

Supplementary Information of **High-pressure synthesis of β - and α -In₂Se₃-like structures in Ga₂S₃**

Samuel Gallego-Parra^{1*}, Rosario Vilaplana^{2*}, Oscar Gomis², Plácida Rodríguez-Hernández³, Alfonso Muñoz³, Jesus Antonio González⁴, Juan Angel Sans¹, Catalin Popescu⁵ and Francisco Javier Manjón¹

¹*Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022 València, Spain*

²Centro de Tecnologías Físicas, MALTA Consolider Team, Universitat Politècnica de València, 46022 Valencia, Spain

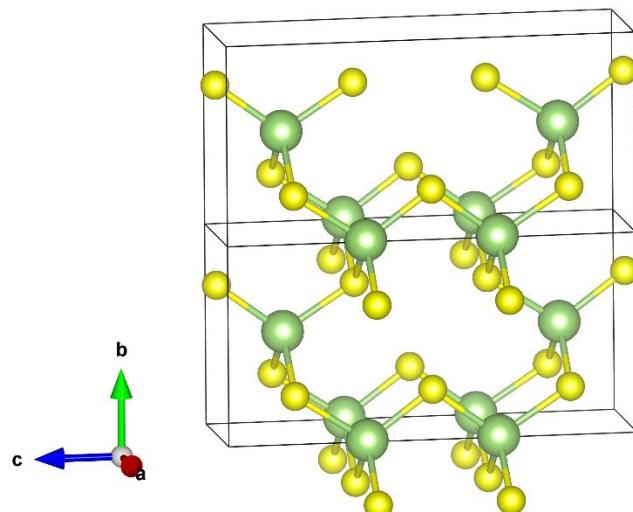
³Departamento de Física, Instituto de Materiales y Nanotecnología, MALTA Consolider Team,
Universidad de La Laguna, 38207 San Cristóbal de La Laguna, Spain

⁴*Ciencias de la Tierra y Fisica de la Materia Condensada, MALTA Consolider Team, Universidad de Cantabria, 39005, Santander, Spain*

⁵ALBA-CELLS, MALTA Consilider Team, 08290 Cerdanyola del Valles (Barcelona), Spain

*Corresponding authors: S. Gallego-Parra (sagalpar@doctor.upv.es), R. Vilaplana (rovilan@fis.upv.es)

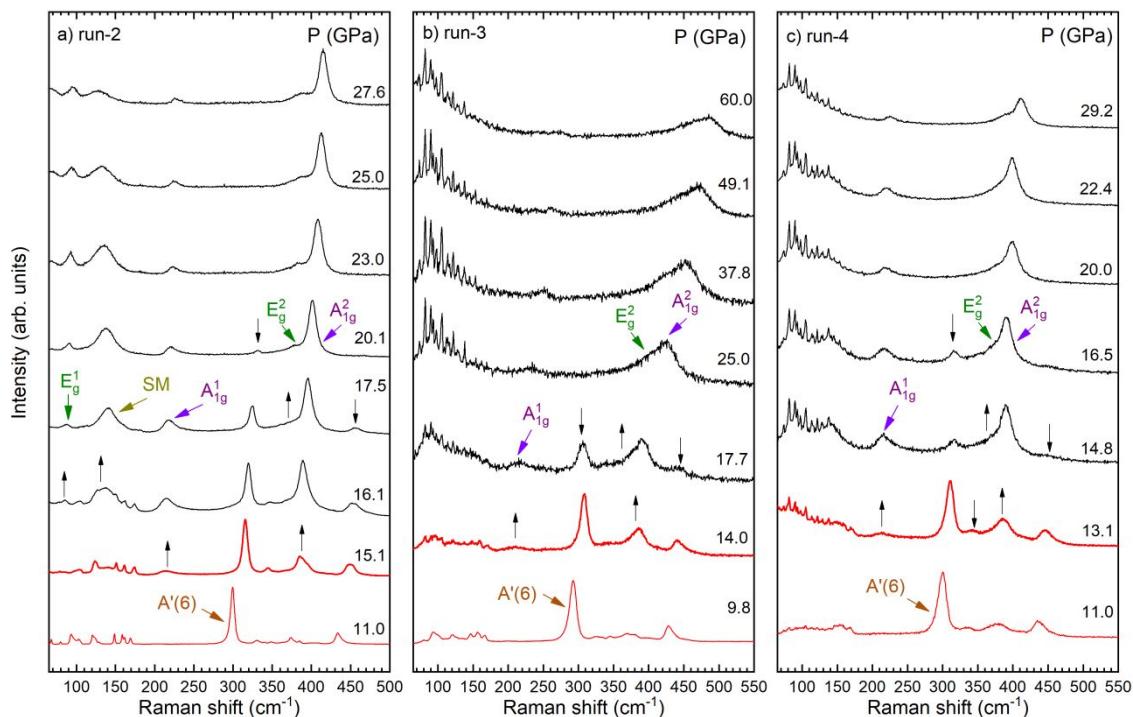
20 **Figure S1.** Crystal structure of ortho- β -Ga₂Se₃ and α -Ga₂Te₃ (orthorhombic, S.G. *Imm2*, No. 44,
21 Z=8). Cations and anions are depicted as yellow and green spheres, respectively.



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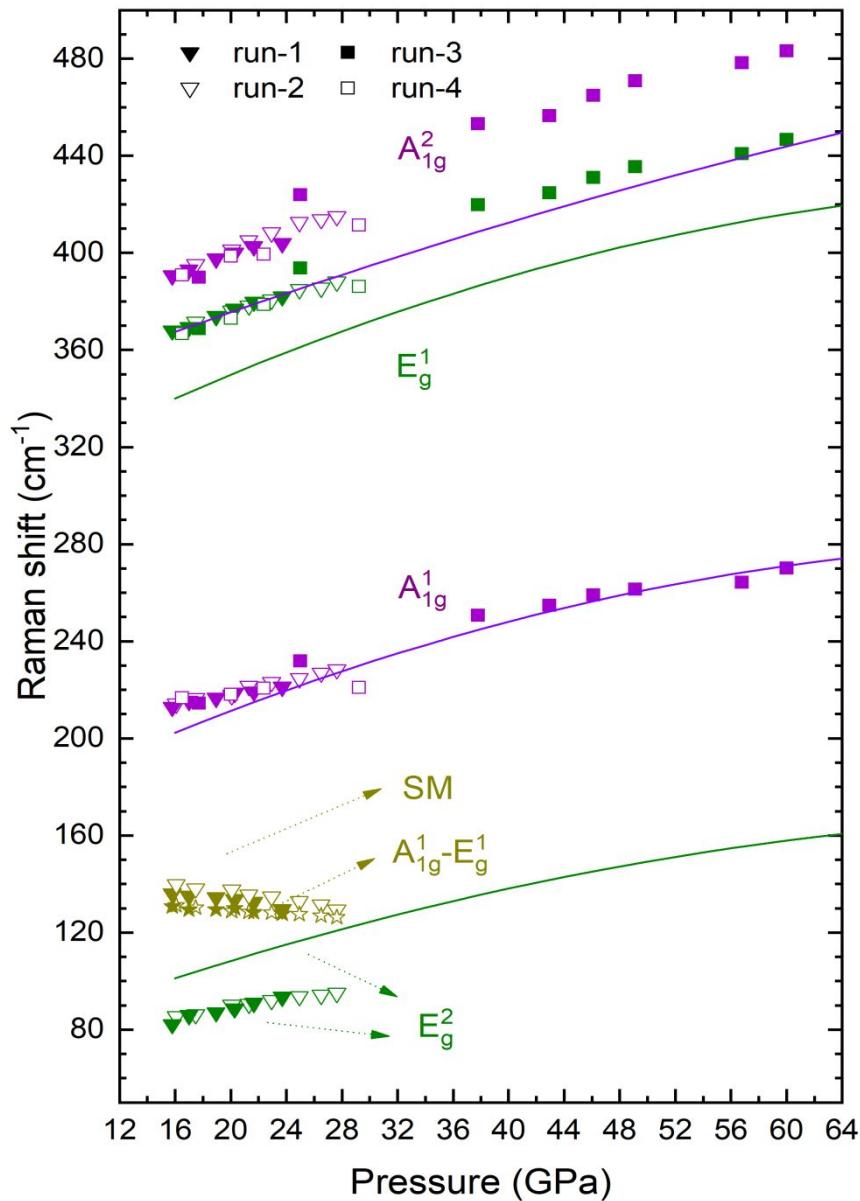
24 **Figure S2.** Selected normalized Raman spectra of α' -Ga₂S₃ under compression from a) run-2, b)
 25 run-3 and c) run-4. Red and black colors represent spectra of α' -Ga₂S₃ and β' -Ga₂S₃, respectively.
 26 For the sake of clarity, only the most intense Raman mode, the A'(6), of α' -Ga₂S₃ is marked.
 27 Down and up black arrows indicate emerging or disappearing peaks under compression. In β' -
 28 Ga₂S₃, the soft mode (with negative pressure coefficient) is labeled as the SM mode. The reader
 29 is referred to our previous work (Ref. [1]) for further information about pressure dependence of
 30 the Raman modes of α' -Ga₂S₃. In runs 3 and 4, rotational N₂ and O₂ modes below 150 cm⁻¹ appear
 31 above 14.0 and 13.1 GPa, respectively.



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 34 * M-E: methanol-ethanol, S: silicon oil.
 35 ^a run-2, M-E, ^b run-3, S, ^c run-4, S.

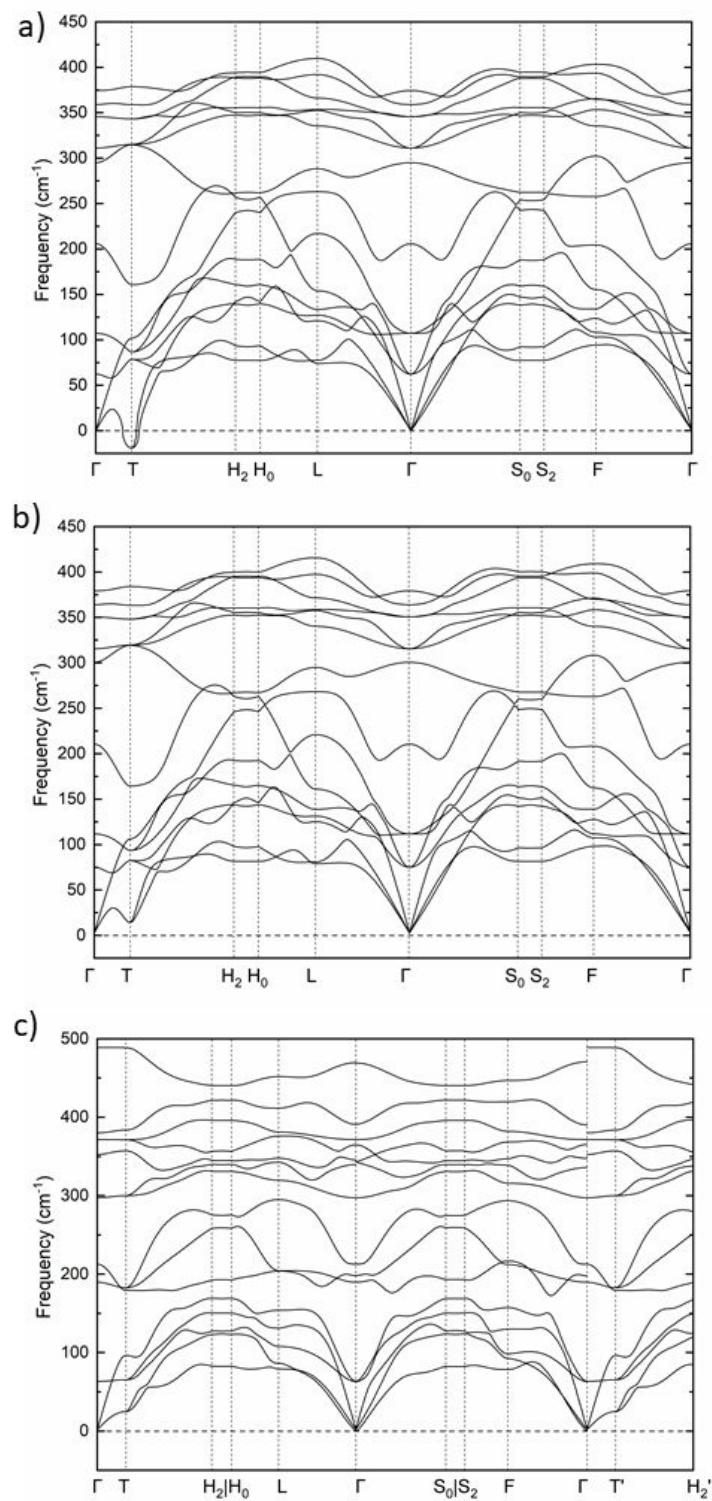
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47 **Figure S3.** Experimental (symbols) and theoretical (solid lines) PBE-D3 pressure dependence of
48 the Raman frequencies of β' - Ga_2S_3 on upstroke (all runs). The experimental A_{1g}^1 - E_g^1 frequency is
49 labeled with hollow star symbols to compare with the SM mode.

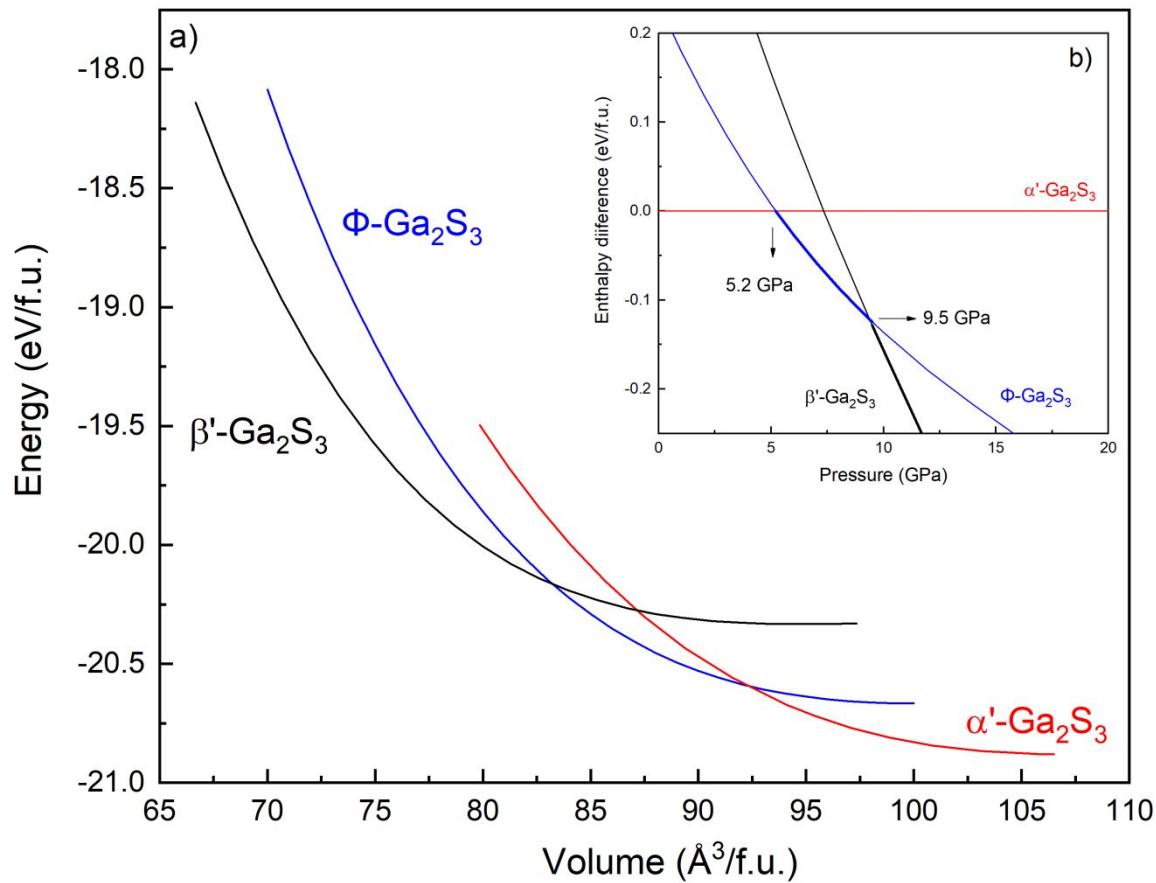


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57 **Figure S4.** Theoretical phonon dispersion curves of β' -Ga₂S₃ at a) 17.9 and b) 18.6 GPa and c) ϕ -
58 Ga₂S₃ at 15 GPa.



60 **Figure S5.** a) Theoretical volume dependence of the total energy of α' -, β' -, and ϕ - Ga_2S_3 and b)
61 theoretical pressure dependence of the enthalpy difference between α' -, β' -, and ϕ - Ga_2S_3 .
62 Enthalpy of α' - Ga_2S_3 is taken as reference.

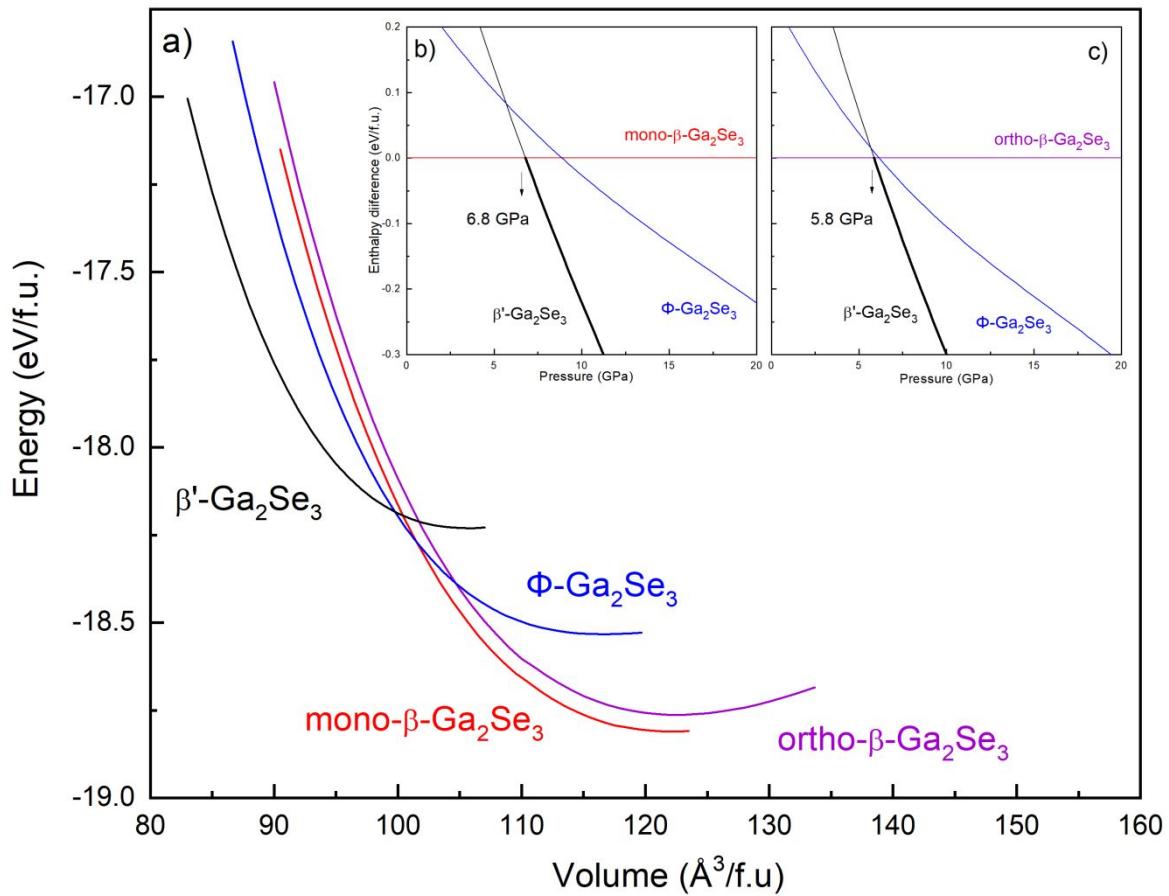


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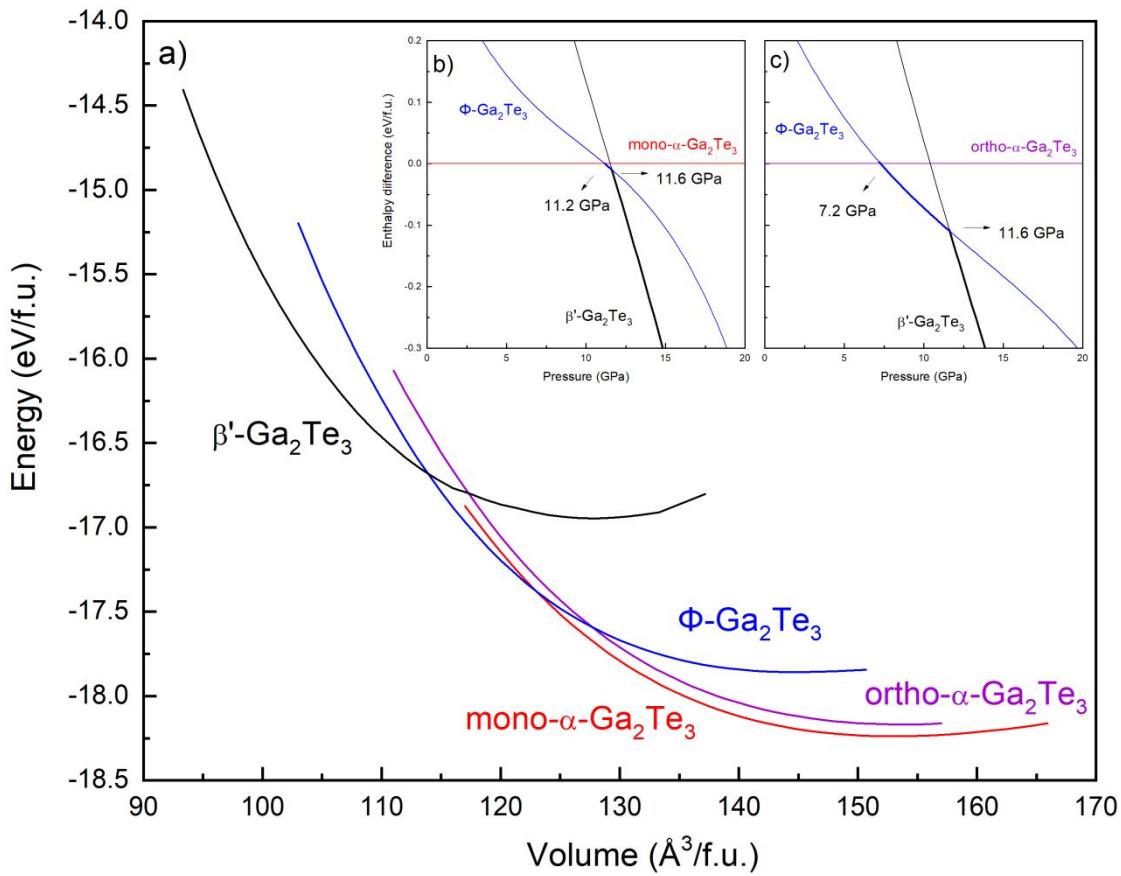
66 **Figure S6.** a) Theoretical volume dependence of the total energy of mono- β -, ortho- β -, β' -, and
67 ϕ - Ga_2Se_3 . b) Theoretical pressure dependence of the enthalpy difference between mono- β -, β' -,
68 and ϕ - Ga_2Se_3 , taking the former as a reference, and c) between ortho- β -, β' -, and ϕ - Ga_2Se_3 ,
69 taking the former as a reference.



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72 **Figure S7.** a) Theoretical volume dependence of the energy of mono- α -, ortho- α -, β' -, and ϕ -
 73 Ga_2Te_3 . b) Theoretical pressure dependence of the enthalpy difference between mono- α' -, β' -,
 74 and $\phi\text{-}\text{Ga}_2\text{Te}_3$, taking the former as a reference, and c) between ortho- α -, β' -, and $\phi\text{-}\text{Ga}_2\text{Te}_3$,
 75 taking the former as a reference.



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78 **References**

- 79 1. Gallego-Parra, S., et al., *Structural, vibrational and electronic properties of α' -Ga₂S₃*
80 under compression. Physical Chemistry Chemical Physics, 2021. **23**(11): p. 6841-6862.
81 DOI <https://doi.org/10.1039/D0CP06417C>.

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