

ENHANCED OPTICAL PROPERTIES OF β -Ga₂O₃- x S_x: A DFT STUDY

G.B. Eshonqulov^{1,*}, A.A. Meyliyeva², Sh. U. Yuldashev^{1,2},
G.R. Berdiyev³

¹Department of Physics, National University of Uzbekistan, Tashkent,
Uzbekistan

²Center for Development of Nanotechnology, National University of Uzbekistan, Tashkent,
Uzbekistan

³Qatar Environment and Energy Research Institute, Hamad Bin Khalifa University, Doha,
Qatar

Crystalline β -Ga₂O₃ has received renewed interest in recent years as a strong candidate for power electronic and optoelectronic devices [1,2], UV photodetectors [3,4], sensors, and solar cells, due to its low-cost, large-area fabrication, suitable UV transmission properties, and high breakdown electric characteristics. The performance of Ga₂O₃-based devices strongly depends on the quality of the material and its structural properties [3]. One of the main drawbacks limiting the use of β -Ga₂O₃-based devices in broader electronic applications is its wide band gap (4.5 to 4.8 eV) [5,6]. Ga₂O₃-based hybrid materials have been proposed as a promising approach for band gap engineering, where the combination of wide and narrow band gap materials optimizes the overall band structure, enhancing complex electronic and optical properties [7].

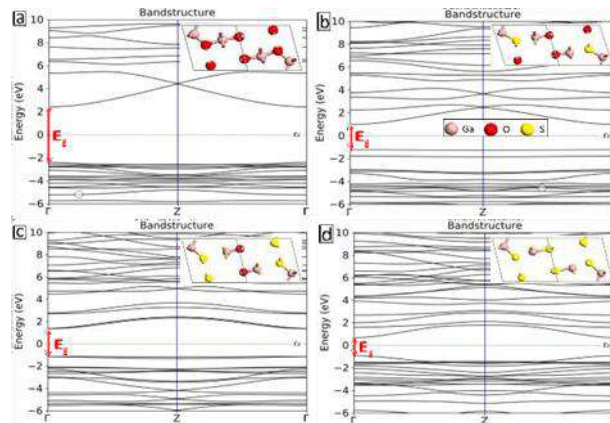


Figure 1. Band structure of β -Ga₂O₃ - x S_x for $x = 0$ (a), $x = 1$ (b), $x = 2$ (c) and $x = 3$ (d). Insets show the optimized structures of the samples.

Here, we use DFT calculations to conduct a systematic study of the structural, electronic, and

optical properties of sulfur-doped $\text{Ga}_2\text{O}_3\text{--}\chi\text{S}_\chi$ material. The structural and electronic properties of the considered samples are studied using DFT with the metageneralized gradient approximation (meta-GGA) of Tran and Blaha (TB09) for the exchange correlation energy. The Brillouin zone sampling was performed using a $15 \times 15 \times 15$ Monkhorst Pack k -point. Norm conserving PseudoDojo pseudopotential with medium basis sets were applied for all atoms in the system with a real space grid with a mesh cutoff energy of 250 Ry. Grimme's PBE-D empirical dispersion correction was used for van der Waals interactions during structural optimizations only.

We start by studying the structural properties of the $\beta\text{-Ga}_2\text{O}_{3-\chi}\text{S}_\chi$ systems. For each doping level, we generated up to 13 distinct configurations by substituting sulfur atoms at different oxygen sites within the 10-atom supercell. These configurations represent all possible symmetry inequivalent arrangements of sulfur atoms for a given doping concentration. Table 1 presents the structural parameters and band gap values of the seven lowest energy configurations selected from this process, corresponding to different sulfur doping levels. Insets in Fig. 1 show the optimized ground state configurations for selected doping levels. It can be seen from Table 1 that the lattice parameters b and c increase with increasing sulfur content. The lattice parameter a increases up to 50% sulfur doping, after which it slightly decreases. A similar trend is observed for the angle β . However, the volume of the unit cell increases consistently with the level of sulfur doping. It is important to note that the lattice type (base centered monoclinic) was kept fixed during the geometry optimization. Next, we study how sulfur doping affects the electronic properties of the material. To obtain accurate band structures of the $\beta\text{-Ga}_2\text{O}_{3-\chi}\text{S}_\chi$ samples, we performed calculations using the TB09 meta-GGA exchange correlation functional. Fig. 1 shows the band structures of several representative systems. For the pristine sample (Fig. 1(a)), we obtained a direct band gap of $E_g = 4.81$ eV, which is in good agreement with previous experimental [5] and theoretical studies using different levels of DFT. Sulfur doping leads to a significant reduction in the band gap (see Fig. 1(b)). Both the valence and conduction bands shift closer to the Fermi level, while the direct nature of the band gap is preserved. As the sulfur concentration increases, the band gap continues to decrease, although the overall band structure topology remains unchanged (see Fig. 1(c)). The smallest band gap, $E_g = 1.59$ eV, is observed for the fully substituted $\beta\text{-Ga}_2\text{S}_3$ system (see Fig. 1(d)). To examine the contribution of sulfur atoms to the electronic structure, we present in Fig. 2 the total density of states (DOS) (solid curves) and the DOS projected onto sulfur atoms (dashed curves) for $\text{Ga}_2\text{O}_2\text{S}_1$ (red curves) and $\text{Ga}_2\text{O}_1\text{S}_2$ (green curves). For reference, the results for Ga_2O_3 (solid black curve) and Ga_2S_3 (solid blue curve) are also included. In both partially doped systems, sulfur atoms contribute significantly to both the valence and conduction band edges. Only minor deviations are observed in the conduction band at energies away from the band edges. These results demonstrate that DFT simulations predict the tunability of the electronic properties of $\beta\text{-Ga}_2\text{O}_3$ materials through sulfur

substitutional doping.

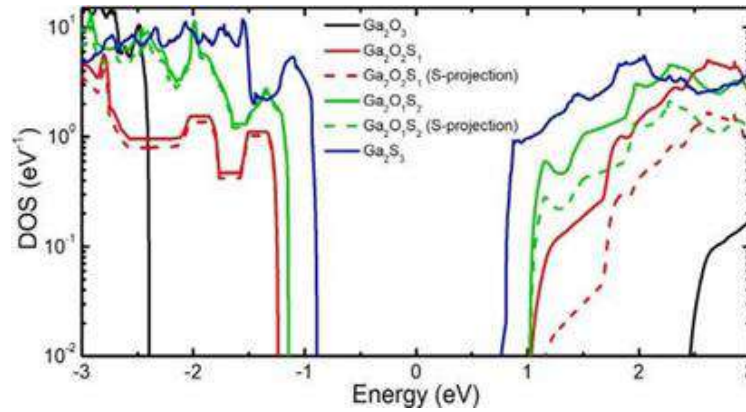


Figure 2. Density of states (DOS) of β -Ga₂O₃ (solid-black curve), β -Ga₂O₂S₁ (solid-red curve), β -Ga₂O₁S₂ (solid-green curve) and β -Ga₂S₃ (solid-blue curve) samples. Dashed-red and dashed-green curves show the DOS of β -Ga₂O₂S₁ and β -Ga₂O₁S₂ samples, respectively, projected on sulfur atoms.

Table 1

System	a (Å)	b (Å)	c (Å)	α	β	γ	Volume (Å ³)	S-concentration (%)	E_g (eV)
β -Ga ₂ O ₃	12.44	3.09	5.88	90°	103.71°	90°	109.87	0	4.81
β -Ga ₂ O _{2.5} S _{0.5}	12.28	3.21	6.28	90°	103.31°	90°	120.34	16.7	2.93
β -Ga ₂ O ₃ S ₁	14.96	3.25	6.29	90°	107.22°	90°	145.96	33.3	2.21
β -Ga ₂ O _{1.5} S _{1.5}	16.25	3.40	6.39	90°	110.08°	90°	165.93	50	2.49
β -Ga ₂ O ₁ S ₂	15.60	3.41	6.90	90°	102.62°	90°	178.99	66.7	2.51
β -Ga ₂ O _{0.5} S _{2.5}	13.85	3.80	7.33	90°	104.32°	90°	186.70	83.3	2.21
β -Ga ₂ S ₃	15.81	3.67	7.07	90°	102.52°	90°	200.20	100	1.59

Structural parameters and band-gap energy of β -Ga₂O_{3- x} S _{x} samples.

Using first principles density functional theory calculations, we studied the effect of sulfur substitutional doping on the structural, electronic, and optical properties of

β -Ga₂O₃ material. We found that the electronic band gap decreases by more than a factor of

two, depending on the level of doping.

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