Electronic Supplementary Material (ESI) for Dalton Transactions.

Hybrid organic-inorganic triguanidine arsenate dihydrate for ultraviolet nonlinear optical application

Dongmei Wang [a, b], Zhuangzhuang Wei [a, b, d], Zhiyong Bai [a, e], Lehui Liu [a, c], Zhoubin Lin[a, c*, e], Lizhen Zhang [a, c*, e]

[a] Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China

[b] College of Chemistry and Materials Science, Fujian Normal University, Fuzhou ,350007, China

[c] Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian, 350108, China

[d] Xiamen Key Laboratory of Rare Earth Photoelectric Functional Materials, Xiamen Institute of Rare Earth Materials, Haixi Institutes, Chinese Academy of Sciences, Xiamen 361021, P. R. China

[e] University of Chinese Academy of Sciences, Beijing 100049, P. R. China

*Corresponding author, E-mail: lzb@fjirsm.ac.cn; lzzhang@fjirsm.ac.cn.

Crystal Growth. As source materials, the chemical reagents $[C(NH_2)_3]_2CO_3$ (99%, Aladdin) and $NH_4H_2AsO_4$ (98%, Alfa Aesar), ethanol (AR) were received without further purification. Initially, the mixture of $[C(NH_2)_3]_2CO_3$ and $NH_4H_2AsO_4$ with molar ratio 3:2 were dissolved in the deionized water and magnetically stirred at 35 ℃ for 1 h. The solution was evaporated at room temperature for several days, and then colorless rod-shaped single crystals with the largest length of about 20 mm were obtained. The obtained crystals were recrystallized in the solvent composed of certain ratio of deionized water and ethanol. Through evaporating the solution at room temperature for days, transparent and wafer well-developed bulk single crystals were obtained.

Powder X-ray Diffraction. X-ray powder diffraction measurement was obtained with the Miniflex 600 diffractometer using Cu Kα radiation (λ = 1.5406 Å). Data were collected from the 2θ range 10~70° with an increment of 8°/min at room temperature. The experimental powder X-ray diffraction results and theoretical simulation patterns present good agreement.

Single Crystal X-ray Diffraction. The single crystal X-ray diffraction data for the compounds were collected using a Rigaku ROD, Synergy Custom system, HyPix diffractometer operating with Ga Kα radiation (λ=1.3405Å) at 100 K (GZCO and GZSO) and 235 K (GAO), respectively. All the collected data were corrected for Lorentz, polarization factors and absorption. Using the Olex2 program, the structure was solved and refined with the ShelXT structure solution program and the ShelXL refinement package, respectively. All of the atom corrections were carried out with anisotropic displacement parameters and secondary extinction correction. The structures were checked by Platon for searching missing symmetry elements and no higher symmetries were found. All of the Crystallographic data are listed in Tables S1 to S6.

UV-Vis-NIR Transmittance Spectrum. The UV-Vis-NIR transmittance spectrum in the wavelength region 200-800 nm was gathered using the Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer.

Thermal Analysis. Thermogravimetric (TG) analysis was characterized with a NETZSCH STA 449F3 technique. Sample powder (~10 mg) was placed in a crucible under the flowing argon atmosphere and the temperature was increased from 30 ℃ to 1000 ℃ with a rate of 10 ℃/ min.

Powder SHG Measurement. The powder SHG characteristic of guanidinium-based crystals were employed for the method described in the reference[1] using Q-switched Nd:YAG solid-state laser at a wavelength of 1064 nm. To investigate its phase-matching behavior and the SHG efficiencies of every crystal, the polycrystalline of all the crystals were ground in a mortar and sieved into several different particle size ranges. Meanwhile, KDP sample particles with corresponding size were used as the standard for comparison.

Computational Descriptions. The band structure and the partial density of state were calculated by the VASP[2], a plane-wave pseudopotential density functional theory (DFT) package. The exchange-correlation functionals were Perdew-Burke-Emzerhof (PBE) functional within the generalized gradient approximation (GGA)[3]. The number of plane waves included in the basis sets was determined by a cutoff energy of 420 eV. And the Γ-centered 3 ×3× 2 *k*-point sampling mesh was used for GZCO and GZSO, the Γ-centered 4 ×2× 2 *k*-point sampling mesh was adopted for GAO. The convergence criteria for energy and force are tightened to 1×10^{-4} eV and -0.05 eV/ Å in all of the calculations.

Birefringence Measurement. The measurements of birefringence were carried out using a polarizing microscope (ZEISS Axio Scope. A1) which equipped with Berek compensator and 546 nm light source.

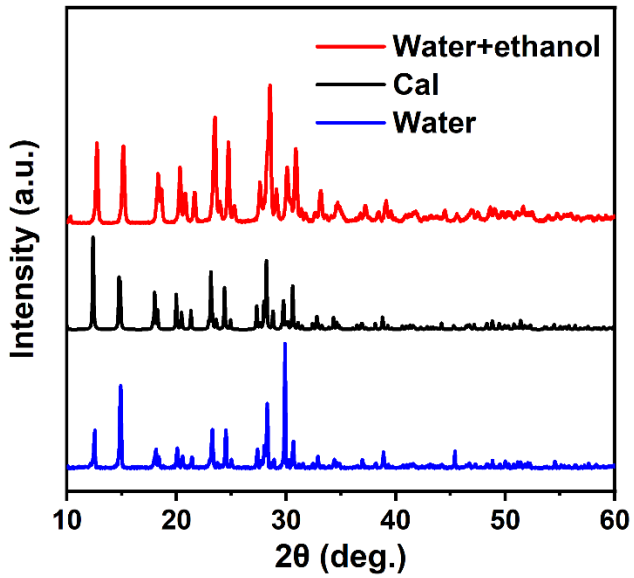

Figure S1. The powder XRD patterns.

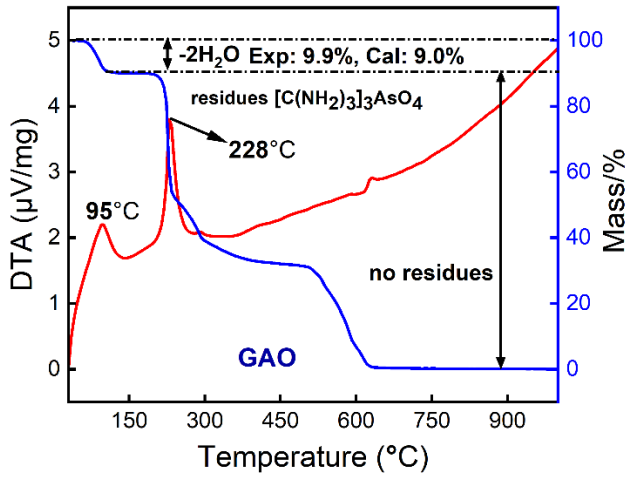

Figure S2. TG/DSC curves.

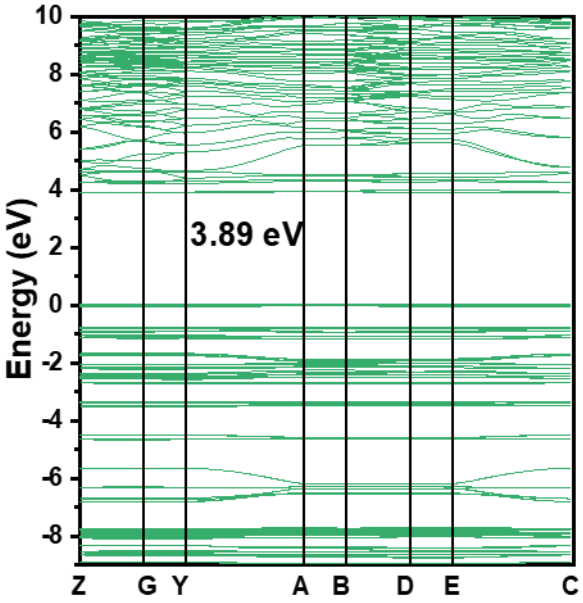

Figure S3. Band structure.

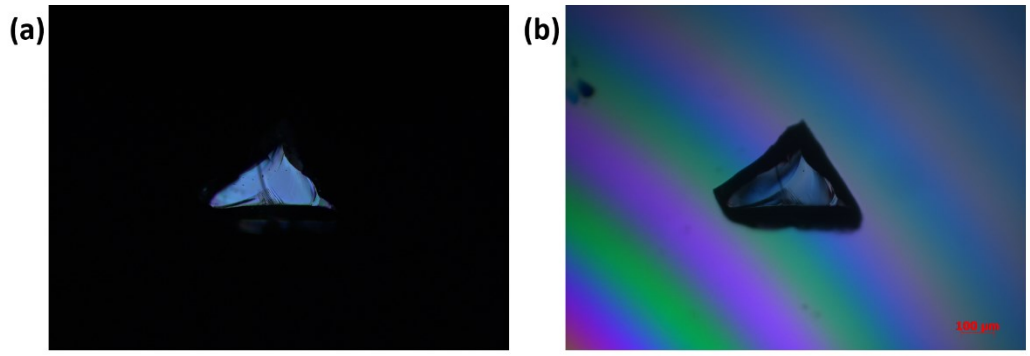

Figure S4. Birefringence measurement of GAO. (a) is complementary color before and (b) is complementary color after.

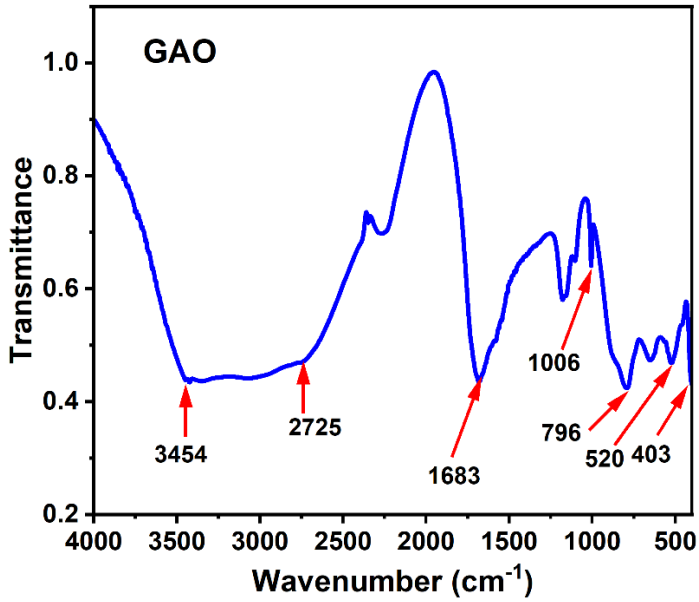

Figure S5. IR spectrum of GAO. The absorption bands from 3454-2725 cm^{-1} are ascribed to vibration of hydron bonds, and the absorption peak at 1683 cm^{-1} can be ascribed to the vibration of N-H bonds in $(NH_2)^{-1}$. The peaks at 1006 cm^{-1} and 796 cm^{-1} were assigned to the asymmetric stretching vibration and symmetric stretching vibration of As-O in AsO_4, respectively, while the bending vibration absorptions could be observed at 403 and 520 cm^{-1}.

Table S1. Crystal data and structure refinement for GAO.

Crystal data and structure refinement for GAO	
Empirical formula	$C_3H_{22}AsN_9O_6$
Formula weight	355.21
Temperature/K	235(30)
Crystal system	monoclinic
Space group	*Cc*
a/Å	6.5850(3)
b/Å	17.7646(7)
c/Å	12.3972(5)
α/°	90
β/°	104.506(4)
γ/°	90
Volume/Å^3	1403.99(11)
Z	4
ρ_{calc} g/cm^3	1.680
μ/mm^{-1}	2.497
F (000)	736.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	GaKα (λ = 1.3405)
2 θ range for data collection/°	8.656 to 103.606
Index ranges	$-7 \le h \le 7$, $-20 \le k \le 20$, $-14 \le l \le 14$
Reflections collected	11259
Independent reflections	2341 [R_{int} = 0.0366, R_{sigma} = 0.0261]
Data/restraints/parameters	2341/6/187
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0183, wR_2 = 0.0431
Final R indexes [all data]	R_1 = 0.0188, wR_2 = 0.0433
Largest diff. peak/hole / e Å^{-3}	0.15/-0.17
Flack parameter	0.003(13)

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for GAO. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
As_1	5227.8(2)	6481.8(2)	5615.8(2)	18.30(13)
N_1	6441(5)	3660.1(18)	7738(3)	31.3(8)
N_2	11609(5)	4324.3(16)	7872(2)	29.7(7)
N_3	11413(5)	3039.9(17)	7859(3)	32.0(8)
O_1	3973(3)	7287.1(12)	5130.9(18)	26.3(5)
C_1	11492(5)	3505.4(17)	3077(3)	22.9(7)
O_2	7459(4)	6410.6(12)	5188(2)	28.1(6)
N_4	6554(5)	4951.6(17)	7808(2)	33.2(7)
N_5	9917(5)	3277.9(19)	3454(3)	32.9(7)
O_3	3640(4)	5746.5(13)	5185.0(19)	30.2(5)
N_6	11103(5)	3925.7(15)	2144(2)	26.6(6)
N_7	10119(5)	3695.4(16)	6247(2)	29.8(7)
C_2	11043(5)	3688.9(19)	7314(3)	24.1(7)
C_3	6021(5)	4321.5(19)	7232(3)	25.3(7)
O_4	5890(4)	6481.0(11)	7024.6(19)	26.7(6)
O_5	5182(6)	2617.4(12)	5673(4)	33.4(5)
O_6	9578(5)	4871.7(15)	39(2)	34.5(6)
N_8	13470(6)	3374.9(18)	3598(3)	37.3(9)
N_9	5084(5)	4353.7(17)	6162(2)	32.3(7)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for GAO. The Anisotropic displacement factor exponent takes the form: -$2π^2[h2a*2U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As_1	18.40(18)	17.27(18)	18.75(17)	0.9(2)	3.78(11)	0.2(2)
N_1	36(2)	24.7(16)	32.8(18)	3.7(14)	7.9(15)	3.8(14)
N_2	36.1(16)	20.9(15)	31.4(15)	0.4(12)	6.9(13)	2.5(13)
N_3	40(2)	22.7(16)	28.4(16)	1.8(13)	0.3(14)	-0.5(14)
O_1	29.0(13)	20.1(12)	28.3(12)	4.0(10)	4.4(10)	3.9(10)
C_1	26.5(19)	17.8(17)	22.9(17)	-6.1(12)	3.8(14)	-0.2(12)
O_2	24.4(13)	28.1(13)	35.1(13)	-3.9(9)	13.5(11)	-0.8(9)
N_4	44.1(18)	22.8(15)	28.1(15)	4.1(12)	0.2(13)	0.2(14)
N_5	26.9(17)	42(2)	29.0(17)	8.9(15)	4.6(13)	-3.1(15)
O_3	28.0(12)	23.1(12)	34.8(13)	2.8(10)	-1.3(10)	-5.6(10)
N_6	27.9(14)	27.3(16)	23.8(14)	0.4(12)	4.8(11)	-1.1(12)
N_7	36.7(18)	25.0(15)	24.8(16)	0.5(13)	2.4(13)	-2.3(13)
C_2	21.1(17)	22.4(18)	31(2)	1.7(15)	9.9(14)	1.5(14)
C_3	22.9(16)	24.7(17)	30.1(18)	3.9(14)	10.0(14)	2.9(14)
O_4	33.2(14)	27.6(13)	18.6(12)	1.3(9)	5.4(10)	1.9(10)
O_5	34.2(12)	24.6(11)	42.7(13)	0.7(17)	11.7(10)	-0.2(17)
O_6	39.7(16)	27.6(15)	35.9(14)	0.9(11)	8.6(12)	1.2(12)
N_8	28.3(19)	44(2)	38.5(19)	11.3(16)	6.3(15)	4.5(15)
N_9	39.9(18)	25.2(16)	28.8(15)	0.4(13)	2.8(13)	1.0(13)

Table S4. Bond Lengths for GAO.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
As_1	O_1	1.686(2)	C_1	N_5	1.304(5)
As_1	O_2	1.687(2)	C_1	N_6	1.346(4)
As_1	O_3	1.675(2)	C_1	N_8	1.322(5)
As_1	O_4	1.691(2)	N_4	C_3	1.326(5)
N_1	C_3	1.328(5)	N_7	C_2	1.311(5)
N_2	C_2	1.328(5)	C_3	N_9	1.317(4)
N_3	C_2	1.327(5)			

Table S5. Bond Angles for GAO.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O_1	As_1	O_2	109.81(11)	N_8	C_1	N_6	118.0(3)
O_1	As_1	O_4	110.22(10)	N_2	C_2	N_3	118.8(3)
O_2	As_1	O_4	107.77(12)	N_7	C_2	N_2	121.1(3)
O_3	As_1	O_1	109.70(12)	N_7	C_2	N_3	120.1(3)
O_3	As_1	O_2	111.38(11)	N_1	C_3	N_4	119.8(3)
O_3	As_1	O_4	107.92(11)	N_9	C_3	N_1	120.2(3)
N_5	C_1	N_6	118.9(3)	N_9	C_3	N_4	119.9(3)
N_5	C_1	N_8	123.1(3)				

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for GAO.

Atom	*x*	*y*	*z*	U(eq)
H_1A	6097.1	3245.98	7361.51	38
H_1B	7060.05	3640.67	8444.81	38
H_2A	11367.99	4754.85	7529.2	36
H_2B	12220.85	4310.29	8580.38	36
H_3A	11042.87	2618.38	7507.2	38
H_3B	12026.73	3036.04	8567.24	38
H_4A	6284.65	5385.64	7477.89	40
H_4B	7172.96	4930.8	8514.77	40
H_5A	10144.95	3027.49	4075.86	40
H_5B	8638.17	3376.36	3083.45	40
H_6A	12138.65	3880.21	1813.41	32
H_6B	9931.18	3787.92	1662.32	32
H_7A	9866.59	4121.22	5891.91	36
H_7B	9757.46	3273.95	5893.55	36
H_5C	4340(60)	2250(20)	5550(40)	50
H_5D	6320(50)	2440(20)	5570(40)	50
H_6C	8880(70)	4480(20)	180(40)	52
H_8A	13769.89	3126.57	4222.53	45
H_8B	14472.85	3537.36	3315.92	45
H_9A	4738.43	3940.6	5783.36	39
H_9B	4811.49	4787.98	5833.12	39
H_6D	10720(70)	4660(20)	0(40)	48(14)

Table S7. The Dipole Moment of AsO_4 and CN_3 (unit: Debye).

Group	*x*-component	*y*-component	*z*-component	total
As(1)O_4	0.18371736	0.3023044	2.544362	2.568836
	0.30639106	0.2327393	2.54448	2.573407
	0.18361532	-0.302304	2.544088	2.568557
	0.30666479	-0.232558	2.544206	2.573152
C(1)N_3	0.05979394	-0.005701	-0.0068	0.060449
	0.05979417	-0.005728	-0.0068	0.060452
	0.05976373	0.0056795	-0.00679	0.060416
	0.05976373	0.0056795	-0.00679	0.060416
C(2)N_3	0.06799913	-0.182762	0.326856	0.380606
	0.06801395	-0.182762	0.326856	0.380608
	0.06800312	0.1827689	0.326858	0.380611
	0.0680477	0.1827488	0.32686	0.380611
C(3)N_3	0.08225378	-1.3523	-0.26458	1.380393
	0.08223093	-1.352288	-0.26458	1.38038
	0.08224616	1.3522873	-0.26457	1.380378
	0.08224616	1.3522873	-0.26457	1.380378

Reference

1. S. K. Kurtz and T. T. Perry, *J. Appl. Phys*., 1968, 39, 3798-3813.
2. G. Kresse, and Furthmüller, *Comput. Mater. Sci*., 1996, 6, 15-50.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, 77, 3865-3868.