0FInfluence of Cu_2S, SnS and $Cu_2ZnSnSe_4$ on optical properties of Cu_2ZnSnS_4

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Abstract

We have studied influence of $Cu_2ZnSnSe_4$ (CZTSe) and secondary phases of Cu_2S and SnS on optical properties of kesterite-type Cu_2ZnSnS_4 (CZTS) by using the effective medium theory. We found that CZTSe and Cu_2S cause band gap reduction and enhance light absorption of CZTS at all photon energies of the sunlight whereas SnS changes optical properties of CZTS only at large photon energies beyond the solar spectrum. Optical spectra of CZTS(Se) has been studied by first principles calculations within hybrid functional that was used as input for the effective medium theory.

Keywords: Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$, kesterite, Cu_2S, SnS, band gap, hybrid functional.

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1. Introduction

Owing to its abundance, non-toxicity, high absorption coefficient of 10^4-10^5 cm^{-1} in the visible range of the solar spectra, and charge carrier concentration that can be tuned in wide range from 1.2×10^{15} to 3.1×10^{20} cm^{-3} [1], Cu_2ZnSnS_4 (CZTS) is one of the promising materials in thin film photovoltaic technology as the light absorber [2] and the Pt-free electrocatalyst in dye-sensitized solar cells [3-5]. Band gap and optical absorption by CZTS are one of the important parameters strongly influencing on the cell efficiency. The experimentally determined band gap for the kesterite CZTS varies between 1.3-1.89 eV [6-8]. Theoretically studies of electronic structure and optical properties of CZTS (see, e.g., Ref. [9]) within hybrid functional and Becke-Johnson potential shows good agreement with experimental data. Cu-Zn related intrinsic defect plays critical role in band gap fluctuations and small open-circuit voltage of the CZTS-based solar cells [10-11]. Possibility of tuning the band gap between 1.0 and 1.5 eV is reported [12] by increasing the S/Se ratio in CZTS. Since CZTS is a quaternary compound, during thermal processing and synthesis secondary phases might be formed [13] that play important role in its electrical and optical properties. Some examples are Cu_2S and SnS_2 (see, e.g., Refs. [6, 14-15]) with band gaps of 1.2-1.8 eV [15] and ~2.2 eV [16], respectively, that can be formed in CZTS at annealing temperatures $T\geq350$ °C. Band gap of SnS is ~1.32 eV [17], so the SnS-based secondary phases might play important role in electro-optical properties of CZTS. The aim of the work is to study influence of CZTSe and secondary phases of Cu_2S and SnS on optical properties of CZTS.

2. Methods, choice of materials, and parameter values

Optical properties of the films has been studied by the Bruggeman effective medium approximation [18], which based on the imaginary ε_2 and real ε_1 parts of the macroscopic dielectric function of the host and secondary phase, allows to estimate ε_2 and ε_1 for the composite material. The following assumptions have been adopted: CZTS films contain only one of secondary phase such as Cu_2S or SnS or only CZTSe. In reality, several secondary phases will co-exist in CZTS(Se). However, that complicates clarification experimentally influence of each secondary phase individually on optical properties of CZTS(Se) as to which of them will enhance/worsen light absorption of CZTS(Se) in the visible spectra. As demonstrated in the paper, effective medium theory can be the efficient tool to solve the problem. Shape of the secondary phases is accepted as spherical. The reason for selection of the Cu_2S and SnS secondary phases is because their band gaps are in the 1.1-1.5 eV range. So, their influence on optical properties of CZTS might be important. Spectral distribution of ε_2 and ε_1 that is used in this work as input is estimated by ab initio calculations within hybrid functional and taken from the Ref. [19] for for CZTS(Se) Ref. [20] for Cu_2S and Ref. [21] for SnS.

Vienna ab initio simulation package (VASP) [22-24] has been used for the first principles calculations together with the potential projector augmented-wave (PAW) method [25-27]. Exchange and correlation effects have been described by the Perdew-Burke-Ernzerhoff (PBE) [28] of generalized gradient approximation (GGA) as well as HSE06 hybrid functional containing a modified portion of the Fock exchange. PAW-PBE pseudopotentials were employed to describe the Cu($4s^1 3d^{10}$), Zn($3d^{10}$,$4s^2$), Sn($4d^{10}5s^2 5p^2$), S($3s^2 3p^4$), and Se ($3d^{10}4s^2 4p^4$) valence states. Hybrid functional was performed as the proposed by Heyd-Scuseria-Ernzerhof (HSE) [29-30] with the standard value of the Hartree-Fock exchange (25%) and a portion of PBE exchange (75%). The screening parameter of 0.25 $Å^{-1}$ has been used. Structural optimization was performed with k-mesh 8x8x8, plane-wave cut-off energy 600 eV, and energy error 10^{-8} eV. The residual forces and pressure are less than 10^{-4} eV/A and 0.06 kB, respectively.

3. Results

Figures 1 (a) and (b) present imaginary part of the macroscopic dielectric function and absorption coefficient for the alloy $CZTS_{1-x}Se_x$, where x=S/(S+Se), for x=0.00, 0.25, 0.50, 0.75, and 1.00 by using the optical data for CZTS and CZTSe from Ref. [19] as input. One can see shift of the main peaks of ε_2 for CZTS toward smaller energies with increasing the Se concentration and approach that of CZTSe. Figure 1(c) and (d) shows the Tauc plot that has been used for estimation of the band gap and its dependence on x. Analysis shows that the dependence of E_g on x is non-monotonic. With increasing x, E_g decreases at smaller x and increases at larger x. This result is consistent with that of Ref. [31], reporting non-monotonic dependence of E_g on x.

Estimation of ε_2 and ε_1 for CZTS and CZTSe has been performed by first-principles calculations within the hybrid functional that have been used as input for calculation of optical properties of $CZTS_xSe_{1-x}$. Band gap has been estimated from Tauc plot and dependence of it has been plotted as a function of the fill factor x of CZTS by CZTSe [Fig. 1 (d)]. Analysis shows that the calculated band gap somehow differs from experimental data. The discrepancy is expected, because of the difficulty to control phase purity, lattice disorder, and defect concentration in CZTS. Furthermore, the hybrid functional calculates the band gap within certain accuracy. Analysis of Fig. 1(d) shows that the dependence of the band gap for the $CZTS_xSe_{1-x}$ on fill factor x estimated from the first principles calculations provides the same tendency as that found experimentally.

Figure 2 (a)-(c) presents imaginary part of the macroscopic dielectric function, absorption coefficient, and Tauc plot for CZTS with different amount of SnS phases. Analysis shows that the influence of SnS phases will cause band gap engineering and influences on optical properties of CZTS. However, the influence is sensible only at larger photon energies beyond the solar spectrum exceeding ~3.5 eV. According to Tauc plot, the band gap of CZTS is slightly reduced by the SnS phases.

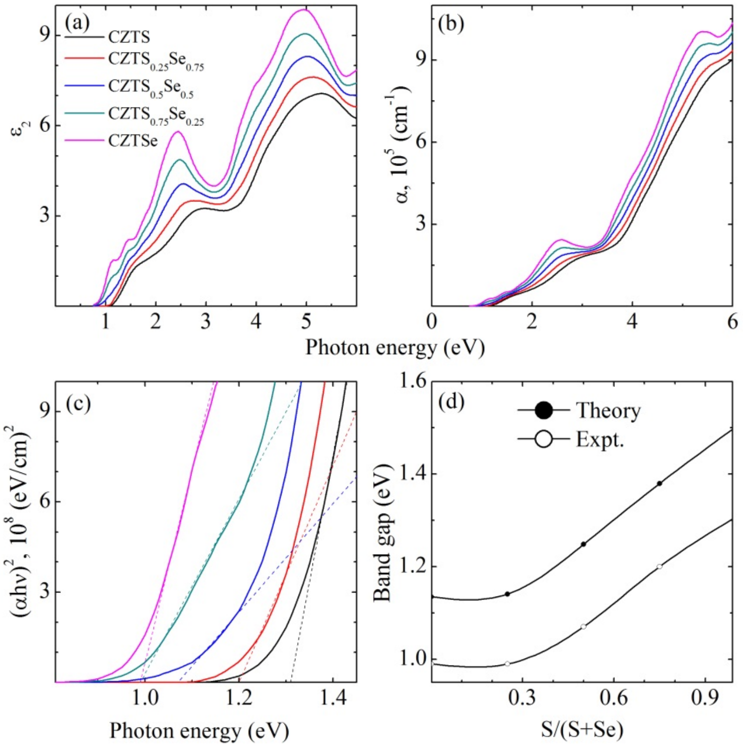

Figure 1. *(a) imaginary part of the dielectric response, (b) absorption coefficient, and (c) Tauc plot for* $CZTS_{1-x}Se_x$ *for x=0, 0.25, 0.5, 0.75, and 1.0. (c) Dependence of the band gap of the* $CZTS_{1-x}Se_x$ *calculated for different values of concentration of Se.*

Figure 3(a)-(c) shows the imaginary part of the macroscopic dielectric function, absorption coefficient, and Tauc plot for CZTS containing secondary phases of Cu_2S. Analysis shows that the Cu_2S phase improves absorption of sunlight by CZTS at all photon energies of the sunlight and the improvement is enhanced with increasing the content of Cu_2S. Furthermore, the band gap of CZTS is reduced by the Cu_2S phases. The influence of the secondary phase is very strong even though for its small concentration. This phenomenon can be explained with large values of permittivity for Cu_2S.

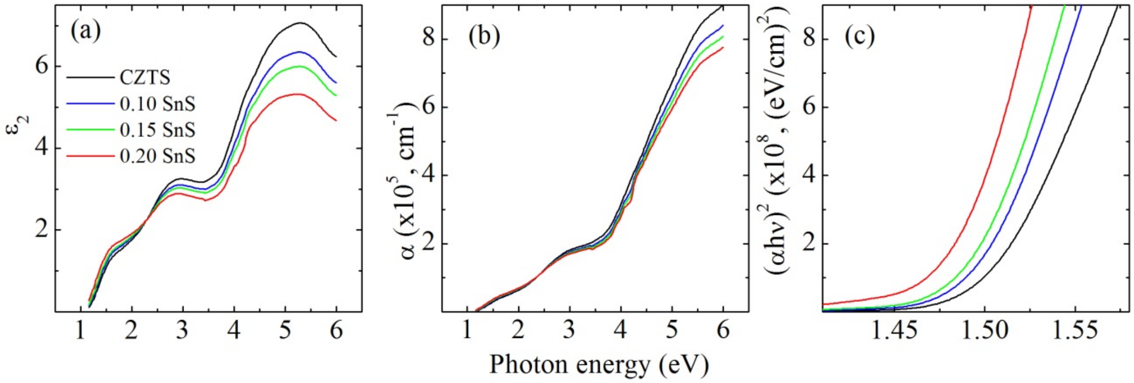

Figure 2. *(a)Imaginary part of the macroscopic dielectric function, (b) absorption coefficient and (c) Tauc plot for CZTS with different concentration of SnS secondary phases.*

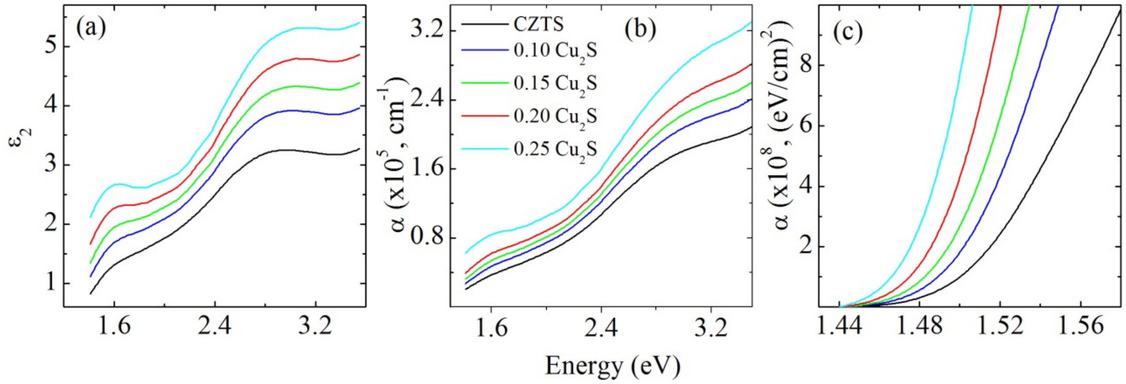

Figure 3. *Spectral distribution of (a) macroscopic dielectric function, (b) absorption coefficient and (c) Tauc plot for CZTS different concentrations of secondary phases of* Cu_2S.

Conclusion

By using the effective mass theory, we have studied influence of CZTSe and secondary phases of SnS and Cu_2S on optical properties of CZTS. We found that CZTSe and Cu_2S cause band gap reduction of and enhance light absorption by CZTS at all photon energies of the sunlight whereas SnS changes optical properties of CZTS only at large photon energies beyond the solar spectrum. Electronic structure and optical properties of CZTS(Se) has been studied by first principles calculations within hybrid functional. The discrepancy between the calculated and experimental band gaps can be because of phase purity, lattice disorder, intrinsic defect concentration of CZTS(Se) as well as accuracy of the computations.

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References

1 S. Chen, A. Walsh, X.-G. Gong, S.-H. Wei. *Adv. Mater.* **25**(11), (2013), 1522-1539.

2 M. Edoff. *Ambio*. **41**(Suppl 2), (2012), 112-118.

3 S. Chen, J. Tao, H. Tao, Y. Shen, L. Zhu, J. Jiang, X. Zeng, T. Wang. *Mater. Technol.* **30**(5), (2015), 306-312.

4 X. Xin, M. He, W. Han, J. Jung, Z. Lin. *Ang. Chem. Int. Ed.* **50**(49), (2011), 11739-11742.

5 P. Sudhagar, D. D. Kirubakaran, C. Ravidhas, P. Selvaraj, M. Klopov, S. Z. Karazhanov, S. Sundaram. *Submitted*. (2017).

6 R. Pandiyan, Z. Oulad Elhmaidi, Z. Sekkat, M. Abd-lefdil, M. A. El Khakani. *Appl. Surf. Sci.* **396**, (2017), 1562–1570.

7 C. Steinhagen, M. G. Panthani, V. Akhavan, B. Goodfellow, B. Koo, B. A. Korgel. *J. Amer. Chem. Soc.* **131**(35), (2009), 12554-12555.

8 Q. Guo, H. W. Hillhouse, R. Agrawal. *J. Amer. Chem. Soc.* **131**(33), (2009), 11672-11673.

9 A. H. Reshak, K. Nouneh, I. V. Kityk, J. Bila, S. Auluck, H. Kamarudin, Z. Sekkat. *Int. J. Electrochem. Sci.,*. **9**, (2014), 955 - 974.

10 J. J. S. Scragg, J. K. Larsen, M. Kumar, C. Persson, J. Sendler, S. Siebentritt, C. Platzer Björkman. *Phys. Stat. Solidi (b)*. **253**(2), (2016), 247-254.

11 J. J. S. Scragg, L. Choubrac, A. Lafond, T. Ericson, C. Platzer-Björkman. *Appl. Phys. Lett.* **104**(4), (2014), 041911.

12 S.-Y. Li, S. Zamulko, C. Persson, N. Ross, J. K. Larsen, C. Platzer-Björkman. *Appl. Phys. Lett.* **110**(2), (2017), 021905.

13 X. Song, X. Ji, M. Li, W. Lin, X. Luo, H. Zhang. *Int. J. Photoenergy*. **2014**, (2014), 11.

14 C.-Y. Su, C. Yen Chiu, J.-M. Ting. *Sci. Rep.* **5**, (2015), 9291.

15 A. Mohd Zubair, K. Neeraj. *J. Phys. D: Appl. Phys.* **47**(18), (2014), 185101.

16 A. Sanchez-Juarez, A. Ortíz. *Semicond. Sci. Technol.* **17**(9), (2002), 931.

17 K. T. Ramakrishna Reddy, N. Koteswara Reddy, R. W. Miles. *Solar Energy Mater. Solar Cells.* **90**(18–19), (2006), 3041-3046.

18 A. G. Bruggemann. *Ann. Physik.* **24**, (1935), 636-664.

19 S. Adachi, editor. *Earth Abundant Materials for Solar Cells. Cu_2-Ii-Iv-Vi_4 Semiconductors*. Chichester, UK: John Wiley & Sons, Ltd; 2015.

20 H. M. Pathan, J. D. Desai, C. D. Lokhande. *Appl. Surf. Sci.* **202**(1–2), (2002), 47-56.

21 A. Otto, L. Ley, J. Azoulay, T. Grandke, R. Eymard, W. Braun, M. Cardona. *Phys. Rev. B.* **16**(10), (1977), 4429-4433.

22 G. Kresse, J. Furthmüller. *Phys. Rev. B.* **54**(16), (1996), 11169-11186.

23 G. Kresse, J. Furthmüller. *Comput. Mater. Sci.* **6**(1), (1996), 15-50.

24 G. Kresse, J. Hafner. *Phys. Rev. B.* **49**(20), (1994), 14251-14269.

25 G. Kresse, D. Joubert. *Phys. Rev. B.* **59**(3), (1999), 1758-1775.

26 G. Kresse, J. Hafner. *Phys. Rev. B.* **47**(1), (1993), 558-561.

27 P. E. Blochl. *Phys. Rev. B.* **50**(24), (1994), 17953-17979.

28 J. P. Perdew, K. Burke, M. Ernzerhof. *Phys. Rev. Lett.* **77**(18), (1996), 3865-3868.

29 A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria. *J. Chem. Phys.* **125**(22), (2006), 224106

30 J. Heyd, G. E. Scuseria, M. Ernzerhof. *J. Chem. Phys.* **118**(18), (2003), 8207.

31 M. Jiang, X. Yan. *Cu2znsns4 Thin Film Solar Cells: Present Status and Future Prospects*. In: Morales-Acevedo A, editor. Solar Cells - Research and Application Perspectives. Rijeka: InTech; Ch. 05, (2013).