Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.


# Supporting Information of

# Joint experimental and theoretical study of

# $PbGa_2S_4$ under compression

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## 1.- Single crystal XRD measurements at room pressure

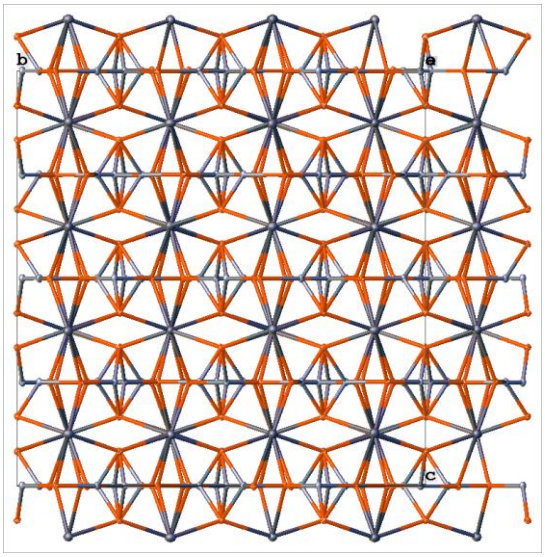


**Figure S1.** Detail of the crystal structure of $PbGa_2S_4$ along the *b* and *c* axes. Pb, Ga, and S atoms are big gray, small gray, and orange circles, respectively.

**Experimental.** Single orange plate crystals of $PbGa_2S_4$ were used. A suitable crystal with dimensions 0.12 × 0.11 × 0.04 $mm^3$ was selected and mounted on a SuperNova, Dualflex, EosS2 diffractometer. The crystal was kept at a steady $T$ = 293(2) K during data collection. The diffraction data was collected with the CrysAlis Pro software **[S1]** and the structure was solved with the ShelXT 2018/2 **[S2,S3]** solution program using dual methods and by using Olex2 **[S4]** as the graphical interface. The model was refined with ShelXL 2018/3 using full matrix least squares minimisation on $\boldsymbol{F^2}$.

The structure was solved and the space group *Fddd* (# 70) determined by the ShelXT 2018/2 **[S2,S3]** structure solution program using using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of ShelXL 2018/3 **[S2,S3]**. All non-hydrogen atoms were refined anisotropically. Sulfur atom positions were calculated geometrically and refined using the riding model.

| **Compound** | **$PbGa_2S_4$** |
|---|---|
| Formula | $PbGa_2S_4$ |
| $D_{calc.}$/ g $cm^{-3}$ | 4.907 |
| $\mu$/$mm^{-1}$ | 35.610 |
| Formula Weight | 474.87 |
| Colour | orange |
| Shape | plate |
| Size/$mm^3$ | 0.12×0.11×0.04 |
| $T$/K | 293(2) |
| Crystal System | orthorhombic |
| Space Group | *Fddd* |
| $a$/Å | 12.1674(2) |
| $b$/Å | 20.4180(4) |
| $c$/Å | 20.7005(5) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| V/$Å^3$ | 5142.71(18) |
| $Z$ | 32 |
| $Z'$ | 1 |
| Wavelength/Å | 0.71073 |
| Radiation type | Mo $K_\alpha$ |
| $\Theta_{min}$/° | 2.183 |
| $\Theta_{max}$/° | 28.278 |
| Measured Refl's. | 24555 |
| Indep't Refl's | 1597 |
| Refl's I≥2 $\sigma$(I) | 1195 |
| $R_{int}$ | 0.0353 |
| Parameters | 66 |
| Restraints | 0 |
| Largest Peak | 1.129 |
| Deepest Hole | -0.841 |
| GooF | 1.185 |
| $wR_2$ (all data) | 0.0520 |
| $wR_2$ | 0.0480 |
| $R_1$ (all data) | 0.0357 |
| $R_1$ | 0.0236 |

**Table S1**: Anisotropic Displacement Parameters (×$10^4$) for $PbGa_2S_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

| **Atom** | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Pb3 | 20.4(2) | 23.2(2) | 22.7(3) | 0 | 0 | 0 |
| Pb2 | 15.20(18) | 24.9(2) | 24.6(2) | 0 | 0 | 3.29(10) |
| Pb1 | 15.9(2) | 33.8(3) | 22.9(3) | 0 | 0 | 0 |
| Ga1 | 7.3(2) | 11.6(2) | 18.8(3) | 0.0(2) | 0.1(2) | -0.98(18) |
| Ga2 | 7.4(2) | 12.1(3) | 19.1(3) | -0.1(2) | 0.3(2) | -0.64(17) |
| S2 | 10.5(5) | 12.4(5) | 14.7(5) | 2.4(8) | -2.4(8) | -0.1(4) |
| S3 | 9.5(4) | 14.6(5) | 14.4(5) | -2.2(8) | 2.3(8) | 1.9(4) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| S4 | 5.7(4) | 10.6(5) | 18.3(5) | -1.4(6) | 0.5(6) | -0.1(3) |
| S1 | 7.7(4) | 10.0(5) | 21.3(6) | -0.4(6) | 1.4(6) | -1.5(4) |

**Table S2**: Bond Lengths in Å for $PbGa_2S_4$.

| Atom | Atom | Length/Å |
|---|---|---|
| Pb3 | $S3^{1}$ | 3.0918(19) |
| Pb3 | $S3^{2}$ | 3.0918(19) |
| Pb3 | $S3^{3}$ | 3.0918(19) |
| Pb3 | $S3^{4}$ | 3.0918(19) |
| Pb3 | $S4^{5}$ | 3.0801(19) |
| Pb3 | $S4^{6}$ | 3.0801(19) |
| Pb3 | $S4^{7}$ | 3.0801(19) |
| Pb3 | S4 | 3.0802(19) |
| Pb2 | $S2^{8}$ | 3.0772(18) |
| Pb2 | $S2^{9}$ | 3.0772(18) |
| Pb2 | $S3^{10}$ | 3.1117(18) |
| Pb2 | $S3^{11}$ | 3.1117(18) |
| Pb2 | $S4^{10}$ | 3.0769(19) |
| Pb2 | $S4^{11}$ | 3.0769(19) |
| Pb2 | $S1^{12}$ | 3.059(2) |
| Pb2 | S1 | 3.059(2) |
| Pb1 | $S2^{6}$ | 3.0973(19) |
| Pb1 | $S2^{13}$ | 3.0973(19) |
| Pb1 | S2 | 3.0974(19) |
| Pb1 | $S2^{12}$ | 3.0973(19) |
| Pb1 | $S1^{12}$ | 3.076(2) |
| Pb1 | $S1^{6}$ | 3.076(2) |
| Pb1 | S1 | 3.076(2) |
| Pb1 | $S1^{13}$ | 3.0762(19) |
| Ga1 | $S2^{8}$ | 2.3026(16) |
| Ga1 | S2 | 2.2952(16) |
| Ga1 | S4 | 2.2443(11) |
| Ga1 | S1 | 2.3010(12) |
| Ga2 | S3 | 2.2987(16) |
| Ga2 | $S3^{4}$ | 2.3031(16) |
| Ga2 | $S4^{9}$ | 2.3023(12) |
| Ga2 | S1 | 2.2451(12) |

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$^{1}$1/4+x,1-y,1/4+z; $^{2}$3/2-x,-1/4+y,1/4+z; $^{3}$1/4+x,-1/4+y,1/2-z; $^{4}$3/2-x,1-y,1/2-z; $^{5}$7/4-x,+y,3/4-z; $^{6}$+x,3/4-y,3/4-z; $^{7}$7/4-x,3/4-y,+z; $^{8}$1-x,1/2-y,1/2-z; $^{9}$-1/4+x,1/4+y,1/2-z; $^{10}$5/4-x,+y,1/4-z; $^{11}$-1/2+x,3/4-y,1/4-z; $^{12}$3/4-x,3/4-y,+z; $^{13}$3/4-x,+y,3/4-z

**Table S3**: Bond Angles (in °) for $PbGa_2S_4$.

| Atom | Atom | Atom | Angle |
|---|---|---|---|
| $S3^{1}$ | Pb3 | $S3^{2}$ | 147.38(4) |
| $S3^{3}$ | Pb3 | $S3^{4}$ | 147.38(4) |
| $S3^{1}$ | Pb3 | $S3^{4}$ | 68.51(7) |
| $S3^{2}$ | Pb3 | $S3^{3}$ | 68.51(7) |
| $S3^{1}$ | Pb3 | $S3^{3}$ | 121.60(7) |
| $S3^{2}$ | Pb3 | $S3^{4}$ | 121.60(7) |
| $S4^{5}$ | Pb3 | $S3^{2}$ | 73.89(3) |
| S4 | Pb3 | $S3^{3}$ | 73.89(3) |
| $S4^{5}$ | Pb3 | $S3^{3}$ | 77.00(3) |
| $S4^{6}$ | Pb3 | $S3^{4}$ | 77.00(3) |
| $S4^{5}$ | Pb3 | $S3^{1}$ | 78.54(3) |
| $S4^{7}$ | Pb3 | $S3^{3}$ | 78.54(3) |
| $S4^{6}$ | Pb3 | $S3^{1}$ | 73.89(3) |
| $S4^{7}$ | Pb3 | $S3^{2}$ | 134.53(3) |
| S4 | Pb3 | $S3^{4}$ | 78.54(3) |
| $S4^{5}$ | Pb3 | $S3^{4}$ | 134.53(3) |
| S4 | Pb3 | $S3^{1}$ | 134.53(3) |
| $S4^{6}$ | Pb3 | $S3^{2}$ | 78.54(3) |
| $S4^{6}$ | Pb3 | $S3^{3}$ | 134.53(3) |
| S4 | Pb3 | $S3^{2}$ | 77.00(3) |
| $S4^{7}$ | Pb3 | $S3^{4}$ | 73.89(3) |
| $S4^{7}$ | Pb3 | $S3^{1}$ | 77.00(3) |
| $S4^{5}$ | Pb3 | S4 | 144.60(5) |
| $S4^{7}$ | Pb3 | S4 | 64.02(5) |
| $S4^{6}$ | Pb3 | S4 | 128.53(5) |
| $S4^{5}$ | Pb3 | $S4^{7}$ | 128.52(5) |
| $S4^{5}$ | Pb3 | $S4^{6}$ | 64.02(5) |
| $S4^{6}$ | Pb3 | $S4^{7}$ | 144.60(5) |
| $S2^{8}$ | Pb2 | $S2^{9}$ | 149.22(5) |
| $S2^{9}$ | Pb2 | $S3^{10}$ | 68.90(6) |
| $S2^{8}$ | Pb2 | $S3^{10}$ | 121.04(6) |
| $S2^{9}$ | Pb2 | $S3^{11}$ | 121.04(6) |
| $S2^{8}$ | Pb2 | $S3^{11}$ | 68.90(6) |
| $S3^{10}$ | Pb2 | $S3^{11}$ | 145.88(5) |
| $S4^{10}$ | Pb2 | $S2^{9}$ | 133.70(3) |
| $S4^{11}$ | Pb2 | $S2^{9}$ | 76.05(3) |
| $S4^{10}$ | Pb2 | $S2^{8}$ | 76.05(3) |
| $S4^{11}$ | Pb2 | $S2^{8}$ | 133.70(3) |
| $S4^{10}$ | Pb2 | $S3^{10}$ | 77.67(3) |
| $S4^{11}$ | Pb2 | $S3^{10}$ | 73.52(3) |
| $S4^{10}$ | Pb2 | $S3^{11}$ | 73.52(3) |
| $S4^{11}$ | Pb2 | $S3^{11}$ | 77.67(3) |
| $S4^{10}$ | Pb2 | $S4^{11}$ | 64.10(5) |
| $S1^{12}$ | Pb2 | $S2^{9}$ | 81.89(4) |
| $S1^{12}$ | Pb2 | $S2^{8}$ | 72.40(3) |
| S1 | Pb2 | $S2^{8}$ | 81.89(4) |
| S1 | Pb2 | $S2^{9}$ | 72.41(3) |
| $S1^{12}$ | Pb2 | $S3^{10}$ | 79.97(4) |
| S1 | Pb2 | $S3^{11}$ | 79.97(4) |
| S1 | Pb2 | $S3^{10}$ | 131.63(4) |
| $S1^{12}$ | Pb2 | $S3^{11}$ | 131.62(4) |
| S1 | Pb2 | $S4^{10}$ | 150.17(3) |
| S1 | Pb2 | $S4^{11}$ | 123.26(4) |
| $S1^{12}$ | Pb2 | $S4^{10}$ | 123.26(4) |
| $S1^{12}$ | Pb2 | $S4^{11}$ | 150.17(3) |
| $S1^{12}$ | Pb2 | S1 | 66.72(6) |
| $S2^{13}$ | Pb1 | S2 | 69.11(7) |
| $S2^{6}$ | Pb1 | S2 | 120.74(7) |
| $S2^{12}$ | Pb1 | S2 | 147.72(4) |
| $S2^{6}$ | Pb1 | $S2^{12}$ | 69.11(7) |
| $S2^{6}$ | Pb1 | $S2^{13}$ | 147.71(4) |
| $S2^{13}$ | Pb1 | $S2^{12}$ | 120.74(7) |

| Atom | Atom | Atom | Angle |
|---|---|---|---|
| S1[6] | Pb1 | S2[6] | 71.58(3) |
| S1 | Pb1 | S2[6] | 79.29(3) |
| S1 | Pb1 | S2 | 71.58(3) |
| S1[12] | Pb1 | S2[12] | 71.58(3) |
| S1[12] | Pb1 | S2[13] | 79.29(3) |
| S1[13] | Pb1 | S2[12] | 79.29(3) |
| S1[6] | Pb1 | S2[13] | 81.40(3) |
| S1[13] | Pb1 | S2[6] | 81.40(3) |
| S1[12] | Pb1 | S2 | 81.40(3) |
| S1[6] | Pb1 | S2[12] | 130.64(4) |
| S1[13] | Pb1 | S2 | 130.64(4) |
| S1 | Pb1 | S2[13] | 130.64(4) |
| S1[13] | Pb1 | S2[13] | 71.58(3) |
| S1[6] | Pb1 | S2 | 79.29(3) |
| S1 | Pb1 | S2[12] | 81.40(3) |
| S1[12] | Pb1 | S2[6] | 130.64(4) |
| S1[6] | Pb1 | S1[13] | 66.30(6) |
| S1[13] | Pb1 | S1 | 156.51(4) |
| S1[6] | Pb1 | S1 | 119.00(5) |
| S1[12] | Pb1 | S1[6] | 156.51(4) |
| S1[12] | Pb1 | S1[13] | 119.00(5) |
| S1[12] | Pb1 | S1 | 66.30(6) |
| S2 | Ga1 | S2[9] | 97.35(4) |
| S2 | Ga1 | S1 | 103.54(7) |
| S4 | Ga1 | S2[9] | 123.09(7) |
| S4 | Ga1 | S2 | 123.61(7) |
| S4 | Ga1 | S1 | 102.62(4) |
| S1 | Ga1 | S2[9] | 103.87(7) |
| S3 | Ga2 | S3[4] | 96.70(4) |
| S3 | Ga2 | S4[8] | 107.46(7) |
| S4[8] | Ga2 | S3[4] | 107.06(7) |
| S1 | Ga2 | S3 | 120.92(7) |
| S1 | Ga2 | S3[4] | 121.33(7) |
| S1 | Ga2 | S4[8] | 102.42(4) |
| Pb2[9] | S2 | Pb1 | 148.47(4) |
| Ga1 | S2 | Pb2[9] | 112.28(7) |
| Ga1[9] | S2 | Pb2[9] | 91.35(6) |
| Ga1 | S2 | Pb1 | 91.99(6) |
| Ga1[9] | S2 | Pb1 | 112.26(7) |
| Ga1 | S2 | Ga1[9] | 82.65(4) |
| Pb3[4] | S3 | Pb2[11] | 146.63(4) |
| Ga2 | S3 | Pb3[4] | 88.97(6) |
| Ga2[4] | S3 | Pb3[4] | 116.12(7) |
| Ga2 | S3 | Pb2[11] | 116.97(7) |
| Ga2[4] | S3 | Pb2[11] | 88.98(6) |
| Ga2 | S3 | Ga2[4] | 83.30(4) |
| Pb2[11] | S4 | Pb3 | 115.94(3) |
| Ga1 | S4 | Pb3 | 118.92(8) |
| Ga1 | S4 | Pb2[11] | 120.06(8) |
| Ga1 | S4 | Ga2[3] | 112.76(5) |
| Ga2[3] | S4 | Pb3 | 89.19(5) |
| Ga2[3] | S4 | Pb2[11] | 89.85(5) |
| Pb2 | S1 | Pb1 | 113.49(3) |
| Ga1 | S1 | Pb2 | 91.84(6) |
| Ga1 | S1 | Pb1 | 92.42(6) |
| Ga2 | S1 | Pb2 | 119.41(8) |
| Ga2 | S1 | Pb1 | 119.40(8) |
| Ga2 | S1 | Ga1 | 112.57(5) |

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[1]1/4+x,1-y,1/4+z; [2]3/2-x,-1/4+y,1/4+z; [3]1/4+x,-1/4+y,1/2-z; [4]3/2-x,1-y,1/2-z; [5]7/4-x,+y,3/4-z; [6]+x,3/4-y,3/4-z; [7]7/4-x,3/4-y,+z; [8]-1/4+x,1/4+y,1/2-z; [9]1-x,1/2-y,1/2-z; [10]-1/2+x,3/4-y,1/4-z; [11]5/4-x,+y,1/4-z; [12]3/4-x,3/4-y,+z; [13]3/4-x,+y,3/4-z

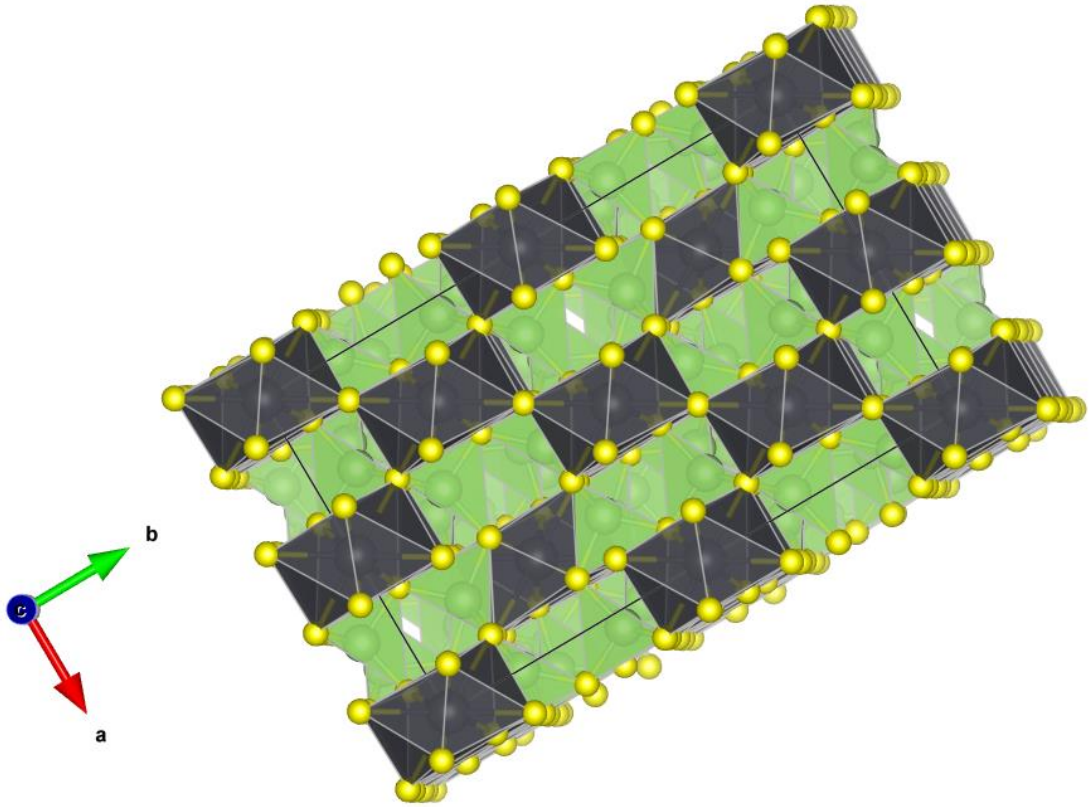
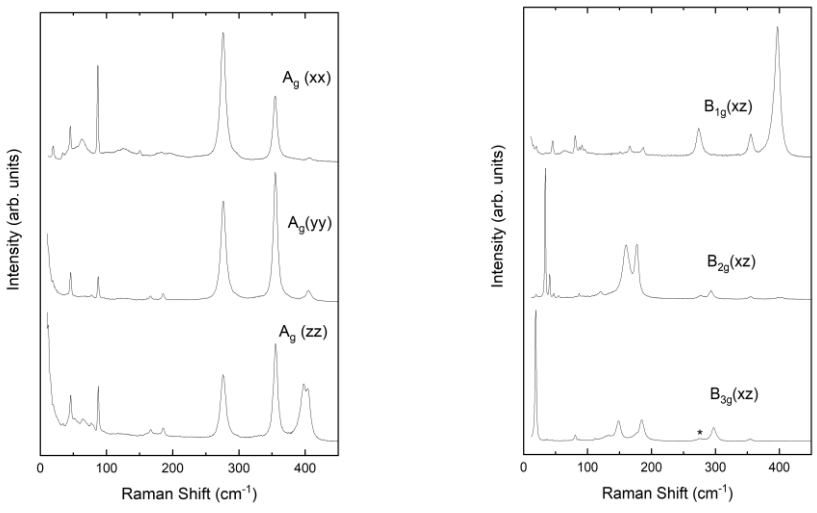



**Figure S2.** Detail of the crystal structure of $PbGa_2S_4$ in a perspective that highlights its layered characteristic. $GaS_4$ tetrahedra are shown in green and $PbS_8$ square antiprismatic polyhedra is black. Sulfur atoms are shown in yellow.

## 2.- RS measurements at room pressure




(a) (b)

**Figure S3.** Normalized Raman spectra of $PbGa_2S_4$ at room pressure. (a) Modes with $A_g$ symmetry. (b) Modes with $B_g$ symmetry. The asterisk in the Raman spectrum corresponding to the $B_{3g}$ symmetry is related to an $A_g$ (xx) mode.

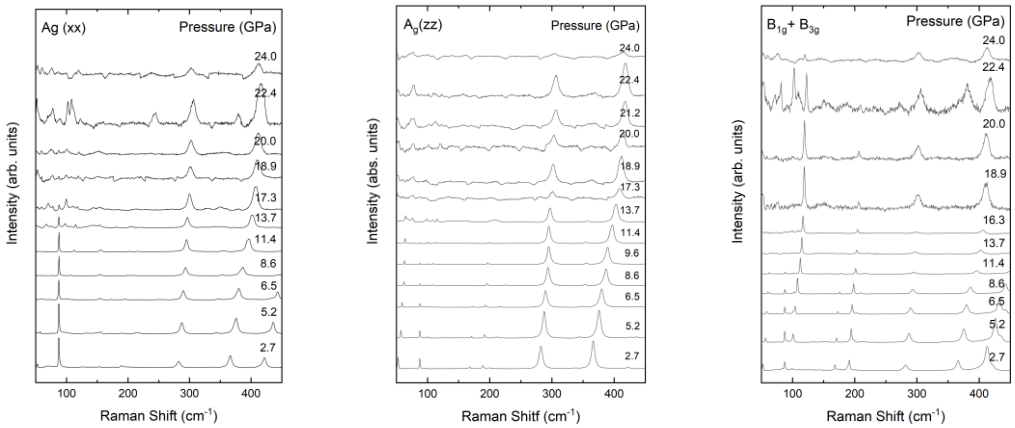



**Figure S4.** Normalized polarized Raman spectra of $PbGa_2S_4$ at high pressure up to 24 GPa.

**Table S4**

Raman-active frequencies of $A_g$, $B_{1g}$, $B_{2g}$ and $B_{3g}$ modes in $PbGa_2S_4$ at room pressure obtained from polarized RS measurements. Data from Ref. Kamenshchikov et al. (2007) (noted with subindex k) are provided for comparison.

| $A_{gk}$ | $A_g$ | $B_{1gk}$ | $B_{1g}$ | $B_{2gk}$ | $B_{2g}$ | $B_{3gk}$ | $B_{3g}$ |
|---|---|---|---|---|---|---|---|
| | 12.2 | | 20 | 19.7 | 20 | 19 | |
| | 19.7 | 25 | | 34 | 33.9 | 31 | 34 |
| | 20.3 | 35 | 34.3 | 41 | 40.7 | | |
| | 22.4 | 42 | | 47 | 47.2 | 47 | 45 |
| | 25 | 46 | 45.6 | 55 | 55.0 | 55 | |
| | 34.1 | 67 | 65 | 89 | 86.5 | 89 | 81 |
| | 34.9 | 83 | 80.5 | 121 | 121 | | 112 |
| | 45.5 | | 87 | 160 | 160.8 | 132 | 131 |
| 46 | 46.2 | 93 | 91.2 | 176 | 177.0 | 150 | 149 |
| 53 | 51.9 | 98 | 96.5 | | 277.0 | 175 | 179 |
| | 62.7 | 152 | | 293 | 293.1 | 187 | 184 |
| 67 | 64.0 | 161 | 166.2 | 362 | 354.8 | 280 | 277 |
| 80 | 77.0 | 167 | | | 398.6 | 298 | 297 |
| | 86.8 | 178 | | | | 336 | 330 |
| 88 | 87.6 | 187 | 187.2 | | | 345 | 355 |
| 118 | | 274 | 273.7 | | | | |
| 127 | 125.7 | 292 | | | | | |
| 159 | 150.8 | 321 | | | | | |
| 166 | 166.6 | 356 | 355 | | | | |
| 172 | | 398 | 396.9 | | | | |
| | 182.0 | | | | | | |
| 185 | 185.4 | | | | | | |
| | 198.5 | | | | | | |
| 277 | 276.4 | | | | | | |
| 332 | | | | | | | |
| 353 | 355.0 | | | | | | |
| | 397.8 | | | | | | |
| 404 | 404.1 | | | | | | |

**Table S5**
Theoretical Raman-active frequencies at zero pressure ($\omega_0$, in $cm^{-1}$) and pressure coefficients ($a_1$, in $cm^{-1}GPa^{-1}$; $a_2$, in $cm^{-1}GPa^{-2}$) in $PbGa_2S_4$ according to fits to $\omega_0+a_1 \cdot P+ a_2 \cdot P^2$.

| Mode | $\omega_0$ | $a_1$ | $a_2$ | Mode | $\omega_0$ | $a_1$ | $a_2$ |
|---|---|---|---|---|---|---|---|
| $B_{2g}^1$ | 17.7(2) | 3.81(0) | -0.1(0) | $B_{2g}^{12}$ | 162.9(2) | 3.3(0) | 0.0(0) |
| $B_{1g}^1$ | 30.4(1) | 2.2(0) | -0.1(0) | $B_{2g}^{13}$ | 167.1(1) | 4.1(0) | 0.0(0) |
| $B_{3g}^1$ | 33.8(1) | 0.7(0) | -0.1(0) | $B_{3g}^{13}$ | 167.3(1) | 4.4(0) | 0.0(0) |
| $B_{2g}^2$ | 36.46(1) | 1.8(0) | 0.0(0) | $B_{2g}^{14}$ | 169.7(1) | 4.3(0) | 0.0(0) |
| $B_{3g}^2$ | 39.2(0) | 1.6(0) | -0.1(0) | $B_{3g}^{14}$ | 173.9(0) | 5.8(0) | 0.0(0) |
| $B_{1g}^2$ | 43.6(1) | 2.4(0) | 0.0(0) | $A_g^9$ | 170.5(2) | 3.2(0) | 0.0(0) |
| $A_g^1$ | 44.0(1) | 2.4(0) | -0.1(0) | $B_{1g}^{12}$ | 174.2(1) | 3.3(0) | 0.0(0) |
| $B_{3g}^3$ | 46.4(0) | 1.8(0) | 0.0(0) | $B_{1g}^{13}$ | 179.6(0) | 5.3(0) | 0.0(0) |
| $B_{2g}^3$ | 50.5(0) | 1.8(0) | 0.0(0) | $A_g^{10}$ | 182.3(0) | 5.4(0) | 0.0(0) |
| $B_{3g}^4$ | 53.8(0) | 1.7(0) | 0.0(0) | $A_g^{11}$ | 195.5(0) | 4.8(0) | 0.0(0) |
| $B_{2g}^4$ | 64.3(0) | 2.7(0) | 0.0(0) | $B_{1g}^{14}$ | 262.9(0) | 2.2(0) | 0.0(0) |
| $B_{3g}^5$ | 79.1(2) | 1.8(0) | -0.1(0) | $A_g^{12}$ | 266.0(0) | 2.0(0) | 0.0(0) |
| $B_{2g}^5$ | 77.8(1) | 2.1(0) | 0.0(0) | $B_{3g}^{15}$ | 266.3(0) | 3.4(0) | 0.0(0) |
| $B_{1g}^3$ | 78.6(0) | 0.6(0) | 0.0(0) | $B_{1g}^{15}$ | 272.1(0) | 3.7(0) | 0.0(0) |
| $B_{1g}^4$ | 81.68(0) | 0.7(0) | 0.0(0) | $B_{2g}^{15}$ | 274.6(0) | 3.7(0) | 0.0(0) |
| $A_g^2$ | 84.3(0) | 0.1(0) | 0.0(0) | $B_{1g}^{16}$ | 276.0(0) | 4.1(0) | 0.0(0) |
| $A_g^3$ | 88.7(1) | 1.1(0) | 0.0(0) | $B_{3g}^{16}$ | 276.4(0) | 4.3(0) | -0.1(0) |
| $B_{1g}^5$ | 88.8(1) | 1.3(0) | 0.0(0) | $A_g^{13}$ | 278.8(0) | 4.0(0) | 0.0(0) |
| $B_{1g}^6$ | 89.8(0) | 1.9(0) | 0.0(0) | $B_{2g}^{16}$ | 278.9(0) | 4.5(0) | -0.1(0) |
| $A_g^4$ | 91.6(0) | 1.1(0) | 0.0(0) | $A_g^{14}$ | 283.3(0) | 5.1(0) | -0.1(0) |
| $B_{3g}^6$ | 98.1(0) | -0.6(0) | 0.0(0) | $B_{2g}^{17}$ | 292.0(0) | 3.1(0) | 0.0(0) |
| $B_{3g}^7$ | 108.3(0) | -0.4(0) | 0.0(0) | $B_{3g}^{17}$ | 292.1(0) | 3.2(0) | 0.0(0) |
| $B_{2g}^6$ | 107.4(0) | -0.7(0) | 0.0(0) | $B_{3g}^{18}$ | 292.7(0) | 3.1(0) | 0.0(0) |
| $B_{2g}^7$ | 110.4(0) | -0.7(0) | 0.0(0) | $B_{2g}^{18}$ | 293.3(0) | 3.0(0) | 0.0(0) |
| $B_{3g}^8$ | 112.7(0) | 0.0(0) | 0.0(0) | $A_g^{15}$ | 320.0(1) | 2.4(0) | 0.0(0) |
| $B_{2g}^8$ | 113.7(0) | -0.1(0) | 0.0(0) | $B_{1g}^{17}$ | 318.9(0) | 3.0(0) | 0.0(0) |
| $B_{3g}^9$ | 114.7(2) | 7.7(0) | -0.2(0) | $B_{3g}^{19}$ | 334.4(0) | 3.0(0) | 0.0(0) |
| $B_{2g}^9$ | 128.8(3) | 6.2(0) | -0.2(0) | $B_{1g}^{18}$ | 334.9(0) | 3.5(0) | 0.0(0) |
| $B_{2g}^{10}$ | 144.7(2) | 4.7(0) | -0.1(0) | $A_g^{16}$ | 335.9(0) | 3.5(0) | 0.0(0) |
| $B_{1g}^7$ | 145.4(1) | 0.8(0) | 0.0(0) | $A_g^{17}$ | 336.9(0) | 4.0(0) | 0.0(0) |
| $A_g^5$ | 145.5(1) | 0.1(0) | 0.0(0) | $B_{2g}^{19}$ | 337.1(0) | 3.0(0) | 0.0(0) |
| $A_g^6$ | 148.7(1) | 2.6(0) | 0.0(0) | $B_{1g}^{19}$ | 338.1(0) | 3.9(0) | 0.0(0) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $B_{1g}^{8}$ | 151.5(1) | 2.2(0) | 0.0(0) | $B_{3g}^{20}$ | 338.1(0) | 3.2(0) | 0.0(0) |
| $B_{3g}^{10}$ | 153.5(2) | 3.7(0) | -0.1(0) | $B_{2g}^{20}$ | 339.1(0) | 3.2(0) | 0.0(0) |
| $A_{g}^{7}$ | 149.7(1) | 4.2(0) | -0.1(0) | $B_{3g}^{21}$ | 363.2(0) | 5.0(0) | 0.0(0) |
| $B_{1g}^{9}$ | 152.9(2) | 4.7(0) | -0.1(0) | $B_{2g}^{21}$ | 369.4(0) | 5.3(0) | -0.1(0) |
| $B_{1g}^{10}$ | 155.2(1) | 5.1(1) | 0.0(0) | $B_{3g}^{22}$ | 370.3(0) | 5.3(0) | -0.1(0) |
| $A_{g}^{8}$ | 160.2(1) | 3.2(2) | 0.0(0) | $B_{1g}^{20}$ | 371.8(0) | 5.8(0) | -0.1(0) |
| $B_{3g}^{11}$ | 166.4(2) | 1.7(0) | 0.0(0) | $B_{2g}^{22}$ | 374.7(0) | 5.4(0) | -0.1(0) |
| $B_{1g}^{11}$ | 163.2(1) | 4.3(0) | 0.0(0) | $A_{g}^{18}$ | 379.2(0) | 5.6(0) | -0.1(0) |
| $B_{2g}^{11}$ | 160.9(2) | 2.8(0) | 0.2(0) | $A_{g}^{19}$ | 380.0(0) | 6.1(0) | -0.1(0) |
| $B_{3g}^{12}$ | 162.8(1) | 4.7(0) | 0.0(0) | $B_{1g}^{21}$ | 381.5(0) | 5.3(0) | 0.0(0) |

**Tabla S6**
Theoretical Raman-active frequencies at 16 GPa ($\omega_{16}$, in $cm^{-1}$) and pressure coefficients ($a_1$, in $cm^{-1}GPa^{-1}$; $a_2$, in $cm^{-1}GPa^{-2}$) in $Pb_6Ga_{10}S_{21}$ according to fits to $\omega_{16}+a_1\cdot(P-16)+ a_2\cdot(P-16)^2$.

| Mode | $\omega_0$ | $a_1$ | $a_2$ |
|---|---|---|---|
| Bg | 43.5 (0) | 2.0 (0) | -0.1 (0) |
| Bg | 49.4 (0) | 2.6 (0) | -0.1 (0) |
| Ag | 48.0 (0) | 0.4 (0) | 0 (0) |
| Ag | 54.4 (0) | 0.9 (0) | 0 (0) |
| Ag | 56.4 (0 | 0.5 (0) | 0 (0) |
| Bg | 59.6 (0) | 1.1 (0) | 0 (0) |
| Bg | 67.7 (0) | 1.0 (0) | 0 (0) |
| Ag | 74.0 (0) | 0.7 (0) | 0 (0) |
| Ag | 84.3 (0) | 1.3 (0) | 0 (0) |
| Bg | 85.6 (0) | 1.2 (0) | 0 (0) |
| Bg | 89.3 (0) | 1.4 (0) | 0 (0) |
| Ag | 91.9 (0) | 0.8 (0) | 0 (0) |
| Ag | 94.7 (0) | 0.9 (0) | 0 (0) |
| Bg | 100.8 (0) | 0.7 (0) | 0 (0) |
| Ag | 103.1 (0) | 1.0 (0) | 0 (0) |
| Ag | 113.4 (0) | 1.2 (0) | 0 (0) |
| Bg | 116.7 (0) | 1.2 (0) | 0 (0) |
| Ag | 124.5 (0) | 1.3 (0) | 0 (0) |
| Ag | 137.6 (0) | 1.5 (0) | 0 (0) |
| Ag | 142.6 (0) | 1.7 (0) | 0 (0) |
| Bg | 161.2 (0) | 2.9 (0) | 0 (0) |
| Ag | 162.0 (0) | 1.1 (0) | 0 (0) |
| Ag | 177.2 (0) | 1.9 (0) | 0 (0) |
| Ag | 183.7 (0) | 1.3 (0) | 0 (0) |
| Ag | 187.8 (0) | 1.5 (0) | 0 (0) |
| Ag | 204.8 (0) | 2.0 (0) | 0 (0) |
| Bg | 216.4 (0) | 3.0 (0) | 0 (0) |
| Ag | 217,9 (0) | 2.2 (0) | 0 (0) |
| Ag | 226.9 (0) | 3.0 (0) | 0 (0) |
| Bg | 242,7 (0) | 3.3 (0) | 0 (0) |
| Ag | 241.7 (0) | 2.5 (0) | 0 (0) |
| Bg | 252.0 (0) | 2.9 (0) | 0 (0) |
| Bg | 259.0 (0) | 3.1 (0) | 0 (0) |
| Ag | 266.0 (0) | 2.9 (0) | 0 (0) |
| Bg | 270.1 (0) | 3.2 (0) | 0 (0) |
| Ag | 271.3 (0) | 2.9 (0) | 0 (0) |
| Ag | 279.6 (0) | 2.6 (0) | 0 (0) |
| Bg | 283.2 (0) | 3.0 (0) | 0 (0) |
| Ag | 284.9 (0) | 2.9 (0) | 0 (0) |
| Bg | 291.2 (0) | 2.7 (0) | 0 (0) |
| Ag | 292.8 (0) | 2.3 (0) | 0 (0) |
| Bg | 297.8 (0) | 2.8 (0) | 0 (0) |

| | | | |
|---|---|---|---|
| Bg | 306.0 (0) | 3.9 (0) | 0 (0) |
| Ag | 315.7 (0) | 2.7 (0) | 0 (0) |
| Ag | 323.6 (0) | 2.5 (0) | 0 (0) |
| Ag | 324.3 (0) | 2.9 (0) | 0 (0) |
| Ag | 331.2 (0) | 2.7 (0) | 0 (0) |
| Ag | 337.4 (0) | 2.7 (0) | 0 (0) |
| Ag | 344.2 (0) | 2.7 (0) | 0 (0) |
| Ag | 349.5 (0) | 3.1 (0) | 0 (0) |
| Ag | 353.7 (0) | 2.6 (0) | 0 (0) |
| Ag | 366.5 (0) | 3.3 (0) | 0 (0) |
| Ag | 371.9 (0) | 4.1 (0) | 0 (0) |
| Ag | 389.0 (0) | 2.9 (0) | 0 (0) |

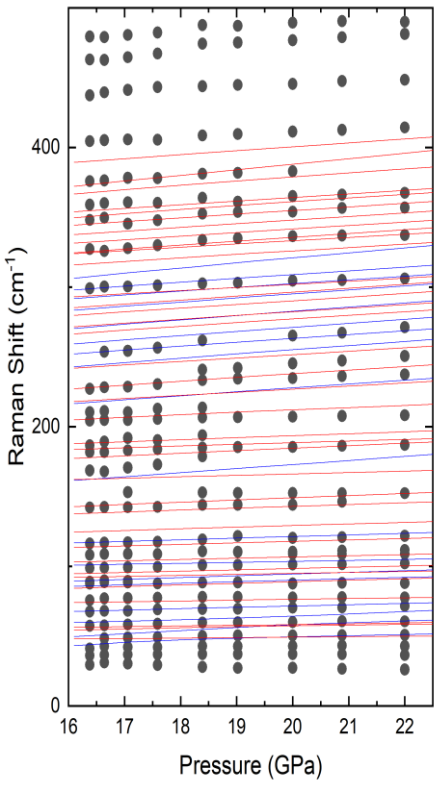
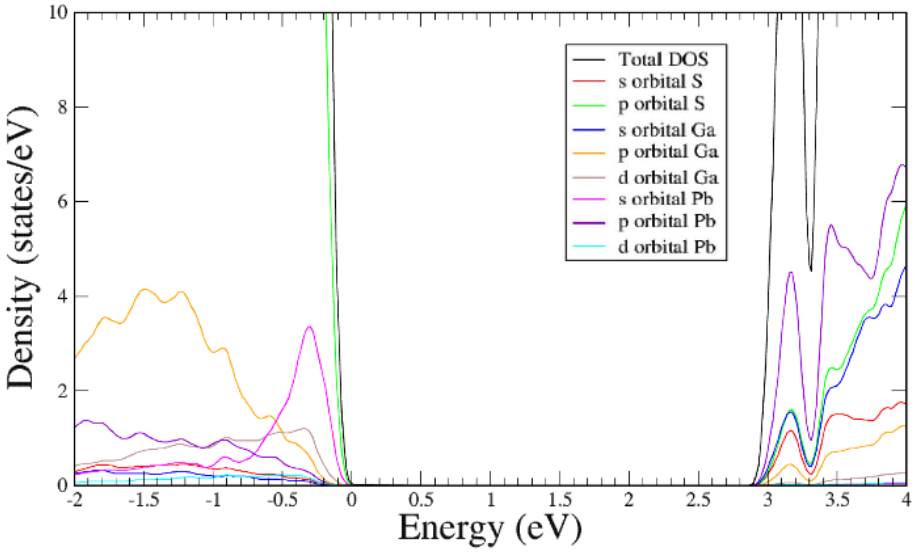



**Figure S5.** Pressure dependence of the experimental (symbols) and theoretical (lines) Raman frequencies of $Pb_6Ga_{10}S_{21}$ during compression. The red (blue) lines correspond to the theoretical $A_g$ ($B_g$) modes.



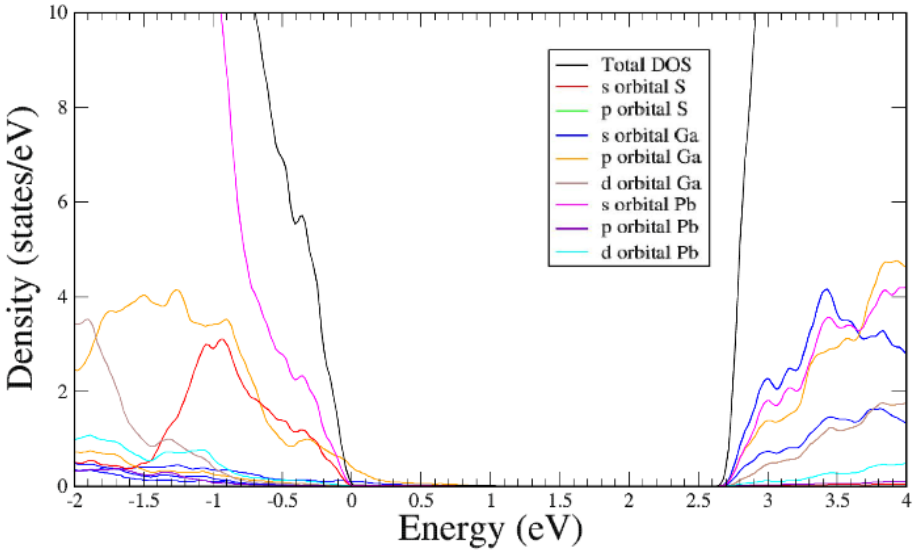




**Figure S6.** (Top) Zoom of the total and partial electronic density of states of $PbGa_2S_4$ at 0 GPa. (Bottom) Zoom of the total and partial electronic density of states of $Pb_6Ga_{10}S_{21}$ at 15.3 GPa

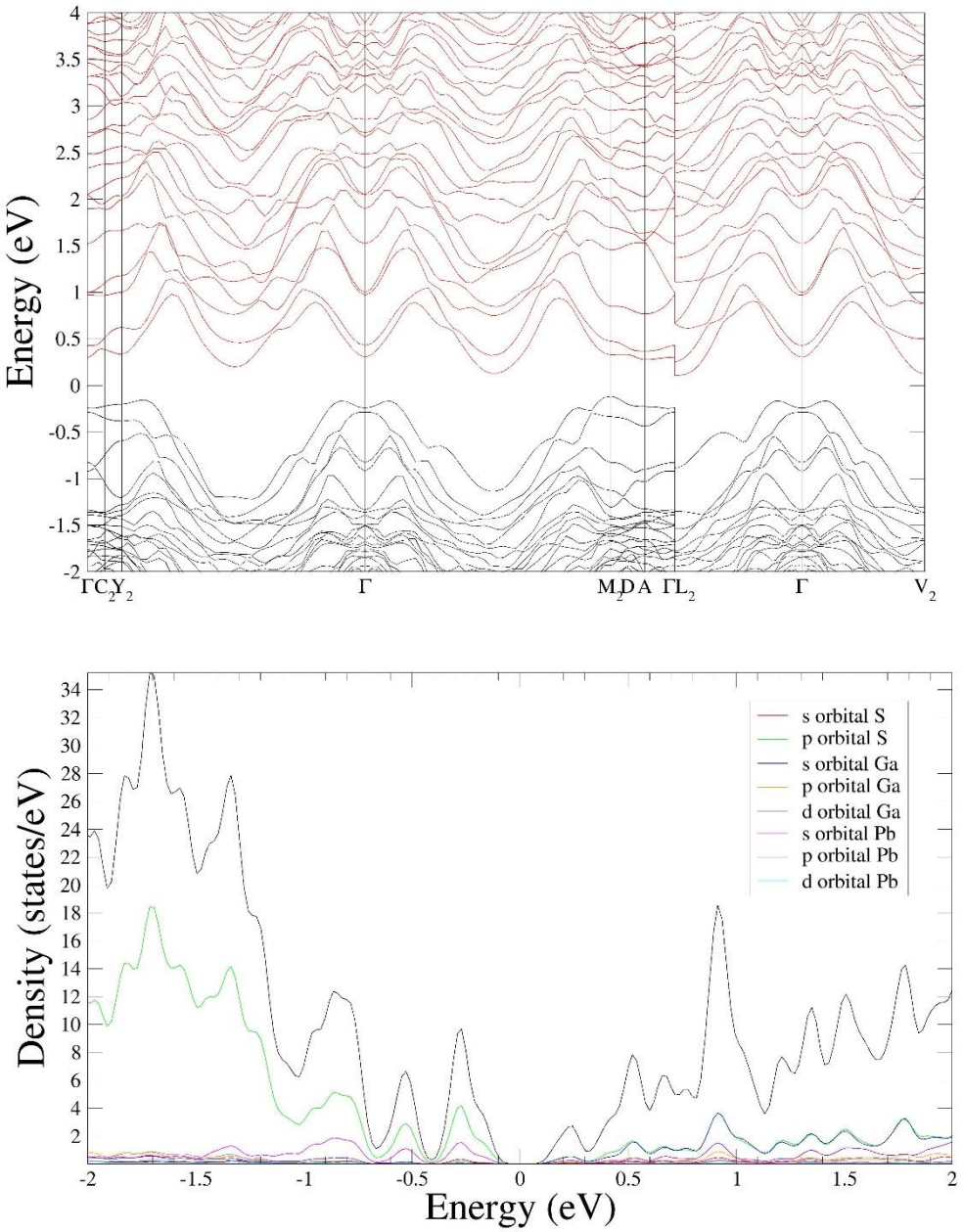



**Figure S7.** (Top) Electronic band structure of $Pb_6Ga_{10}S_{21}$ at 15.3 GPa. (Bottom) Total and partial electronic density of states at 15.3 GPa

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