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Thermoelectric Properties Of Doped $BaHfO_3$

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Abstract. We have studied the structural stability, electronic structure, optical properties and thermoelectric properties of doped $BaHfO_3$ by full potential linearized augmented plane wave (FP-LAPW) method. The electronic structure of $BaHfO_3$ doped with Sr shows enhances the indirect band gaps of 3.53 eV, 3.58 eV. The charge density plots show strong ionic bonding in Ba-Hf, and ionic and covalent bonding between Hf and O. Calculations of the optical spectra, viz., the dielectric function, refractive index and extinction coefficient are performed for the energy range are calculated and analyzed. Thermoelectric properties of semi conducting are also reported first time. The doped $BaHfO_3$ is approximately wide band gap semiconductor with the large p-type Seebeck coefficient. The power factor of $BaHfO_3$ is increased with Sr doping, decreases because of low electrical resistivity and thermal conductivity.

INTRODUCTION

As a result of a raising demand involving renewable energy, thermoelectric materials nowadays usually are attracting very much attention since they directly change thermal energy into electrical energy. For example, thermoelectric oxides usually are interesting because of the low producing costs, environmentally friendly, availability within nature, in addition to high support temperatures, high service temperatures. $BaHfO_3$, cubic pervoskite which find wide range of applications such as special interest for memory, ferroelectricity semi conductivity, logic, memory storage capacitors and thermoelectricity, passive microelectronic applications [1-4]. Yangthaisong et al. investigated the electronic structure and lattice vibrational properties of $BaHfO_3$ by screened exchange local density approximation (sX-LDA) [5]. Ohta et.al. measured thermoelectric properties of heavily La/Nb-doped $SrTiO_3$ at high temperature and have found ZT values of 0.27 and 0.37 at 1000 K for 20% doping respectively [6-7]. Liu et al. studied the mechanical, electronic, chemical bonding and optical properties of cubic $BaHfO_3$ by plane-wave ultra soft pseudo-potential method based on the density-functional theory (DFT) [8]. Earlier work on to enhance the thermo power involving doped $SrTiO_3$ different atomic substitutions and defects are researched. In this work, $BaHfO_3$ is a semiconductor we focus on the Sr, doped analog and systematically study their structural, electronic and transport properties using first-principles density-functional calculations.

METHODOLOGY

The structure of $BaHfO_3$ are calculated using the WIEN2K package, which is an implementation of the hybrid full potential linear augmented plane wave method (GGA) within the density-functional theory (DFT). The atomic sphere radii R_{mt} are chosen to be 2.43, 1.73, 1.75 and 1.64 a.u. for Ba, Sr, Hf and O atoms, respectively. The convergence parameter RKmax (Rmt × Kmax, where Kmax is the plane wave cut-off and Rmt represents the smallest among all atomic sphere radii), which determines the matrix size in these calculations, is set to be 7.0. The self-consistent calculations are carried out with a total energy convergence tolerance of less than 0.1mRy. We have used 1000 k-points in the entire Brillouin zone. We assume that $BaSrHfO_3$ has a similar structure to $BaHfO_3$ using Sr, as a substitute for Hf. The transport properties have been calculated using semi-classical Boltzmann theory as implemented in the BoltzTraP interfaced program with Wien2k [9,10]. The lattice parameters and other properties are summarized in Table 1.

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RESULT& DISCUSSION

$BaHfO_3$ ideal cubic pervoskite structure with space group Pm3m.The lattice sites remain in the ideal cubic perovskite positions with Ba in (0,0,0), Hf in (1/2,1/2,1/2) and O in (1/2,1/2,0).The energy band structure and densities of states (DOSs) of $BaHfO_3$ are shown in Figs. 1. The energy band structure is calculated along the way that contains the highest number of high symmetry points of the Brillouin zone. The top of the valence bands (VBs) and the bottom of conduction bands (CBs) are composed of O $2p$ and Ba 3d states, respectively. The VB maximum of $BaSrHfO_3$ is located at the Γ point, whereas the CB minimum is located at the Γ point, suggesting an indirect band gap. The VB show a slight shift to low energy, while the CB move to high energy. As a result, the energy gap of $BaSrHfO_3$ increases from 3.53 eV of $BaHfO_3$ to 3.58 eV. The bands between −10 and −12 eV mainly consist of O $2s$ states, and those at about −4 eV arise from Hf $3d$ states with a sharp peak due to its strong localization character. The Ba $6s$ states are located at about −10 eV with a bandwidth of 2 eV. Since the O $2p$ states have some admixture with the Ba, Sr and Hf sp states. In the VB region, the energy levels of Sr and Hf are clearly lower than that of Ba and O. This indicates that the hybridization of Ba-O is stronger than those of Sr-O and Hf-O. In the energy range from 3 eV to 10 eV, the bands are mainly derived from the Ba $6p$ states with some admixture from Sr and Hf sp states. From the analysis of DOS, it can be observed that there is strong orbital hybridization between the Hf $3d$ and O $2p$ states.

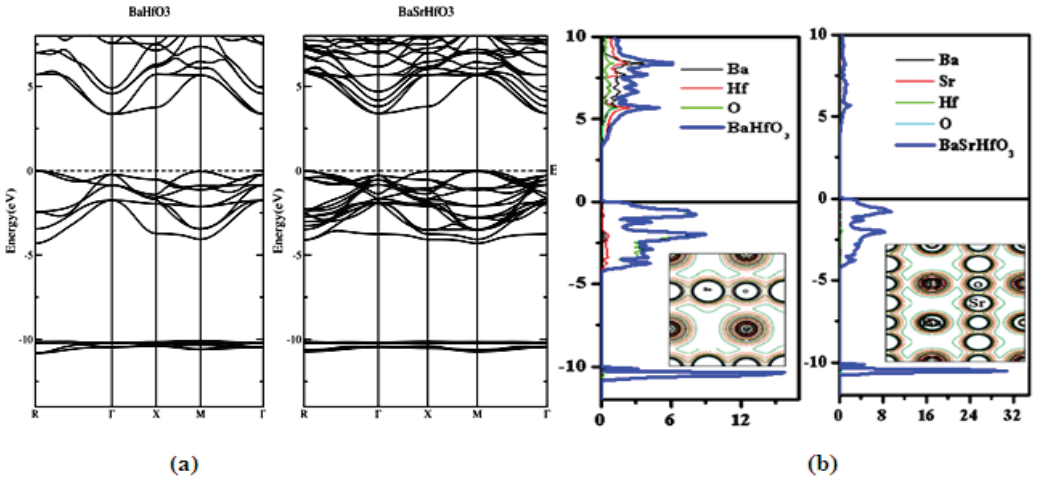

FIGURE 1. (a) Energy bands (b) Density of states

For, the contour plots of valence charge distribution have been calculated by considering the nature of the corresponding Ba–O, Hf–O, Sr–O and Hf-Sr bonds, which are displayed in the (1 1 1) plane. From Figs. 1(b), the given plots show a strong ionic but week covalent character of Ba–O bond that can be attributed to the larger charge transfer among Ba and O atoms with very small contour extension. Figure 1(b) reveals the strong sharing and distribution of electrons along the Hf–O bond. As a result, their bond is strongly covalent nature is observed along the Sr–O and Hf–O bond.

The determination of the optical properties of a compound in the spectral range above its band gap plays an important role in the understanding of the nature of that material and also gives a clear picture of its applications in optoelectronic devices. The calculated imaginary part of dielectric function for $BaHfO_3$ and $BaSrHfO_3$ in the radiation range 0–12 eV are shown in Fig .2 (a).Our analysis $\varepsilon_2(\omega)$ curve shows that the threshold energy (the first critical point) of the dielectric function occurs at 2.05 and 1.27 eV for $BaHfO_3$ and $BaSrHfO_3$, respectively. These points give the threshold for direct optical transitions between the highest valence and the lowest conduction bands. It is known as the fundamental absorption edge. Beyond these points, the curve increases rapidly because the number of points contributing towards $\varepsilon_2(\omega)$ increases abruptly. The main features in the spectrum of the real part $\varepsilon(\omega)_1$ are a peak with a magnitude of 7.22,7.70 at around 4.29 eV, a decrease between 5.76 and 9.57 eV, for $BaHfO_3$ and $BaSrHfO_3$ respectively. After which $\varepsilon(\omega)_1$ becomes negative, and a minimum at around 10.56 eV, followed by a slow increase toward zero. The most important quantity is the zero frequency limit $\varepsilon\ (0)_1$, which is the electronic part of the static dielectric constant and depends strongly on the band gap.

The efficiency of thermoelectric devices is determined by the dimensionless figure of merit, $zT = \sigma S^2 T / \kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, T is the temperature, and κ is the thermal conductivity. The latter comprises lattice (κlattice) and electronic (κelectron) contributions, κtotal = κlattice + κelectron. In order to achieve a high efficiency, the thermoelectric material, in general, should be a good electrical and poor thermal conductor and, at the same time, possess a high Seebeck coefficient. Fig.2 (b), shows the temperature dependence of the thermo power for $BaHfO_3$ and $BaSrHfO_3$ with p-type carrier concentration at fixed to 10^{19} cm^{-3}. High thermopower S is observed in p-type $BaHfO_3$ and $BaSrHfO_3$ over whole temperature range. Room temperature thermo powers are 267 μV/K and 127 μV/K for p-type $BaHfO_3$ and $BaSrHfO_3$, respectively. While in p-type both materials shows similar behavior. This value is quite similar to their iso-structural compounds like $SrTiO_3$. Previously reported pervoskites such as $SrTiO_3$, $BaTiO_3$ and $PbTiO_3$ have band-gaps around 3 eV (insulators) which is far from the visible region and Seebeck values are always high for large band gap materials. The electrical conductivity is very low, this results in small $S^2\sigma$ (Power factor) at low temperature, but after doping of Sr in $BaHfO_3$, the power factor of $BaSrHfO_3$ increases from room temperature. In our study, bandgap is around 3.5 eV which half of them and a moderate doping could make these materials as good candidate for optoelectronic and thermoelectric devices. The Seeback coefficient of $BaHfO_3$ has high at room temperature in comparison to $BaSrHfO_3$ and gradually decreases at RT and both value of S is positive, suggesting that the holes to be the majority carriers. We have reported first time the ZT of Sr doped $BaHfO_3$ is decreases.

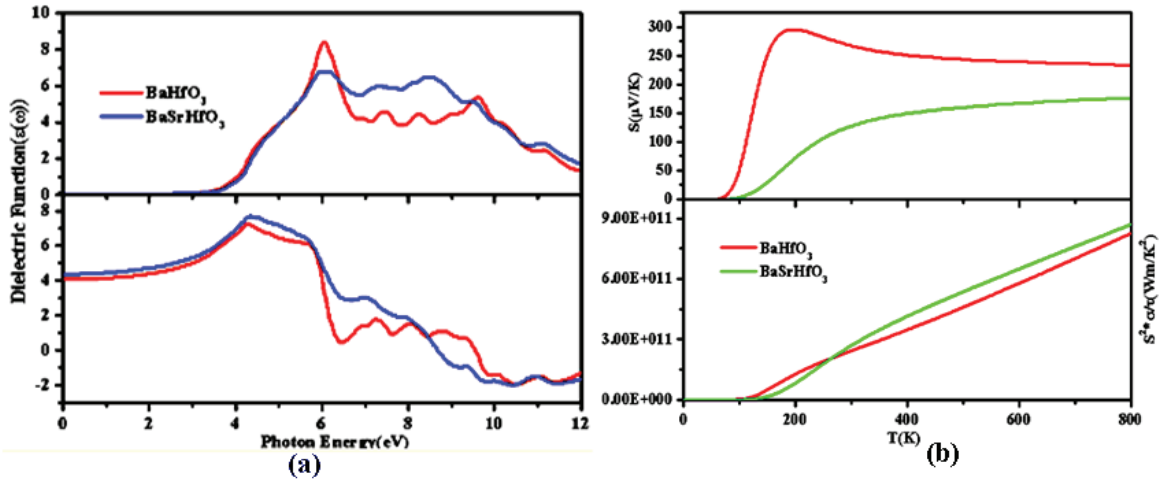

FIGURE 2. (a) Optical property (b) (c) Transport property

TABLE 1. Out parameters

Parameters	$BaHfO_3$	$BaSrHfO_3$
Band gap (eV)	3.53[Ref.5]	3.58
S (μV/K)	267	127
$R_H(10^{-8})(m^3/C)$	2.10	4.07
ZT	0.81	0.43

SUMMARY

The electronic structure and thermoelectric properties are calculated for doped $BaHfO_3$ .The calculated optimized structural parameters, band gaps are in good agreement with the experimental data. The band structure of $BaSrHfO_3$ shows the indirect band gap (R-Γ=3.58eV) semiconductors. The electronic structures of $BaSrHfO_3$ reveal that the top of a VB and the bottom of a CB are decided by O 2*p* and Ba 6*p* states, respectively. Furthermore, BaSrHfO3 shows some covalent features which can reduce the total energy and help maintain the stability of the semiconductor property. High thermo power 267 μV/K is observed in n-type $BaHfO_3$ as compared to $BaSrHfO_3$ (S = 127 μV/K) at room temperature. It is expected that the present study will provide better insight in understanding electronic as well as thermoelectric properties of these materials.

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REFERENCES

1. C.B. Samantaray, H. Sim, H. Hwang, J. Microelectron. **36**, 725 (2005).
2. V.E. Henrich, Rep. Prog. Phys. **11**, 1481(1985).
3. H. Muta, K. Kurosaki, S. Yamanaka, J. Alloys Compd. **350**, 292(2003).
4. C B Samantaray and H Sim and H Hwang. Phys. B: Condens. Matter, **351**, 158(2004).
5. A. Yangthaisong Phys. Let.A. **377**, 927-931 (2013).
6. S. Ohta, T. Nomura, H. Ohta, M. Hirano, H. Hosono, and K. Koumoto, Appl. Phys. Lett. **87**, 092108 (2005).
7. S. Ohta, T. Nomura, H. Ohta, and K. Koumotoa, J. Appl. Phys. **97**, 034106 (2005).
8. Q.J. Liu, Z.T. Liu, L.P. Feng, H. Tian Phys. B: Cond. Mat. **405**, 4032–4039 (2010)**.**
9. P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka and J. Luitz, Wien2k, Vienna University of Technology, Vienna, Austria.
10. G.K.H Madsen and D.J Singh Comp.Phys.Comm.**175,** 67-71 (2006).