

**Cs₄Mo₅P₂O₂₂: A First Strandberg-Type POM with 1D straight chains
of polymerized [Mo₅P₂O₂₃]⁶⁻ units and Moderate Second Harmonic
Generation Response**

(Supporting Information: 14 pages)

Ying Wang,^{ab} Shilie Pan,^{*a} Hongwei Yu,^{ab} Xin Su,^a Min Zhang^a, Fangfang Zhang^a
and Jian Han^{*a}

^a *Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang
Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, 40-1 South
Beijing Road, Urumqi 830011, China;*

^b *University of Chinese Academy of Sciences, Beijing 100039, China;*

*To whom correspondence should be addressed. Phone: (86)991-3674558.

Fax: (86)991-3838957. E-mail: slpan@ms.xjb.ac.cn (S. Pan).

Section S1. Synthesis and general characterization	S-2
Section S2. Single crystal X-ray diffraction data collection, Structure solution and refinement procedures	S-4
Section S3. IR Spectroscopy	S-9
Section S4. UV-Vis-NIR diffuse-reflectance spectroscopy	S-10
Section S5. Second-harmonic generation measurements	S-11
Section S6. Out-of-center distortion and local dipole moment calculation for Cs₄Mo₅P₂O₂₂	S-12
Section S7. Comparison of the DSC curves	S-13
Section S8. References	S-14

Section S1. Synthesis and general characterization

Synthesis of Cs₄Mo₅P₂O₂₂: All reagents for synthesis were commercially available and used as received. Polycrystalline samples of Cs₄Mo₅P₂O₂₂ were synthesized via solid-state reactions of the stoichiometric starting components (0.02mol) of Cs₂CO₃ (99.0%), MoO₃ (99.5%) and NH₄H₂PO₄ (99.5%). The sample was placed in an alumina crucible and heated to 500 °C slowly in air, held for 3 d with several intermediate grindings and mixings. Purity was confirmed by PXRD. The single crystals of Cs₄Mo₅P₂O₂₂ were grown by spontaneous crystallization from the melt of polycrystalline samples (5g). The reaction was completed in a platinum crucible under air by applying the following temperature program: heating up to 700 °C in air, holding at this temperature for 24 h, cooling slowly down to 450 °C (2 °C/h), before rapid cooling to RT. Several colorless block crystals were separated mechanically from the crucible for the further structural characterization.

General characterization: PXRD data were collected on a Bruker D2 PHASER diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The 2θ range was 5-70° with a step size of 0.02° and a fixed counting time of 1s/step. Vibrational spectra were obtained at room temperature via a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer. The sample was mixed thoroughly with dried KBr (5 mg of the sample, 500 mg of KBr). It was collected in a range from 400 to 4000

cm^{-1} with a resolution of 4 cm^{-1} . The UV-Vis-NIR optical diffuse reflectance spectrum was measured at room temperature with a Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected in the wavelength range 250-2600 nm. The reflectance spectrum was converted to absorbance with the Kubelka–Munk function.^{S1} Thermal analysis was carried out on NETZSCH STA 449C instrument at a temperature range of 40 - 800 °C with a heating rate of 5 °C /min in an atmosphere of flowing N_2 .

Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures

Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer using monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). A colorless block crystal of Cs₄Mo₅P₂O₂₂ (dimensions 0.047 mm \times 0.10 mm \times 0.165 mm) was glued on to a glass fiber at room-temperature. A total of 7424 reflections were collected of which 2833 were independent in the range $2.30 < \theta < 27.77^\circ$. The reduction of data was carried out with the Bruker Suite software package. Face-indexed absorption correction was performed numerically with the program SADABS.^{S2} The crystal structure of Cs₄Mo₅P₂O₂₂ was solved by direct methods using the SHELXTL program package with anisotropic displacement parameters for all atoms.^{S3} The structure was examined using the *Adsym* subroutine of PLATON to assure that no additional symmetry could be applied to the models.^{S4} Crystal data and structure refinement information are given in Table S1. Selected bond lengths for Cs₄Mo₅P₂O₂₂ are listed in Table S2.

Table S1. Crystal data and structure refinement for Cs₄Mo₅P₂O₂₂

Empirical formula	Cs ₄ Mo ₅ P ₂ O ₂₂
Formula weight	1425.28
Temperature	296(2) K
Crystal system	Orthorhombic
Space group	C222 ₁
<i>a</i> / Å	6.622(5)
<i>b</i> / Å	20.485(15)
<i>c</i> / Å	17.748(13)
Volume / Å ³	2408(3)
Z	4
$\rho_{\text{calcd}} / \text{g}\cdot\text{cm}^{-3}$	3.932
μ / mm^{-1}	8.715
F(000)	2544
Crystal size / mm ³	0.165 × 0.10 × 0.047
Θ range for data collection	2.30 to 27.77°
Index ranges	-8 ≤ <i>h</i> ≤ 7, -23 ≤ <i>k</i> ≤ 26, -23 ≤ <i>l</i> ≤ 19
Reflections collected	7424
Independent reflections	2833 [R(int) = 0.0406]
Completeness to theta = 27.77	99.4 %
Data / restraints / parameters	2833 / 0 / 153
Goodness-of-fit on F ²	1.009
Final R indices [<i>I</i> > 2σ(<i>I</i>)] ^[a]	R ₁ = 0.0314, wR ₂ = 0.0483
Final R indices (all data) ^[a]	R ₁ = 0.0383, wR ₂ = 0.0503
Largest diff. peak/hole / e·Å ⁻³	0.971 and -0.905
Absolute structure parameter	0.03(2)

^[a]R₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$ and wR₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Selected bond lengths (Å) for Cs₄Mo₅P₂O₂₂.

Cs(1)-O(2)	2.960(5)	Cs(3)-O(9)	3.378(6)
Cs(1)-O(2)#1	2.960(5)	Mo(1)-O(8)	1.694(5)
Cs(1)-O(4)#1	2.973(5)	Mo(1)-O(6)	1.704(6)
Cs(1)-O(4)	2.973(5)	Mo(1)-O(10)#11	1.903(4)
Cs(1)-O(6)	3.068(6)	Mo(1)-O(7)	1.906(2)
Cs(1)-O(6)#1	3.068(6)	Mo(1)-O(2)#3	2.328(5)
Cs(1)-O(8)#2	3.280(6)	Mo(1)-O(3)	2.485(5)
Cs(1)-O(8)#3	3.280(6)	Mo(2)-O(4)	1.699(5)
Cs(1)-O(7)	3.439(3)	Mo(2)-O(4)#1	1.699(5)
Cs(1)-O(7)#2	3.439(3)	Mo(2)-O(5)	1.910(5)
Cs(2)-O(4)#1	2.919(5)	Mo(2)-O(5)#1	1.910(5)
Cs(2)-O(11)#4	2.972(5)	Mo(2)-O(12)#2	2.267(5)
Cs(2)-O(5)#5	2.987(5)	Mo(2)-O(12)#3	2.267(5)
Cs(2)-O(11)#2	3.203(6)	Mo(3)-O(9)	1.692(5)
Cs(2)-O(9)	3.324(6)	Mo(3)-O(11)	1.708(5)
Cs(2)-O(8)	3.353(6)	Mo(3)-O(10)	1.923(4)
Cs(3)-O(6)#6	3.174(6)	Mo(3)-O(5)#5	1.930(5)
Cs(3)-O(6)#7	3.174(6)	Mo(3)-O(3)#6	2.263(5)
Cs(3)-O(8)#4	3.249(6)	Mo(3)-O(12)	2.364(4)
Cs(3)-O(8)#8	3.249(6)	P(1)-O(2)	1.500(5)
Cs(3)-O(10)#9	3.318(5)	P(1)-O(3)	1.526(5)
Cs(3)-O(10)#2	3.318(5)	P(1)-O(12)#12	1.529(5)
Cs(3)-O(9)#10	3.378(6)	P(1)-O(1)	1.597(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2; #2 x+1,y,z; #3 -x,y,-z+1/2; #4 x+1/2,-y+3/2,-z; #5 x-1,y,z; #6 x-1/2,y+1/2,z; #7 x-1/2,-y+3/2,-z; #8 x+1/2,y+1/2,z; #9 x+1,-y+2,-z; #10 x,-y+2,-z; #11 x+1/2,y-1/2,z; #12 -x-1/2,y-1/2,-z+1/2.

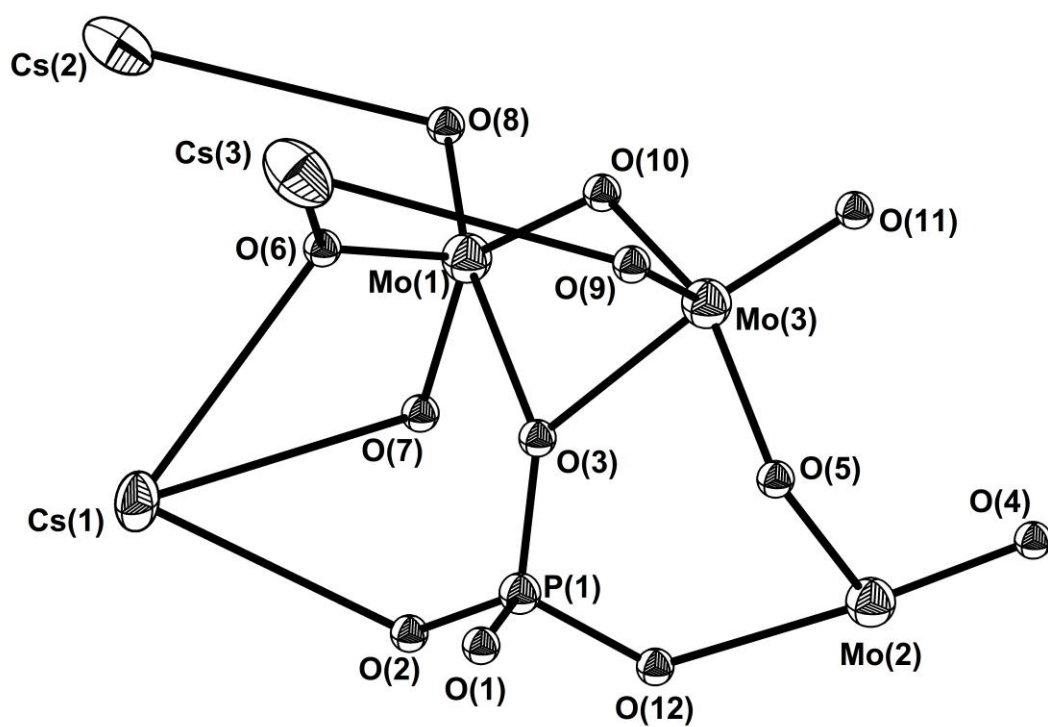


Fig. S1 ORTEP drawing of the asymmetric unit of $\text{Cs}_4\text{Mo}_5\text{P}_2\text{O}_{22}$. Thermal ellipsoids are drawn at a 50% probability level.

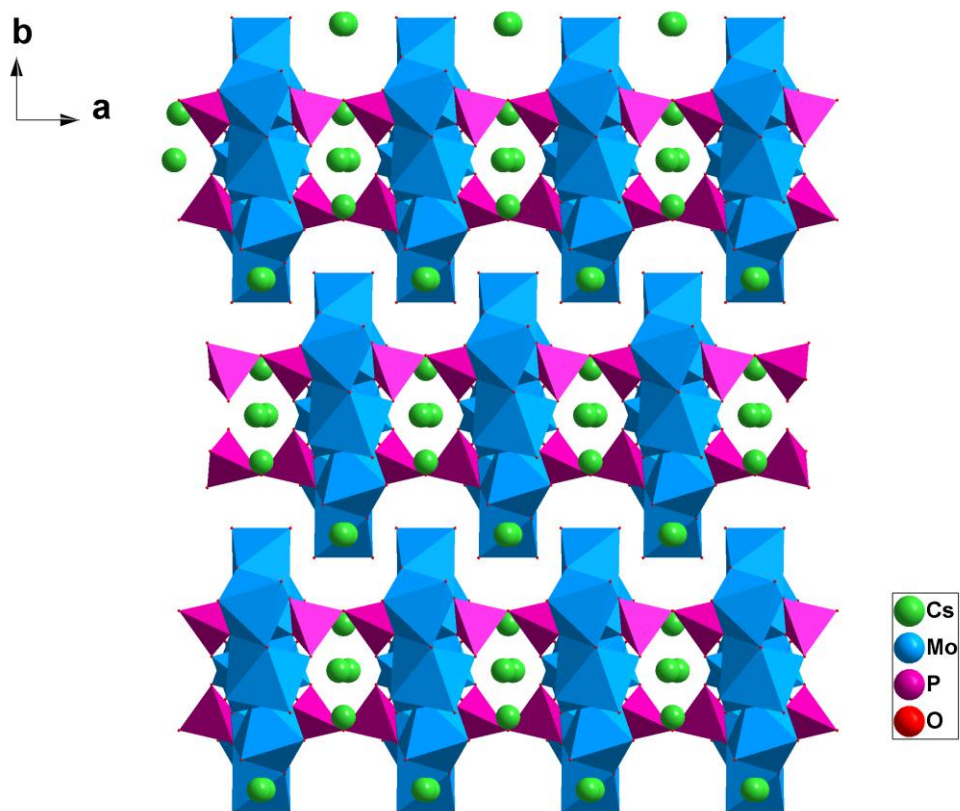


Fig. S2 The polyhedra representation of $\text{Cs}_4\text{Mo}_5\text{P}_2\text{O}_{22}$ along the $[001]$ direction. The figure shows the crystallographic 2_1 screw axis in the c direction.

Section S3. IR Spectroscopy

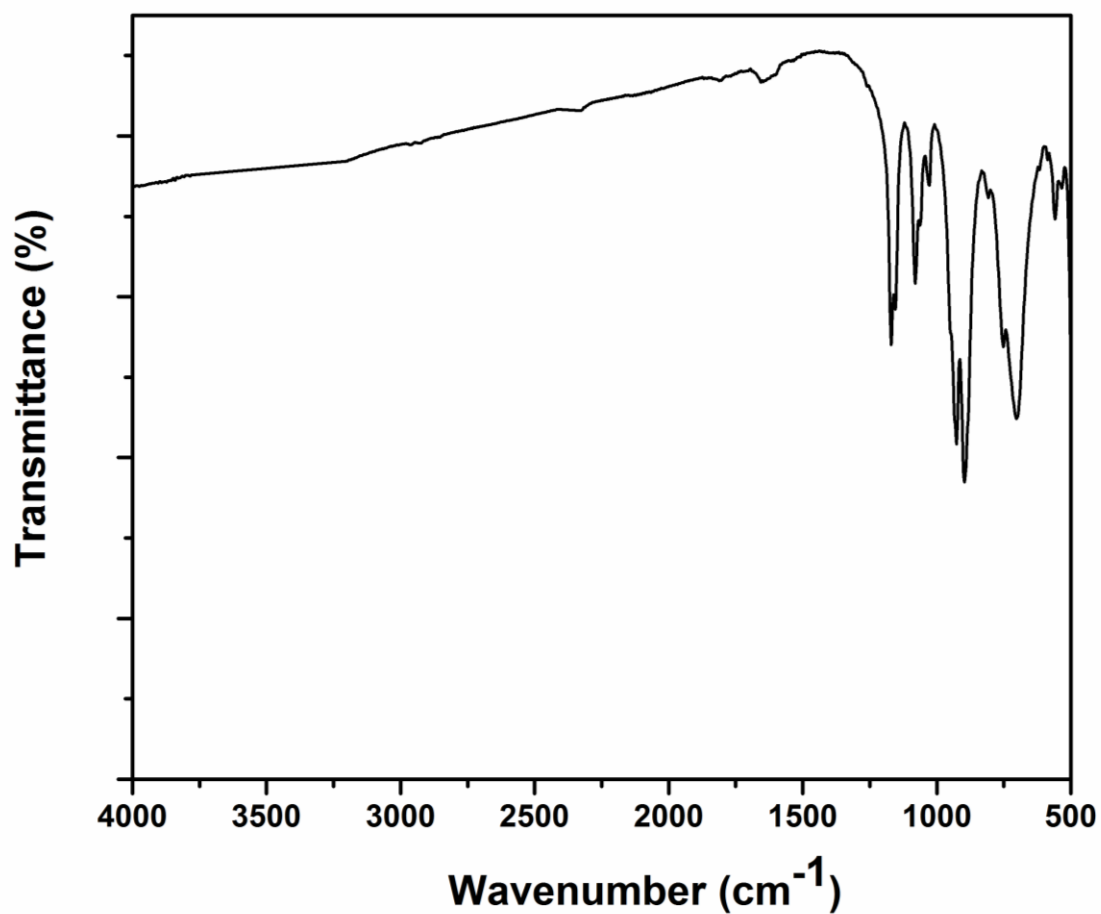


Fig. S3 IR Spectroscopy of as-synthesized Cs₄Mo₅P₂O₂₂. Characteristic FTIR bands at 1170 and 1078 cm⁻¹ confirmed the presence of P-O-P bridges, and bands at 927, 891, 704, and 559 cm⁻¹ are characteristic of phosphomolybdate anion.

Section S4. UV-Vis-NIR diffuse-reflectance spectroscopy

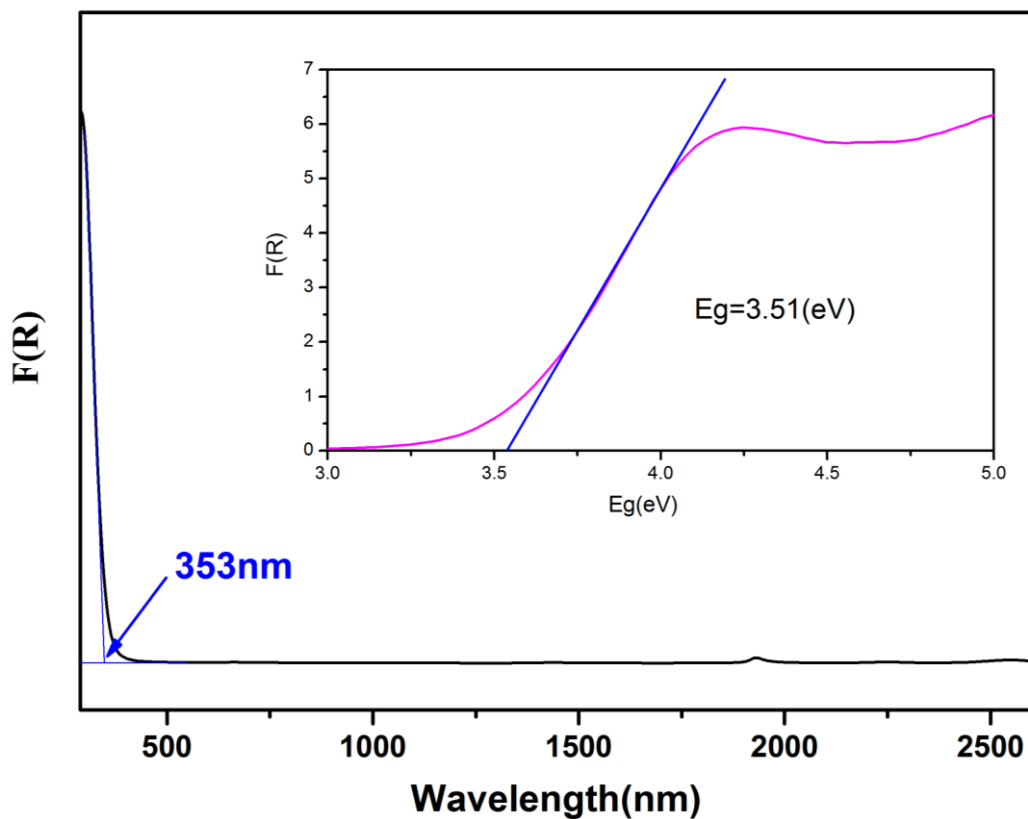


Fig. S4 UV-Vis-NIR diffuse-reflectance spectroscopy of $\text{Cs}_4\text{Mo}_5\text{P}_2\text{O}_{22}$.

Section S5. Second-harmonic generation measurements

Second-harmonic generation (SHG) test was performed on a modified Kurtz-NLO system.^{S5} About 100 mg of the powder samples were hand-pressed into a 1 cm diameter round box with two glass windows, which were irradiated with a pulsed infrared beam (1064 nm, 10 ns, 10 kHz) produced by a Q-switched Nd: YAG laser. A 532 nm filter was used to absorb the fundamental light and pass the visible light onto a photomultiplier. A digital oscilloscope was used to receive the laser SHG signal. Because the SHG efficiency has been shown to depend on particle size,^{S6} polycrystalline samples were ground and sieved into distinct particle size ranges: <20, 20–38, 38–55, 55–88, 88–105, 105–150, and 150–200 μm , and the microcrystalline KDP (150–200 μm) also served as a reference.

Section S6. Out-of-center distortion and local dipole moment

calculation for Cs₄Mo₅P₂O₂₂

Table S3. The direction and magnitude of the MoO₆, PO₄, and CsO_n (n=10, 6, and 8) polyhedra in Cs₄Mo₅P₂O₂₂

species	octahedron distortion, $\Delta_d^{[a]}$		dipole moment				
	direction	magnitude	$x (a)$	$y (b)$	$z (c)$	deby	magnitude $\times 10^{-4}$ esu·cm /Å ³
Mo(1)O ₆	C ₂ [110]	1.433	-0.6743	-6.118	2.090	6.501	108.0
Mo(2)O ₆	C ₂ [110]	1.171	0	7.043	0	7.043	117.0
Mo(3)O ₆	C ₂ [110]	1.302	-1.196	0.2933	7.122	7.227	120.0
PO ₄	–	–	1.865	-1.882	-0.3181	2.669	44.33
[Mo ₅ P ₂ O ₂₃] ⁶⁻ unit ^[b]	–	–	0	-8.371	0	8.371	139.0
[Mo ₅ P ₂ O ₂₃] ⁶⁻ unit ^[b]	–	–	0	8.371	0	8.371	139.0
Cs(1)O ₁₀	–	–	0	-3.772	0	3.772	62.66
Cs(2)O ₆	–	–	-1.465	1.282	-0.6708	2.059	34.20
Cs(3)O ₈	–	–	1.372	0	0	1.372	22.78
Asymmetric unit	–	–	-0.0988	-3.154	8.223	8.808	146.3
Unit cell	–	–	0	0	0	0	0

^[a] Octahedron distortion, Δ_d parameter, is defined as below:

$$\Delta_d = \frac{|(M - O1) - (M - O4)|}{|\cos \theta_1|} + \frac{|(M - O2) - (M - O5)|}{|\cos \theta_2|} + \frac{|(M - O3) - (M - O6)|}{|\cos \theta_3|}$$

where the pairs (O1, O4), (O2, O5), and (O3, O6) are the oxygen atoms that constitute the octahedron and are located in opposite positions from each other.

$\theta_1 = \angle O1-M-O4$, $\theta_2 = \angle O2-M-O5$, and $\theta_3 = \angle O3-M-O6$

^[b] Representation of two opposite directions of the POM units

Section S7. Comparison of the DSC curves

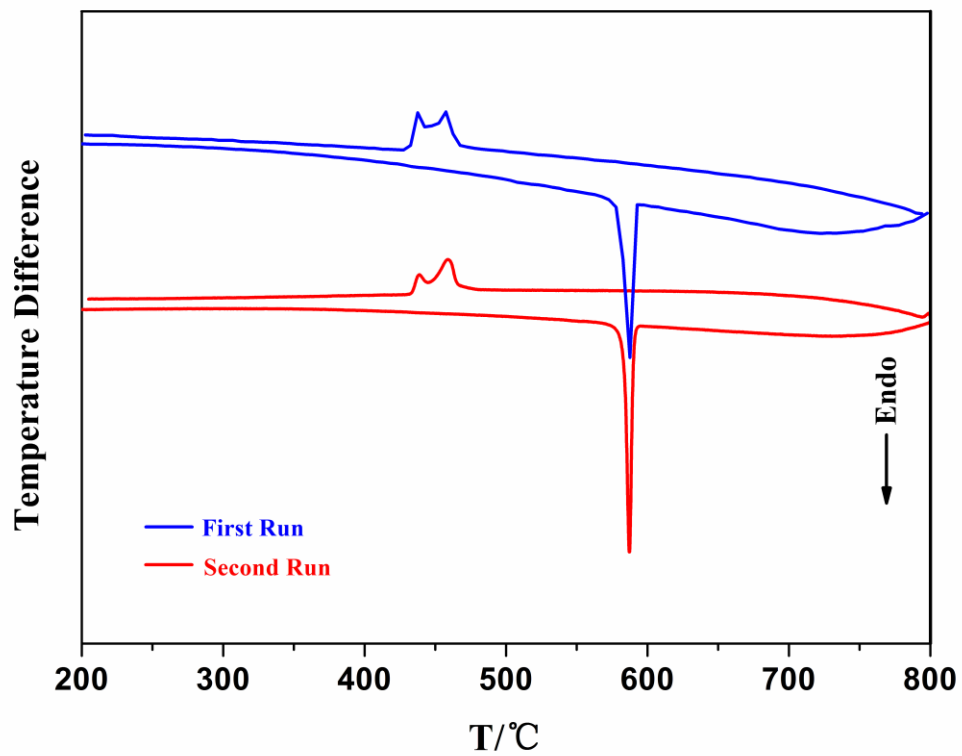


Fig. S5 Comparison of the DSC curves for $\text{Cs}_4\text{Mo}_5\text{P}_2\text{O}_{22}$. The second run performed right after the first run.

Section S8. References

- S1. (a) J. Tauc, *Mater. Res. Bull.*, 1970, **5**, 721; (b) P. Kubelka and F. Z. Munk, *Tech. Phys.*, 1931, **12**, 593.
- S2. SAINT, *Version 7.60A, Bruker Analytical X-ray Instruments, Inc., Madison, WI*, 2008.
- S3. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2010, **64**, 112.
- S4. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- S5. S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
- S6. J. P. Dougherty and S. K. Kurtz, *J. Appl. Crystallogr.*, 1976, **9**, 145.