

## **Creating two-dimensional layered Zintl phase by dimensional manipulation of the crystal structure**

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Creation of 2D layered ZnSb. (A) Schematic illustration of the dimensional manipulation of a crystal structure from 3D-ZnSb to 2D-ZnSb via Li alloying



and etching processes. The Li alloying into 3D-ZnSb was conducted by thermal and electrochemical reactions (ERs). The selective etching of Li ions was conducted by reacting with polar solvent solution reaction (SR). A reversible process of alloying and etching occurs in the mean of electrochemical reaction (ER). (B) XRD patterns of 3D-ZnSb and 2D-LiZnSb. The 2D-LiZnSb polycrystal and single crystal were synthesized by using the synthesized 3D-ZnSb as a precursor. All patterns are well matched with the simulated patterns of corresponding compounds. a.u., arbitrary units. (C) XRD patterns of 2D-ZnSb crystals obtained by solution reaction and electrochemical reaction processes. For the solution reaction process, water-based solutions [DI water and dimethyl sulfoxide (DMSO) with 1 volume % of DI water, and hexamethyl phosphoric triamide (HMPA) with 1 volume % of DI water] were used. For the electrochemical reaction process, 1 M LiPF6 dissolved in 1:1 mixture of ethylene carbonate and diethyl carbonate solution was used as an electrolyte. The interlayer distances were calculated from the angle of highest intensity. (D to I) Scanning electron microscopy (D to F) and optical images (G to I) of 2D-LiZnSb and 2D-ZnSb created by the solution reaction and electrochemical reaction processes. The flakes of 2D-ZnSb were exfoliated by mechanical cleaving using 3M tape. (J to L) X-ray photoelectron spectroscopy (XPS) spectra of Li 1s (J), Zn 2p (K), and Sb 3d (L) for 3D-ZnSb, 2D-LiZnSb, and 2D-ZnSb, respectively. The Li 1s peak (54.6 eV) of 2D-LiZnSb indicates the Li1+ state. While the binding energies of the Zn 2p3/2 (1019.8 eV) and Sb 3d5/2 (525.8 eV) are significantly lower than the Zn 2p3/2 (1021.5 eV) and Sb 3d5/2 (527.6 eV) in 3D-ZnSb, the binding energies of Zn 2p3/2 (1022.1 eV) and Sb 3d5/2 (528.2 eV) of 2D-ZnSb are slightly higher than those of 3D-ZnSb. Credit: Science Advances, doi: 10.1126/sciadv.aax0390

The discovery of new families of two-dimensional (2-D) layered materials beyond graphene has always attracted great attention, but it remains challenging to artificially recreate the honeycomb atomic lattice structure with multi-components such as hexagonal boron nitride in the lab. In a new study now published on *Science Advances*, Junseong Song and colleagues at the departments of Energy Science, Nanostructure



Physics, Environmental Science and Materials Science in the Republic of Korea developed an unprecedented structure of the Zintl phase.

They constructed the material by staking  $sp^2$ -hybridized honeycomb ZnSb layers and via the dimensional manipulation of a crystal structure from the  $sp^3$ -hybridized 3-D-ZnSb state. The <u>materials scientists</u> combined <u>structural analysis</u> with theoretical calculations to form a stable and robust layered structure of 2-D-ZnSb. This phenomenon of bidimensional polymorphism was not previously observed at ambient pressure in Zintl families. Therefore, the new work provides a rational design strategy to search and create new 2-D layered materials in various compounds. The new results will allow the unlimited expansion of 2-D libraries and their corresponding physical properties.

The advent of Dirac physics of graphene triggered an explosive interest in research on two-dimensional (2-D) materials with varied applications in <u>electronics</u>, <u>magnetics</u>, <u>energy</u> and chemistry to <u>quantum physics</u>. At present, 2-D research is primarily focused on a <u>few 2-D materials</u> containing a single or <u>several atomic layers</u> exfoliated from their mother compounds, in contrast to <u>2-D atomic crystals such as silicone</u>. This can restrict the method of 2-D materials development to two approaches of <u>exfoliation</u> and <u>chemical vapor deposition</u>. It is therefore highly desirable to expand on 2-D materials research to artificially create a new 2-D material with a new synthetic approach and form a variety of material groups.

In new materials discovery, transformation of a crystal structure is a widely recognized key factor. Where the temperature-pressure and electrostatic-doping induced structural phase transitions are core to <u>explore a new crystal structure</u> or to <u>switch 2-D materials</u> properties. For instance, most transition <u>metal dichalcogenides</u> exhibit polymorphic phase transition to access inherently diverse properties including superconducting and topological states. The transition has led to



promising applications including <u>electronic homojunction</u>, photonic memory devices and <u>catalytic energy materials</u>.



Crystal structure of 2D layered ZnSb. (A and B) Atomic resolution STEM-HAADF (high-angle annular dark-field) images of 2D-LiZnSb along the [110] (A) and [001] (B) zone axes, respectively. (C) Atomic resolution STEM-EDS elemental mapping for 2D-LiZnSb along the [110] (top) and [001] (bottom) zone axes. (D and E) Atomic resolution STEM-HAADF images of 2D-ZnSb along the [110] (D) and [211] (E) zone axes. The determined crystal structure of 2D-ZnSb. The atomic distances of 2D-ZnSb are compared with those of 3D-ZnSb and 2D-LiZnSb. From the observation at [211] zone axis of 2D-ZnSb, the honeycomb lattice is slightly tilted. For the detection of lithium, the STEM–EELS (electron energy-loss spectroscopy) technique was used, showing the clear existence and absence of lithium in 2D-LiZnSb and 2D-ZnSb. (G) Cohesive energy ( $\Delta$ Ecoh) calculation of predictable 2D-ZnSb structures. Structure I that is determined from the STEM observations exhibits the lowest energy compared with other candidates, showing excellent agreement between experiments and calculations. Credit: Science Advances, doi: 10.1126/sciadv.aax0390

These polymorphic transitions only occurred between different layered structures in the same two dimensions and remain to be realized between



different dimensions of a crystal structure at ambient pressure. To reach ultimate crystal engineering and alter the structural dimension of multicomponent compounds is a promising next frontier in <u>materials</u> <u>science</u> beyond the <u>allotropes of carbon</u>.

In the present work, Song et al. established <u>bidimensional polymorphism</u> via the discovery of 2-D layered structures in Zintl phases <u>containing a</u> large number of chemical compositions. Due to the sp<sup>2</sup> hybrid orbital bonding of honeycomb-structured 2-D atomic crystals such as graphene and hexagonal boron nitride, the scientists expected the 3-D structured Zintl phases (with sp<sup>3</sup> hybrid orbital bonding) to transform to sp<sup>2</sup> honeycomb structured 2-D layered materials, as well, via electron transfer. As a proof-of-concept, Song et al. selected a 3-D orthorhombic ZnSb (3-D-ZnSb) Zintl phase and created the unprecedented, 2-D layered structure of ZnSb (2-D-ZnSb).

In the new method, Song et al. first synthesized layered AZnSb (2-D-AZnSb) ternary compounds; where A referred to an alkali metal such as Na, Li and K. The materials contained a layered structure of ZnSb by transforming 3-D-ZnSb via A alloying, although the phases could be independently synthesized. Song et al. performed selective etching of A ions to create the 2-D-ZnSb in two different processes, including (1) chemical reaction in deionized water-incorporated solutions, and (2) electrochemical ion etching reaction in alkali-based electrolyte.





Electronic properties of 2D layered ZnSb. (A to C) Temperature dependence of electrical resistivity (A), Hall mobility (B), and carrier concentration (C) for 3D-ZnSb, 2D-LiZnSb, and 2D-ZnSb. The bidimensional polymorphs of 3D-ZnSb and 2D-ZnSb show the metal-insulator transition. (D to F) Electronic band structures of 3D-ZnSb (D), 2D-LiZnSb (E), and 2D-ZnSb (F). The band structures of 3D-ZnSb (D) and 2D-LiZnSb (E) indicate that both are semiconductors with a well-defined indirect bandgap of 0.05 and 0.29 eV, respectively. A low electrical resistivity and a high carrier concentration of 2D-LiZnSb indicate a heavily doped semiconducting behavior. Credit: Science Advances, doi: 10.1126/sciadv.aax0390

For example, they synthesized the polycrystalline and single crystalline 2-D-LiZnSb intermediate substrate by first alloying Li into polycrystalline 3-D-ZnSb, followed by Li ion etching to form a 2-D-ZnSb crystal. The scientists easily cleaned the Li-etched 2-D-ZnSb crystals using adhesive tape exfoliation as mechanical cleaving to exhibit a typical flat surface as reported for 2-D materials.



To understand the effect of the manufacturing process, they examined the role of Li alloying and etching on structural transformations using Xray photoelectron spectroscopy (XPS) measurements to reveal the difference between the 2-D and 3-D crystals. To further validate their findings, Song et al. used X-ray diffraction spectroscopy (XRD) patterns, transmission electron microscopy (TEM) observations and scanning tunneling electron microscopy (STEM) combined with energydispersive spectroscopy (EDS) elemental mapping to confirm the atomic structure of 2-D-ZnSb.

Based on the results, the scientists interpreted the stretchable interlayer distances between both Zn-Zn and Sb-Sb atoms as weak interlayer bonds and verified that the 2-D-ZnSb could be exfoliated as a layered material. The newly evolved layered structure of 2-D-ZnSb in the present work, completed the first discovery of bidimensional polymorphism in Zintl phases at ambient pressure.



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C Material	ΔE <sub>coh</sub> (eV/ZnSb)	D Material	ΔE <sub>Li alloying</sub> (eV/Li)
3D-ZnSb	-5.23	3D-ZnSb	-2.19
2D-ZnSb	-4.65	2D-ZnSb	-2.77
E		F	
Material	E <sub>inter</sub> (meV/atom)	Material	E <sub>exf</sub> (meV/atom)
3D-ZnSb (1)	872	2D-ZnSb	183
3D-ZnSb (2)	697	Graphene	66
2D-ZnSb (3)	328	h-BN	59

2D layered behavior of 2D-ZnSb. (A) [100] view of 3D-ZnSb. (B) [100] view of 2D-ZnSb. (C) Cohesive energy (ΔEcoh) calculation of 3D-ZnSb, 2D-ZnSb. From the cohesive energy calculation, 3D-ZnSb is more stable but the cohesive energy of 2D-ZnSb is reasonably large enough, indicating that the 2D-ZnSb exists as a stable material. (D) Li alloying energy (ΔELi alloying) calculation of 3D-ZnSb and 2D-ZnSb indicating reaction Li alloying process in 2D-ZnSb and 3D-ZnSb are energetic favor. Compare two ΔELi alloying, Li ions alloying into 2D-ZnSb is favorable than 3D-ZnSb. (E) Interlayer binding energy (Einter) of 3D-ZnSb and 2D-ZnSb. Large difference of Einter between 3D-ZnSb and 2DZnSb indicates the characteristics of 2D layered materials for 2D-ZnSb. (F) Exfoliation energy (Eexf) calculation of 2D-ZnSb and other 2D materials. Eexf of 2D-ZnSb is rather higher than those of conventional van der Waals (vdW) bonded 2D materials such as graphene and h-BN, indicating that the 2D-ZnSb is



not a vdW-type layered material. However, the Eexf of 2D-ZnSb is lower than that of antimonene, which can be exfoliated or grown into monolayer indicating that free-standing monolayer or few layers of 2D-ZnSb can be possible as conventional 2D vdW layered materials. Credit: Science Advances, doi: 10.1126/sciadv.aax0390.

Accordingly, Song et al. manipulated the sp<sup>3</sup>-hybridized bonding state in 3-D-ZnSb into the sp<sup>2</sup> state in 2-D-ZnSb honeycomb lattice. Previous studies on polymorphic transitions between 3-D and 2-D structures in Zintl phases were only <u>observed under high pressure</u>. The present results on bidimensional polymorphism between 3-D-ZnSb and 2-D-ZnSb emphasized the potential and broad availability of such an electron transfer to transform the crystal structure.

Song et al. next investigated electrical transport properties of bidimensional ZnSb polymorphs and 2-D-LiZnSb crystals alongside first principles calculations of their electronic energy band <u>structure</u>. In contrast to the semiconducting nature of 3-D-ZnSb, both 2-D-LiZnSb and 2-D-ZnSb showed metallic conduction behavior. When they decreased the temperature, the electrical mobilities of both 2-D-LiZnSb and 2-D-ZnSb increased to a value higher than that of 3-D-ZnSb. The scientists credited the observed enlarged bandwidths for 2-D-ZnSb to the enhanced sp<sup>2</sup> nature of honeycomb-structured layers with weakened interlayer interactions that formed the semi-metal. They used theoretical calculations to confirm that 2-D-ZnSb could be mechanically exfoliated into the bilayer to exist in an energetically stable form as a 2-D material, while the monolayer of 2-D-ZnSb was energetically unfavorable.





Dimensional manipulation of a crystal structure for the bidimensional polymorphic ZnSb. (A and B) In situ synchrotron powder XRD patterns using 3D-ZnSb (A) and 2D-ZnSb (B) via the electrochemical reaction. The alloying and etching processes were controlled by reducing and increasing voltage potential, respectively. The inset (bottom left) of (A) shows the peak shift of (002) plane for 3D-ZnSb. The inset (top left) of (A) shows the disappearance of diffraction peaks' corresponding (002) and (101) planes at 11.1° and 11.7° of 2D-LiZnSb with Li etching, indicating the transformation to 2D-ZnSb. The inset (middle) shows the appearance and disappearance of Li1+xZnSb by-product with discharging and charging reactions, respectively. The insets of (B) show the same changes observed in the insets (top left and middle) of (A). No diffraction peaks of 3D-ZnSb were observed during the reversible structural transformation by Li alloying and etching processes. (C) Schematic illustration of the dimensional manipulation of a crystal structure, along with the transition of hybridized bonding characters from sp3 of 3D-ZnSb to sp2 of 2D-LiZnSb and 2D-ZnSb. The displacement of the blue arrow in Sb fifth to Zn fourth orbital depicts the covalent bonding character between Zn and Sb in the honeycomb



lattice. The electron transfer from Li to sp3-hybridized state of 3D-ZnSb enables the transition to sp2-hybridized state of honeycomb ZnSb lattice in 2D-LiZnSb and 2D-ZnSb. Credit: Science Advances, doi: 10.1126/sciadv.aax0390.

To demonstrate structural transformation of bidimensional ZnSb polymorphs during 2-D-LiZnSb formation, the scientists conducted synchrotron XRD - during the electrochemical reaction. They observed peaks corresponding to Li alloying of 3-D-ZnSb at pure 2-D-LiZnSb formation, followed by the final product of 2-D-ZnSb. During the electrochemical reaction, the Li atoms selectively penetrated into 3-D-ZnSb to break the Zn-Sb and Sb-Sb bonds. At the level of electron transfer, the hybridized bonding state changed from sp<sup>3</sup> in 3-D-ZnSb to sp<sup>2</sup> in 2-D-LiZnSb to form the puckered honeycomb lattice.

The outcome of Li alloying based 2-D-LiZnSb transformation yielded the 2-D-ZnSb product, which did not return to its 3-D form. Song et al. showed that once formed, the layered 2-D-ZnSb was a stable material with a honeycomb architecture, validating the stable bidimensional polymorphic transition. The scientists anticipate applications of the new material in sustainable alkali ion batteries.

In this way, Junseong Song and co-workers performed rigorous experimental and theoretical studies to demonstrate the creation of 2-D layered Zintl phases by manipulating the structural dimensionality. The new method is a first to establish the bidimensional polymorphic family in Zintl phases at ambient pressure, to allow new phase transformations as a general route of synthesis. This work provides a rational design strategy to explore new 2-D layered materials and unlock further properties of interest within materials, such as 2-D magnetism, ferroelectricity, thermoelectricity and topological states for further applications.



**More information:** Paul F. McMillan. New materials from highpressure experiments, *Nature Materials* (2003). <u>DOI: 10.1038/nmat716</u>

Manish Chhowalla et al. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets, *Nature Chemistry* (2013). DOI: 10.1038/nchem.1589.

Kenneth S. Burch et al. Magnetism in two-dimensional van der Waals materials, *Nature* (2018). DOI: 10.1038/s41586-018-0631-z

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