

This is the accepted manuscript made available via CHORUS. The article has been published as:

Phase stability and transition of BaSi_2 -type disilicides and digermanides

Jian-Tao Wang, Changfeng Chen, and Yoshiyuki Kawazoe

Phys. Rev. B **91**, 054107 — Published 17 February 2015

DOI: [10.1103/PhysRevB.91.054107](https://doi.org/10.1103/PhysRevB.91.054107)

Phase stability and transition of BaSi₂-type disilicides and digermanides

Jian-Tao Wang,^{1,2,*} Changfeng Chen,² and Yoshiyuki Kawazoe^{3,4}

¹*Beijing National Laboratory for Condensed Matter Physics,*

Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

²*Department of Physics and High Pressure Science and Engineering Center,
University of Nevada, Las Vegas, Nevada 89154, USA*

³*New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan*

⁴*Institute of Thermophysics, Siberian Branch of Russian Academy of Sciences, Novosibirsk 630090, Russia*

(Dated: December 29, 2014)

BaSi₂-type disilicides and digermanides hold great promise for solar-cell applications, but their structural stability and phase transition mechanisms remain unresolved. Here we present *ab initio* calculations of pressure induced structural phase transitions of BaSi₂, BaGe₂ and SrGe₂ and show that Si-tetrahedra in orthorhombic BaSi₂ tend to convert to corrugated layers in the trigonal phase under high pressure with bond breaking along the *b*-axis, and a three-dimensional Si-net in the cubic phase is stabilized energetically at low pressure. The orthorhombic semiconductor to trigonal metal conversion is also preferred for SrGe₂ by both energetics and kinetics. However, Ge-tetrahedra in BaGe₂ tends to convert to a ThSi₂-type tetragonal net with bond breaking around the *c*-axis. The kinetic barriers are large for both the reaction (~ 0.43 eV under compression) and counterreaction (~ 0.39 eV under decompression) for BaSi₂, which explains the stability of the trigonal and cubic phases at room temperature and the high-temperature requirement for the phase transitions.

PACS numbers: 61.50.Ks, 62.50.-p, 64.70.kg

BaSi₂-type disilicides and digermanides BaSi₂, SrSi₂, BaGe₂, and SrGe₂ are semiconductors with larger band gaps of 0.9~1.3 eV and high optical absorption coefficients,¹⁻⁴ which make them ideal candidates as silicon-based solar cell materials. Great interest in these materials has been reignited by recent success in preparing well-crystalline *a*-axis-oriented BaSi₂ and Ba_{1-x}Sr_xSi₂ epitaxial films on Si(111) and Si(100) substrates.⁵⁻¹⁰ It was demonstrated that the electronic band gap can reach the ideal value of approximately 1.4 eV by replacing half of the Ba atoms with iso-electric Sr atoms.⁵ Meanwhile, there are a rich variety of pressure-induced structural phase transitions similar to those observed in Si and Ge.¹¹ At ambient conditions, BaSi₂, BaGe₂, and SrGe₂ all adopt the BaSi₂-type orthorhombic structure, but SrSi₂ has the SrSi₂-type cubic structure.¹²⁻¹⁹ Under high-pressure and high-temperature (HPHT) conditions, orthorhombic BaSi₂ transforms into SrSi₂-type cubic and EuGe₂-type trigonal structure,²⁰⁻²² and the trigonal phase can exist at ambient conditions, showing a metallic and superconducting behavior.²³ On the other hand, orthorhombic BaGe₂ and SrGe₂²⁴⁻²⁶ transform into tetragonal and trigonal structure, respectively. Each phase of disilicides and digermanides is characterized by an unique three-connected Si or Ge configuration: isolated tetrahedra in the orthorhombic phase, two-dimensional three-connected (2D3C) corrugated layers in the trigonal phase, and three-dimensional three-connected (3D3C) nets in both cubic and tetragonal phases. As far as we know, a metallic phase formed under high pressure rarely exists at atmospheric pressure and room temperature. Past studies have explored the electronic, thermoelectric and optical properties of these materials,²⁷⁻²⁹ but the

more complicated and important atomistic mechanisms for the phase stability and pressure induced phase transformations remain unresolved.

In this paper, we present a comprehensive study on the phase stability and transition of BaSi₂ compared with BaGe₂ and SrGe₂ under a wide pressure range of 0 ~ 10 GPa. We examine the energetics and kinetics that govern the phase stability and drive the structural conversion. In particular, we identify the pathways from the tetrahedra configurations in the orthorhombic phase toward the 2D3C corrugated layers in the trigonal phase and the 3D3C nets in the cubic phase with the Si-Si bond breaking and reconstruction parallel to the *b*[010] axis. The Si-tetrahedra in orthorhombic BaSi₂ convert to corrugated layers dynamically under high pressure, which further convert to 3D3C cubic net under low pressure (< 7 GPa) driven by energetics. Direct conversion from the orthorhombic (semiconductor) to trigonal (metal) structure is also favored for SrGe₂ by both energetics and kinetics. Moreover, Ge-tetrahedra in BaGe₂ tend to form 3D3C tetragonal net structure with bond breaking and rebonding around the *c*[001] axis. Pressure plays a key role in enhancing the high-pressure phase stability, but it has little effect on the conversion barrier. The large counterreaction barriers (~ 0.39 eV) are comparable to the compression process reaction barriers (~ 0.43 eV) for BaSi₂, which explains the high stability of the HPHT metastable (cubic or trigonal) phases at room temperature and the requirement of high temperature for the phase transitions,²⁰ in contrast to low-kinetic-barrier cold-compressed phase transitions in Si and Ge.¹¹

Our calculations are carried out using density functional theory as implemented in the Vienna *ab initio* simulation package (VASP)³⁰ with the spin-polarized gener-

TABLE I: Calculated equilibrium lattice parameters a, b, c (in Å), volume (in Å³ per atom), and bulk modulus (B_0 in GPa) for BaSi₂, BaGe₂ and SrGe₂ in orthorhombic (ort), cubic (cub), tetragonal (tet), and trigonal (tri) symmetry at 0 GPa, compared to available experimental data.^{17–19,22,24,25}

Phase	Method	a (Å)	b (Å)	c (Å)	V_0 (Å ³)	B_0 (GPa)
BaSi ₂ -ort	Cal	9.224	6.827	11.716	30.78	28.23
	Exp ^{19,22}	8.942	6.733	11.555	28.99	27.94
BaSi ₂ -tri	Cal	4.102	4.102	5.445	26.41	44.46
	Exp ¹⁹	4.047	4.047	5.330	25.21	
BaSi ₂ -cub	Cal	6.820	6.820	6.820	26.43	48.24
	Exp ¹⁹	6.715	6.715	6.715	25.24	
BaSi ₂ -tet	Cal	4.736	4.736	14.287	26.71	40.84
	Exp ²⁴	9.078	6.829	11.653	30.10	
BaGe ₂ -ort	Cal	9.471	6.942	11.861	32.53	25.14
BaGe ₂ -tri	Cal	4.344	4.344	5.435	29.59	38.60
	Exp ²⁵	4.769	4.769	14.737	27.93	
BaGe ₂ -cub	Cal	7.088	7.088	7.088	29.68	38.31
BaGe ₂ -tet	Cal	4.882	4.882	15.031	29.86	35.64
	Exp ²⁵	4.769	4.769	14.737	27.93	
SrGe ₂ -ort	Cal	9.058	6.674	11.351	28.61	29.12
	Exp ¹⁷	8.739	6.567	11.215	26.82	
SrGe ₂ -tri	Cal	4.204	4.204	5.256	26.83	41.50
	Exp ¹⁸	4.104	4.104	5.165	25.11	
SrGe ₂ -cub	Cal	6.887	6.887	6.887	27.23	41.62
	Cal	4.693	4.693	14.716	27.01	39.78

alized gradient approximation.³¹ The all-electron projector augmented wave (PAW) method³² was adopted with $4s^2 4p^6 5s^2$ for Sr, $5s^2 5p^6 6s^2$ for Ba, $3s^2 3p^2$ for Si, and $3d^{10} 4s^2 4p^2$ for Ge treated as valence electrons. A plane-wave basis set with an energy cutoff of 500 eV was used. The phase conversion barrier was calculated using a generalized solid-state nudged elastic band method³³ with the cell and atomic position optimization. Forces on the ions are calculated through the Hellmann-Feynman theorem allowing a full geometry optimization. Convergence criteria employed for both the electronic and the ionic relaxation were set to 10^{-6} eV and 0.02 eV/Å for energy and force, respectively.

We first discuss the energetic stability of silicides and germanides. The results show that the most favorable structures are orthorhombic with relatively large volumes of 30.78, 32.53, and 28.61 Å³ per atom for BaSi₂, BaGe₂, and SrGe₂ [see Fig. 1(a,c,e)], respectively. Meanwhile, the second stable phases have distinct cubic, tetragonal, or trigonal structures with a relatively small volume of 26.43, 29.86, and 26.83 Å³ per atom. Upon compression, for BaSi₂ as shown in Fig. 1(b), the cubic structure becomes more stable than the orthorhombic structure at 1.9 GPa, and the trigonal structure becomes more stable than the cubic structure above 7.2 GPa. The larger enthalpy change between the orthorhombic and cubic phases shows a strong pressure dependence with a large volume change, while the small enthalpy change be-

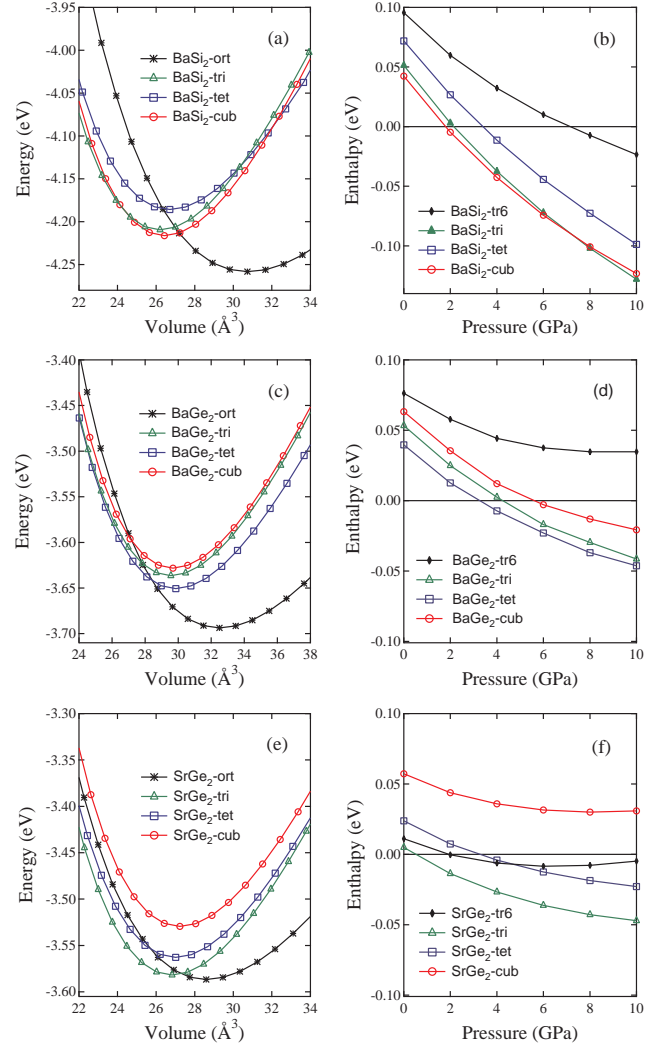


FIG. 1: (color online) Energy versus volume per atom for BaSi₂ (a), BaGe₂ (c), and SrGe₂ (e). Enthalpy per atom versus pressure for BaSi₂ (b), BaGe₂ (d), and SrGe₂ (f), relative to that of BaSi₂-type orthorhombic structure. The BaSi₂-type orthorhombic (*ort*), SrSi₂-type cubic (*cub*), α -ThSi₂ type tetragonal (*tet*) and EuGe₂-type trigonal (*tri*) phases are in D_{2h}^{16} - $Pnma$, O^6 - $P4_332$, D_{4h}^{19} - $I4_1/amd$, and D_{3d}^3 - $P\bar{3}m1$ symmetry, respectively. The enthalpy of CaSi₂-type structure (*tr6* in $R\bar{3}m$ symmetry)²² is shown for comparison.

tween the cubic and trigonal phases has a corresponding small volume change (see Table I). On the other hand, for BaGe₂ and SrGe₂ as shown in Fig. 1(d,f), no stable cubic phase exists up to 10 GPa. The tetragonal and trigonal structure become more stable than the orthorhombic structure above 3.2 GPa and 0.52 GPa, respectively. The enthalpy of the CaSi₂-type structure (*tr6* in $R\bar{3}m$ symmetry) is also shown in Fig. 1(b,d,f) for comparison,²² but it is clearly unfavorable for BaSi₂, BaGe₂, and SrGe₂ under a wide pressure range of 0 ~ 10 GPa.

It is worth noting that all of the Si and Ge sublattices satisfy the (8-N) rule that requires a formal transfer of

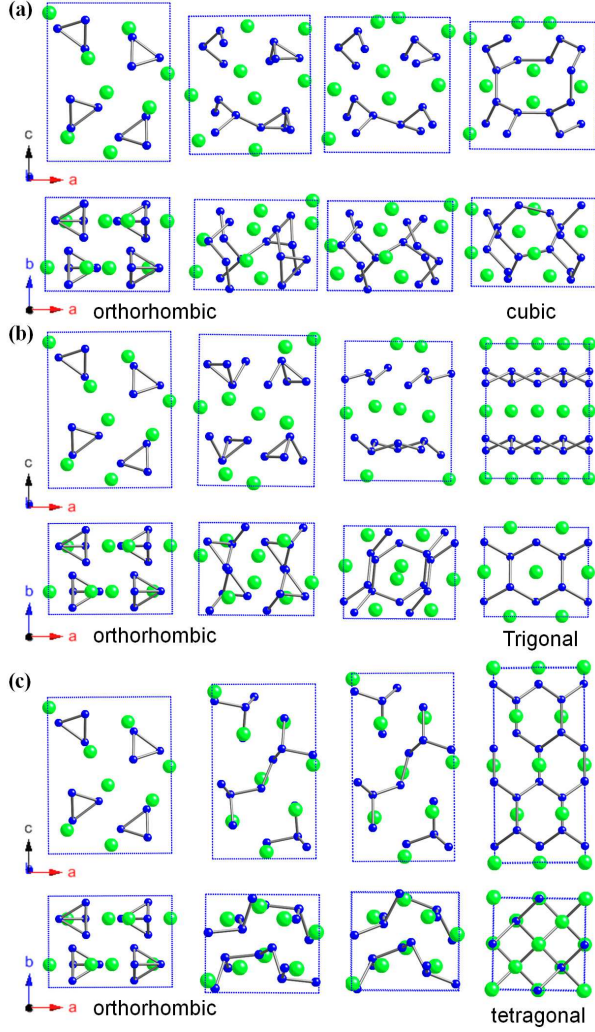


FIG. 2: (color online) Top and side views of the structures along the pathways to form cubic, trigonal and tetragonal BaSi_2 starting from the orthorhombic phase at 4 GPa. (a) Conversion process orthorhombic \rightarrow cubic with bond breaking along the $b[010]$ direction. The intermediate structures along the pathway are in $P2_1$ (No. 4) monoclinic symmetry. (b) Conversion process orthorhombic \rightarrow trigonal with the shortening in the a_{ort} and c_{ort} direction and elongation in the b_{ort} direction. The intermediate structures along the pathway are in $P2_1/C$ (No. 14) monoclinic symmetry. (c) Conversion process orthorhombic \rightarrow tetragonal with the shortening in the a_{ort} direction and elongation in the c_{ort} direction. The intermediate structures along the pathway are in $P2_12_12_1$ (No. 19) orthorhombic symmetry. The small (blue) and large (green) circles denote Si and Ba atoms, respectively.

valence electrons of the divalent metal atoms to Si or Ge atoms,²⁴ which then become isoelectronic with group V elements. One can regard BaSi_2 formally as $\text{Ba}^{2+}[\text{Si}^-]_2$ and accordingly Si_4 tetrahedra is preferred in the orthorhombic phase, which is similar to the structural arrangement in white phosphorus.³⁴ Since the orthorhombic phases have high compressibility with a larger vol-

ume and a smaller bulk modulus (see Table I), thus the more densely packed cubic, trigonal, or tetragonal phases can be produced under pressure. Here the corrugated layers of Si in the trigonal phase are similar to the crystal structures adopted by black phosphorus at high pressures;³⁵ and the cubic Si nets are congruent to the pressure-induced structure of cubic gauche nitrogen (cg-N).³⁶

We next examine the kinetic process at the atomic scale using a generalized solid-state climbing image nudged elastic band method³³ with the cell and atomic positions optimization under a wide pressure range of 0~8 GPa. According to above results, there are three possible phase transformations from BaSi_2 -type orthorhombic structure toward the SrSi_2 -type cubic, ThSi_2 -type tetragonal, and EuGe_2 -type trigonal phases under pressure. For the transformation of the orthorhombic BaSi_2 to the cubic BaSi_2 phase [see Fig. 2(a)], $b_{\text{ort}} = 6.827 \text{ \AA} \rightarrow a_{\text{cub}} = 6.820 \text{ \AA}$, $c_{\text{ort}} = 11.716 \text{ \AA} \rightarrow \sqrt{2}a_{\text{cub}} = 9.645 \text{ \AA}$, and $a_{\text{ort}} = 9.224 \text{ \AA} \rightarrow \sqrt{2}a_{\text{cub}} = 9.645 \text{ \AA}$, with about -18% shortening in the c_{ort} direction and about +4.6% elongation in the a_{ort} direction. Meanwhile, four Si_4 tetrahedra convert to four fourfold helices with bond breaking along the $b[010]$ direction and rebonding with torsion angles of 60° between the helical chains to form the 3D3C cubic net.³⁷ Throughout this pathway, the intermediate structures are all in $P2_1$ (No. 4) monoclinic symmetry, and the $\angle\text{Si-Si-Si}$ bond angle changes from 60° in Si_4 tetrahedra to 118° in fourfold helices. As a result, one orthorhombic unit-cell is converted into two cubic unit-cells with four fourfold helices. For the transformation of the orthorhombic BaSi_2 into the trigonal BaSi_2 phase [see Fig. 2(b)], $b_{\text{ort}} = 6.827 \text{ \AA} \rightarrow \sqrt{3}a_{\text{tri}} = 7.105 \text{ \AA}$, $a_{\text{ort}} = 9.224 \text{ \AA} \rightarrow 2a_{\text{tri}} = 8.204 \text{ \AA}$, and $c_{\text{ort}} = 11.716 \text{ \AA} \rightarrow 2c_{\text{tri}} = 10.890 \text{ \AA}$, with about -7% shortening in the c_{ort} , -11% shortening in a_{ort} and +4% elongation in the b_{ort} direction. Along this pathway, four Si_4 tetrahedra convert to four distorted chains (parallel to the $b[010]$ direction) with the bond breaking perpendicular to the $c[001]$ axis, and then four chains rebond to each other to form corrugated Si layers with distorted six-membered rings. Throughout this pathway, the intermediate structures are all in $P2_1/C$ (No. 14) monoclinic symmetry, and the $\angle\text{Si-Si-Si}$ bond angle changes from 60° to 111.6° . As a result, one orthorhombic unit-cell turns into four hexagonal cells. On the other hand, for the transformation of the orthorhombic BaSi_2 into the tetragonal BaSi_2 phase [see Fig. 2(c)], $b_{\text{ort}} = 6.827 \text{ \AA} \rightarrow \sqrt{2}a_{\text{tet}} = 6.698 \text{ \AA}$, $a_{\text{ort}} = 9.224 \text{ \AA} \rightarrow \sqrt{2}a_{\text{tet}} = 6.698 \text{ \AA}$, and $c_{\text{ort}} = 11.716 \text{ \AA} \rightarrow c_{\text{tet}} = 14.287 \text{ \AA}$, with about -27% shortening in the a_{ort} direction and about +22% elongation in the c_{ort} direction. Along the pathway, four Si_4 tetrahedra convert to four flat Si_4 groups with bond breaking around the $c[001]$ axis, and then the four flat Si_4 groups rebond to each other to form a 3D3C tetragonal net [see Fig. 2(c)]. Throughout this pathway, the intermediate structures are all in $P2_12_12_1$ (No. 19) orthorhombic symmetry, and the $\angle\text{Si-Si-Si}$ bond angle changes from 60° to

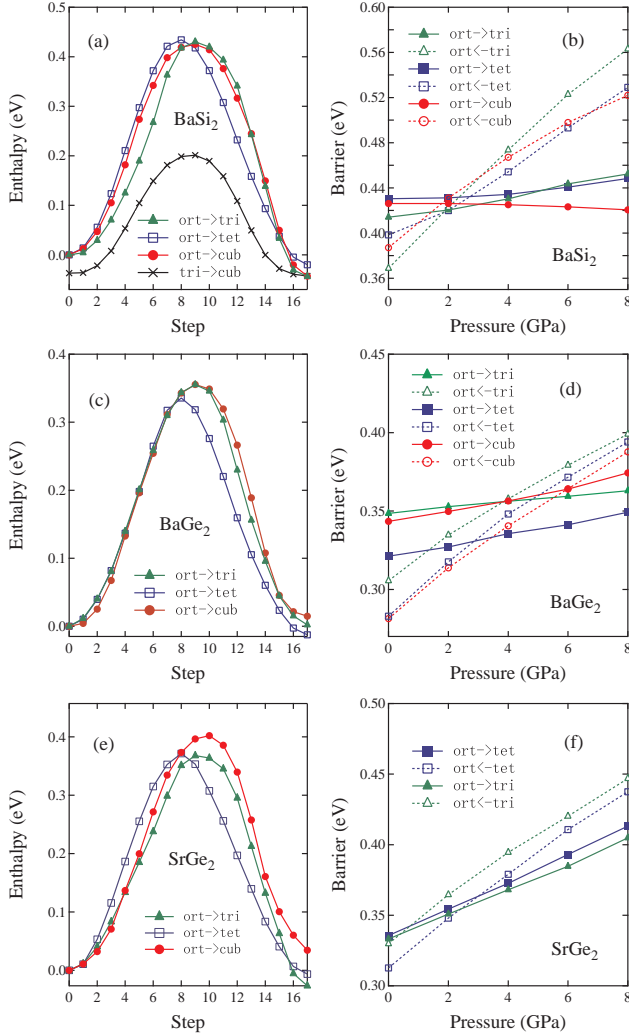


FIG. 3: (color online) (a,c,e) Enthalpy versus transformation pathways orthorhombic \rightarrow cubic, trigonal, or tetragonal at 4 GPa for BaSi₂, BaGe₂, and SrGe₂, respectively. (b,d,f) Enthalpy barriers versus pressure for orthorhombic \rightarrow cubic, tetragonal, and trigonal, respectively.

120°. As a result, one orthorhombic unit-cell is converted into two tetragonal unit-cells.

Figure 3(a) shows the enthalpy along the pathways starting from orthorhombic BaSi₂ toward the formation of the cubic, tetragonal, and trigonal BaSi₂ phase at 4 GPa. The enthalpy increases initially due to the bond twisting and breaking of the Si₄ tetrahedra in the orthorhombic phase, and then it decreases with the relinking of Si-Si bonds. The conversion barriers are estimated to be 0.424 eV for orthorhombic \rightarrow cubic, 0.430 eV for orthorhombic \rightarrow trigonal, and 0.434 eV for orthorhombic \rightarrow tetragonal. These results suggest the strong competing nature to form the cubic, trigonal and tetragonal structures. Similar competing nature is also found in the hypothetical conversion of orthorhombic SrSi₂ [see Fig. S1 in Supplemental Material³⁸]. Among these re-

actions, however, the pathway toward the trigonal phase has the lowest enthalpy up to step 8 as shown in Fig. 3(a). Thus the orthorhombic-to-trigonal transition is more favored than the orthorhombic-to-cubic transition dynamically. Experimentally, a two-stage reaction process of orthorhombic \rightarrow trigonal \rightarrow cubic is shown at 5.2 GPa up to 1133 K.²⁰ To clarify this point, we have also examined the second stage trigonal-to-cubic conversion process [see Fig. S2 in Supplemental Material³⁸] and the corresponding enthalpy is plotted in Fig. 3(a). The conversion barrier is estimated to 0.24 eV at 4 GPa, which is smaller than 0.43 eV for the first stage orthorhombic-to-trigonal conversion. Consequently, cubic BaSi₂ can be easily synthesized by a two-stage reaction process.

We plot in Fig. 3(b) the enthalpy barriers versus pressure. With increasing pressure from 0 to 8 GPa, the barriers undergo only small changes from 0.429 to 0.421 eV for orthorhombic \rightarrow cubic, 0.411 to 0.452 eV for orthorhombic \rightarrow trigonal, and 0.430 to 0.448 eV for orthorhombic \rightarrow tetragonal, respectively. These results show that pressure has little effect on the conversion barrier, which means these phase conversions require high temperature to overcome the large energy barriers. This is similar to the situation of phase conversion of graphite to diamond.³⁹

Experimentally, it has been reported that both the cubic and trigonal phases of BaSi₂ can be quenched to the ambient conditions.²⁰ To clarify this point, the counterreaction barriers are also plotted in Fig. 3(b). With decreasing pressure from 8 to 0 GPa, the barriers decrease from 0.522 to 0.387 eV for cubic \rightarrow orthorhombic, 0.563 to 0.369 eV for trigonal \rightarrow orthorhombic, and 0.529 to 0.398 eV for tetragonal \rightarrow orthorhombic. These results suggest that pressure has a considerable effect on lowering the kinetic barrier upon decompression. However, the counterreaction barriers remain at high values (\sim 0.39 eV at 0 GPa) that are comparable to the barriers encountered during the compression process (\sim 0.43 eV). As a result, the cubic and trigonal phases can be stabilized at ambient conditions due to a combination of the large counterreaction barriers (\sim 0.39 eV) and small energy differences (\sim 0.05 eV per atom) relative to the BaSi₂-type orthorhombic structure [see Fig. 1(b)].

For BaGe₂, as shown in Fig. 3(c,d), the orthorhombic \rightarrow tetragonal conversion is clearly favorable by both kinetics and energetics. On the other hand, for SrGe₂ compound, the cubic structure is unfavorable in enthalpy as shown in Fig. 1(f) in a wide pressure range of 0~10 GPa. There is a strong competing conversion pathway under pressure to form the trigonal or tetragonal structure [see Fig. 3(e,f)]; however, the orthorhombic \rightarrow trigonal conversion is more favorable dynamically, similar to the case for BaSi₂ shown above.

In summary, our *ab initio* calculations have revealed the phase stability and transformation mechanisms for several BaSi₂-type semiconductors. The results show that the tetrahedra in orthorhombic BaSi₂ and SrGe₂ tend to convert to corrugated layers dynamically under

high pressure with bond breaking along the $b[010]$ axis, and the Si-corrugated layers in trigonal BaSi_2 can further convert to cubic Si-net under low pressure driven by energetics. Moreover, Ge-tetrahedra in BaGe_2 tend to form a tetragonal-net structure with bond breaking around the $c[001]$ axis. The large counterreaction barriers (~ 0.39 eV) are comparable to that for the compression process reaction barriers (~ 0.43 eV) for BaSi_2 , which explains the high stability of the metastable phases at the ambient conditions. Our results provide a comprehensive understanding of the experimental findings by unveiling the underlying energetic and kinetic mechanisms, which

may shed light on other disilicides and digermanides.

This study was supported by the National Natural Science Foundation of China (Grant No. 11274356) and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB07000000). C.F.C. acknowledges support by DOE under Cooperative Agreement DE-NA0001982. Y.K. acknowledges support by the CREST project headed by Professor M. Kotani and the Russian Megagrant Project No. 14.B25.31.0030. We are thankful to the crew of the Center for Computational Materials Science at IMR, Tohoku University for their support at the SR16000 supercomputing facilities.

* e-mail address: wjt@aphy.iphy.ac.cn

- ¹ T. Nakamura, T. Suemasu, K. Takakura, F. Hasegawa, A. Wakahara, and M. Imai, *Appl. Phys. Lett.* **81**, 1032 (2002).
- ² S. Kishino, T. Imai, T. Iida, Y. Nakaishi, M. Shinada, Y. Takanashi, and N. Hamada, *J. Alloys Compd.* **428**, 22 (2007).
- ³ Y. Matsumoto, D. Tsukada, R. Sasaki, M. Takeishi, and T. Suemasu, *Appl. Phys. Express* **2**, 021101 (2009).
- ⁴ M. Imai, *Phys. Status Solidi C* **10**, 1728 (2013).
- ⁵ T. Suemasu, K. Morita, and M. Kobayashi, *J. Cryst. Growth* **301-302**, 680 (2007).
- ⁶ M. Kobayashi, Y. Matsumoto, Y. Ichikawa, D. Tsukada, and T. Suemasu, *Appl. Phys. Express* **1**, 051403 (2008).
- ⁷ M. A. Khan, T. Saito, K. Nakamura, M. Baba, W. Du, K. Toh, K. Toko, and T. Suemasu, *Thin Solid Films* **522**, 95 (2012).
- ⁸ W. J. Du, M. Suzuno, M. Ajmal Khan, K. Toh, M. Baba, K. Nakamura, K. Toko, N. Usami, and T. Suemasu, *Appl. Phys. Lett.* **100**, 152114 (2012).
- ⁹ M. Ajmal Khan, K. O. Hara, W. Du, M. Baba, K. Nakamura, M. Suzuno, K. Toko, N. Usami, and T. Suemasu, *Appl. Phys. Lett.* **102**, 112107 (2013).
- ¹⁰ S. Koike, K. Toh, M. Baba, K. Toko, K. O. Hara, N. Usami, N. Saito, N. Yoshizawa, and T. Suemasu, *J. Crystal Growth* **378**, 198 (2013).
- ¹¹ J. T. Wang, C. F. Chen, H. Mizuseki, and Y. Kawazoe, *Phys. Rev. Lett.* **110**, 165503 (2013).
- ¹² H. K. Janzon, H. Schäfer, and A. Weiss, *Z. Anorg. Allg. Chem.* **372**, 87 (1970).
- ¹³ H. Schäfer, K. H. Janzon, and A. Weiss, *Angew. Chem. Int. Ed. Engl.* **2**, 393 (1963).
- ¹⁴ J. Evers, G. Oehlinger, and A. Weiss, *Angew. Chem. Int. Ed. Engl.* **17**, 538 (1978).
- ¹⁵ J. Evers, G. Oehlinger, and A. Weiss, *Angew. Chem. Int. Ed. Engl.* **16**, 659 (1977).
- ¹⁶ M. Pani and A. Palenzona, *J. Alloys Compd.* **462**, L9 (2008).
- ¹⁷ A. Palenzona and M. Pani, *J. Alloys Compd.* **402**, 136 (2005).
- ¹⁸ J. Evers, G. Oehlinger, and A. Weiss, *Z. Naturforsch. B* **32**, 1352 (1977).
- ¹⁹ J. Evers, *J. Solid State Chem.* **32**, 77 (1980).
- ²⁰ M. Imai, T. Hirano, T. Kikegawa, and O. Shimomura, *Phys. Rev. B* **55**, 132 (1997); *ibid.* **58**, 11 922 (1999).
- ²¹ J. Evers, *J. Solid State Chem.* **24**, 199 (1978); *J. Phys. Chem. Solid* **40**, 951 (1979).
- ²² M. Imai and T. Kikegawa, *Chem. Mater.* **15**, 2543 (2003).
- ²³ M. Imai and T. Hirano, *J. Alloys Compd.* **224**, 111 (1995).
- ²⁴ J. T. Vaughey, G. J. Miller, S. Gravelle, E. A. Leon-Escamilla, and J. D. Corbett, *J. Solid State Chem.* **133**, 501 (1997).
- ²⁵ J. Evers, G. Oehlinger, and A. Weiss, *Z. Naturforsch. B* **35**, 397 (1980).
- ²⁶ A. Palenzona and M. Pani, *J. Alloys Compd.* **402**, 136 (2005).
- ²⁷ K. Hashimoto, K. Kurosaki, Y. Imamura, H. Muta, and S. Yamanaka, *J. Appl. Phys.* **102**, 063703 (2007).
- ²⁸ D. B. Migas, V. L. Shaposhnikov, and V. E. Borisenko, *Phys. Stat. Sol.* **244**, 2611 (2007).
- ²⁹ M. Kumar, N. Umezawa, and M. Imai, *J. Appl. Phys.* **115**, 203718 (2014).
- ³⁰ G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); G. Kresse and J. Hafner, *ibid.* **47**, 558 (1993).
- ³¹ Y. K. Zhang and W. T. Yang, *Phys. Rev. Lett.* **80**, 890 (1998).
- ³² P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994); G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ³³ J. T. Wang, C. F. Chen, and Y. Kawazoe, *Phys. Rev. Lett.* **106**, 075501 (2011).
- ³⁴ A. Simon, H. Borrmann, and H. Craubner, *Phosphorus and Sulfur and the Related Elements*, **30**, 507 (1987); H. Okudera, R. E. Dinnebier, and A. Simon, *Z. Kristallogr.* **220**, 259 (2005).
- ³⁵ J. C. Jamieson, *Science* **139**, 1291 (1963).
- ³⁶ M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, *Nature Mater.* **3**, 558 (2004).
- ³⁷ J. T. Wang, C. F. Chen, and Y. Kawazoe, *Sci. Rep.* **3**, 03077 (2013).
- ³⁸ See Supplemental Material for the phase stability of hypothetical orthorhombic SrSi_2 (Fig. S1) and the conversion pathway between trigonal and cubic BaSi_2 (Fig. S2).
- ³⁹ J. T. Wang, C. F. Chen, and Y. Kawazoe, *Phys. Rev. B* **84**, 012102 (2011).