

Supporting Information for

Na₃Ca₄(TeO₃)(PO₄)₃: New Noncentrosymmetric Tellurite Phosphate with Fascinating Multimember-Ring Architectures and Intriguing Nonlinear Optical Performance

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1. Syntheses of Na₃Ca₄(TeO₃)(PO₄)₃
2. Structure determination
3. Property characterization
4. Computational methods
5. Figure S1.
6. Figure S2.
7. Table S1.
8. Table S2.
9. Table S3.

Experimental details

1. Synthesis

Single crystals of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ were grown through a high temperature solid state reaction. The mixtures of stoichiometric amounts of Na_2CO_3 (1.5 mmol, 0.159 g), CaCO_3 (4 mmol, 0.4 g), TeO_2 (1 mmol, 0.1596 g) and $\text{NH}_4\text{H}_2\text{PO}_4$ (3 mmol, 0.345 g) were put into a platinum crucible, heated up to 900 °C and held at this temperature for 24 h. Then the mixtures were cooled to 500 °C at a rate of 3 °C h⁻¹ and cooled to room temperature by switching off the furnace. A transparent prism shaped crystal with dimensions of 0.1 × 0.1 × 0.2 mm³ was selected for single crystal structure determination. Polycrystalline powder samples of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ were synthesized by a traditional solid state reaction with stoichiometric amounts of Na_2CO_3 , CaCO_3 , TeO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$. The mixtures were ground, presintered at 300 °C for 12 h and heated to its sintering temperature of 600 °C. Pure powder samples of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ were obtained by maintaining this temperature for three days with several intermittent grindings.

2. Structure determination

Single crystal X-ray diffraction data were recorded on a Xcalibur Ecos diffractometer equipped with a graphite-monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation at 293 K. The structure was solved with direct method by SHELXS-97 and refined by the full matrix least squares on F² by SHELXL-97, respectively. The detailed crystallographic data were summarized in Table S1. The atomic coordinates, occupancy and equivalent displacement parameters are given in Table S2. The important bond lengths are listed in Table S3.

3. Property Characterization

Powder X-ray Diffraction

The powder X-ray diffraction pattern of the as-obtained polycrystalline powder was performed at room temperature on a Bruker D8 Focus diffractometer with Cu K_α ($\lambda = 1.5418$ Å) radiation. The scanning step width of 0.1° and a fixed counting time 0.2 s/step were applied to record the patterns in the 2θ range of 10 – 70°.

Element Analysis

Elemental analysis of compositions of the single crystal was performed on an energy-dispersive X-ray (EDX)-equipped Hitachi S-4800 scanning electron microscopy (SEM) instrument.

Diffuse reflectance spectroscopy

A Cary 5000 UV-vis-NIR spectrophotometer with a diffuse reflectance accessory was used to measure the spectrum of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ and BaSO_4 (as a reference) in the range 200 nm (6.2 eV) to 2500 nm (0.496 eV).

Infrared spectrum: Infrared (IR)

Spectroscopy was collected on a Varian Excalibur 3100 spectrometer in the 400 – 4000 cm^{-1} range. The $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ and KBr samples with mass ratio about 1:100 were mixed thoroughly.

Raman Spectroscopy.

The unpolarized Raman scattering spectrum was recorded from ground powder sample at room temperature with an in Via-Reflex instrument with a line of 532 nm of solid state laser. The spectral resolution was 2 cm^{-1} , and the scanning range was 100–1200 cm^{-1} .

SHG Measurement

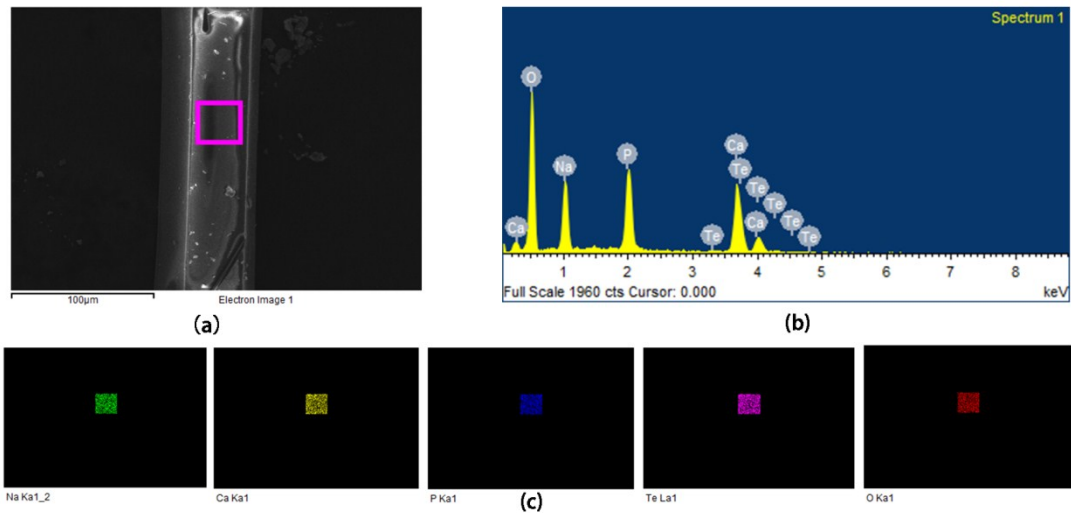
The optical SHG response of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ was measured by means of the Kurtz–Perry method. The fundamental light was the 1064 nm light generated with a Q switched Nd: YAG laser. The polycrystalline powder of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ was thoroughly ground and sieved into a series of distinct particle size ranges of 20 – 41, 41 – 74, 74 – 105, 105 – 150, 150 – 200 μm , respectively, which were then pressed into a disk with diameter of 8 mm that was put between glass microscope slides and secured with tape in a 1 mm thick aluminum holder. Microcrystalline KH_2PO_4 (KDP) was ground and sieved into the same particle size ranges as a reference.

4. Computational methods

The first–principles calculation for $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ was implemented by the plane–wave pseudo–potential method based on the density functional theory (DFT). The CASTEP package was employed to determine the electronic structures, including total density of states (DOS) and

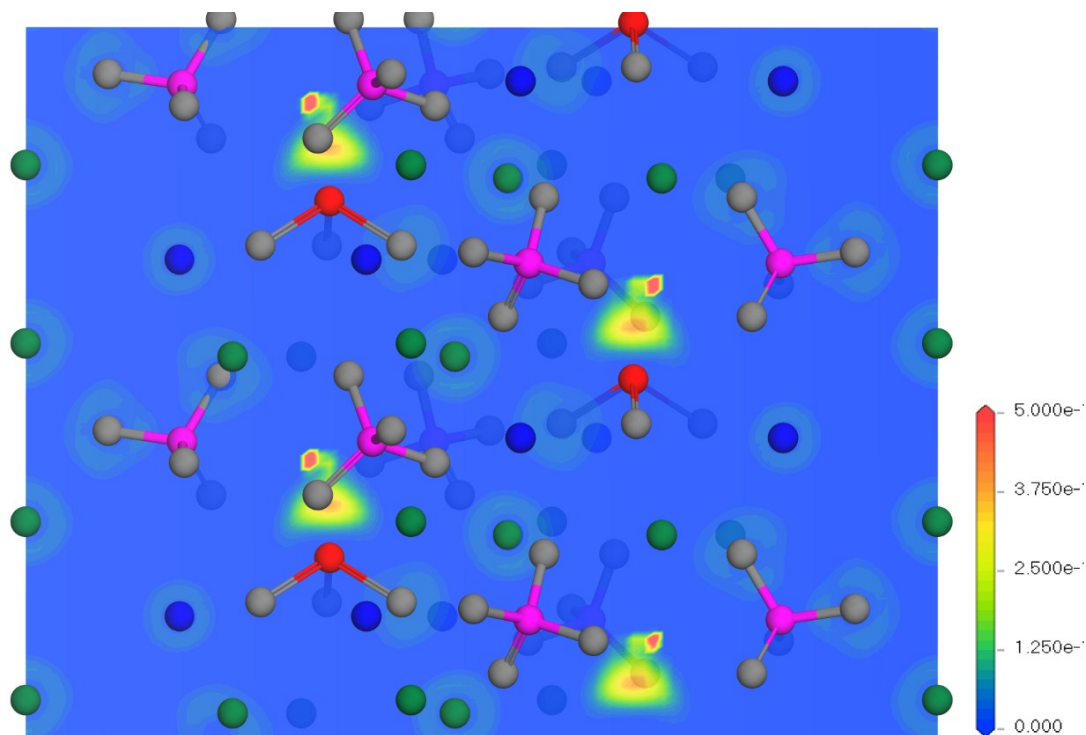
partial DOS (PDOS). The ion–electron interactions were modeled by the optimized ultrasoft pseudo–potentials for elements in the compound. The optimized norm–conserving pseudopotentials in the Kleinman–Bylander form for all the elements are used to model the effective interaction between atom cores and valence electrons. And Na $2p^64s^1$, Ca $3p^64s^2$, P $3s^23p^3$, Te $5s^25p^4$, O $2s^22p^4$ electrons were treated as valence electrons, allowing the adoption of a relatively small basis set without compromising the computational accuracy. The high kinetic energy cutoff 700 eV and dense $4\times4\times4$ Monkhorst–Pack k–point meshes in the Brillouin zones were chosen for $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$. Our tests showed that the above computational set ups are sufficiently accurate for present purposes.

5. Figure S1



(a) Scanning electron microscopy (SEM) image of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ (b) Elemental analysis of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ by EDX spectroscopy. (c) Elemental distribution of the as-grown crystal (from left to right: Na Ca P Te O).

6. Figure S2



The electron localization function (ELF) isosurfaces for the (110) plane of $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$ (Red balls represent Te atoms).

7. Table S1 Crystallographic data and structure refinement for $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$.

Empirical formula	$\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$
Formula weight	689.80
Space group	$P6_3$
$a/\text{\AA}$	10.7110(3)
$b/\text{\AA}$	10.7110(3)
$c/\text{\AA}$	6.8995(3)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	120.00
$V/\text{\AA}^3$	685.50(5)
Z	2
$\rho_{\text{calc}} \text{ g/cm}^3$	3.342
μ/mm^{-1}	4.197
$F(000)$	660.0
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)
2θ range for data collection/ $^\circ$	7.36 to 52.7
Index ranges	$-13 \leq h \leq 11, -12 \leq k \leq 13, -8 \leq l \leq 8$
Reflections collected	7380
Independent reflections	470 [$R_{\text{int}} = 0.0785$]

Data/restraints/parameters	896/1/80
GOF on F^2	1.196
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0409$, $wR_2 = 0.0965$
Final R indexes [all data]	$R_1 = 0.0409$, $wR_2 = 0.0965$

8. Table S2 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	Wyckoffsite	U(eq)
Na1	-1594(5)	-3213(6)	-16557(9)	6c	8.9(11)
Ca1	-575(3)	-5300(3)	-9263(4)	6c	12.6(7)
Ca2	0	-10000	-13765(14)	2a	42.3(17)
P1	-1727(4)	-8242(4)	-11596(5)	6c	10.9(8)
Te1	-3333	-6667	-14815(2)	2b	8.1(5)
O1	-4070(30)	-5700(40)	-16113(18)	6c	105(11)
O2	-750(20)	-6870(20)	-12600(40)	6c	88(9)
O3	-3020(20)	-9170(20)	-12800(40)	6c	90(9)
O4	-948(14)	-9063(14)	-11160(20)	6c	31(3)
O5	-2205(13)	-7824(13)	-9720(20)	6c	32(3)

9. Table S3 Selected bond lengths (\AA) and angles ($^\circ$) for $\text{Na}_3\text{Ca}_4(\text{TeO}_3)(\text{PO}_4)_3$.

P–O \times 1	1.480(16)	O–P–O \times 1	106.3(12)
P–O \times 1	1.489(15)	O–P–O \times 1	110.1(9)
P–O \times 1	1.514(12)	O–P–O \times 1	111.3(16)
P–O \times 1	1.536(14)	O–P–O \times 1	109.3(13)
Te–O \times 3	1.822(13)	O–P–O \times 1	108.4(9)
O–P–O \times 1	111.4(8)	O–Te–O \times 3	97.9(5)