Supplementary Information

Optically decomposed near-band-edge structure and excitonic transitions in Ga_2S_3

Ching-Hwa Ho[1,2,*] and Hsin-Hung Chen[1]

[1]*Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan*

[2]*Graduate Institute of Electro-Optical Engineering and Department of Electronic and Computer Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan.*

[*]Corresponding author; E-mail: chho@mail.ntust.edu.tw

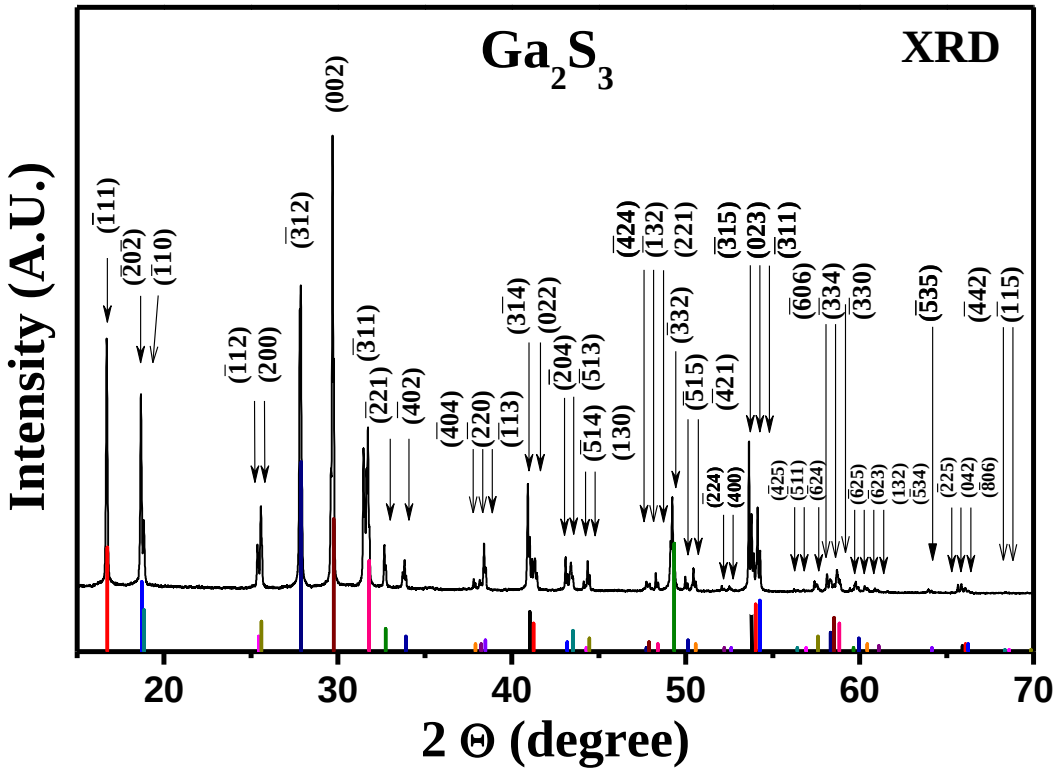
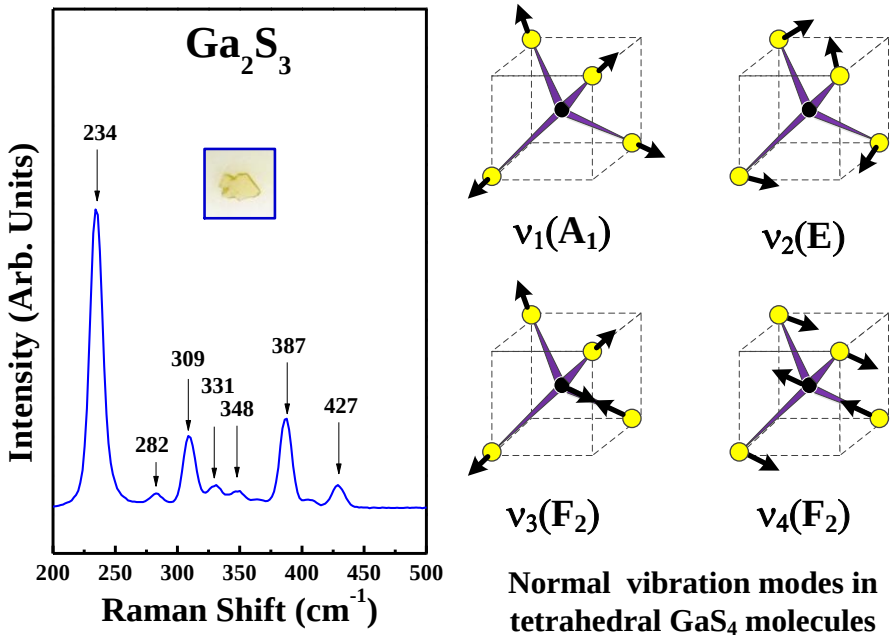


Figure SI-1. X-ray diffraction (XRD) pattern of Ga_2S_3. The XRD sample was prepared by finely grinding the small crystals of Ga_2S_3 into a powered form. The measurement range is from 15° to 70°. A JCPDS diffraction data of Ga_2S_3 with the monoclinic phase is also included for comparison.

To confirm the crystalline phase of the as-grown Ga_2S_3, powdered X-ray diffraction (XRD) measurement by using the small (ground) crystals of Ga_2S_3 (i.e. powdered form) was implemented. Figure SI-1 shows the XRD result of the as-grown Ga_2S_3. Many diffraction peaks are observed in the angular range (2Θ) between 10 and 70° owing to the lower symmetry of monoclinic structure of Ga_2S_3 comprised in the unit cell. The relative narrowed line-width broadening for each diffraction peak feature indicated that high crystalline quality of Ga_2S_3 was existed in the as-grown crystals as comparing to those of the other polycrystalline thin-film forms. The monoclinic symmetry of the as-grown Ga_2S_3 is confirmed by comparing the data with previous XRD result of monoclinic Ga_2S_3 (Card No. 48-1432).[32]



(a) **(b)**

Raman modes (cm^{-1})	Attribution
234	ν_s-GaS_4 (A_1)
282	ν_s-GaS_4 (A_1)
309	ν_d-GaS_4 (A')
331	ν_d-GaS_4 (A')
348	ν_d-GaS_4 (F_2)
387	ν_d-GaS_4 (F_2)
427	ν_d-GaS_4 (Ga-S-Ga)

(c)

Figure SI-2. (a) Raman spectrum of Ga_2S_3 done on the *c* plane. The morphology of a polished as-grown Ga_2S_3 crystal is also included, which shows transparent and light-yellow colored. (b) Representative schemes of the normal vibration modes of $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ in the GaS_4 tetrahedra molecular inside the digallium trisulfide. (c) The assignments of vibration frequencies detected in the Raman spectrum of Ga_2S_3 that correlated with the oscillation modes in the GaS_4 molecules.

Figure SI-2(a) shows the Raman spectrum of the Ga_2S_3 in the energy range of 200-500 cm^{-1}. The crystal morphology and crystal color of the Ga_2S_3 sample are also

displayed in the inset of Fig. SI-2(a). The Ga_2S_3 crystal essentially shows transparent and yellow colored. The crystal color indicates that Ga_2S_3 is a wide-band-gap semiconductor with its corresponding wavelength shorter than that of visible light. As shown in the Raman spectrum of Fig. SI-2(a), there are seven peak features at 234, 282, 309, 331, 348, 387, and 427 cm^{-1} detected in the Ga_2S_3 crystal. Most of the frequencies can be assigned in terms of internal and external vibrations of tetrahedral GaS_4 groups.[21,22] The symmetric GaS_4 molecule has four fundamental vibration modes expressed by $\Gamma=A_1+E+F_1+F_2$ as indicated in Fig. SI-2(b). For the Raman scattering of the monoclinic Ga_2S_3, the dominant peaks are located at 234 and 387 cm^{-1} [see Fig. SI-2(a)], which can be primarily associated with the $\nu_1(A_1)$ and $\nu_4(F_2)$ modes of the GaS_4 molecular unit. Listed in Fig. SI-2(c) are the assignments of Raman modes observed in the Fig. SI-2(a) of Ga_2S_3 and that associated with the vibrations of the GaS_4 molecules are also shown in Fig. SI-2(b). The structure of monoclinic Ga_2S_3 is close to a defective wurtzite structure (like γ-In_2Se_3), and which exhibits tetrahedral bonding and one-third Ga sites (on the average) are vacant tend to broaden the line widths of the Raman peak features. The Raman peak features of Fig. SI-2(a) reveal relative narrowed line widths and clear peak positions as comparing to those of the thin-film forms. It indicates that the as-grown Ga_2S_3 crystals possess high quality and are crystallized in the monoclinic structural phase.

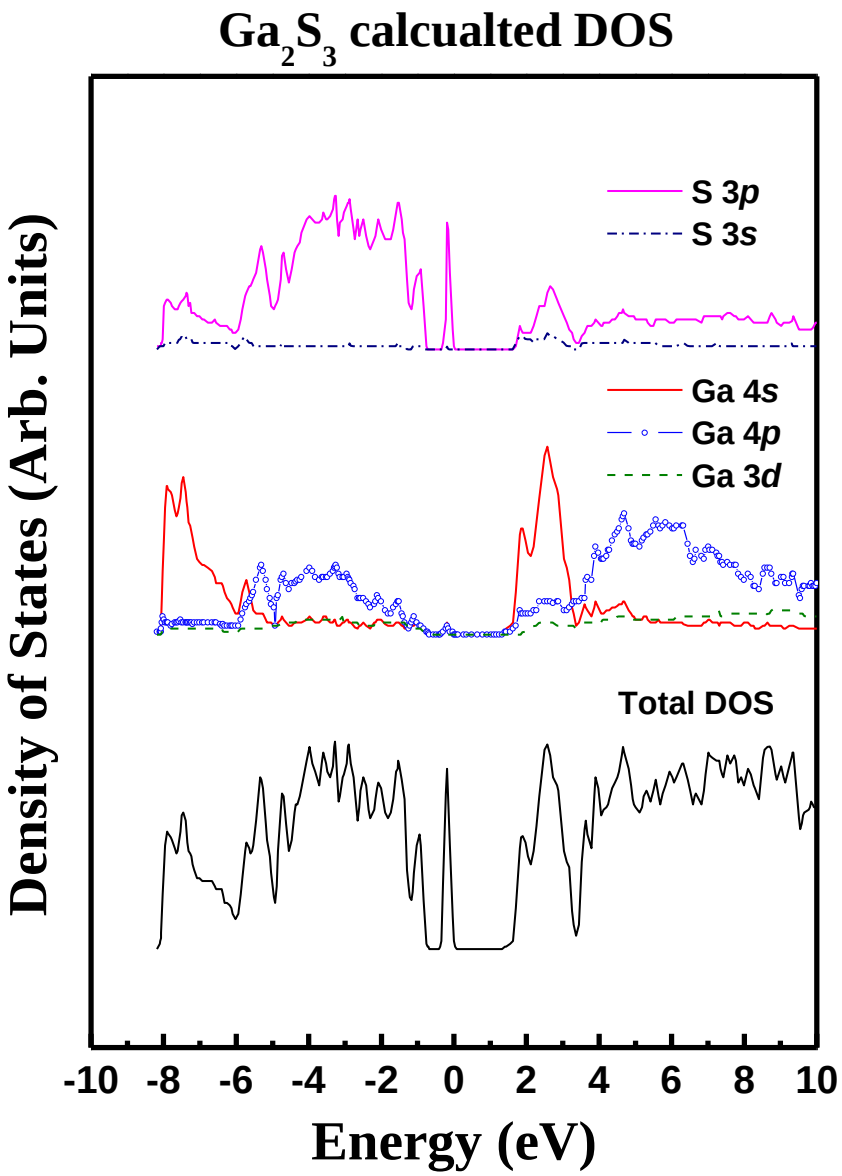


Figure SI-3. The calculated partial and total density of states (DOS) of Ga_2S_3. The band edge is consisted of mainly S 3*p* and a little Ga 4*p* electron in the valence band. The largely Ga 4*s* and a little S 3*p* state are comprised in the conduction band. The highly oriented *p* electron consisted in the top of the valence band may render strongly optical anisotropy of Ga_2S_3 detected by orientation-dependent and polarization-dependent TR spectra.

For the computational work, we utilized WEIN97 software to calculate the electronic density of states for the Ga_2S_3. This program package is capable of performing the electronic structure calculations of solid using full-potential Linearized-Augmented-Plane-Wave (LAPW) method.[33] By taking the information of lattice parameters, space group, and atomic coordination of Ga_2S_3 into the WIEN 97 software, the partial density of states of Ga atoms and S atoms and total density of states of the digallium trisulfide compound can be respectively determined.

Supplementary Information References:

32. Pardo, M. P., Guittard, M., Chilouet, A., Tomas, A., Diagrammme de phases gallium-soufre et etudes structurales des phases soildes, *J. Soild State Chem.* **102**, 423-433 (1993).

33. Blaha, P., Schwarz, K., Luitz, J. WIEN97 - A Full-Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties, Vienna University of Technology **1997**, Vienna, Austria.