Research Article

Electronic Structure and Momentum Density of BaO and BaS

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The electronic structure and electron momentum density distribution in BaO and BaS are presented using Compton spectroscopy. The first-ever Compton profile measurements on polycrystalline BaO and BaS were performed using 59.54 keV gamma-rays. To interpret the experimental data, we have computed the theoretical Compton profiles of BaO and BaS using the linear combination of atomic orbitals method. In the present computation, the correlation scheme proposed by Perdew-Burke-Ernzerhof and the exchange scheme of Becke were considered. The hybrid B3PW and Hartree-Fock based profiles were also computed for both compounds. The ionic configurations are performed to estimate the charge transfer on compound formation, and the present study suggests charge transfer from Ba to O and S atoms. On the basis of equal-valence-electron-density profiles, it is found that BaO is more ionic as compared to BaS.

1. Introduction

The II–VI alkaline earth compounds have interesting bond characteristics and simple crystal structures. BaO and BaS have potential applications in light-emitting diodes (LEDs), laser diodes (LDs), and magneto-optical devices [1–4]. BaO is an indirect bandgap, whereas BaS is a direct bandgap material. At normal conditions, BaO and BaS crystallize in NaCl (B1) structure, but under pressure, they show structural phase transition from B1 to B2 structure [5, 6]. Using the full-potential linearized augmented plane wave (FP-LAPW) method, Drablia et al. [7] reported the electronic and optical properties of BaO and BaS in cubic phase at normal and under hydrostatic pressure. Lin et al. [8] observed that the electronic structure of these compounds containing oxygen atoms always obeys a different relationship from the compounds not containing oxygen atoms using density functional theory (DFT).

Most of the earlier studies, both experimental and theoretical, involve the electronic, optical, and structural properties of BaO and BaS [5–15]. To the best of our knowledge, no one attempted the electronic structure and momentum density of BaO and BaS using Compton spectroscopy. It is well established that Compton spectroscopy provides a

useful test to examine the bonding in solids [16, 17]. Thus, we found it worth to study the electronic structure in BaO and BaS using Compton profile. The Compton profile, $J(p_z)$, is related to the ground state electron momentum density $n(\mathbf{p})$ as [16, 17]

$$J(p_z) = \iint_{-\infty}^{+\infty} n(\mathbf{p}) dp_x dp_y, \quad (1)$$

where integration is performed over a constant- p_z plane, z is scattering vector direction, and $n(\mathbf{p})$ is given as

$$n(\mathbf{p}) \propto \sum_i \left| \int \psi_i(\mathbf{r}) \exp(-i\mathbf{p} \cdot \mathbf{r}) d\mathbf{r} \right|^2, \quad (2)$$

where $\psi_i(\mathbf{r})$ is the electron wave function and summation extends over all occupied states. In this paper, the results of a Compton scattering study on BaO and BaS are presented. For the theoretical Compton profiles, first-principles calculations based on linear combination of atomic orbitals (LCAO) method are performed using CRYSTAL06 code [18]. The ionic model has been applied to estimate the charge transfer in these compounds. The nature of bonding in isostructural

and isovalent BaO and BaS is also compared using equal-valence-electron-density (EVED) profiles. The paper is organized as follows. Section 2 gives the experimental details and data analysis. The theoretical calculations are presented in Section 3 and Section 4 is devoted to the results and discussion. Finally, the conclusions are drawn in Section 5.

2. Experimental Details and Data Analysis

The measurements on BaO and BaS were performed using 5 Ci ^{241}Am gamma-rays Compton spectrometer. The details of the experimental setup are available in [19]. The incident gamma-rays of 59.54 keV were scattered at an angle of $166^\circ \pm 3.0^\circ$ by the polycrystalline sample of BaO and BaS (pellet of 18 mm dia, 3.2 mm thickness, and effective density for BaO 2.9329 gm/cm³ and BaS 1.7815 gm/cm³). The scattered radiation was analyzed using an HPGe detector (Canberra model, GL0110S) which was cooled with liquid nitrogen providing overall momentum resolution of 0.6 a.u. The spectra were recorded with a multichannel analyzer (MCA) with 4096 channels. The calibration of the spectrometer was checked regularly using weak ^{241}Am gamma-rays source. The Compton spectra were measured for BaO near about 48.529 h to collect 2×10^4 counts and BaS around 56.25 h to collect 2.5×10^4 counts at the Compton peak. To deduce the true Compton profile, the raw data were processed for several systematic corrections like background, instrumental resolution, sample absorption, scattering cross-section, and multiple scattering using the computer code of the Warwick Group [20, 21]. Finally, the corrected profiles were normalized to 23.200 for BaO and 26.434 for BaS electrons in the range of 0 to +5 a.u., being the area of free atom Compton profile [22] in the given range. The 1s electrons of Ba were neglected for both compounds since these do not contribute in the present experimental setup.

3. Theoretical Details

3.1. DFT-LCAO Method. To compute the theoretical Compton profiles of BaO and BaS, the LCAO method embodied in the CRYSTAL06 code [18, 23] was employed. This code provides a platform to calculate electronic structure of periodic systems considering Gaussian basis sets. In the LCAO technique, each crystalline orbital is built from the linear combination of Bloch functions. The Bloch functions are defined in terms of local functions constructed from the atom-centered certain number of Gaussian functions. For Ba, O, and S, the local functions were constructed from the Gaussian type basis sets [24]. In the present DFT calculation, the crystal Hamiltonian was generated using the correlation functional proposed by Perdew et al. [25] and exchange scheme of Becke [26]. The hybrid B3PW and Hartree-Fock (HF) based profiles were also computed for both compounds [18]. The computations were performed by taking B1 structure and 145 k points in the irreducible wedge of the Brillouin zone for BaO and BaS.

3.2. Ionic Model. The theoretical ionic profiles of BaO and BaS for various charge transfer configurations were calculated

from the free atom Compton profiles of Ba, O, and S atoms [22]. The valence profiles for various $(\text{Ba})^{+x}(\text{O}^{-x})$ and $(\text{Ba})^{+x}(\text{S}^{-x})$ ($0.0 \leq x \leq 2.0$) configurations were computed by transferring x electrons from the s shell of Ba to the p shell of O and S atoms. The valence profiles for $(\text{Ba})^{+x}(\text{O}^{-x})$ and $(\text{Ba})^{+x}(\text{S}^{-x})$ configurations were then added to the core contribution to get total profiles. All these profiles were then convoluted and normalized to compare with the measured profiles of BaO and BaS.

4. Results and Discussion

The numerical values of unconvoluted spherically averaged theoretical Compton profiles (DFT-PBE, B3PW, HF, and Ionic) of BaO and BaS are presented in Table 1. The experimental Compton profiles of BaO and BaS are also given in the table including experimental errors at selected points.

In Figures 1 and 2, the experimental Compton profiles of BaO and BaS are compared with various ionic arrangements to estimate the charge transfer. For a quantitative comparison of the ionic and experiment, the difference profiles $\Delta J = J^{\text{Theory}}(p_z) - J^{\text{Expt}}(p_z)$ have been deduced after convoluting all ionic profiles with a Gaussian function of 0.6 a.u. FWHM. All ionic profiles are normalized to 23.200 electrons for BaO and 26.434 electrons for BaS in the range of 0 to +5 a.u. Figure 1 depicts that the effect of charge transfer from Ba to O atoms is largely visible within 0.0 to 3.0 a.u. for BaO. The best agreement is found for $x = 1.0$. Figure 2 shows that the charge transfer configuration $x = 1.5$ is closest to the experiment for BaS. Beyond 3.0 a.u., all configurations show identical behavior for both compounds. On the basis of χ^2 checks and from Figures 1 and 2, it is found that $\text{Ba}^{+1.0}\text{O}^{-1.0}$ and $\text{Ba}^{+1.5}\text{S}^{-1.5}$ configurations give the best agreement for BaO and BaS, respectively. Thus, the model suggests the transfer of 1.0 and 1.5 electrons from the valence s state of Ba to the p states of O and S for BaO and BaS, respectively.

The differences ($\Delta J = J^{\text{Theory}}(p_z) - J^{\text{Expt}}(p_z)$) between experimental and LCAO scheme based Compton profiles are presented in Figures 3 and 4 for BaO and BaS, respectively. Figure 3 shows that for BaO all theories (DFT-PBE, B3PW, and HF) predict lower momentum density as compared to experiment in the momentum range of $0.0 < p_z < 0.5$ a.u., while the trend reversed in the momentum range of $0.5 < p_z < 2.0$ a.u. The difference between theory and experiment is negligible in the high momentum region, because the contribution in this region is mostly due to core electrons, which remain unaffected in the compound formation. Similar features are also visible in Figure 4, but the effect of exchange and correlation is not seen for BaS.

The directional Compton profiles of BaO and BaS along [100], [110], and [111] directions have been computed to examine the anisotropies [100]–[110], [110]–[111], and [100]–[111] in the electron momentum density. All these anisotropies are derived from convoluted B3PW hybrid scheme and presented in Figures 5 and 6 for BaO and BaS, respectively. Figure 5 depicts that all anisotropies are positive in nature at $p_z = 0.0$ a.u. for BaO. It indicates larger occupied states along [100] direction with low momentum. A close

TABLE 1: The unconvoluted theoretical (DFT-PBE, DFT-B3PW, HF, and Ionic) and experimental Compton profiles for BaO and BaS. The experimental errors at few points are also presented, and all profiles are normalized to the free atom area.

p_z (a.u.)	$J(p_z)$ in e/a.u.									
	BaO					BaS				
	DFT-PBE	DFT-B3PW	HF	Ionic	Experiment	DFT-PBE	DFT-B3PW	HF	Ionic	Experiment
0.0	12.516	12.626	12.605	13.775	12.498 ± 0.050	14.410	14.417	14.412	15.455	14.718 ± 0.053
0.1	12.419	12.528	12.508	13.275	12.400	14.290	14.296	14.291	15.119	14.567
0.2	12.271	12.377	12.358	12.333	12.148	14.094	14.101	14.096	14.499	14.259
0.3	12.023	12.125	12.107	11.509	11.786	13.656	13.663	13.659	13.702	13.791
0.4	11.613	11.709	11.693	10.890	11.339	13.242	13.249	13.247	13.073	13.148
0.5	11.079	11.167	11.155	10.362	10.804	12.519	12.526	12.527	12.273	12.347
0.6	10.434	10.511	10.504	9.792	10.181	11.739	11.746	11.750	11.363	11.450
0.7	9.715	9.777	9.776	9.176	9.496	10.847	10.854	10.861	10.436	10.539
0.8	8.957	9.002	9.008	8.525	8.791	9.913	9.920	9.929	9.521	9.668
1.0	7.472	7.476	7.494	7.286	7.426 ± 0.037	8.141	8.148	8.163	7.918	8.081 ± 0.037
1.2	6.200	6.163	6.186	6.250	6.225	6.708	6.712	6.722	6.638	6.798
1.4	5.307	5.248	5.266	5.483	5.371	5.932	5.932	5.932	5.921	5.933
1.6	4.719	4.662	4.670	4.922	4.786	5.368	5.367	5.362	5.375	5.288
1.8	4.314	4.267	4.268	4.494	4.341	4.966	4.965	4.960	4.983	4.915
2.0	4.005	3.966	3.965	4.149	4.023 ± 0.027	4.638	4.637	4.633	4.662	4.627 ± 0.028
3.0	2.781	2.769	2.767	2.826	2.811 ± 0.022	3.268	3.268	3.267	3.291	3.260 ± 0.022
4.0	1.887	1.884	1.883	1.902	1.986 ± 0.018	2.207	2.207	2.207	2.223	2.270 ± 0.018
5.0	1.394	1.393	1.393	1.404	1.391 ± 0.014	1.602	1.602	1.602	1.611	1.653 ± 0.015

FIGURE 1: Difference (ΔJ) between convoluted ionic and experimental Compton profiles of BaO. Experimental errors ($\pm\sigma$) are also shown at points. All ionic profiles are convoluted with the Gaussian of 0.6 a.u. FWHM.

FIGURE 2: Difference (ΔJ) between convoluted ionic and experimental Compton profiles of BaS. Experimental errors ($\pm\sigma$) are also shown at points. All ionic profiles are convoluted with the Gaussian of 0.6 a.u. FWHM.

inspection of this figure reveals that maximum anisotropy is seen between [100] and [111] directions at 0.6 a.u. and 1.2 a.u. All anisotropies are visible up to 3.0 a.u. In Figure 6, the

anisotropies are plotted for BaS. This figure shows similarity with BaO, but all anisotropies are diminished beyond 2.0 a.u. Measurements on single crystalline samples of BaO and BaS

FIGURE 3: The difference of DFT-PBE, B3PW, and HF with experimental Compton profile of BaO. All profiles are convoluted with the Gaussian of 0.6 a.u. FWHM.

FIGURE 4: The difference of DFT-PBE, B3PW, and HF with experimental Compton profile of BaS. All profiles are convoluted with the Gaussian of 0.6 a.u. FWHM.

along principal directions would be valuable to examine these findings.

The nature of bonding in isostructural and isovalent BaO and BaS has been compared and plotted in Figure 7. In this figure, the experimental EVED profiles of these compounds are considered. We also plot the theoretical EVED profiles in the inset. The EVED profiles were derived by normalizing valence electron profiles to 4.0 electrons and scaling the resulting profiles by the Fermi momentum (p_F). For BaO and BaS, p_F turned out to be 0.938 and 0.813 a.u., respectively,

FIGURE 5: Directional anisotropies, $\Delta J(p_z)$, for BaO for the pair of directions [100]–[110], [110]–[111], and [100]–[111].

FIGURE 6: Directional anisotropies, $\Delta J(p_z)$, for BaS for the pair of directions [100]–[110], [110]–[111], and [100]–[111].

using the expression $(3\pi^2 n)^{1/3}$, where n is the valence electron density. A number of researchers have proved that this scheme offers a way to understand the nature of bonding in isovalent and isostructural compounds [27–31]. It is seen from Figure 7 that, near $p_z = 0$ a.u., the sharpness of Compton profiles is higher for BaS, which suggests more localization of charges in BaS in the bonding direction as compared to BaO. It is worth mentioning here that the covalent bonding is a result of sharing of electrons, and hence, it increases localization of charge in bonding direction which results in a sharper Compton line shape [32, 33].

FIGURE 7: The equal-valence-electron-density (EVED) profiles of BaO and BaS ($p_F = 0.938$ and 0.813 a.u., resp.). These profiles are deduced from the experimental valence profiles. The inset shows the EVED profiles derived from the theoretical valence profiles of these compounds. All these profiles are normalized to 4.0 electrons.

Therefore, we conclude that the ionic character is higher for BaO as compared to BaS. The larger ionic character of BaO as compared to BaS is well supported by the bulk modulus and cohesive energy data [34].

5. Conclusions

Electronic structure and momentum density in BaO and BaS using Compton scattering technique are reported. The experimental values of Compton profiles are compared with the LCAO based values for both compounds. The anisotropies in momentum densities depict larger occupied states along [100] direction with low momentum. In addition, the ionic model based calculations have also been used to estimate the charge transfer in the compounds, and the model suggests a transfer of 1.0 and 1.5 electrons from s state of Ba atom to p state of O and S atoms. The EVED profiles for the compounds conclude higher ionic character in BaO as compared to BaS.

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References

[1] P. Cervantes, Q. Williams, M. Côté, M. Rohlffing, M. L. Cohen, and S. G. Louie, "Band structures of CsCl-structured BaS and CaSe at high pressure: implications for metallization pressures

of the alkaline earth chalcogenides," *Physical Review B*, vol. 58, no. 15, pp. 9793–9800, 1998.

- [2] T. Lv, D. Chen, and M. Huang, "Quasiparticle band structures of BaO and BaS," *Journal of Applied Physics*, vol. 100, Article ID 086103, 3 pages, 2006.
- [3] S. Drablia, H. Meradji, S. Ghemid, G. Nouet, and F. El Haj Hassan, "First principles investigation of barium chalcogenide ternary alloys," *Computational Materials Science*, vol. 46, no. 2, pp. 376–382, 2009.
- [4] M. Uludoan, T. Çain, A. Strachan, and W. A. Goddard III, "Ab-initio studies of pressure induced phase transitions in BaO," *Journal of Computer-Aided Materials Design*, vol. 8, no. 2-3, pp. 193–202, 2001.
- [5] M. Alfredsson, J. P. Brodholt, P. B. Wilson et al., "Structural and magnetic phase transitions in simple oxides using hybrid functionals," *Molecular Simulation*, vol. 31, no. 5, pp. 367–377, 2005.
- [6] S. T. Weir, Y. K. Vohra, and A. L. Ruoff, "High-pressure phase transitions and the equations of state of BaS and BaO," *Physical Review B*, vol. 33, no. 6, pp. 4221–4226, 1986.
- [7] S. Drablia, H. Meradji, S. Ghemid, N. Boukhris, B. Bouhaf, and G. Nouet, "Electronic and optical properties of BaO, BaS, BaSe, BaTe and BaPo compounds under hydrostatic pressure," *Modern Physics Letters B*, vol. 23, no. 26, pp. 3065–3079, 2009.
- [8] G. Q. Lin, H. Gong, and P. Wu, "Electronic properties of barium chalcogenides from first-principles calculations: tailoring wide-band-gap II-VI semiconductors," *Physical Review B*, vol. 71, no. 8, Article ID 085203, 2005.
- [9] M. Ameri, A. Touia, H. Khachai, Z. Mahdjoub, M. Z. Chekroun, and A. Slamani, "Ab initio study of structural and electronic properties of barium chalcogenide alloys," *Materials Sciences and Applications*, vol. 3, pp. 612–618, 2012.
- [10] Y. Kang, Y. S. Kim, Y. C. Chung, H. Kim, D. S. Kim, and J. J. Kim, "The evaluation of ultrasoft pseudopotential in predicting material properties of ionic systems by an ab-initio pseudopotential method," *Journal of Ceramic Processing Research*, vol. 3, no. 3, pp. 171–173, 2002.
- [11] R. K. Singh, A. S. Verma, and S. K. Rathi, "Ground state properties of rock salt, CsCl, diamond and zinc blende structured solids," *The Open Condensed Matter Physics Journal*, vol. 2, pp. 25–29, 2009.
- [12] M. Teng and X. Hong, "Phase transition and thermodynamic properties of BaS: an Ab initio study," *Wuhan University Journal of Natural Sciences*, vol. 16, no. 1, pp. 33–37, 2011.
- [13] F. El Haj Hassan and H. Akbarzadeh, "First-principles elastic and bonding properties of barium chalcogenides," *Computational Materials Science*, vol. 38, no. 2, pp. 362–368, 2006.
- [14] R. Khenata, M. Sahnoun, H. Baltache et al., "Structural, electronic, elastic and high-pressure properties of some alkaline-earth chalcogenides: an ab initio study," *Physica B*, vol. 371, no. 1, pp. 12–19, 2006.
- [15] Z. Feng, H. Hu, Z. Lv, and S. Cui, "First-principles study of electronic and optical properties of BaS, BaSe and BaTe," *Central European Journal of Physics*, vol. 8, no. 5, pp. 782–788, 2010.
- [16] M. J. Cooper, P. E. Mijnarends, N. Shiotani, N. Sakai, and A. Bansil, *X-Ray Compton Scattering*, Oxford Publishing Press, Oxford, UK, 2004.
- [17] M. J. Cooper, "Compton scattering and electron momentum determination," *Reports on Progress in Physics*, vol. 48, no. 4, pp. 415–481, 1985.

- [18] R. R. Dovesi, V. R. Saunders, C. Roetti et al., *CRYSTAL06 User's Manual*, University of Torino, Torino, Canada, 2006.
- [19] B. K. Sharma, A. Gupta, H. Singh, S. Perkiö, A. Kshirsagar, and D. G. Kanhere, "Compton profile of palladium," *Physical Review B*, vol. 37, no. 12, pp. 6821–6826, 1988.
- [20] D. N. Timms, *Compton scattering studies of spin and momentum densities [Ph.D. thesis]*, University of Warwick, Coventry, UK, 1989.
- [21] J. Felsteiner, P. Pattison, and M. Cooper, "Effect of multiple scattering on experimental Compton profiles: a Monte Carlo calculation," *Philosophical Magazine*, vol. 30, no. 3, pp. 537–548, 1974.
- [22] F. Biggs, L. B. Mendelsohn, and J. B. Mann, "Hartree Fock Compton profiles for the elements," *Atomic Data and Nuclear Data Tables*, vol. 16, no. 3, pp. 201–309, 1975.
- [23] R. Dovesi, R. Orlando, C. Roetti, C. Pisani, and V. R. Saunders, "The periodic Hartree-Fock method and its implementation in the CRYSTAL code," *Physica Status Solidi B*, vol. 217, no. 1, pp. 63–88, 2000.
- [24] <http://www.tcm.phy.cam.ac.uk/> .
- [25] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters*, vol. 77, no. 18, pp. 3865–3868, 1996.
- [26] A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Physical Review A*, vol. 38, no. 6, pp. 3098–3100, 1988.
- [27] M. C. Mishra, G. Sharma, R. K. Kothari, Y. K. Vijay, and B. K. Sharma, "Electronic structure of CaX (X = O, S, Se) compounds using Compton spectroscopy," *Computational Materials Science*, vol. 51, no. 1, pp. 340–346, 2012.
- [28] N. Munjal, G. Sharma, V. Vyas, K. B. Joshi, and B. K. Sharma, "Ab-initio study of structural and electronic properties of AlAs," *Philosophical Magazine*, vol. 92, pp. 3101–3112, 2012.
- [29] G. Sharma, K. B. Joshi, M. C. Mishra et al., "Electronic structure of AlAs: a Compton profile study," *Journal of Alloys and Compounds*, vol. 485, no. 1-2, pp. 682–686, 2009.
- [30] R. Kumar, N. Munjal, G. Sharma, V. Vyas, M. S. Dhaka, and B. K. Sharma, "Electron momentum density and phase transition in SrO," *Phase Transitions*, vol. 85, no. 12, pp. 1098–1108, 2012.
- [31] W. A. Reed and P. Eisenberger, "Gamma-ray compton profiles of diamond, silicon, and germanium," *Physical Review B*, vol. 6, no. 12, pp. 4596–4604, 1972.
- [32] G. Sharma, K. B. Joshi, M. C. Mishra, S. Shrivastava, Y. K. Vijay, and B. K. Sharma, "Electron momentum density in multiwall carbon nanotubes," *Physica E*, vol. 43, no. 5, pp. 1084–1086, 2011.
- [33] M. C. Mishra, R. Kumar, G. Sharma, Y. K. Vijay, and B. K. Sharma, "Size dependent electron momentum density distribution in ZnS," *Physica B*, vol. 406, no. 22, pp. 4307–4311, 2011.
- [34] A. S. Verma, "An empirical model for bulk modulus and cohesive energy of rocksalt-, zincblende- and chalcopyrite-structured solids," *Physica Status Solidi B*, vol. 246, no. 2, pp. 345–353, 2009.