*Supporting Information for*

# Highly Polarized [$GeOTe_3$] Motif-Driven Structure Order Exaltation and Enhanced Second Harmonic Generation Response in the New Nonlinear Optical Oxytelluride $Ba_3Ge_2O_4Te_3$

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**Table S1**: Atomic Coordinates, equivalent isotropic displacement parameters, and bond valence sums (BVS) for $Ba_3Ge_2O_4Te_3$.

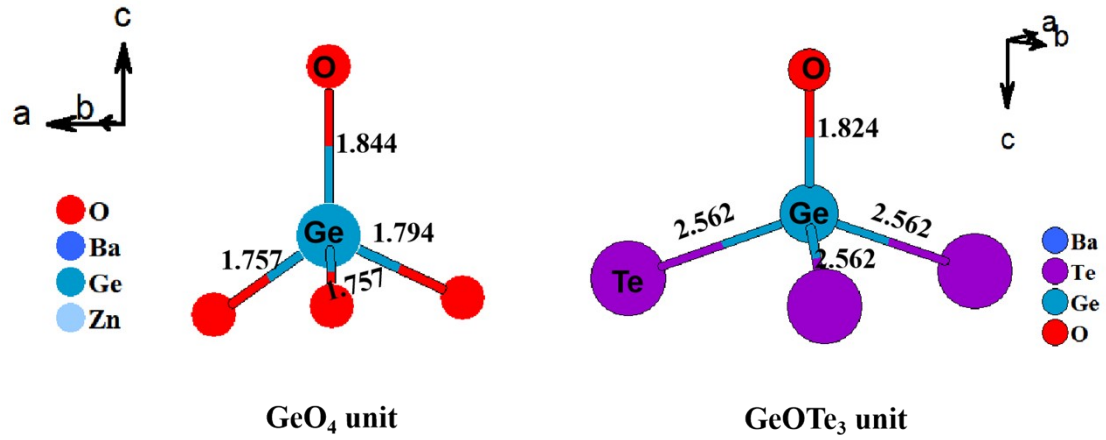
| Atom | Wyckoff site | x | y | z | $U_{eq}$ | BVS |
|---|---|---|---|---|---|---|
| Ba1 | 9b | 0.47554(6) | 0.5244.6(6) | 0.39915(10) | 0.0133(4) | 2.087 |
| Ge1 | 3a | 0.6667 | 0.3333 | 0.6785(4) | 0.0146(7) | 3.772 |
| Ge2 | 3a | 0.6667 | 0.3333 | 0.2899(4) | 0.0144(8) | 4.166 |
| O1 | 9b | 0.5818(6) | 0.4182(6) | 0.2210(14) | 0.014(2) | −2.125 |
| O2 | 9b | 0.64303(0) | 0.3570(30) | 0.4800(50) | 0.0402(0) | −1.821 |
| Te1 | 9b | 0.53959(7) | 0.46041(7) | 0.77531(14) | 0.0161(4) | −1.954 |

**Table S2**: Selected bond Lengths (Å) and Angles (°) for $Ba_3Ge_2O_4Te_3$.

| | | | |
|---|---|---|---|
| Lengths (Å) | | | |
| Ba1− O1[3] | 2.732(7) | Ge1− O2[9] | 1.83(4) |
| Ba1− O1[1] | 2.732(7) | Ge1− O2 | 1.83(4) |
| Ba1− O1 | 2.573(12) | Ge1− Te1[9] | 2.5625(18) |
| Ba1− O2 | 3.26(5) | Ge1− Te1 | 2.5625(18) |
| Ba1− Te1[4] | 3.6580(12) | Ge1− Te1[8] | 2.5625(18) |
| Ba1− Te1[5] | 3.7967(8) | Ge2− O1[8] | 1.723(12) |
| Ba1− Te1[6] | 3.6580(12) | Ge2− O1[9] | 1.723(12) |
| Ba1− Te1 | 3.5877(15) | Ge2− O1 | 1.723(12) |
| Ba1− Te1[7] | 3.7967(8) | Ge2− O2 | 1.76(4) |
| Ge1− O2[8] | 1.83(4) | Ge2− O2[8] | 1.76(4) |
| Angles (°) | | | |
| O2[8]− Ge1− O2[9] | 24(3) | O1[8]− Ge2− O2[9] | 117.7(8) |
| O2[8]− Ge1− O2 | 24(3) | O1− Ge2− O2[8] | 117.7(8) |
| O2[9]− Ge1− O2 | 24(3) | O1[9]− Ge2− O2[9] | 96.4(18) |
| O2[8]− Ge1− Te1[8] | 95.8(17) | O1− Ge2− O2[9] | 117.7(8) |
| O2− Ge1− Te1 | 95.8(17) | O1[9]− Ge2− O2 | 117.7(8) |
| O2− Ge1− Te1[8] | 116.3(7) | O1[8]− Ge2− O2[8] | 96.4(18) |
| O2[9]− Ge1− Te1[8] | 116.3(7) | O1[8]− Ge2− O1[9] | 107.9(5) |
| O2[8]− Ge1− Te1[9] | 116.3(7) | O1[8]− Ge2− O1 | 107.9(5) |
| O2[8]− Ge1− Te1 | 116.3(7) | O1[9]− Ge2− O1 | 107.9(5) |
| O2[9]− Ge1− Te1[9] | 95.8(17) | O1−Ge2−O2 | 96.4(18) |
| O2− Ge1− Te1[9] | 116.3(7) | O1[8]− Ge2− O2 | 117.7(8) |
| O2[9]− Ge1− Te1 | 116.3(7) | O1[9]− Ge2− O2[8] | 117.7(8) |
| Te1[9]− Ge1− Te1[8] | 109.11(8) | O2[8]− Ge2− O2 | 25(3) |
| Te1[9]− Ge1− Te1 | 109.11(8) | O2[9]− Ge2− O2[8] | 25(3) |
| Te1[8]− Ge1− Te1 | 109.11(8) | O2[9]− Ge2− O2 | 25(3) |

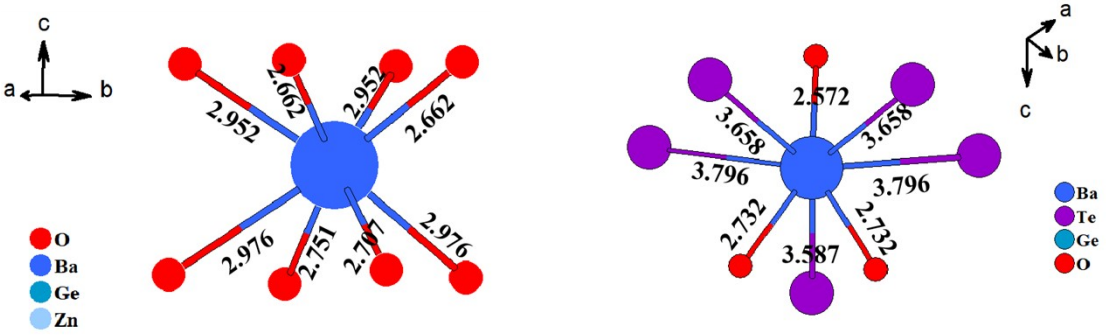
Symmetry codes: [1]-1/3+X,1/3+Y,1/3+Z; [2]2/3+Y-X,4/3-X,1/3+Z; [3]2/3+Y-X,4/3-X,-2/3+Z; [4]1/3+Y-X,2/3-X,-1/3+Z; [5]2/3-Y,1/3+X-Y,-2/3+Z; [6]4/3-Y,2/3+X-Y,-1/3+Z; [7]2/3-Y,1/3+X-Y,1/3+Z; [8]1-Y,+X-Y,+Z; [9]1+Y-X,1-X,+Z; [10]1/3+X,-1/3+Y,-1/3+Z; [11]4/3-Y,2/3+X-Y,2/3+Z; [12]1/3+Y-X,2/3-X,2/3+Z

**Figure S1.** The basic building unit of $GeO_4$ and $GeOTe_3$ polyhedron in $Ba_2ZnGe_2O_7$ and $Ba_3Ge_2O_4Te_3$, respectively.




**$GeO_4$ unit** **$GeOTe_3$ unit**

**Figure S2.** The basic building unit of $BaO_8$ and $BaO_3Te_5$ polyhedron in $Ba_2ZnGe_2O_7$ and $Ba_3Ge_2O_4Te_3$, respectively.




**$BaO_8$ unit** **$BaO_3Te_5$ unit**