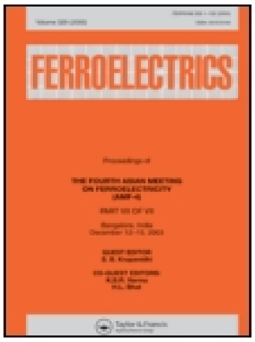

Ferroelectrics

ISSN: 0015-0193 (Print) 1563-5112 (Online) Journal homepage: https://www.tandfonline.com/loi/gfer20

Optical and electronic properties of orthorhombic and trigonal AXO_3 (A=Cd, Zn; X=Sn, Ge): First principle calculation

Haci Ozisik, Sevket Simsek, Engin Deligoz, Amirullah M. Mamedov & Ekmel Ozbay

To cite this article: Haci Ozisik, Sevket Simsek, Engin Deligoz, Amirullah M. Mamedov & Ekmel Ozbay (2016) Optical and electronic properties of orthorhombic and trigonal AXO_3 (A=Cd, Zn; X=Sn, Ge): First principle calculation, Ferroelectrics, 498:1, 73-79, DOI: 10.1080/00150193.2016.1168207

To link to this article: https://doi.org/10.1080/00150193.2016.1168207

FERROELECTRICS
2016, VOL. 498, 73–79
http://dx.doi.org/10.1080/00150193.2016.1168207

Taylor & Francis
Taylor & Francis Group

Optical and electronic properties of orthorhombic and trigonal AXO_3 (A=Cd, Zn; X=Sn, Ge): First principle calculation

Haci Ozisik[a], Sevket Simsek[b], Engin Deligoz[c], Amirullah M. Mamedov[d,e], and Ekmel Ozbay[d]

[a]Department of BOTE, Faculty of Education, Aksaray University, Aksaray, Turkey; [b]Department of Material Science and Engineering, Faculty of Engineering, Hakkari University, Hakkari, Turkey; [c]Department of Physics, Faculty of Science, Aksaray University, Aksaray, Turkey; [d]Nanotechnology Research Center (NANOTAM), Bilkent University, Bilkent, Ankara, Turkey; [e]International Scientific Center, Baku State University, Baku, Azerbaijan

ABSTRACT
Electronic structure and optical properties of the $CdXO_3$ and $ZnXO_3$ (X=Ge, Sn) compounds have been investigated based on density functional theory. According to the predictive results, reveal that the $CdXO_3$ and $ZnXO_3$ would be candidates for a high performance lead free optical crystal, which will avoid the environmental toxicity problem of the lead-based materials.

ARTICLE HISTORY
Received 28 June 2015
Accepted 12 November 2015

KEYWORDS
Ab initio calculation; ABO_3; electronic structure; optical properties

1. Introduction

$CdXO_3$ and $ZnXO_3$ (X=Sn, Ge) are multifunctional materials, that have structure of perovskite oxides [1–3]. There are two points of view on the structures of $ZnXO_3$ and $CdXO_3$, perovskite-type oxide [4] and ilmenite structures [5]. It was found that ilmenite-type $ZnXO_3$ contains only cations with the electronic configuration of $(n\text{-}1)d^{10}ns^0$. However, until now little attention has been paid to oxides containing only main group cations with such electronic configuration, so these compounds gave us a new strategy to search more polar crystals [6]. To search for new high performance ferroelectrics based on the above strategy we have investigated $CdXO_3$ and $ZnXO_3$(X=Ge, Sn), because the investigation of perovskite- and ilmenite-based oxide systems with ferroelectric properties has gained large interest within the scientific community in recent years [7, 8]. It is well known that $LiNbO_3$ compounds is so important optical materials with a wide applications in optoelectronics and other nonlinear systems. Therefore, it seems to us noncentrosymmetric (NCS) compounds $CdXO_3$ and $ZnXO_3$ with the same ilmenite structure will be used in different application areas, like optoelectronics, too

In present work, we investigated the electronic and optical properties of the $CdXO_3$ and $ZnXO_3$(X=Ge, Sn) compounds. The method of calculation is given in section 2; the results are discussed in section 3. Finally, the summary and conclusion are given in section 4.

CONTACT Amirullah M. Mamedov ✉ mamedov@bilkent.edu.tr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gfer.

2. Method of calculation

In the present paper, all of our calculations that are performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) [9–12] developed within the density functional theory (DFT) [13], the exchange-correlation energy function is treated within the GGA (generalized gradient approximation) by the density functional of Perdew et al. [14]. The potentials used for the GGA calculations take into account the $3d^{10}4s^{2}4p^{2}$ valence electrons of each Ge-, and $4d^{10}5s^{2}5p^{2}$ valence electrons of each Sn. The valence electronic configuration were $4d^{10}5s^{2}$ for each Cd-, $3d^{10}4s^{2}$ for each Zn-, and $2s^{2}2p^{4}$ for each O- atom. When including a plane-wave basis up to a kinetic-energy cutoff equal to 19 Ha (the electronic energy convergence is 10^{-8} eV), the properties investigated in this work are well converged. The Brillouin-zone integration was performed using special k points sampled within the Monkhorst-Pack scheme [15]. We found that a mesh of 9×9×9 k-points was required to describe well of these the density of states and electronic structures. In structure relaxations, the force convergence for ionic is set to 10^{-3} eV/A. This k-point mesh guarantees a violation of charge neutrality less than 0.008eV. Such a low value is a good indicator for an adequate convergence of the calculations.

The primitive cell structures ($ZnXO_3$ and $CdXO_3$) contains 2 molecules and 10 atoms. When we started the calculations, we have optimized the structural properties first. The lattice parameters obtained as a result of this optimization are shown in Table 1 with the experimental and theoretical results. The structural parameters obtained are in a good agreement with the experimental and theoretical values [1, 16–26]. We have used these structural properties in all our subsequent calculations. Following geometry optimization, the Kohn-Sham electronic band structures and the partial densities of states per atom and per orbital were calculated.

3. Results and discussion

In the first step of our calculations, we have carried out the equilibrium lattice constants of $CdXO_3$ and $ZnXO_3$(X=Ge, Sn) compounds. The optimization lattice parameters obtained after the geometry optimization are presented in Table 1. Experimental value are shown as well, for comparison. The lattice parameters very close to experimental data when we look at the GGA result. We have also calculated formation energies for these compounds. The results are also presented in Table 1. The calculated negative formation energies mean that these phases for $CdXO_3$ and $ZnXO_3$ compounds are thermodynamically stable at ground state. Generally, ilmenite type rhomboedric structures exhibit a higher structural stability than that of perovskite type orthorhombic structures since the ilmenite type rhomboedric structures possesses the lower formation energies, and $ZnGeO_3$ compound in ilmenite type rhomboedric structures may be the most stable among them.

The Kohn-Sham electronic band structure gives a picture of electronic eigenenergies as a function of a set of quantum numbers which form the components of a wavevector **k** in the first Brillouin zone (BZ). For perovskite and ilmenite $CdXO_3$ and $ZnXO_3$, the path in the BZ used for the DFT computations are formed straight segments connecting a set of high symmetry points. Figure 1 present the electronic band structures obtained for the $CdXO_3$ and $ZnXO_3$ crystals using GGA, together with the respective partial and total DOS in a manner

Table 1. The calculated equilibrium lattice parameters (a, b, and c in Å) and electronic bandgaps (E_g in eV) for **A**XO_3 (**A** = Zn, Cd and **X** = Ge, Sn) in orthorhombic perovskite and rhomboedric ilmenite structures.

Lattice	Material	a	b	c	E_0 (eV/f.u.)	V_0 (Å^3/f.u.)	E_g (eV)*	ΔH_f (eV/p.a)	Refs.
Ilmenite type	$ZnGeO_3$	5.046		14.077	−28.1930	51.73	2.106 (**I**)	−1.6806	Present
Rhomboedric R-3(148)		4.9568		13.860		49.15			Exp.[16]
A: 6c (0, 0, z)	$ZnSnO_3$	5.378		14.29	−27.3057	59.66	1.302 (**I**)	−1.5802	Present
B: 6c (0, 0, z)		5.419		14.348					US-PBE [17]
O: 18f (x, y, z)		5.284		14.091					Exp. [18]
		5.2118		13.90		56.29			LDA-CA [19]
		5.419		14.348		60.82			GGA-PBE[20]
		5.284		14.091		56.78			Exp. [21]
	$CdGeO_3$	5.193		15.257	−27.2324	59.38	1.398 (**I**)	−1.5602	Present
		5.098		14.883		55.83			Exp. [22]
	$CdSnO_3$	5.556		15.272	−26.5540	68.05	0.981 (**I**)	−1.5016	Present
Perovskite type	$ZnGeO_3$	5.074	5.14	7.451	−27.7240	48.59	1.588 (**D**)	−1.5868	Present
Orthorhombic Pnma (62)	$ZnSnO_3$	5.383	5.375	7.922	−27.1404	57.31	1.069 (**D**)	−1.5471	Present
A:4c (x, 0.25, z)		5.428	5.422	7.994					US-PBE [17]
B:4b (0, 0, 0.50)	$CdGeO_3$	5.31	5.362	7.582	−26.7519	53.97	0.817 (**D**)	−1.4641	Present
O:8d (x, y, z)		5.209	5.253	7.434		50.86			Exp. [22]
4c (x, 0.25, z)		5.2114	5.2608	7.4263		50.90			Exp [23]
		5.3165	5.3750	7.5903		54.23			GGA-PW91 [24]
		5.136	5.369	7.579		49.10	0.82		US-PBE [25]
		5.152	5.197	7.334		54.08	1.67		US-LDA [25]
		5.211	5.261	7.443		51.01			Exp. [25]
	$CdSnO_3$	5.556	5.676	8.041	−26.4046	63.40	0.650 (**D**)	−1.4717	Present
		5.4989	5.6068	7.9488		61.27	0.94		PAW-PBE [26]
		5.1927	5.2856	7.4501		51.12	1.7		PAW-LDA [26]
		5.4588	5.5752	7.8711		59.89	3.0		Exp. [1]
						0.42			US-PBE [26]
							1.14		US-LDA [26]

* (I) and (D) refers indirect and direct bandgap, separately.

similar to our previous work [27]. Each ilmenite unit cell has two units (Z = 2), which leads to 68 valence electrons per cell, while the corresponding values for perovskite are Z = 4, and 136 valence electrons.

The band structure of $CdXO_3$ and $ZnXO_3$ along the principal symmetry directions have been calculated by using the equilibrium lattice constants as shown in Table 1 in perovskite orthorhombic and ilmenite phases. As a result of our calculations the band structure of the $ZnGeO_3$ and $ZnSnO_3$ have a direct gap (Γ-high symmetry point), which are 1.588 eV and 1.069 eV in the perovskite phase, respectively. For $CdGeO_3$ and $CdSnO_3$, we received the same results in perovskite phase. They have a direct band at Γ-high symmetry point with the forbidden gap 0.817 eV and 0.650 eV, respectively. In the ilmenite phase, the gaps are 2.106 eV and 1.302 eV for $ZnGeO_3$ (indirect band transition between B-Γ high symmetry points) and $ZnSnO_3$ (X-Γ), respectively. For $CdGeO_3$ (B-Γ) and $CdSnO_3$ (Z-Γ) in ilmenite phase, the gaps are 1.398 eV and 0.981 eV, respectively. The general features of the energy bands such as band gaps, DOS and orbital hybridization are similar for all investigated compounds. Furthermore our results are in agreement with the results obtained in previous calculations [1, 25, 26]. We have summarized the band gap energies for $ZnXO_3$ and $CdXO_3$ in Table 1 with the available theoretical and experimental results. Our results in perovskite type orthorhombic structures can roughly compare with band structure for $SrSnO_3$ and $CaGeO_3$ compound in same structure [8, 25]. The band structures of $CdXO_3$ and $ZnXO_3$ is qualitatively similar to that of $SrSnO_3$ and $CaGeO_3$. The band gap for $SrSnO_3$ (2.9 eV) [8] is higher than that for $CdXO_3$ and $ZnXO_3$ compounds.

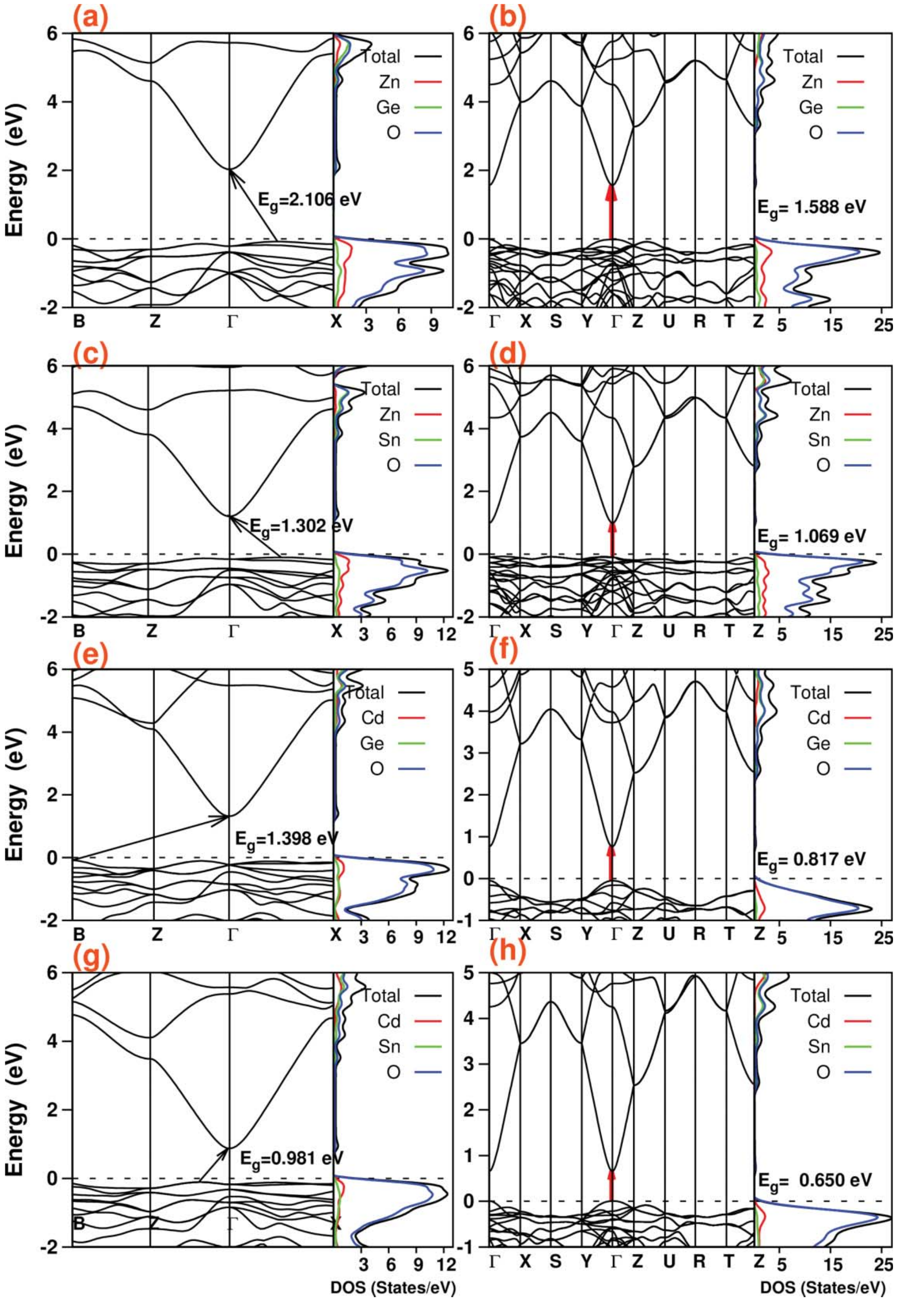

Figure 1. The calculated electronic band structure of AXO_3 (A = Zn, Cd and X = Ge, Sn) compounds. **(a)** Ilmenite-$ZnGeO_3$, **(b)** Perovskite-$ZnGeO_3$, **(c)** Ilmenite-$ZnSnO_3$, **(d)** Perovskite-$ZnSnO_3$, **(e)** Ilmenite-$CdGeO_3$, **(f)** Perovskite-$CdGeO_3$, **(g)** Ilmenite-$CdSnO_3$, **(h)** Perovskite-$CdSnO_3$.

The real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of $\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega)$ were calculated by using Kramers-Kroning transformation [28]. Figure 2 shows the real and imaginary parts of $\varepsilon(\omega)$ for both ilmenite and perovskite $ZnXO_3$ and $CdXO_3$ compounds in a manner similar to our

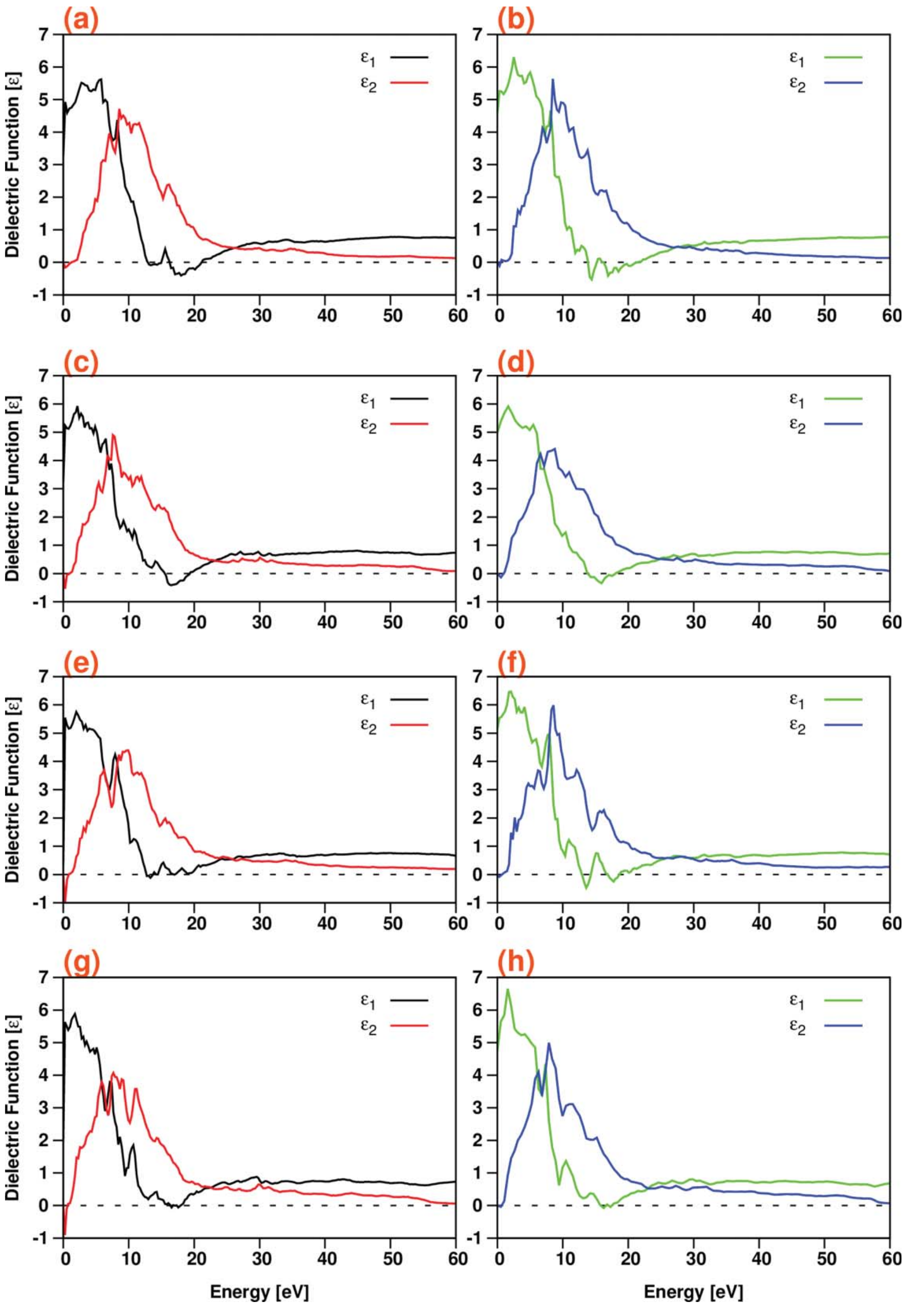

Figure 2. The calculated real and imaginary parts of linear dielectric function of AXO_3 (A = Zn, Cd and X = Ge, Sn) compounds. **(a)** $ZnGeO_3$ (Ilmenite-type), **(b)** $ZnGeO_3$ (Perovskite-type), **(c)** $ZnSnO_3$ (Ilmenite-type), **(d)** $ZnSnO_3$ (Perovskite-type), **(e)** $CdGeO_3$ (Ilmenite-type), **(f)** $CdGeO_3$ (Perovskite-type), **(g)** $CdSnO_3$ (Ilmenite-type), **(h)** $CdSnO_3$ (Perovskite-type).

recent work [29]. The calculated $\varepsilon_2(\omega)$ show main peaks in the range of 2.0 to 20 eV for both phases. These peaks related for $\varepsilon_2(\omega)$ are related to the interband transition from the valence to conduction bands (interband transition from O2s and O2p to Ge and Sn s- and p- states).

Conclusion

This work present ab initio studies of electronic structure and optical properties of $CdXO_3$ and $ZnXO_3$(X=Ge, Sn) compounds. By a search of the total energy minimum the equilibrium volume are found, which are in good agreement with experimentally determined one. The DFT calculations of the electronic structure and optical properties of the investigated compounds have been performed using the calculated equilibrium lattice parameters. It is shown that all compounds considered are semiconductor nature. The lowest CB is formed of the valence orbitals of the Cd(Zn) and X (Sn,Te) atoms and major contribution comes from d-orbitals of Cd(Zn) and p-orbitals of X(Ge, Sn) atoms. Topmost valence band is formed of the valence orbitals of the O-atoms and major contribution comes from p-orbitals of O. Finally, optical properties were investigated. The relations of the optical properties to the interband transitions were also discussed.

Acknowledgments

This work is supported by the projects DPT-HAMIT, DPT-FOTON, NATO-SET-193 and TUBITAK under Project Nos., 113E331, 109A015, 109E301. One of the authors (Ekmel Ozbay) also acknowledges partial support from the Turkish Academy of Sciences. The numerical calculations reported in this paper were fully performed at Aksaray University, Science and Technology Application and Research Center.

References

1. E. Mizoguchi, H. Eng and P. Woodward: Probing the electronic structure of ternary perovskite and pyrochlore oxides containing Sn(4^+) or Sr(5^+). *Inorg. Chem.* **43**, 1667–1680 (2004).
2. E. Mizoguchi and P. Woodward: Electronic Structure Studies of Main Group Oxides Possessing Edge-Sharing Octahedra: Implications for the Design of Transparent Conducting Oxides. *Chem. Mater.* **16**, 5233–5248 (2004).
3. S. Matar, I. Baraille, M. Subramanian: First principle studies of $SnTiO_3$ perovskite as potentially environmentally benigh ferroelectric material. *Chem. Phys.* **355**, 43–49 (2009).
4. A. Smith: The system cadmium oxide-stannic oxide.*Acta. Crystallogr.* **13**, 749–752 (1960).
5. R. Shannon, J. Gillson, R. Bouchard: Single crystal synthesis and electrical properties of $CdSnO_3$, Cd_2SnO_4, In_2TeO_6 and $CdIn_2O_4$. *J. Phys. Chem Solids.* **38**, 877–891 (1977).
6. P. Ferraro, S. Grilli, P. Natali: Ferroelectric Crystals for Photonic Applications. (Springer, Berlin, 2009).
7. M. Okayama, Y. Ishibashi: *Ferroelectric Thin Films: basic properties and device physics for memory applications.* (Springer, Berlin, 2005).
8. K. P. Ong, X. Fan, A. Subedi, M. B. Sullivan, and D. J. Singh: Transparent conducting properties of $SrSnO_3$ and $ZnSnO_3$.*APL. Materials.* **3**, 062505–062513 (2015).
9. G. Kresse, J. Hafner: Ab initio molecular dynamics for liquid metals. *Phys. Rev. B.* **47**, 558–561 (1993).
10. G. Kresse, J. Furthmüller: Ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
11. G. Kresse, D. Joubert: From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B.* **59**, 1758–1775 (1999).
12. G. Kresse, J. Furthmüller: Efficient iterative schemes for ab initio total- energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
13. P. Hohenberg, W. Kohn: Inhomogeneous Electron Gas. *Phys. Rev.* **136**, A1133–A1138 (1964).
14. J. P. Perdew, S. Burke, M. Ernzerhof: Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).

15. H. J. Monkhorst, J. D. Pack: Special points for Brillouin-zone integrations. *Phys. Rev. B.* **13**, 5188–5192 (1976).
16. N. L. Ross, K. Leinenweber: Single crystal structure refinement of high-pressure $ZnGeO_3$ ilmenite. *Zeitschrift für Kristallographie.* **191**, 93–104 (2010).
17. H. Gou, J. Zhang, Z. Li, G. Wang, F. Gao, R. C. Ewing, and J. Lian: Energetic stability, structural transition, and thermodynamic properties of $ZnSnO_3$. *Appl. Phys. Lett.* **98**, 091914–091917 (2011).
18. Y. Inaguma, M. Yoshida, and T. Katsumata: A Polar Oxide $ZnSnO_3$ with a $LiNbO_3$-Type Structure. *J. Am. Chem. Soc.* **130**, 6704–6705 (2008).
19. N. N. Ge, C. M. Liu, Y. Cheng, X. R. Chen, and G. F. Ji: First-principles calculations for elastic and electronic properties of $ZnSnO_3$ under pressure. *Physica. B.* **406**, 742–748 (2011).
20. H. Y. Gou, F. M. Gao, and J. M. Zhang: Structural identification, electronic and optical properties of $ZnSnO_3$: First principle calculations. *Comput. Mater. Sci.* **49**, 552–555 (2010).
21. D. Kovacheva, K. Petrov: Preparation of crystalline $ZnSnO_3$ from Li_2SnO_3 by low-temperature ion exchange. *Solid State Ionics.* **109**, 327–332 (1998).
22. J. I. Susaki: $CdGeO_3$ -phase transformations at high pressure and temperature and structural refinement of the perovskite polymorph. *Phys. Chem. Minerals.* **16**, 634–641 (1989).
23. S. Tateno, K. Hirose, N. Sata, and Y. Ohishi: High-pressure behavior of $MnGeO_3$ and $CdGeO_3$ perovskites and the post-perovskite phase transition. *Phys. Chem. Miner.* **32**, 721–725 (2006).
24. C. M. Fang, R. Ahuja: Structures and stability of ABO_3 orthorhombic perovskites at the Earth's mantle conditions from first-principles theory. *Physics of the Earth and Planetary Interiors.* **157**, 1–7 (2006).
25. C. A. Barboza, J. M. Henriques, E. L. Albuquerque, E. WS. Caetano, V. N. Freire, and J. A. P. da Costa: Structural, electronic and optical properties of orthorhombic CdGeO3 from first principles calculations. *J. Solid State Chem.* **183**, 437–443 (2010).
26. P. D. Jr Sesion, J. M. Henriques, C. A. Barboza, E. L. Albuquerque, V. N. Freire and E. WS. Caetano: Structural, electronic and optical properties of ilmenite and perovskite $CdSnO_3$ from DFT calculations. *J. Phys.: Condens. Matter.* **22**, 435801 (2010).
27. H. Ozisik, E. Deligoz, K. Colakoglu, G. Surucu: Mechanical and lattice dynamical properties of the Re_2C compound. *Physica status solidi (RRL)-Rapid Research Letters* **4**(12), 347–349 (2010).
28. H. R. Philipp and H. Ehrenreich: Optical properties of semiconductors. *Phys. Rev.* **129**, 1550–1560 (1963).
29. H. Koc, A. M. Mamedov, E. Deligoz, H. Ozisik: First principles prediction of the elastic, electronic, and optical properties of Sb_2S_3 and Sb_2Se_3 compounds. *Solid State Sciences* **14** (8), 1211–1220 (2012).