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Structural, electronic and optical characteristics of $SrGe_2$ and $BaGe_2$: A combined experimental and computational study

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ABSTRACT

$SrGe_2$ and $BaGe_2$ were characterized for structural, electronic and optical properties by means of diffuse reflectance and first-principles density functional theory. These two germanides crystallize in the $BaSi_2$-type structure, in which Ge atoms are arranged in tetrahedral configuration. The calculation indicates a charge transfer from Sr (or Ba) atoms to Ge atoms along with the formation of covalent bonds among Ge atoms in Ge tetrahedral. The computational results confirm that these two germanies are Zintl phase described as Sr_2Ge_4 (or Ba_2Ge_4), which are characterized by positively charged $[Sr_2 \text{ (or } Ba_2)]^{2.59+}$ and negatively charged $[Ge_4]^{2.59-}$ units acting as cation and anion, respectively. These compounds are indirect gap semiconductors with band gap estimated to be $E_g = 1.02$ eV for $BaGe_2$ and $E_g = 0.89$ eV for $SrGe_2$ which are in good agreement with our experimental measured values ($E_g = 0.97$ eV for $BaGe_2$ and $E_g = 0.82$ eV for $SrGe_2$). Our calculations demonstrate that the band gaps are narrowed by application of hydrostatic pressure; the pressure coefficients are estimated to be -10.54 for $SrGe_2$ and -10.06 meV/GPa for $BaGe_2$. Optical properties reveal that these compounds have large absorption coefficient ($\sim 7.5 \times 10^4\ \text{cm}^{-1}$ at 1.5 eV) and the estimated high frequency (static) dielectric constant are, $\varepsilon_\infty(\varepsilon_0) \approx 12.8(20.97)$ for $BaGe_2$ and $\varepsilon_\infty(\varepsilon_0) \approx 14.27(22.87)$ for $SrGe_2$.

1. Introduction

Silicon and germanium intermetallic compounds also known as silicides and germanides are very useful functional materials [1–3]. Extensive works have been carried out in the past decade on these compounds to understand their suitability for many technological applications such as solar-cells, thermoelectric, superconductivity, and optoelectronics [4–10]. However, it is worth to mention that compared to silicides [5–15], very few systematic studies have been carried out for germanides [16–19] in this context.

$SrGe_2$ and $BaGe_2$ have been reported way back in 1974 as semiconductors [19], which crystallize with the $BaSi_2$-type structure (orthorhombic, space group $D_{2h}^{16} - Pnma$ no. 62, $Z = 8$) [20]. Fig. 1a illustrates the crystal structure of $SrGe_2$ or $BaGe_2$. In a conventional unit cell of 24 atoms, eight Sr (Ba) cations (green big balls) occupy two inequivalent 4*c* Wyckoff sites, and 16 Ge anions (small blue balls) occupy three inequivalent positions (4*c* and 8*d* Wyckoff sites). In these digermanides, Ge atoms form a characteristic configuration, tetrahedral. This structure has been understood by the Zintl–Klemann concept [21] as follows. According to an electron counting based on formal charge of constituent elements, each of electropositive atoms Sr (or Ba) provides two electrons to singly ionize two of electronegative Ge atoms. As a result, Ge atoms have five valence electrons ($3s^2 3p^3$), forming covalent bonds with neighbor three Ge atoms according to the octet (8-N) rule. However, the charge transfer from Sr (or Ba) to Ge atoms and covalent bonding formation have not been demonstrated clearly yet. One first-principles density functional theory (DFT) calculation is available for these compounds [17], where electronic properties are discussed by using generalized gradient approximation (GGA). However, DFT studies within the local density approximation (LDA), or GGA are commonly underestimate band gaps by the order of 50%. Despite all these reports on germanides [16–19], a systematic detailed analysis of physical properties of $SrGe_2$ and $BaGe_2$ is missing. For example, it is important to understand the chemical bonding and nature of bonds in these compounds. Similarly, the energy gap, an important fundamental physical quantity in semiconductors, was measured way back in 1974 from the temperature dependence of electrical resistivity measurements [19], although the details were not shown. Therefore, E_g needs to be determined using a complementary method, such as optical measurements or a better theoretical methods, to confirm and

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establish its values. Moreover, optical properties of these compounds were rarely discussed.

On the other hand, use of Ge in electronic devices with metal-oxide-semiconductors (MOSs) has attracted attention recently due to the higher mobility of Ge [22,23]. However, one of the technical problem in Ge MOSs device is the thermal instability at interface of insulator and Ge substrate. This is particularly caused by the degasing of reducing gas GeO from the interface. This problem deteriorates the characteristics of interface and finally Ge mobility fall down. In order to fabricate a high-performance Ge MOSs devices, it is necessary to address the instability at the interface between Ge substrate and MOSs. Among various Ge based stable compounds of Sr (or Ba), $SrGe_2$ and $BaGe_2$ have good lattice matching with Ge (the *c*-axis values of these compounds is very close to twice the lattice constant of Ge). Therefore, it is expected that good electric characteristics can be obtained when these compounds are grown epitaxially. Hence, $SrGe_2$ and $BaGe_2$ are the promising candidates as a non-metallic Ge based semiconductors which have been recently proposed as a sandwich layer to reduce the instability at the interface of Ge and MOSs [24]. Therefore, a detailed understanding of the fundamental properties of these compounds is very essential to meet the aforementioned future potential application.

A detailed analysis of material properties can only be achieved using combined application of experimental and theoretical (especially quantum mechanical calculations) methods. Therefore, in this study, $SrGe_2$ and $BaGe_2$ were synthesized by Ar arc-melting technique and then characterized by X-ray diffractometry and diffuse reflectance spectroscopy. Furthermore, a detailed theoretical analysis was carried out to analyze the structural, electronic, and optical properties by employing a first-principles method within DFT. We used Heyd-Scuseria-Ernzerhof (HSE06) screened hybrid functional in present study to overcome the shortcomings of LDA/GGA methods. Details are discussed in this article.

2. Experimental and computational methods

2.1. Experimental details

$SrGe_2$ and $BaGe_2$ were synthesized by Ar arc-melting of a 1.03:2 molar mixture of Sr and Ge or Ba and Ge, respectively. These two germanides seem to be sensitive to moisture because the color of samples changed when they were exposed to air. The formation of $SrGe_2$ and $BaGe_2$ was confirmed using powder X-ray diffractometry. We measured X-ray diffraction (XRD) patterns (Cu Kα radiation) of the powdered samples sealed in an Ar-filled sample holder with a polyimide film window. Si (NIST, 640c) was used as an external standard material. We measured diffuse reflectance spectra of the samples sealed in a cell designed for moisture-sensitive samples in wavelength region from 190 to 2000 nm. Spectralon® (Labsphere) was used as a standard material. Optical absorbance spectra were calculated from the diffuse reflectance spectra using the Kubelka–Munk equation: $\alpha/S = (1 - R)2/R$, where α, R, and S are the absorption coefficient, the diffuse reflectance relative to the standard material, and the scattering coefficient, respectively [17].

2.2. Computational details

All DFT calculations were performed with plane-wave code VASP [25] using the hybrid HSE06 functional [26], in which the short-range exchange potential is mixed 25% Hartree–Fock exchange potential with the 75% Perdew–Burke–Ernzerhof (PBE) potential. The lattice constants and the atomic positions were relaxed with an accuracy of 0.01 eV/Å for the forces on each atom. A 3 × 4 × 2 Monkhorst-Pack **k**-point mesh with an energy cutoff of 400 eV was employed for convergence. The optical properties were determined in the independent-particle approximation using a 6 × 6 × 4 Monkhorst-Pack **k**-point mesh along with sufficient conduction bands. In order to investigate optical properties, the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ (where ε_1 is the real part and ε_2 is the imaginary part) was calculated. The imaginary part ε_2 of the dielectric function was calculated from the joint density of states and the optical momentum matrix in the long wavelength limit $q = |\mathbf{k}' - \mathbf{k}| = 0$ The real part $\varepsilon_1(\omega)$ of the dielectric function was obtained from the Kramers–Kronig transformation. The absorption coefficient $\alpha(\omega)$ was obtained directly from the dielectric function. The details were described elsewhere [27].

3. Results and discussion

In this section we discuss the structural, electronic, and optical properties of $SrGe_2$ and $BaGe_2$ and compare them with previous available experimental and computational results.

3.1. Structural analysis

Fig. 2 shows X-ray diffraction patterns of $SrGe_2$ and $BaGe_2$ together with patterns calculated using parameters reported in Ref. [20]. The observed pattern was almost the same as the calculated pattern for both $SrGe_2$ and $BaGe_2$. Most of the reflections were indexed by an orthorhombic structure. The lattice parameters determined from the observed patterns are consistent with those reported previously, shown in Table 1.

Table 1 lists the measured and calculated lattice parameters of $SrGe_2$ and $BaGe_2$. The lattice parameters determined from the observed patterns are $a = 8.732(9)$ Å, $b = 6.559(4)$ Å, and $c = 11.210(8)$ Å for $SrGe_2$ and $a = 9.063(7)$ Å, $b = 6.803(7)$ Å, and $c = 11.63(2)$ Å for $BaGe_2$, in which the figure in parentheses represents standard deviations, are in excellent agreement with our theoretically calculated lattice parameters $a = 8.754$ Å, $b = 6.566$ Å, and $c = 11.223$ Å for $SrGe_2$ and $a = 9.111$ Å, $b = 6.854$ Å, and $c = 11.696$ Å for $BaGe_2$. Hence, it is worth to

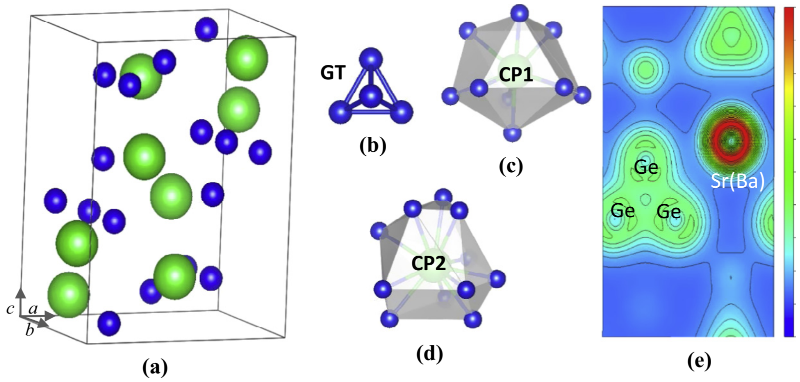

Fig. 1. One representative case of a crystal structure of $SrGe_2$ (or $BaGe_2$), here large green balls represent cation Sr (or Ba) and small blue balls represent anion Ge; (a) conventional unit cell of orthorhombic structure, containing 8 cation atoms and 16 Ge atoms. (b) Ge tetrahedron (GT) where each Ge atom is bonded with three neighboring Ge atoms and thus forms an isolated distorted tetrahedral. Coordination polyhedra (c) CP1 and (d) CP2 formed by two different cation atoms with nearest Ge atoms, and (e) a contour plot of charge density along 1 0 0 plane which start from 0.02 electrons/Å^3 (red color as highest electron density) and change successively till lowest electron density 0.002 electrons/Å^3 (blue color). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)