Supporting Information

New Cuprates Featuring Ladder-like Periodic Arrays of $[\text{Cu}_3\text{O}_8]^{10-}$ Trimeric Magnetic Nanostructures

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Table S1. Crystallographic Data for $\text{Li}_2\text{Cu}_3\text{Si}_4\text{O}_{12}$ and $\text{Na}_2\text{Cu}_3\text{Ge}_{4-x}\text{Si}_x\text{O}_{12}$ ($x = 0, 0.862(6), 1.72(1)$).

Chemical formula	$\text{Li}_2\text{Cu}_3\text{Si}_4\text{O}_{12}$	$\text{Na}_2\text{Cu}_3\text{Ge}_{4-x}\text{Si}_x\text{O}_{12}$		
		$x = 0$	$x = 0.862(6)$	$x = 1.72(1)$
Crystal color, shape	royal blue, sphenoid	blue, plate	blue, plate	blue, plate
Crystal size (mm)	$0.10 \times 0.10 \times 0.05$	$0.16 \times 0.12 \times 0.03$	$0.14 \times 0.10 \times 0.04$	$0.12 \times 0.10 \times 0.04$
Formula weight (amu)	508.6	718.96	680.27	642.33
Space group	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
Cell parameters				
a, (Å)	5.835(2)	6.187(1)	6.172(1)	6.152(1)
b, (Å)	7.451(3)	7.698(2)	7.678(2)	7.655(2)
c, (Å)	5.180(4)	5.480(1)	5.420(1)	5.365(1)
α , (°)	100.46(4)	102.36(3)	102.22(3)	102.01(3)
β , (°)	95.96(4)	93.28(3)	93.26(3)	93.37(3)
γ , (°)	86.65(3)	87.53(3)	87.84(3)	88.13(3)
V, (Å ³)	220.1(2)	254.43 (9)	250.53(9)	246.65(8)
Z	1	1	1	1
ρ_{calcd} , g/cm ³	3.838	4.693	4.509	4.324
Linear abs. coeff., mm ⁻¹	7.82	17.95	15.78	13.59
F ₀₀₀	334	333	317.3	302
T (K) of data collection	296	293(2)	293(2)	293(2)

Refinement Program	SHELXS-86	SHELXL-97	SHELXL-97	SHELXL-97
Reflections collected	1118	1195	2655	2630
Unique Reflections	805 (I > 3.0σ(I))	1103 (Fo > 2.0σ(Fo))	1140 (Fo > 2.0σ(Fo))	1133 (Fo > 2.0σ(Fo))
parameters refined (restraints)	97(0)	98(0)	98(0)	100(0)
Final R1/wR2/goodness of fit	0.063/0.082/2.79 ^a (I > 3.0σ(I))	0.0460/0.123/1.036 ^b (all data)	0.0317/0.0911/1.08 ^b (all data)	0.0299/0.0769/0.914 ^b (all data)
Largest difference peak (e ⁻ / Å ³)		-1.706/1.551	-1.096/1.170	-0.934/0.965

$$^a R1 = \Sigma ||F_O| - |F_C|| / \Sigma |F_O|; R_w = [\Sigma w\{|F_O| - |F_C|\}^2 / \Sigma w|F_C|^2]^{1/2}$$

$$^b R1 = \Sigma ||F_O| - |F_C|| / \Sigma |F_O|; wR2 = \{[\Sigma [w(F_O^2 - F_C^2)^2] / [\Sigma w(F_O^2)^2]]\}^{1/2};$$

$$w = 1 / [\sigma^2(F_O^2) + (0.0727 P)^2 + 2.794 P], \text{ where } P = (F_O^2 + 2F_C^2)/3 \text{ for Na}_2\text{Cu}_3\text{Ge}_4\text{O}_{12};$$

$$w = 1 / [\sigma^2(F_O^2) + (0.0428 P)^2 + 2.285 P] \text{ for } x = 0.862(6);$$

$$w = 1 / [\sigma^2(F_O^2) + (0.0630 P)^2 + 0.06302 P] \text{ for } x = 1.72(1).$$

Table S2. Comparison of selected distances (d , Å) and angle ($\angle$, °) in $\text{Na}_2\text{Cu}_3\text{Ge}_{4-x}\text{Si}_x\text{O}_{12}$, where $x = 0, 0.862(6), 1.72(1)$.

	$x = 0$	$x = 0.862(6)$	$x = 1.72(1)$
Intra-trimer			
$d_{\text{Cu-O}}$	1.918(4)-1.979(5)	1.927(3)-1.974(3)	1.929(3)-1.977(3)
$d_{\text{Cu(1)-Cu(2)}}$	3.026(1)	3.0133(8)	3.0055(8)
$\angle\text{Cu(1)-O(1)-Cu(2)}$	102.2(1)	101.2(1)	100.9(2)
$\angle\text{Cu(1)-O(4)-Cu(2)}$	100.0(2)	99.4(1)	99.0(1)
Inter-trimer			
$d_{\text{Cu(1)-Cu(2)}}$	3.349(1)	3.3257(8)	3.3023(8)
$d_{\text{Cu(2)-Cu(2)}}$	3.273(1)	3.303(1)	3.331(1)
$d_{\text{Cu(1)-O(5)}}$	2.691(5)	2.690(3)	2.685(3)
$d_{\text{Cu(2)-O(4)}}$	2.553(5)	2.559(3)	2.571(3)
$\angle\text{Cu(1)-O(5)-Cu(2)}$	91.4(2)	90.4(1)	90.1(1)
$\angle\text{Cu(1)-O(4)-Cu(2)}$	94.6(2)	93.5(1)	92.2(1)
$\angle\text{Cu(2)-O(4)-Cu(2)}$	91.6(2)	92.6(1)	93.3(1)

Fig. S1. A volume vs. x plot showing the correlation for the $\text{Na}_2\text{Cu}_3\text{Ge}_{4-x}\text{Si}_x\text{O}_{12}$ (where $x = 0, 0.862(6), 1.72(1)$) compound series. The dotted line is drawn to guide viewing.

Fig. S2. (a) Unit cell structure of $\text{Na}_2\text{Cu}_3\text{Ge}_4\text{O}_{12}$ showing the anisotropic thermal ellipsoids (90% probability). (b) Perspective view of the $\text{Na}_2\text{Cu}_3\text{Ge}_4\text{O}_{12}$ structure showing the $[\text{Cu}_3\text{O}_9]^{10-}$ (ball and stick) nanostructures imbedded in meta-germanate matrices (yellow tetrahedra). The sodium cations reside in the channels with a window made of the edges of $2\times\text{CuO}_4$ and $4\times\text{GeO}_4$ polyhedra.

(a)

(b)

Fig. S3. Perspective view of the reported $\text{Na}_2\text{Cu}_3\text{Si}_4\text{O}_{12}$ structure (ref.11), for comparison, showing the $[\text{Cu}_3\text{O}_9]_\infty^{12-}$ (ball and stick) chains (propagating along b) imbedded in meta-silicate matrices (yellow tetrahedra) made of $[\text{SiO}_3]_\infty^{2-}$ chains (propagating along a). The sodium cations reside in the channels with a window made of the edges of $2\times\text{CuO}_4$ and $4\times\text{SiO}_4$ polyhedra.

Fig. S4. χT vs. T plots of $\text{Na}_2\text{Cu}_3\text{Ge}_4\text{O}_{12}$ taken at applied fields of $H = 100$ G (open circles) and 5000 G (solid triangles) showing the field effect of magnetization. The inset shows the plots of magnetic susceptibility of the polycrystalline sample measured in zero-field-cooling (ZFC) and field-cooling (FC) at $H = 100$ G.

Fig. S5. UV-vis diffuse reflectance spectra of $\text{Na}_2\text{Cu}_3\text{Ge}_4\text{O}_{12}$. The spectrum was taken in the range 200 nm (6.2 eV) to 2400nm (0.50 eV) according to the reported procedures^{3c} using ground powder of selected crystals (blue). It shows obvious absorptions attributed to $d-d$ transition of Cu^{2+} cation at 1.2-2.2eV and ligand-to-metal-charge-transfer (LMCT) at higher energy ca. 3.1eV.