:5	unpublished
$Na_7HgSb_5S_{12}$	$R\bar{3}$	Hg/Sb = 1 : 5	This work
$Na_7CdSb_5S_{12}$	$R\bar{3}$	Cd/Sb = 1:5	This work
$Na_7ZnSb_5S_{12}$	$R\bar{3}$	Zn/Sb = 1 : 5	This work

Table S3 Comparison on the selected compounds with positional disorder of M^{II}/M^{III} sites ($M^{II} = Zn$, Cd, Hg; $M^{III} = Ga$, In) and title compounds.

* Cif data of $Na_7HgIn_5S_{12}$ is also uploaded for the review.

Compounds	(M ^{II} /Sb)S ₄ : (M ^{II} /Sb)-S (Å)	NaS ₆ : Na-S (Å)
Na7ZnSb5S12	(Zn/Sb)-S1: 2.403, 2.951 (Zn/Sb)-S2: 2.675, 2.503	Na1-S2: 2.894, 2.896, 2.895 × 4 Na2-S1: 2.834, 2.886, 2.819 Na2-S2: 3.070, 2.874, 2.991
$Na_7CdSb_5S_{12}$	(Cd/Sb)-S1: 2.403, 2.954 (Cd/Sb)-S2: 2.676, 2.502	Na1-S2: 2.901, 2.903, 2.902 × 4 Na2-S1: 2.840, 2.888, 2.826 Na2-S2: 3.086, 2.882, 2.996
Na7HgSb5S12	(Hg/Sb)-S2: 2.391, 2.962 (Hg/Sb)-S1: 2.673, 2.496	Na1-S1: 2.902 × 6 Na2-S1: 2.995, 3.081, 2.893 Na2-S2: 2.843, 2.821, 2.899

Table S4. Bond lengths of (M^{II}/Sb) -S and Na-S $(M^{II} = Zn, Cd, Hg)$ in title

compounds

Compounds	Space group	<i>n</i> in SbS _n	Link mode of SbS _n	<i>n</i> in NaS _n	Link mode of NaS _n	Ref.
Na9Gd5Sb8S26	Pnma	<i>n</i> = 3, 4	1D (Sb ₃ S ₇) _n chain; 0D (SbS ₃)	<i>n</i> = 6	3D network	14
α -NaSbP ₂ S ₆	$P2_{1}/c$	<i>n</i> = 6	1D $(SbS_4)_n$ chain	<i>n</i> = 6	$(NaS_6)_n$ layer	15
β -NaSbP ₂ S ₆	$P2_1$	<i>n</i> = 6	1D $(SbS_4)_n$ chain	<i>n</i> = 5	$(NaS_5)_n$ layer	15
Na ₂ CuSbS ₃	$P2_1/n$	<i>n</i> = 3	0D (SbS ₃)	<i>n</i> = 6	$(NaS_6)_n$ layer	16
NaCdSbS ₃	C2/c	<i>n</i> = 3	0D (SbS ₃)	<i>n</i> = 6	$(NaS_6)_n$ layer	17
Na ₇ ZnSb ₅ S ₁₂	$R\bar{3}$	<i>n</i> = 4	(Zn/Sb) ₃ S ₉ ; 2D layer	<i>n</i> = 6	12-MR	This work
Na7CdSb5S12	$R\bar{3}$	<i>n</i> = 4	(Cd/Sb) ₃ S ₉ ; 2D layer	<i>n</i> = 6	12-MR	This work
Na7HgSb5S12	$R\bar{3}$	<i>n</i> = 4	(Hg/Sb) ₃ S ₉ ; 2D layer	<i>n</i> = 6	12-MR	This work

Table S5. Structural comparisons on series of quaternary Na-based thioantimonates and title compounds.



Fig. S1 The whole crystal structures of (a) Na_6MnS_4 and (b) Na_2BaGeS_4 .



Fig. S2 Na₉Gd₅Sb₈S₂₆: (a) isolated $(Sb_3S_7)_n$ chains and (SbS_3) units; (b) crystal structure of Na₉Gd₅Sb₈S₂₆; (c) 3D network composed of NaS_n units.



Fig. S3 α- NaSbP₂S₆: (a) crystal structure of α- NaSbP₂S₆; (b) isolated (SbS₄)_n chains;
(c) edges and corners-sharing (NaS₆)_n layers.



Fig. S4 β- NaSbP₂S₆: (a) crystal structure of β- NaSbP₂S₆; (b) isolated (SbS₄)_n chain;
(c) corners-sharing (NaS₅)_n layer.



Fig. S5 Na₂CuSbS₃: (a) isolated (SbS₃) unit; (b) crystal structure of Na₂CuSbS₃; (c) corners and edges sharing $(NaS_6)_n$ layer.



Fig. S6 NaCdSbS₃: (a) isolated (SbS₃) unit; (b) corners and edges sharing $(NaS_6)_n$ layer.



Fig. S7 Band structures of (a) $Na_7ZnSb_5S_{12}$, (b) $Na_7CdSb_5S_{12}$, and (c) $Na_7HgSb_5S_{12}$, respectively.



Fig. S8 The partial density states (PDOS) of (a) Na₇ZnSb₅S₁₂, (b) Na₇CdSb₅S₁₂, and (c) Na₇HgSb₅S₁₂, respectively.



Fig. S9 The calculated electron density difference (EDD) and electron localization function (ELF) of $Na_7CdSb_5S_{12}$ (top panels) and $Na_7CdSb_5S_{12}$ (bottom panels), respectively.



Fig. S10 The calculation of spin-orbit coupling for $Na_7HgSb_5S_{12}$.

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