Supporting Information

A Promising Mid-Infrared Nonlinear Optical Crystal with Well-balanced Properties

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Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) and the bond valence sum of $PbZnGeO_4$ in asymmetric unit.

Atom	x	y	z	U(eq)	BVS
Pb(01)	3507(1)	5570(1)	1048(2)	13(1)	1.66
Pb(02)	4600(1)	7667(1)	10737(2)	15(1)	1.735
Ge(03)	2974(2)	6764(1)	5477(5)	9(1)	4.008
Ge(04)	7673(2)	5736(1)	377(5)	8(1)	3.958
Zn(5)	10035(3)	4436(1)	457(5)	10(1)	2.03
Zn(6)	6800(3)	6565(1)	5421(6)	10(1)	1.986
O(1)	6013(17)	5218(8)	-400(30)	11(3)	1.586
O(007)	4707(19)	6452(9)	3860(30)	15(4)	1.955
O(008)	7922(19)	5784(8)	3740(30)	12(4)	2.46
O(009)	3270(20)	6800(9)	8810(30)	19(4)	1.62
O(00A)	9395(18)	5345(8)	-930(30)	12(4)	2.43
O(2)	7500(18)	6560(8)	-930(30)	13(3)	2.03
O(3)	2790(20)	7594(9)	4060(30)	18(4)	2.06
O(4)	1438(19)	6261(9)	4430(30)	19(4)	2.12

Table S2. Selected bond lengths (Å) and angles (deg.) for $PbZnGeO_4$.

Pb(01)-O(1)	2.331(14)	Ge(04)-O(2)	1.738(16)
Pb(01)-O(1)#1	2.419(15)	Ge(04)-O(008)	1.747(16)
Pb(01)-O(007)	2.454(17)	Ge(04)-O(1)	1.760(15)
Pb(01)-O(009)#2	2.652(18)	Ge(04)-O(00A)	1.763(15)
Pb(01)-Ge(03)	3.280(3)	Zn(5)-O(4)#5	1.904(17)
Pb(02)-O(009)	2.246(18)	Zn(5)-O(00A)#6	1.972(16)
Pb(02)-O(3)#3	2.293(17)	Zn(5)-O(00A)	1.972(16)
Pb(02)-O(2)#4	2.465(16)	Zn(5)-O(008)#7	1.976(16)
Pb(02)-Ge(03)#3	3.299(3)	Zn(6)-O(007)	1.944(16)
Ge(03)-O(4)	1.702(17)	Zn(6)-O(3)#8	1.957(16)
Ge(03)-O(009)	1.740(17)	Zn(6)-O(2)#3	1.971(16)
Ge(03)-O(3)	1.770(17)	Zn(6)-O(008)	1.981(16)
Ge(03)-O(007)	1.782(16)	O(2)-Ge(04)-O(1)	111.6(7)
O(1)-Pb(01)-O(1)#1	84.7(3)	O(008)-Ge(04)-O(1)	110.4(7)
O(1)-Pb(01)-O(007)	91.3(5)	O(2)-Ge(04)-O(00A)	108.3(7)
O(1)#1-Pb(01)-O(007)	85.5(5)	O(008)-Ge(04)-O(00A)	107.6(7)
O(1)-Pb(01)-O(009)#2	101.1(5)	O(1)-Ge(04)-O(00A)	108.5(7)
O(1)#1-Pb(01)-O(009)#2	155.2(5)	O(4)#5-Zn(5)-O(00A)#6	124.9(7)
O(007)-Pb(01)-O(009)#2	70.3(5)	O(4)#5-Zn(5)-O(00A)	110.8(7)
O(009)-Pb(02)-O(3)#3	87.5(6)	O(00A)#6-Zn(5)-O(00A)	102.6(5)
O(009)-Pb(02)-O(2)#4	86.7(6)	O(4)#5-Zn(5)-O(008)#7	106.5(7)
O(3)#3-Pb(02)-O(2)#4	80.0(6)	O(00A)#6-Zn(5)-O(008)#7	105.2(6)
O(4)-Ge(03)-O(009)	116.3(9)	O(00A)-Zn(5)-O(008)#7	105.4(7)
O(4)-Ge(03)-O(3)	108.9(8)	O(007)-Zn(6)-O(3)#8	109.2(7)
O(009)-Ge(03)-O(3)	112.5(8)	O(007)-Zn(6)-O(2)#3	131.7(6)
O(4)-Ge(03)-O(007)	105.9(8)	O(3)#8-Zn(6)-O(2)#3	102.6(7)
O(009)-Ge(03)-O(007)	111.3(8)	O(007)-Zn(6)-O(008)	99.2(7)
O(3)-Ge(03)-O(007)	100.6(8)	O(3)#8-Zn(6)-O(008)	105.9(7)
O(2)-Ge(04)-O(008)	110.2(7)	O(2)#3-Zn(6)-O(008)	105.9(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+2 #2 -x+3/2,y-1/2,-z+2
#3 x-1/2,y-1/2,z #4 -x+1,y+1,-z+2
#5 x,y+1,z #6 x-1/2,y+1/2,z
#7 -x+3/2,y+1/2,-z+2 #8 -x+3/2,y-1/2,-z+1
#9 x+1/2,y+1/2,z #10 x-1,y,z
#11 x,y-1,z #12 x+1/2,y-1/2,z
#13 -x+2,y,-z+1 #14 -x+2,y-1,-z+1
#15 -x+3/2,y+1/2,-z+1 #16 -x+2,y+1,-z+1

Table S3. The calculated dipole moments for the ZnO_4, GeO_4, and PbO_3, and PbO_4 structural units for $PbZnGeO_4$.

structure units	dipole moments (Debye)
ZnO_4(5)	1.9892
ZnO_4(6)	2.9125
GeO_4(3)	2.8052
GeO_4(4)	0.8281
PbO_3	14.2245
PbO_4	10.9407

Table S4. The key physical properties of PZGO and some advanced NIR and mid-IR NLO crystals.

material	bandgap (eV)	birefrigence	SHG response	IR cutoff (μm)	Ref.
$KTiOPO_4$	~ 3.52	0.092@1064 nm	~ 15 × KDP	~ 4.3	1,2,3
$KTiOAsO_4$	~ 3.50	0.086@1064 nm	~ 12 × KDP	~ 5.3	2,3
$ZnGeP_2$	~ 2.25	0.04@2 μm	~ 160 × KDP	~ 12	4,5
$AgGaS_2$	~ 2.58	0.04@2 μm	~ 35 × KDP	~ 12	6
PZGO	~ 3.70	0.044@1064 nm	~ 2.5 × KDP	~ 5.9	This work

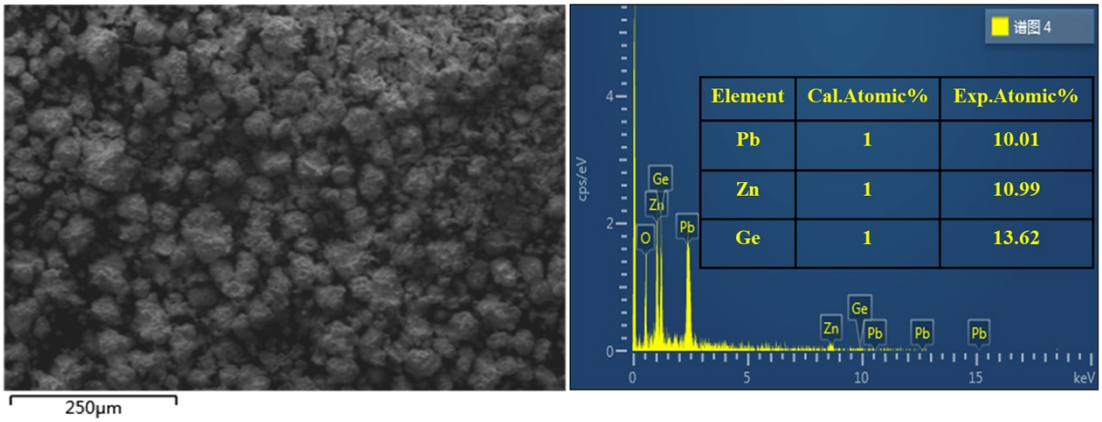

Figure S1. The EDS spectra of PZGO

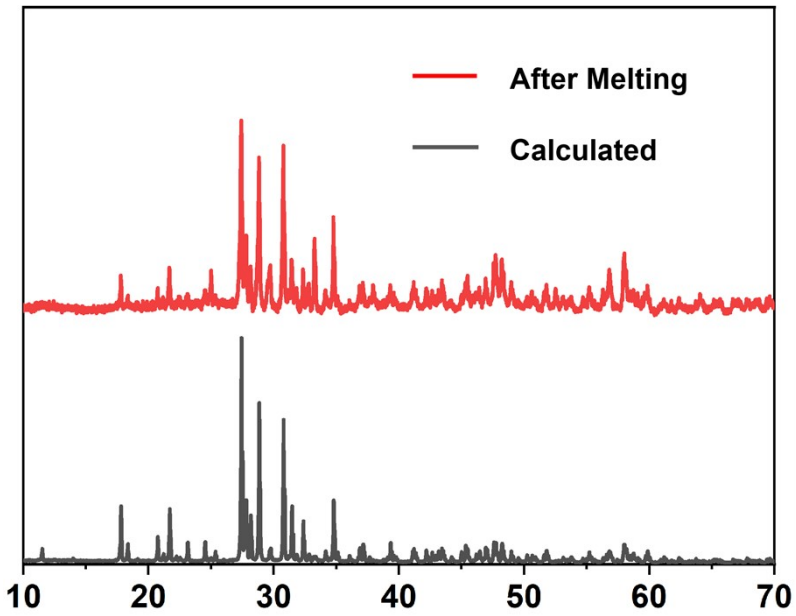

Figure S2. The melted and calculated PXRD patterns of PZGO, respectively

Reference

1. F. Yang, L. Huang, X. Zhao, L. Huang, D. Gao, J. Bi, X. Wang and G. Zou, An energy band engineering design to enlarge the band gap of $KTiOPO_4$ (KTP)-type sulfates via aliovalent substitution., *J. Mater. Chem. C*, 2019, 7, 8131-8138.

2. H. Zhou, X. He, W. Wu, J. Tong, J. Wang, Y. Zuo, Y. Wu, C. Zhang and Z. Hu, Hydrothermal growth of $KTiOPO_4$ crystal for electro-optical application., *Light: Science & Applications*, 2023, **12**, 23.

3. M. V. Pack, D. J. Armstrong and A. V. Smith, Measurement of the $\chi^{(2)}$ tensors of $KTiOPO_4$, $KTiOAsO_4$, $RbTiOPO_4$, and $RbTiOAsO_4$ crystals., *Appl. Opt*., 2004, **43**, 3319-3323.

4. H. Xie, S. Fang, H. Zhao, X. Xu, N. Ye and W. Zhuang, Quasiparticle effects on the linear and nonlinear susceptibility of $ZnGeP_2$., *RSC Adv*., 2019, **9**, 35771-35779.

5. G. D. Boyd, E. Buehler and F. G. Storz, LINEAR AND NONLINEAR OPTICAL PROPERTIES OF $ZnGeP_2$ AND CdSe., *Appl. Phys. Lett*., 1971, **18**, 301-304.

6. H.-M. Zhou, L. Xiong, L. Chen, L.-M. Wu, Dislocations that Decrease Size Mismatch within the Lattice Leading to Ultrawide Band Gap, Large Second-Order Susceptibility, and High Nonlinear Optical Performance of $AgGaS_2$., *Angew. Chem. Int. Ed*., 2019, **58**, 9979-9983.