Electronic Supplementary Information

$Na_6Si_3S_8O$: first example of sulfide silicate exhibiting unusual tri-polymerized $[Si_3S_8O]^{6-}$ units without the S−O bonds

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Experimental Section

Synthesis

All starting reactants with high purities (4N) were commercially purchased and used without further refinement. An Ar-filled glovebox was used to avoid the oxidation of Na metals. A mixture of Na, Si, and S with the molar ratio of 9 : 4 : 12, and additional 1mmol Na_2CO_3 as the flux. Firstly, the mixture was filled into a graphite crucible in an vacuum-sealed quartz tube, then put the tube into a furnace with the following procedure: heated to 1073 K within 2 days and left at this temperature about 4 days, then slowly cooled to 573 K with 6 days, finally rapidly down to room temperature. The products were carefully washed with N,N-dimethylformamide (DMF) to remove the Na_2CO_3 flux and other byproducts. Colorless transparent single-crystals were found and the yield is about 90 %, and this compound was stable in air after several months.

Structural Refinement and Crystal Data

High quality single-crystal was carefully picked and used for data collections with a Bruker SMART APEX II 4K CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 296 K. The structure was solved by direct method and refined using the SHELXTL program package.[1] Multi-scan method was used for absorption correction.[2] Rational anisotropic thermal parameters for all atoms were obtained by the anisotropic refinement and extinction correction. PLATON was also used to check the final structures and no other symmetries were found. Energy-dispersive X-ray (EDX) equipped Hitachi S-4800 SEM was also used to analyze the element composition and proportion. Measured results ensure the presence of Na, Si, S and O with the molar ratio about 6 : 3 : 8 : 1, and no other elements were detected, which is consistent with the result from the X-ray structure determination. Crystal data and structure refinements were shown in Table S1, atomic coordinates and isotropic displacement parameters were shown in Table S2.

Powder XRD Characterization

Powder X-ray diffraction (XRD) analysis was measured on a Bruker D2 X-ray diffractometer with Cu Kα radiation (λ = 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. The simulated pattern was obtained by the Mercury program and single-crystal reflection data.

UV−Vis−Near-IR (NIR) Diffuse-Reflectance Spectroscopy

Diffuse-reflectance spectrum was measured by Shimadzu SolidSpec-3700DUV spectrophotometer at the wavelength range from 190 to 2600 nm.

IR Spectroscopy

As for IR test, single-crystals were picked and mixed with KBr powder, then performed on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer in the wavenumber range from 400 to 4000 cm^{-1}.

Raman Spectroscopy

Raman spectrum was measured on a LABRAM HR Evolution spectrometer using 532 nm radiations at an integration time of 5 s. The laser power of 50 mW with beam diameter about 35 μm was used.

Computational Description

In order to further investigate the relationship of structure–property, the electronic structure of title compound was studied by density functional theory (DFT) based on ab initio calculations.[3] The exchange-correlation potential was calculated using Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme.[4] The following orbital electrons were treated as valence electrons, Na: $2s^2$ $2p^6$ $3s^1$, Si: $3s^2$ $3p^2$, S: $3s^2$ $3p^4$ O: $2s^2$ $2p^4$. To achieve energy convergence, a plane-wave basis set energy cutoff was 830.0 eV within normal-conserving pseudo-potential (NCP),[5] and the Monkhorst–Pack scheme was 4 × 2 × 2 in the Brillouin Zone (BZ) of the primitive cell are chosen.

Table S1 Crystal data and structure refinement for $Na_6Si_3S_8O$.

Empirical formula	$Na_6Si_3S_8O$
Formula weight	494.69
Temperature	296 (2) K
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.8006(8) Å b = 14.3414(18) Å c = 16.207(2) Å β = 90.561(8)°
Z , V	4, 1580.6(3) $Å^3$
Density (calculated)	2.079 g/cm^3
Absorption coefficient	1.497 mm^{-1}
Crystal size	0.107×0.124× 0.157 mm^3
Completeness to theta = 27.51	99.9 %
Goodness-of-fit on F^2	1.024
Final R indices $[F_o^2 > 2\sigma(F_o^2)]$[a]	R_1=0.0368 wR_2 = 0.0611
R indices (all data) [a]	R_1=0.0752 wR_2 = 0.0835
Largest diff. peak and hole	0.861 and −0.749 e $Å^{-3}$

[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 $F_o^2 > 2\sigma (F_o^2)$

Table S2 Atomic coordinates, isotropic displacement parameters, bond valence sums and global instability index (GII) for $Na_6Si_3S_8O$.

Atom	*x*	*y*	*z*	U_{eq}	*BVS*
Na1	4463(2)	5009(1)	7918(1)	27(1)	1.364
Na2	7465(2)	5625(1)	4722(1)	30(1)	1.014
Na3	-765(2)	5765(1)	9119(1)	32(1)	1.069
Na4	7805(2)	6860(1)	6731(1)	34(1)	1.068
Na5	9700(2)	8296(1)	5127(1)	36(1)	1.017
Na6	7917(2)	8488(1)	8616(1)	44(1)	0.772
Si1	3197(1)	6436(1)	6243(1)	15(1)	4.099
Si2	4570(1)	8538(1)	6509(1)	17(1)	4.148
Si3	3143(1)	7331(1)	8228(1)	18(1)	4.115
S1	1530(1)	6415(1)	7391(1)	19(1)	2.189
S2	5951(1)	6774(1)	8407(1)	21(1)	2.128
S3	5340(1)	5390(1)	6229(1)	20(1)	2.172
S4	2864(1)	9387(1)	5746(1)	22(1)	2.109
S5	1109(1)	6358(1)	5308(1)	25(1)	1.917
S6	1400(1)	7476(1)	9262(1)	25(1)	1.949
S7	3372(1)	8707(1)	7738(1)	29(1)	2.071
S8	7548(1)	8844(1)	6577(1)	30(1)	2.013
O1	4417(3)	7423(2)	6277(1)	21(1)	2.114
		GII			**0.131**

GII can be derived from the bond valence concepts, which represent the tension of lattice parameters and always used to evaluate the rationality of structure. While the value of GII is less than 0.05 vu (valence unit), the tension of structure is not proper, whereas the value of GII is larger than 0.2 vu, its structure is not stable. Thus, the value of GII in a reliable structure should be limited at 0.05−0.2 in general. **As for $Na_6Si_3S_8O$, calculated GII value is 0.131 vu, which illustrates that its crystal structure is reasonable.**

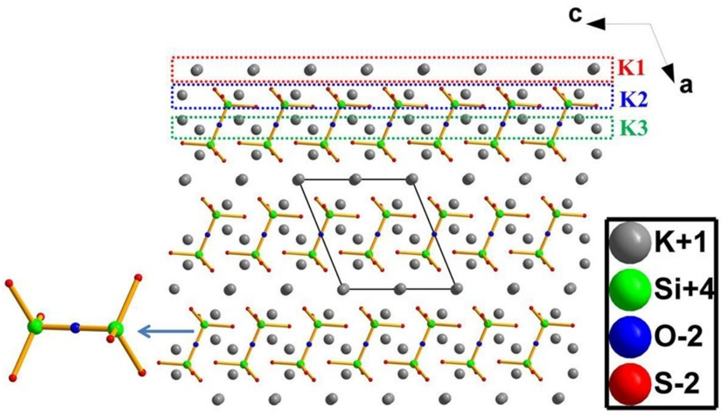

Figure S1. Crystal structure of $K_6Si_2S_6O$.

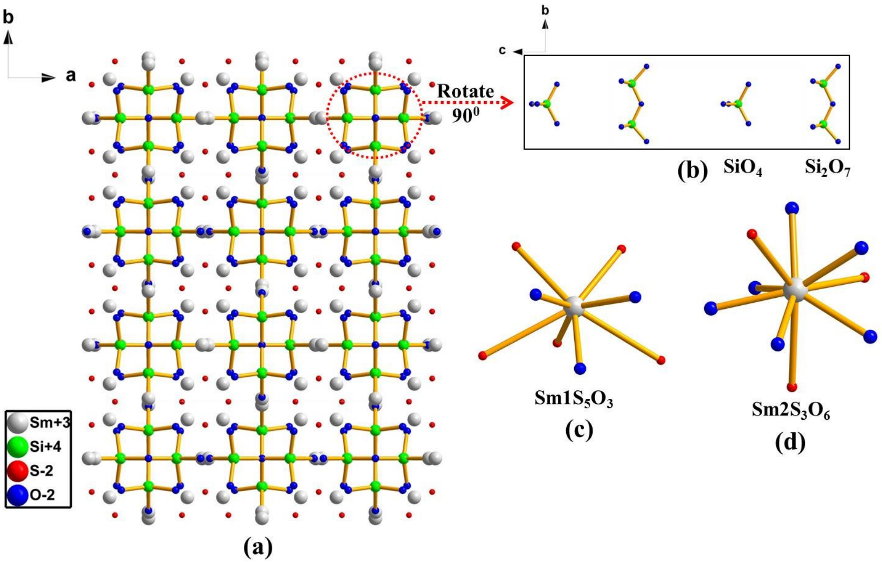

Figure S2. (a) Crystal structure of $Sm_4Si_2S_3O_7$; (b) Isolated SiO_4 and Si_2O_7 units; (c) Coordination environment of $Sm1S_5O_3$; (d) Coordination environment of $Sm2S_3O_6$.

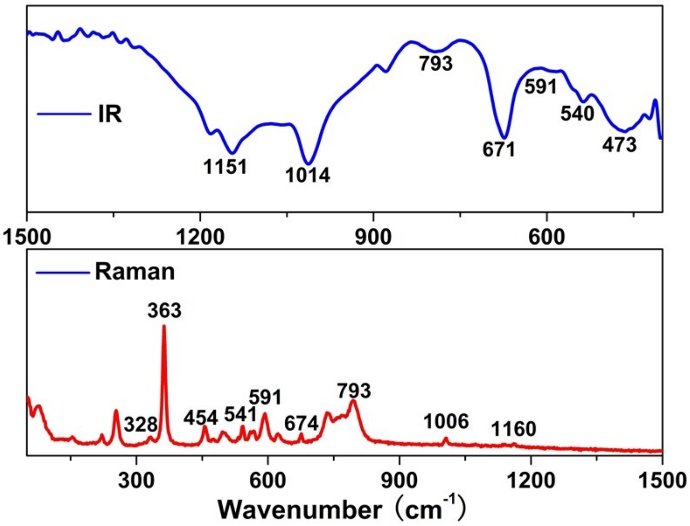

Figure S3. IR and Raman spectra of $Na_6Si_3S_8O$.

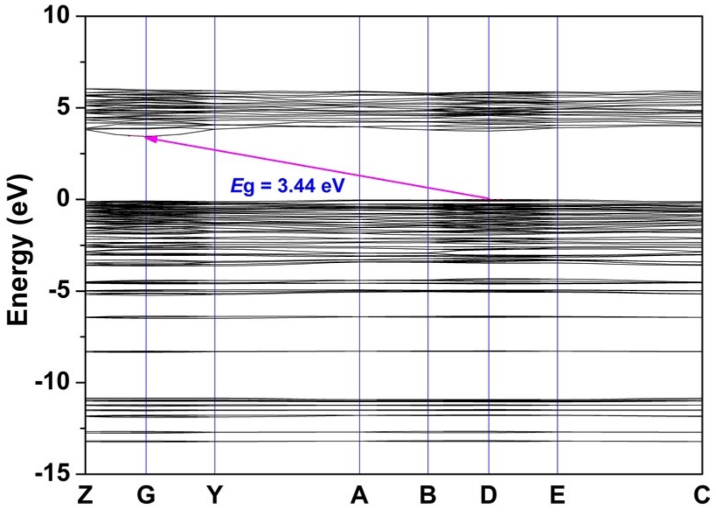

Figure S4. Band structure of $Na_6Si_3S_8O$.

References

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