Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

Band-Resolved Optical Properties of Rock-Salt BaSe and BaS from FP-LAPW Density Functional Theory

Fasih Ud Din*
Department of Physics, Grand Asian University, Sialkot, 7 km Pasrur Road, Sialkot, Punjab 51310, Pakistan
fasih.uddin@gaus.edu.pk, uddin.fasih@gmail.com

Ammar Younis
Department of Physics, Grand Asian University, Sialkot, 7 km Pasrur Road, Sialkot, Punjab 51310, Pakistan

Varda Jabbar
Department of Physics, Grand Asian University, Sialkot, 7 km Pasrur Road, Sialkot, Punjab 51310, Pakistan

Atlas Noreen
Department of Physics, Grand Asian University, Sialkot, 7 km Pasrur Road, Sialkot, Punjab 51310, Pakistan

Alveena Altaf
Department of Physics, Grand Asian University, Sialkot, 7 km Pasrur Road, Sialkot, Punjab 51310, Pakistan

ABSTRACT

The optical properties of the alkaline-earth chalcogenides barium selenide (BaSe) and barium sulfide (BaS) are investigated from first principles within density functional theory (DFT), using the full-potential linearized augmented plane-wave plus local-orbitals (FP-LAPW+lo) method as implemented in the WIEN2k code, building on the structural and electronic-structure results reported in a companion paper. The interband contribution to the optical response — which underlies the imaginary part of the frequency-dependent dielectric function, $\varepsilon_2(\omega)$, and from which the real part, the refractive index, the absorption coefficient, and the reflectivity can in turn be obtained via the Kramers–Kronig relations — was calculated for photon energies up to 14 eV. The principal spectral features were identified and assigned to specific valence-to-conduction-band transitions at high-symmetry points and lines of the Brillouin zone, including transitions at Γ, Λ, W, K, and L. The fundamental absorption onset occurs at lower photon energy in BaSe than in

Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

BaS, consistent with the smaller band gap expected for the larger, more polarisable Se^{2-} anion, while the ordering of the higher-energy spectral features between the two compounds varies from peak to peak, reflecting differences in the higher conduction-band dispersion. Both compounds show strong interband optical activity extending from the visible into the ultraviolet, consistent with their potential use in optoelectronic devices such as light-emitting diodes and semiconductor lasers, and the results are shown to be consistent with the wider body of experimental and computational work on the barium and alkaline-earth chalcogenides.

Keywords: Optical properties; dielectric function; refractive index; absorption; BaSe; BaS; WIEN2k; density functional theory

1. Introduction

The interaction of light with semiconductors underlies the operation of a wide range of optoelectronic devices, including light-emitting diodes, semiconductor lasers, and photodetectors, and the frequency-dependent dielectric response of a candidate material is therefore a key quantity for assessing its suitability for such applications. The alkaline-earth chalcogenides BaSe and BaS, which crystallise in the rock-salt (B1) structure and are indirect-gap semiconductors, have attracted interest in this context because of their wide, tunable optical response and their structural and chemical relationship to other II–VI and lead-chalcogenide optoelectronic materials.

The optical constants of a semiconductor — the frequency-dependent dielectric function, refractive index, absorption coefficient, and reflectivity — are directly connected to its electronic band structure through the joint density of states and the interband momentum matrix elements [1]. For wide-gap ionic semiconductors such as the alkaline-earth chalcogenides, these optical constants are also comparatively sensitive to alloying and to chemical substitution, which has motivated a substantial body of work on optical bowing and band-gap tuning across related chalcogenide alloy systems [2] and on the size-dependent optical response of chalcogenide nanostructures and quantum dots [3].

In a companion paper we reported the structural and electronic-structure properties of BaSe and BaS, computed within the full-potential linearized augmented plane-wave plus local-orbitals (FP-LAPW+lo) method as implemented in the WIEN2k code [4]. There we showed that both compounds crystallise in the six-fold-coordinated B1 structure at ambient pressure and are indirect-gap ($\Gamma \rightarrow X$) semiconductors whose fundamental gap narrows with increasing chalcogen atomic number, in agreement with the wider structural and electronic systematics established for the barium and alkaline-earth chalcogenide family by earlier first-principles studies [5–9].

The optical properties of the barium chalcogenides specifically have been examined in a smaller number of earlier first-principles studies. Feng et al. computed the electronic and optical properties of BaS, BaSe, and BaTe [10], and an earlier study by Pourghazi and Dadsetani examined the band structure and optical spectra of the same three compounds using a full-potential approach [11]. These optical studies, together with the structural, elastic, and high-pressure characterisation of the

Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

barium chalcogenides reported elsewhere [5,12–18], provide the background against which the present, more detailed band-resolved analysis of BaSe and BaS is set.

In the present work we build directly on the electronic structure reported in the companion paper to compute the interband optical response of BaSe and BaS within the same FP-LAPW+lo framework. We identify the principal features of the optical spectrum of each compound, assign them to specific interband transitions at high-symmetry points and lines of the Brillouin zone, and discuss the implications of the computed absorption onset and spectral range for optoelectronic applications, drawing comparisons with the optical and electronic trends established for the wider alkaline-earth and II–VI chalcogenide families [19].

2. Computational Methodology

The ground-state electronic structure of BaSe and BaS was computed as described in the companion paper [4], within the framework of density functional theory (DFT) [22,23], using the FP-LAPW+lo method as implemented in WIEN2k [20], with the generalized gradient approximation [24] used for the exchange-correlation potential and a basis-set cut-off of RMT×Kmax = 7 (RMT = 2.5 a.u.) for both compounds; the Engel–Vosko GGA [25] and the Tran–Blaha modified Becke–Johnson potential [26] were used in the companion paper to improve the description of the band gap that underlies the transitions discussed below. The optical properties reported here were obtained from this electronic structure using the WIEN2k optic module, which evaluates the momentum matrix elements between occupied and unoccupied Kohn–Sham states directly within the LAPW basis [21].

Within the random-phase and dipole approximations, the imaginary part of the frequency-dependent dielectric function, $\varepsilon_2(\omega)$, is given by a Brillouin-zone sum of the squared momentum matrix elements between valence (v) and conduction (c) bands, weighted by a delta function that enforces energy conservation at each photon energy $\hbar\omega$. The energy-conserving delta function alone, without the matrix-element weighting, defines the joint density of states, which identifies the photon energies at which vertical (k-conserving) interband transitions are allowed by the band structure; Figures 1 and 2 show this interband transition spectrum for BaS and BaSe, respectively. The real part of the dielectric function, $\varepsilon_1(\omega)$, follows from $\varepsilon_2(\omega)$ via the Kramers–Kronig relation, and the refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption coefficient $\alpha(\omega)$, and normal-incidence reflectivity $R(\omega)$ are in turn obtained from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ in the standard way [21]:

$$n(\omega) = \sqrt{\{ [\sqrt{(\varepsilon_1^2 + \varepsilon_2^2)} + \varepsilon_1] / 2 \}} \qquad k(\omega) = \sqrt{\{ [\sqrt{(\varepsilon_1^2 + \varepsilon_2^2)} - \varepsilon_1] / 2 \}}$$

$$\alpha(\omega) = 2\omega k(\omega) / c \qquad R(\omega) = [(n-1)^2 + k^2] / [(n+1)^2 + k^2]$$

The structural parameters (lattice constants) used as input for these calculations are the equilibrium GGA values reported for the B1 phase of BaSe and BaS in the companion paper [4].

3. Results and Discussion

3.1 Interband Optical Transition Spectrum

Figures 1 and 2 show the calculated interband optical transition spectrum of BaS and BaSe, respectively, as a function of photon energy up to 14 eV. Both spectra show a strong, sharp onset at low photon energy, followed by a rapid decay and a broader, weaker structure in the 5–9 eV range before tailing off toward 14 eV. This near-edge response is stronger and occurs at slightly

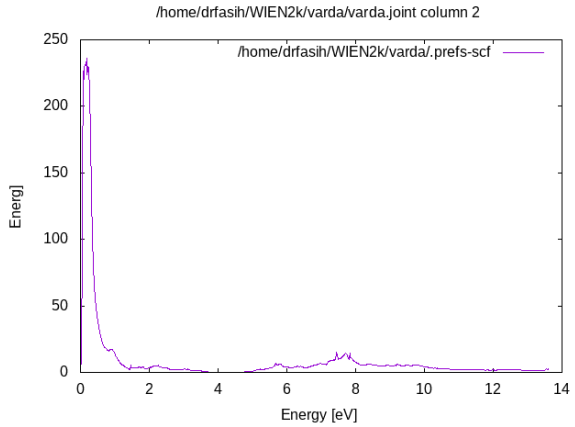
Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

lower photon energy in BaS than in BaSe. Because standard GGA is known to underestimate the fundamental band gap, as discussed in the companion paper [4], the absolute energy scale of the onset should be regarded as a lower bound on the true absorption edge; the relative ordering between the two compounds and the overall two-region shape of the spectrum — a strong near-edge response followed by a weaker, broader feature at higher energy associated with transitions deeper in the valence and conduction bands — are expected to be more robust than the absolute energy scale.

This two-region spectral shape is qualitatively consistent with the optical spectra reported for BaS, BaSe, and BaTe by Feng et al. [10] and by Pourghazi and Dadsetani [11], both of whom likewise found the strongest optical response concentrated within a few eV of the absorption onset, with a weaker, more structured response extending to higher photon energy. The same general shape — a dominant near-edge feature followed by weaker higher-energy structure — is also characteristic of the optical spectra reported for the isostructural cadmium chalcogenides [19] and for chalcogenide alloys more generally [12], suggesting that it reflects a bonding pattern common to this wider class of compounds rather than a feature specific to the barium compounds alone.



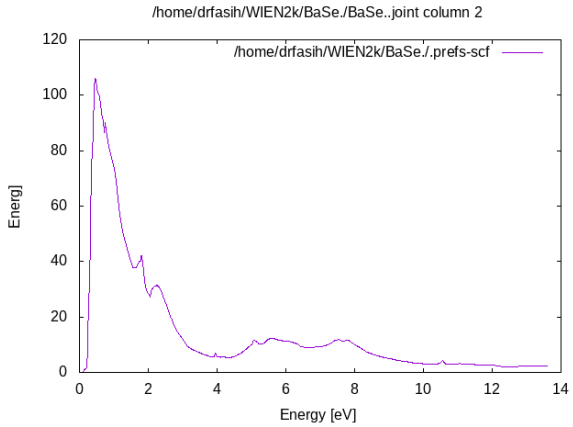


Figure 1. Calculated interband optical transition spectrum of BaS (left) and Figure 2. BaSe (right), as a function of photon energy.

3.2 Dielectric Function Peaks and Transition Assignment

Table 1 lists the peak positions of the imaginary part of the dielectric function, $\varepsilon_2(\omega)$, for BaSe and BaS, together with the dominant valence-to-conduction-band transitions responsible for each peak and its location in the Brillouin zone. Six principal peaks, labelled A–F, are identified for each compound.

Table 1. Peak positions of the imaginary part of the dielectric function, $\varepsilon_2(\omega)$, for BaSe and BaS, with the dominant interband transitions and their location in the Brillouin zone.

Peak	Peak position (eV)		Dominant transition		Location in BZ
	BaSe	BaS	From band(s)	To band	
A	3.55	4.35	6 and 7	8	Γ–Γ

Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

Peak	Peak position (eV)		Dominant transition		Location in BZ
	BaSe	BaS	From band(s)	To band	
B	5.48	5.88	7	9	Λ
C	6.95	6.4	7	10	W–W
D	7.27	7.14	6 and 7	11	W–W and K–K
E	9.85	9.36	6 and 7	14	L–L
F	17.29	17.91	2 and 3	10	W–W and L–L

Peak A, the lowest-energy feature, occurs at 3.55 eV in BaSe and 4.35 eV in BaS, and in both compounds is dominated by transitions from bands 6 and 7 to band 8 at the zone centre (Γ→Γ); the lower energy of this peak in BaSe is consistent with the smaller fundamental gap expected for the larger, more polarisable Se^{2-} anion, following the same trend discussed for the band structure in the companion paper [4]. The remaining peaks (B–F) originate predominantly from transitions along the Λ direction and at the W, K, and L points of the Brillouin zone. Their relative ordering between the two compounds is less systematic than that of peak A: peaks B and F occur at lower energy in BaSe than in BaS, while peaks C, D, and E occur at higher energy in BaSe than in BaS. This mixed ordering reflects differences in the dispersion of the higher conduction bands between the two compounds, rather than a uniform rigid shift of the whole spectrum, and is consistent with the band-structure comparison presented in the companion paper [4].

The assignment of the low-energy peak A to zone-centre transitions is consistent with the direct optical response generally reported at Γ for the barium chalcogenides in earlier band-structure calculations [8,15,16], even though, as established in the companion paper, the fundamental (lowest-energy) gap of both compounds is indirect, between the valence-band maximum at Γ and the conduction-band minimum at X. The narrowing of peak A from BaS to BaSe reproduces the same chalcogen-dependent trend reported for the wider barium chalcogenide series by Feng et al. and by Lin, Gong, and Wu [10,8], and is consistent with the general pattern of gap bowing and gap narrowing with increasing anion size documented for chalcogenide alloys more broadly [2,12].

3.3 Implications for Optoelectronic Applications

Taken together, the interband transition spectra (Figs. 1, 2) and the ε_2 peak positions (Table 1) place the onset of strong interband absorption for both compounds below about 4–5 eV, with measurable optical activity persisting up to nearly 18 eV (peak F). BaSe and BaS are therefore optically active across essentially the entire visible range and well into the ultraviolet. Combined with the indirect Γ→X fundamental gap established in the companion paper [4], this places both compounds among the materials of interest for UV–visible optoelectronic applications, including photoluminescent and electroluminescent devices, consistent with the motivation for this and earlier studies of the barium chalcogenides [10,11].

This spectral range is broadly comparable to that reported for the related compound BaTe and for BaS and BaSe by Feng et al. [10], and is consistent with the general trend, established across the

Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

isostructural cadmium chalcogenide series [19] and in size-tunable chalcogenide quantum dots [3], that the onset of strong interband absorption in this class of compound tracks the fundamental electronic gap closely enough to make band-gap engineering — whether by alloying [12,2], doping [15], or pressure [14,17] — a viable route to tuning the optical response for specific device applications. A quantitative comparison with experimental absorption or reflectivity spectra, where these become available, and an extension of the present GGA-level calculation to the EV-GGA and mBJ schemes used for the band structure in the companion paper, would help to place the absolute energy scale of the computed spectra on a firmer footing.

3.4 Comparison with Related Barium and Alkaline-Earth Chalcogenide Optical Studies

The two-region spectral shape and the chalcogen-dependent trend in the absorption onset established here for BaSe and BaS are consistent with the broader pattern reported across the barium chalcogenide series, including BaTe, by earlier first-principles optical studies [10,11]. They are also consistent with the general relationship between structural, electronic, and optical properties documented for the wider alkaline-earth chalcogenide family [5,6,7] and for the isostructural cadmium chalcogenides [19], in which the optical absorption edge tracks the fundamental electronic gap and both narrow systematically as the chalcogen atomic number increases.

Taken together with the gap-bowing behaviour reported for barium chalcogenide alloys [12] and for isoelectronic zinc chalcogenide alloys [2], and with the size-dependent optical tunability demonstrated in chalcogenide quantum dots [3], these results reinforce the view that the barium chalcogenides form part of a chemically and structurally coherent family whose optical response can be tuned systematically through chalcogen substitution, alloying, doping [15], or applied pressure [14,17,18,16]. This consistency across independent studies, obtained with a range of first-principles methods, supports the reliability of the present band-resolved assignment of the BaSe and BaS optical spectra and provides a point of reference for future experimental or higher-level theoretical work on these compounds.

4. Conclusion

We have presented a first-principles study of the interband optical response of the alkaline-earth chalcogenides BaSe and BaS, computed within the FP-LAPW+lo method as implemented in WIEN2k, building on the structural and electronic-structure results reported in a companion paper. The calculated interband transition spectra of both compounds show a strong near-edge response followed by a weaker, broader structure extending to nearly 18 eV, and the principal features of the imaginary dielectric function were assigned to specific transitions at Γ, Λ, W, K, and L. The absorption onset occurs at lower photon energy in BaSe than in BaS, consistent with the smaller fundamental gap of BaSe, while the ordering of the higher-energy features varies from peak to peak between the two compounds. These trends are consistent with, and extend, the wider body of experimental and computational work on the optical and electronic properties of the barium and alkaline-earth chalcogenides. Taken together with the electronic-structure results of the companion paper, these results support the potential use of BaSe and BaS in optoelectronic devices operating from the visible into the ultraviolet.

Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

References

[1] Yu, P. Y., & Cardona, M. (2010). Fundamentals of Semiconductors: Physics and Materials Properties (4th ed.). Springer-Verlag Berlin Heidelberg.

[2] Bernard, J. E., & Zunger, A. (1986). Optical bowing in zinc chalcogenide semiconductor alloys. Physical Review B, 34(8), 5992–5995.

[3] Al-Douri, Y., Khachai, H., & Khenata, R. (2015). Chalcogenides-based quantum dots: optical investigation using first-principles calculations. Materials Science in Semiconductor Processing, 39, 276–282.

[4] Jabbar, V., & Ud Din, F. Structural and electronic properties of BaSe and BaS: A first-principles study. Companion paper.

[5] Bouhemadou, A., Khenata, R., Zegrar, F., Sahnoun, M., Baltache, H., & Reshak, A. H. (2006). Ab initio study of structural, electronic, elastic and high-pressure properties of barium chalcogenides. Computational Materials Science, 38(2), 263–270.

[6] Khenata, R., Sahnoun, M., Baltache, H., Rérat, M., Rached, D., Driz, M., & Bouhafs, B. (2006). Structural, electronic, elastic and high-pressure properties of some alkaline-earth chalcogenides: An ab initio study. Physica B: Condensed Matter, 371(1), 12–19.

[7] El Haj Hassan, F., & Akbarzadeh, H. (2006). First-principles elastic and bonding properties of barium chalcogenides. Computational Materials Science, 38(2), 362–368.

[8] Lin, G. Q., Gong, H., & Wu, P. (2005). Electronic properties of barium chalcogenides from first-principles calculations: Tailoring wide-band-gap II-VI semiconductors. Physical Review B, 71(8), 085203.

[9] Tuncel, E., Colakoglu, K., Deligoz, E., & Ciftci, Y. O. (2009). A first-principles study on the structural, elastic, vibrational, and thermodynamical properties of BaX (X = S, Se, and Te). Journal of Physics and Chemistry of Solids, 70(2), 371–378.

[10] Feng, Z., Hu, H., Lv, Z., & Cui, S. (2010). First-principles study of electronic and optical properties of BaS, BaSe and BaTe. Open Physics, 8(5), 782–788.

[11] Pourghazi, A., & Dadsetani, M. (2005). Electronic and optical properties of BaTe, BaSe and BaS from first principles. Physica B: Condensed Matter, 370(1–4), 35–45.

[12] Drablia, S., Meradji, H., Ghemid, S., Nouet, G., & Hassan, F. E. H. (2009). First-principles investigation of barium chalcogenide ternary alloys. Computational Materials Science, 46(2), 376–382.

[13] Benamrani, A., Kassali, K., & Bouamama, K. (2010). Pseudopotential study of barium chalcogenides under hydrostatic pressure. High Pressure Research, 30(1), 207–218.

[14] Zagorac, D., Doll, K., Zagorac, J., Jordanov, D., & Matović, B. (2017). Barium sulfide under pressure: Discovery of metastable polymorphs and investigation of electronic properties on ab initio level. Inorganic Chemistry, 56(17), 10644–10654.

[15] Berriah, K., Doumi, B., Mokaddem, A., Elkeurti, M., Sayede, A., Tadjer, A., & Araújo, J. P. (2018). Theoretical investigation of electronic performance, half-metallicity, and magnetic properties of Cr-substituted BaTe. Journal of Computational Electronics, 17(3), 909–919.

Annual Methodological Archive Research Review
http://amresearchreview.com/index.php/Journal/about
Volume 3, Issue 12 (2025)

Online ISSN 3007-3197
Print ISSN 3007-3189

http://amresearchreview.com/index.php/Journal/about

[16] Carlsson, A. E., & Wilkins, J. W. (1984). Band-overlap metallization of BaS, BaSe, and BaTe. Physical Review B, 29(10), 5836.
[17] Grzybowski, T. A., & Ruoff, A. L. (1983). High-pressure phase transition in BaSe. Physical Review B, 27(10), 6502–6503.
[18] Jha, P. K., Sakalle, U. K., & Sanyal, S. P. (1998). High pressure structural phase transition in alkaline earth chalcogenides. Journal of Physics and Chemistry of Solids, 59(9), 1633–1637.
[19] Ouendadji, S., Ghemid, S., Meradji, H., & Hassan, F. E. H. (2011). Theoretical study of structural, electronic, and thermal properties of CdS, CdSe and CdTe compounds. Computational Materials Science, 50(4), 1460–1466.
[20] Blaha, P., Schwarz, K., Madsen, G. K. H., Kvasnicka, D., & Luitz, J. (2001). WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties. Vienna University of Technology, Austria.
[21] Ambrosch-Draxl, C., & Sofo, J. O. (2006). Linear optical properties of solids within the full-potential linearized augmented planewave method. Computer Physics Communications, 175(1), 1–14.
[22] Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. Physical Review, 136(3B), B864–B871.
[23] Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. Physical Review, 140(4A), A1133–A1138.
[24] Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized gradient approximation made simple. Physical Review Letters, 77(18), 3865–3868.
[25] Engel, E., & Vosko, S. H. (1993). Exact exchange-only potentials and the virial relation as microscopic criteria for generalized gradient approximations. Physical Review B, 47(20), 13164–13174.
[26] Tran, F., & Blaha, P. (2009). Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. Physical Review Letters, 102(22), 226401.