Electronic Supplementary Information

$Pb_3(SeO_3)Br_4$: A New Nonlinear Optical Material with Enhanced SHG Response Designed via Ion Substitution Strategy

Xiaoxiao Wang[a], Xingxing Jiang[b], Hongming Liu[a], Lei Yang[b], Zheshuai Lin*[,b], Zhanggui Hu[b], Xianggao Meng[c], Xingguo Chen*[a], Jingui Qin[a]

[a] *Hubei Key Laboratory on Organic and Polymeric Opto-electronic Materials, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China. Email: xgchen@whu.edu.cn*

[b] *Beijing Center for Crystal R&D, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Email: zslin@mail.ipc.ac.cn*

[c] *College of Chemistry, Central China Normal University, Wuhan 430079, China.*

Figure S1. Simulated and measured powder X-ray diffraction patterns of $Pb_3(SeO_3)Br_4$.

Figure S2. The EDX spectrum of $Pb_3(SeO_3)Br_4$ crystal.

Figure S3. The different bonding environments of three Pb atoms in $Pb_3(SeO_3)Br_4$.

Figure S4. The comparison of the different Pb-O bond lengths around SeO_3^{2-} group in $Pb_3(SeO_3)Br_4$ in this work and TeO_3^{2-} group in $Pb_3(TeO_3)Cl_4$.

Figure S5. IR and Raman spectra of $Pb_3(SeO_3)Br_4$。

Figure S6. Oscilloscope traces of the SHG signals of KDP and $Pb_3(SeO_3)Br_4$ at the powder size of 200–300 μm.

Figure S7. The TGA curve of $Pb_3(SeO_3)Br_4$.

Figure. S8 The calculated refractive index of $Pb_3(SeO_3)Br_4$.

Table S1. Selected bond lengths (Å) and calculated bond valenses for $Pb_3(SeO_3)Br_4$.

Table S2. Selected bond angles (°) for $Pb_3(SeO_3)Br_4$.

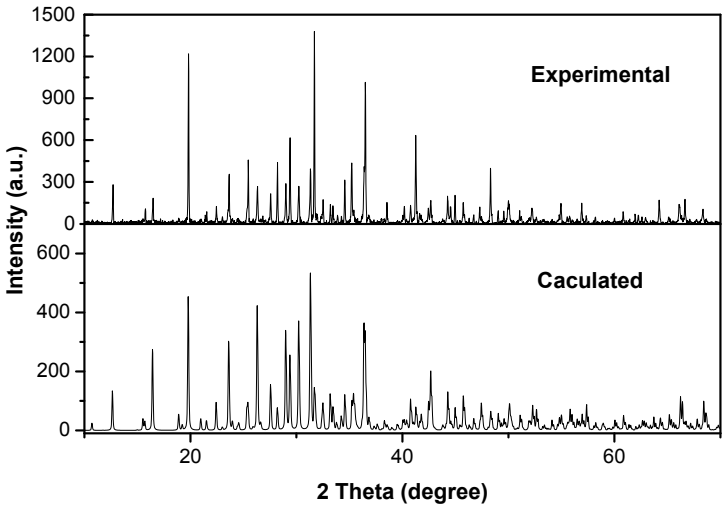

Figure S1. Simulated and measured powder X-ray diffraction patterns of $Pb_3(SeO_3)Br_4$.

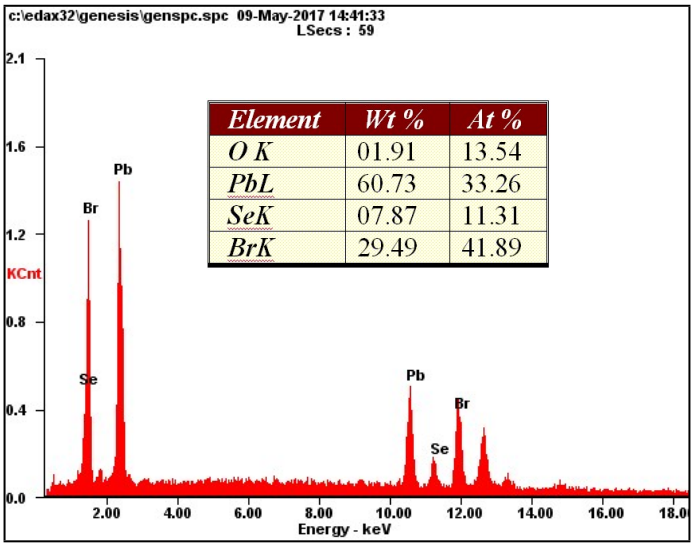

Figure S2. The EDX spectrum of $Pb_3(SeO_3)Br_4$ crystal.

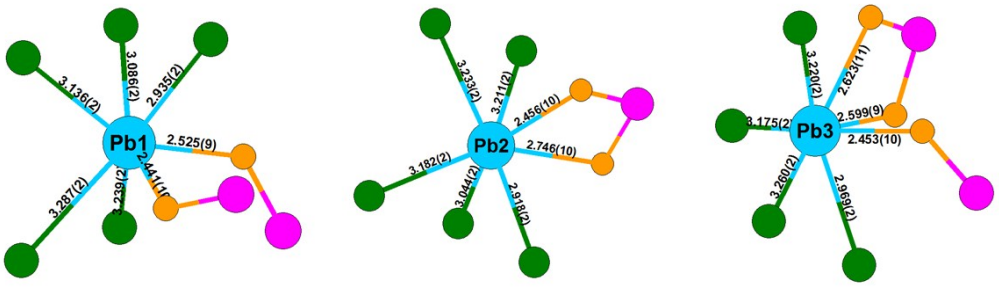

Figure S3. The different bonding environments of three Pb atoms in $Pb_3(SeO_3)Br_4$

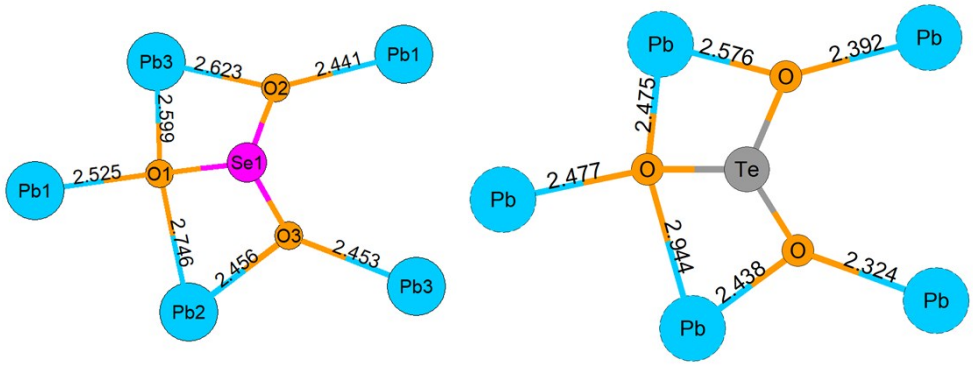

Figure S4. The comparison of the different Pb-O bond lengths around SeO_3^{2-} group in $Pb_3(SeO_3)Br_4$ (in this work) and TeO_3^{2-} group in $Pb_3(TeO_3)Cl_4$ (in ref. 1)。

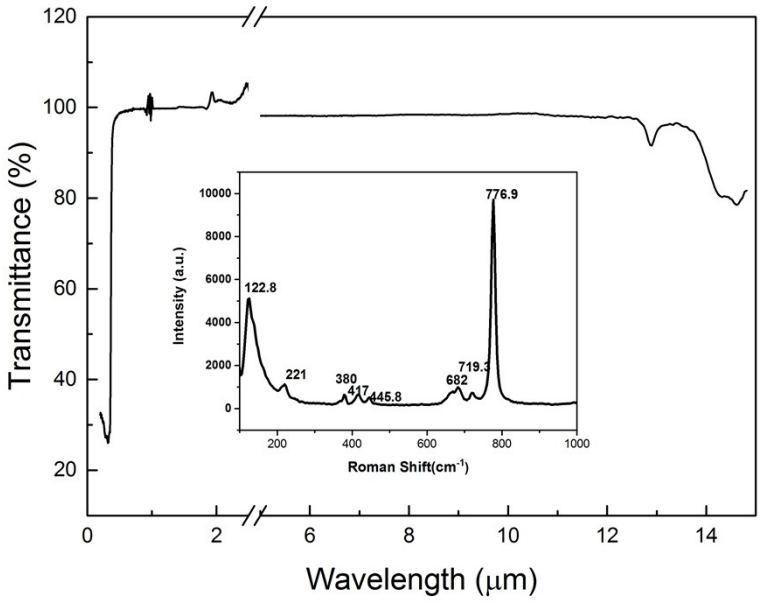

Figure S5. IR and Raman spectra of $Pb_3(SeO_3)Br_4$.

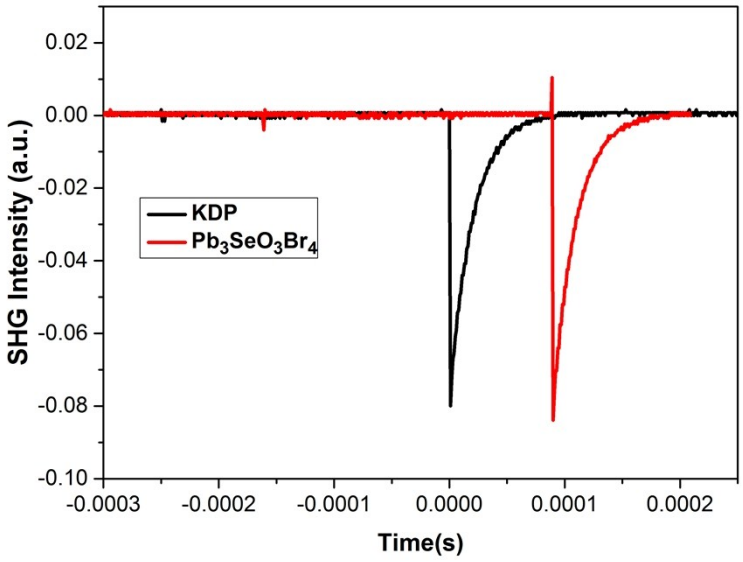

Figure S6. Oscilloscope traces of the SHG signals of KDP and $Pb_3(SeO_3)Br_4$ at the powder size of 200–300 μm.

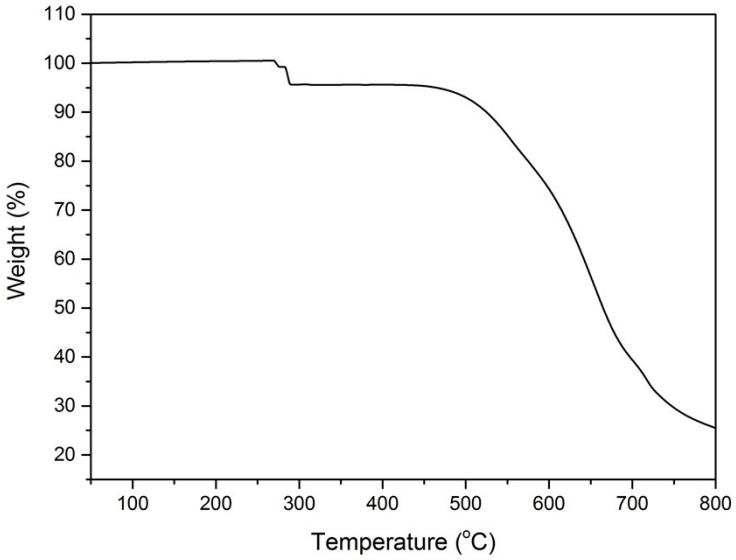

Figure S7. The TGA curve of $Pb_3(SeO_3)Br_4$.

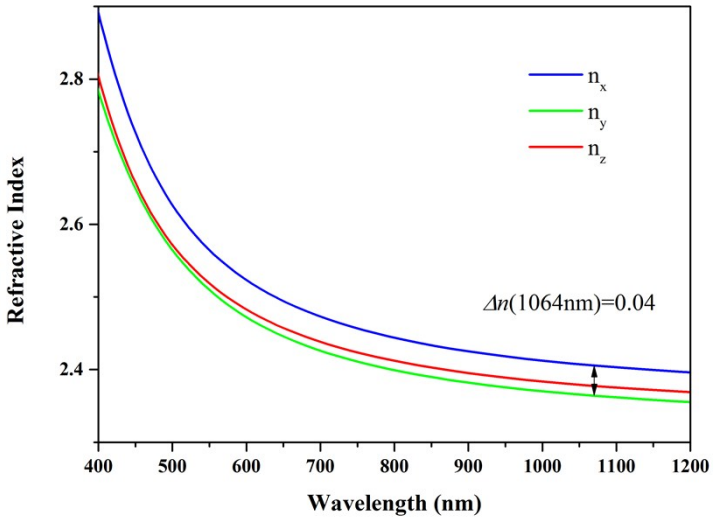

Figure S8. The calculated refractive index of $Pb_3(SeO_3)Br_4$.

Table S1. Selected bond lengths (Å) and calculated bond valenses for $Pb_3(SeO_3)Br_4$.

	bond length (Å)	bond valence		bond length (Å)	bond valence
Pb(1)-O(2)#1	2.441(10)	0.409	Pb(2)-O(3)#5	2.457(10)	0.391
Pb(1)-O(1)	2.525(10)	0.335	Pb(2)-O(1)#5	2.747(10)	0.178
Pb(1)-Br(3)	2.9354(18)	0.425	Pb(2)-Br(1)#6	2.9185(19)	0.444
Pb(1)-Br(4)#2	3.0863(17)	0.283	Pb(2)-Br(4)#7	3.0463(17)	0.315
Pb(1)-Br(2)	3.1360(17)	0.246	Pb(2)-Br(2)	3.1827(17)	0.217
Pb(3)-O(3)#3	2.453(10)	0.400	Pb(2)-Br(4)	3.2114(18)	0.201
Pb(3)-O(1)#4	2.599(9)	0.265	Pb(2)-Br(2)#8	3.2322(17)	0.189
Pb(3)-O(2)#4	2.623(11)	0.253	Se(1)-O(3)	1.698(10)	1.361
Pb(3)-Br(3)#4	2.9691(17)	0.388	Se(1)-O(2)	1.701(11)	1.350
Pb(3)-Br(1)	3.1754(18)	0.221	Se(1)-O(1)	1.733(9)	1.213
Pb(3)-Br(2)	3.2197(16)	0.196			

Table S2. Selected bond angles (°) for $Pb_3(SeO_3)Br_4$.

O(2)#1-Pb(1)-O(1)	90.8(4)	O(2)#1-Pb(1)-Br(3)	80.3(3)
O(1)-Pb(1)-Br(3)	77.3(2)	O(2)#1-Pb(1)-Br(4)#2	159.4(3)
O(1)-Pb(1)-Br(4)#2	80.9(2)	Br(3)-Pb(1)-Br(4)#2	79.44(5)
O(2)#1-Pb(1)-Br(2)	94.0(3)	O(1)-Pb(1)-Br(2)	151.6(2)
Br(3)-Pb(1)-Br(2)	75.91(4)	Br(4)#2-Pb(1)-Br(2)	84.98(4)
O(2)#1-Pb(1)-Br(4)#3	115.3(3)	O(1)-Pb(1)-Br(4)#3	68.1(2)
Br(3)-Pb(1)-Br(4)#3	141.61(5)	Br(4)#2-Pb(1)-Br(4)#3	79.13(2)
Br(2)-Pb(1)-Br(4)#3	132.91(4)	O(3)#4-Pb(3)-O(1)#5	76.0(3)
O(3)#4-Pb(3)-O(2)#5	71.2(3)	O(1)#5-Pb(3)-O(2)#5	59.4(3)
O(3)#4-Pb(3)-Br(3)#5	79.1(2)	O(1)#5-Pb(3)-Br(3)#5	75.6(2)
O(2)#5-Pb(3)-Br(3)#5	130.4(2)	O(3)#4-Pb(3)-Br(1)	147.8(3)
O(1)#5-Pb(3)-Br(1)	71.9(2)	O(2)#5-Pb(3)-Br(1)	94.0(3)
Br(3)#5-Pb(3)-Br(1)	90.70(5)	O(3)#4-Pb(3)-Br(2)	76.6(2)
O(1)#5-Pb(3)-Br(2)	123.6(2)	O(2)#5-Pb(3)-Br(2)	65.4(2)
Br(3)#5-Pb(3)-Br(2)	143.05(5)	Br(1)-Pb(3)-Br(2)	124.02(5)
O(3)#6-Pb(2)-O(1)#6	58.9(3)	O(3)#6-Pb(2)-Br(1)#7	92.8(3)
O(1)#6-Pb(2)-Br(1)#7	74.3(2)	O(3)#6-Pb(2)-Br(4)#8	136.3(2)
O(1)#6-Pb(2)-Br(4)#8	78.4(2)	Br(1)#7-Pb(2)-Br(4)#8	83.19(5)
O(3)#6-Pb(2)-Br(2)	135.8(2)	O(1)#6-Pb(2)-Br(2)	151.4(2)
Br(1)#7-Pb(2)-Br(2)	79.95(5)	Br(4)#8-Pb(2)-Br(2)	86.51(4)
O(3)#6-Pb(2)-Br(4)	75.1(3)	O(1)#6-Pb(2)-Br(4)	66.3(2)
Br(1)#7-Pb(2)-Br(4)	139.50(5)	Br(4)#8-Pb(2)-Br(4)	80.20(2)
Br(2)-Pb(2)-Br(4)	134.96(4)	O(3)#6-Pb(2)-Br(2)#9	76.3(2)
O(1)#6-Pb(2)-Br(2)#9	129.4(2)	Br(1)#7-Pb(2)-Br(2)#9	133.83(5)
Br(4)#8-Pb(2)-Br(2)#9	134.70(5)	Br(2)-Pb(2)-Br(2)#9	78.04(2)
Br(4)-Pb(2)-Br(2)#9	81.42(4)	O(3)-Se(1)-O(2)	102.8(5)
O(3)-Se(1)-O(1)	97.0(5)	O(2)-Se(1)-O(1)	97.9(5)
Pb(1)-Br(2)-Pb(2)	86.66(4)	Pb(1)-Br(2)-Pb(3)	116.67(5)
Pb(2)-Br(2)-Pb(3)	122.28(5)	Pb(1)-Br(2)-Pb(2)#2	89.67(5)
Pb(2)-Br(2)-Pb(2)#2	153.87(5)	Pb(3)-Br(2)-Pb(2)#2	82.27(4)
Pb(2)#10-Br(4)-Pb(1)#9	84.84(4)	Pb(2)#10-Br(4)-Pb(2)	152.84(6)
Pb(1)#9-Br(4)-Pb(2)	90.95(5)	Pb(2)#10-Br(4)-Pb(1)#6	91.88(5)
Pb(1)#9-Br(4)-Pb(1)#6	152.75(5)	Pb(2)-Br(4)-Pb(1)#6	79.73(4)
Pb(1)-Br(3)-Pb(3)#11	91.80(5)	Pb(2)#12-Br(1)-Pb(3)	96.49(5)
Se(1)-O(1)-Pb(1)	128.8(5)	Se(1)-O(1)-Pb(3)#11	101.3(4)
Pb(1)-O(1)-Pb(3)#11	111.7(4)	Se(1)-O(1)-Pb(2)#3	95.0(4)
Pb(1)-O(1)-Pb(2)#3	103.2(3)	Pb(3)#11-O(1)-Pb(2)#3	116.6(4)
Se(1)-O(3)-Pb(3)#13	131.7(5)	Se(1)-O(3)-Pb(2)#3	107.1(5)
Pb(3)#13-O(3)-Pb(2)#3	119.6(4)	Se(1)-O(2)-Pb(1)#14	127.5(5)
Se(1)-O(2)-Pb(3)#11	101.3(4)	Pb(1)#14-O(2)-Pb(3)#11	125.5(4)

References

1. S. Y. Zhang, C. L. Hu, P. X. Li, H. L. Jiang, J. G. Mao, *Dalton. Trans.*, 2012, 41, 9532-9542.