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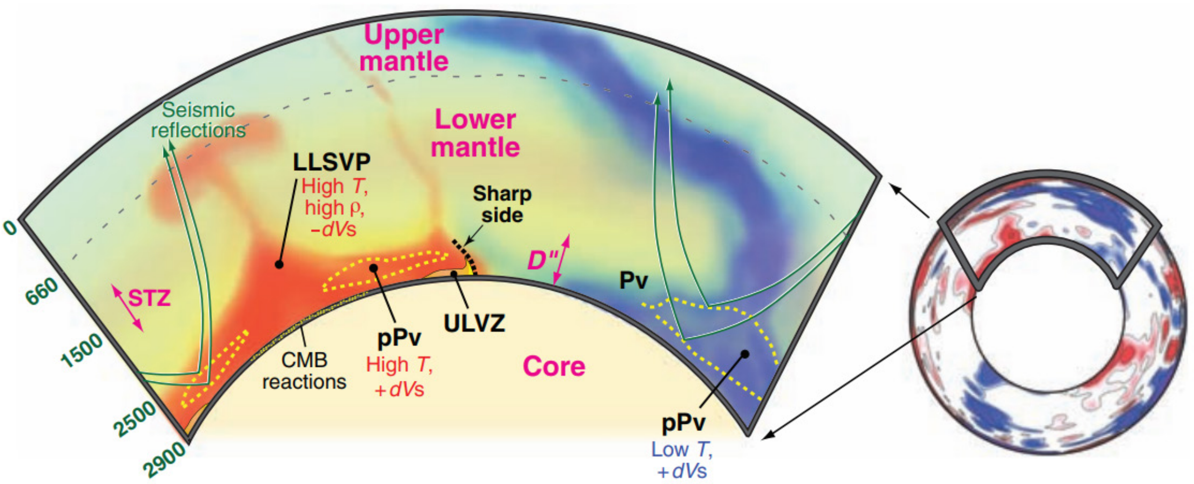
科研亮点
Research Highlight



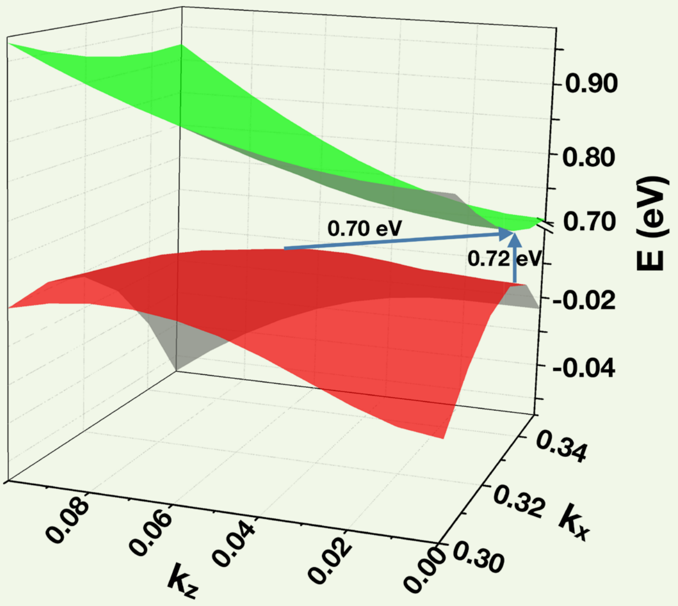
Exotic ST12-Gemanium

锗作为典型的 IVA 族元素具有丰富的结构多样性。常温常压条件下，锗以金刚石结构存在，是当今最常见的一种半导体材料。当室温压缩金刚石结构的锗时，它将在 10GPa 的压力之上转变成金属性的四方 β- 锡结构的高密度锗。然而这种相变呈现不可逆性，在缓慢的降压过程中，β- 锡结构的锗将转变成动力学上更稳定的另一种简单四方结构的亚稳锗（ST12-Ge）。对于 ST12 锗，过去人们较多的关注于其相变机理的研究，对其能带结构及光学的研究虽然也有不少的理论和实验报道，但是由于前人在样品制备方面的局限性以及理论预测的差异，因此对其能带结构和光学特性一直以来都存在着很大的争议。本工作中，当前的研究团队通过大腔体压机合成了毫米级别、纯相的锗多晶块材，并通过 X 射线衍射、透射电镜、拉曼光谱等确定了其晶体结构。光学和电输运测试结果表明 ST12 锗是一种半导体材料，具有间接带隙 0.59eV 和直接带隙 0.74eV，这与他们的第一性原理计算结果相吻合。与常见的金刚石结构的锗相比，ST12 锗具有更小的带隙，这意味着 ST12 锗可以更好地应用于红外光学器件中。本研究结束了 50 多年以来对 ST12 锗电子结构和光学特性的长期争论。

JANUARY. 03, 2017-Scientists at Geophysical Lab, Yanshan University and HPSTAR combined experimental and theoretical methods to probe the exotic properties of one special form-ST12-Ge of the element germanium. The results solve the long-standing debate on the optical and electronic properties of semiconducting Ge and suggest ST12-Ge to be a better material for infrared detection and imaging instead of single-junction solar absorbing.

Germanium as a frequently studied element in IVa element group, has the applications for next-generation computer architecture as well as implications for fundamental condensed matter physics. Germanium is used in fiber-optic systems, specialized camera and microscope lenses, circuitry, and solar cells. It is also an attractive anode material for lithium-ion batteries because it has a large theoretical charge-discharge capacity compared to graphite as well as high lithium ion diffusivity at room temperature compared to silicon. ST12 phase for Germanium comes from its simple tetragonal structure containing 12 atoms per unit cell, resulting from slow decompression process. ST12-Ge was first observed about six decades ago, attracting both theoretical and experimental studies as a great solar absorber candidate. However, great controversies exist about its electronic structure and thermal stability due to lack of bulk pure sample.

New research published in ***Nature Communications*** (doi:10.1038/ncomms13909) from an international team Geophysical Laboratory, Yanshan Universtiy and HPSTAR, of scientists describe their work probing intrinsic semiconductor properties of bulk (~2 mm in diameter) ST12-Ge, a



Caption:A schematic diagram of the valence and conduction bands. It is worth noting that the fundamental indirect gap is not along a high-symmetry direction.

metastable phase of element gemanium.

“Bulk pure sample will allow for more accurate and concise electrical and optical measurements,” said Dr. Zhao, lead author of the study. “However, the intrinsic properties have never been realized in ST12-Ge because the samples obtained in previous studies were either impure or too small to probe their practical performance.”

To synthesize bulk ST12-Ge, the researchers utilized a large volume high-pressure facility called multi-anvil press. To get ST12-Ge, they slowly decompressed the sample from 14 gigapascals at room temperature according to kinetic origins. ~15 mg (~2mm in diameter and length) recovered pellets were then polished for the following serials of measurements.

Bulk ST12-Ge shows both very small so-called "indirect electronic band gap", meaning that light is easily absorbed or emitted. and "direct band gap" meaning that it is much more difficult to absorb or emit light. “The smaller band gaps suggest ST12-Ge could be a good candidate for infrared detection, imaging and high-frequency and low-voltage electronic applications.” said Dr. Zhao. “Our work solves the long-standing debate regarding the band structure of ST12-Ge,”

“Future research is required to understand its structure conversion pathways, but the result of this study, experimental and theoretical, pinpoint a clear picture of the intrinsic properties of ST12-Ge, added Dr. Kim, a co-author of the study who carry out the theoretical calculation of the work and also a staff scientist of HPSTAR.

Ref: Dr. Duckyoung Kim
Nature Communications
volume8, Article number: 13909 (2017)

New Stories for Viologen Materials

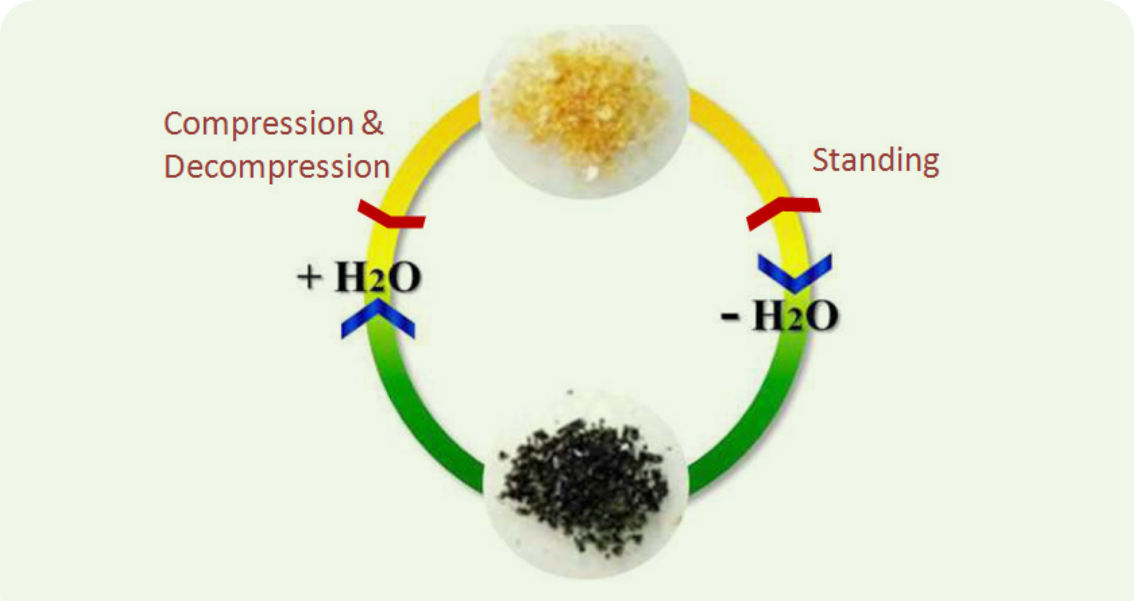
变色现象是指物质在外界环境的影响下，而产生的一种对光的反应的改变。这种现象普遍存在于自然界中，比如变色龙，它的体色会随着周围环境的变化而改变。人们感兴趣的是一类具有可逆变色现象的材料，即可利用一定的外界条件将它们的颜色进行改变并且在另一种条件下将其还原。目前发现的变色现象主要有4 类：电致变色、光致变色、热致变色和压致变色。紫罗精是一种最具有代表性的有机电致变色材料，具有良好的变色性能，选择合适的取代基，通过改变分子轨道能级和分子间电荷的迁移能可以方便地调节其电色效应。人们发现紫精同时具有电致变色及光致变色的性能。华东师范大学及北京高压科学研究中心带领的研究团队发现紫精化合物也表现出压致变色及吸水脱水变色的行为。压力及水虽然一个是通过物理过程，一个是化学的方法使紫罗精变色，但具有一个共同的机理—改变分子间距，转移电荷，产生阳离子自由基。本工作不仅发现了紫罗精化合物新的变色现象，也是首次在有机物中同时发现由于电荷转移形成的自由基而导致压致变色及水致变色的现象。

JANUARY. 23, 2017 Viologen materials have been well known for electrochromism and photochromism from electro and photo stimulus. New work from a team led by Prof. Enqing Gao of East China Normal University and Dr. Lin Wang from hpstar found piezochromis in viologen compounds. This is not only a new chromic phenomena for viologen compounds but also represents the first example of organic mechanochromism and hydrochromism associated with radical formation via electron transfer, proposed in the paper published in the journal ***Chemical Science*** (DOI: 10.1039/C6SC04579K).

Colour change or chromic phenomenon plays an important role in our daily lives. Chamaeleo changes colour in different environments via the active tuning of a lattice of nanocrystals contained in some cells. There are many ways in which colour can be caused to arise both by chemical and physical forces, all of which are used or have the potential to be used in technological applications. These colour change phenomena are classified and named after the stimulus that causes the change. Such as photochromism, electrochromism, mechanochromism and solvatochromism.

Piezochromism refers to the reversible color change of a solid in response to external pressure. We know that pressure will lead to structural changes, it may also lead to color change through modulation of electronic energy gaps or irreversible inter-/intramolecular chemical transformations such as polymerization and isomerization, concomitant with irreversible (undesirable) color change. Stress/pressure could also lead to free colored radicals - often referred to free radicals which are atomic or molecular species with unpaired electrons on an otherwise open shell configuration- to develop colour change.

Viologen derivatives have long been known for electrochromism and photochromism through reversible redox acitivty- electron/charge transfer, to form colored cation radicals. In this work, researchers demonstrated that a viologen-carboxylate zwitterionic molecule - with both positive and negative charges (equal positive and



Caption: Pressure/water induced colour change in viologen.

negative charge) in the crystalline state exhibits piezochromic phenomenon.

The yellow viologen comound will turn to red under several gigapascals, to green after pressure release, and finally return to yellow at ambient conditions.

"External pressure will force the molecules in the lattice to move closer, shortening donor-acceptor distances - be favorable to electron transfer from the electron-rich carboxylate group to the electron-deficient viologen unit," explained Prof. Gao.

"Pressure could be a more powerful than light for induction of intermolecular electron transfer (and chromic phenomena) in viologen crystals. Light can be absorbed by individual molecules and have no direct effect on intermolecular distances, so it would not induce electron transfer if the donor and the acceptor were not placed at a favorable distance. While pressure works directly on intermolecular distances, so it can proactively reduce the distance between the donor and the acceptor in favor of electron transfer," Dr. Lin Wang added.

In addition, they found that hydration-dehydration will also change the color of the viologen compound just like what pressure does.

"The compound behaves like a "chromic sponge": the yellow sample in moist atmosphere will turn to green upon heating to be dried, then return to yellow when put back in the air." Said Prof. Gao.

"We could assume that the loss of lattice water will also lead to closer crystal packing of the zwitterionic molecules so that the distance between electron donors and acceptors is reduced in favor of electron transfer.

"So despite the remarkably different nature, the physical stimuli (compression/decompression) and the chemical stimuli (dehydration/rehydration) have one thing in common: the ability to modulate intermolecular donor-acceptor contacts in favor of electron transfer," Prof. Gao explained.

Ref：Dr. Lin Wang

Chemical Science

2017, 8, Pages: 2758-2768

Exotic two dimensional silica

SiO_2 是我们日常生活中最常见的材料，也是人类从石器时代开始使用的使用时间最长的材料。其中 SiO_2 的一个最主要应用是作为电容器中的介电材料。而经典电子学告诉我们，电介质越薄其电容就越大。因此对只有几个原子层厚度的二维 SiO_2 材料的研究就具有重要意义。董校领导的团队通过遗传算法预测了三种新型准二维的 SiO_2 结构。计算发现他们都具有负泊松比的特殊性质。理论上分析负泊松比来源是三维的结构化学规律在低维条件下被破坏。即证明这三种新型的二维 SiO_2 材料的负泊松比来源是低维效应。除此之外，我们还发现二维的二氧化硅具有所有已发现二维材料中最大的能隙，同时还要薄于其他准二维材料。因为材料的透光性与材料的厚度和能隙具有很大关系。二维二氧化硅可以认为是实际上已知的最透明材料。二维二氧化硅将在纳米力学和纳米电子学方面具有重要的潜在应用价值。

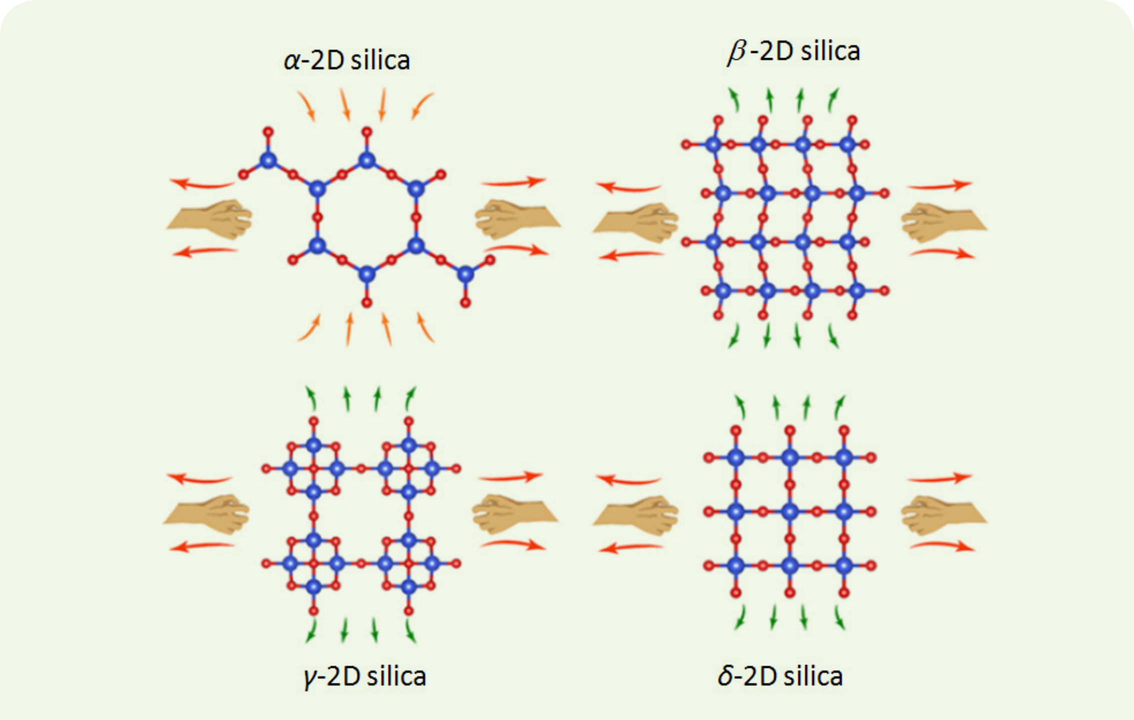
JANUARY 31, 2017 - Using computer modeling, scientists from HPSTAR and Tongji University have found out three new forms of 2D-silica with exotic mechanical and electrical properties-large negative Poisson's ratios and widest electric bandgap among all reported 2D materials . They detailed their work in the latest issue of the journal ***Nano Letters*** (DOI: 10.1021/acs.nanolett.6b03921).

Silicon dioxide is the fundamental component of glass, sand and most minerals, which is also known as one of the building units of earth crust and mantle. There are a large number of polymorphs of silica in crystalline and amorphous forms, such as quartz, and glassy SiO_2. It is well known that bulk silicon dioxide is a good insulator and building materials. What about two-dimensional (2D) silicon dioxide-a layered polymorph of silicon dioxide? Will the low dimentional structural silica show novelphenomenon? These are the focus of the present work.

A team co-led by Dr. Xiao Dong, a scientist of HPSTAR, use ab initio evolutionary algorithm for crystal structure and compound prediction-USPEX (Universal Structure Predictor: Evolutionary Xtallography) to predict intrinsic mechanical and electronicporperties of 2D crystalline freestanding silicon dioxide.

They discovered three more new 2D-silica structures in their simulations. The three new 2D-silica display comparable thermal, dynamical and mechanical properties- superhardness, wide band gap - refers to the lowest energy of light that a semiconductor can absorb and a fundamental parameter required for controlling light receiving, conversion, and transport technologies, with many typical bulk forms of silica.

What surprised the scientists most is that all the three 2D silica have large inplane negative



Caption: α-2D silica with positive Posson's ratio (up left), β-2D silica, γ-2D silica, and δ-2D silica with large in-plane negative Poisson’ s ratios

Poisson’s ratios with the largest one being double of penta-graphene and three times of borophenes.

Usually when a material is stretched in one direction, it usually contracts in the other two directions, are said to have a positive Poisson's ratio which characterizes how a material behaves when stretched. However, some materials becoming fatter when stretched, which means they have negative Poisson’s ratio.

"A negative Poisson's ratio is theoretically possible long ago. While Two-dimensional (2D) materials-single-layer graphene, single-layer graphene ribbons, single-layer black phosphorus, cubic metals and α-Cristobalite, changed the case in their single layer structure,” said Dr. Xiao Dong.

“This surprising negative Poisson’s ratio in 2D-silica originates from the interplay of lattice symmetry and Si-O tetrahedron symmetry” explained Dr. Xiao Dong.

Furthermore, they pointed out that 2D-silica are the most insulating 2D material among reported 2D structures with the widest gap.

These exotic 2D silica with negative Poisson’s ratios and widest band gaps are expected to have great potential applications in nanomechanics and nanoelectronics.

Ref: Dr. Xiao Dong
Nano Letters
2017, 17 (2), Pages: 772–777

Freeing hydrogen in Earth's lower mantle

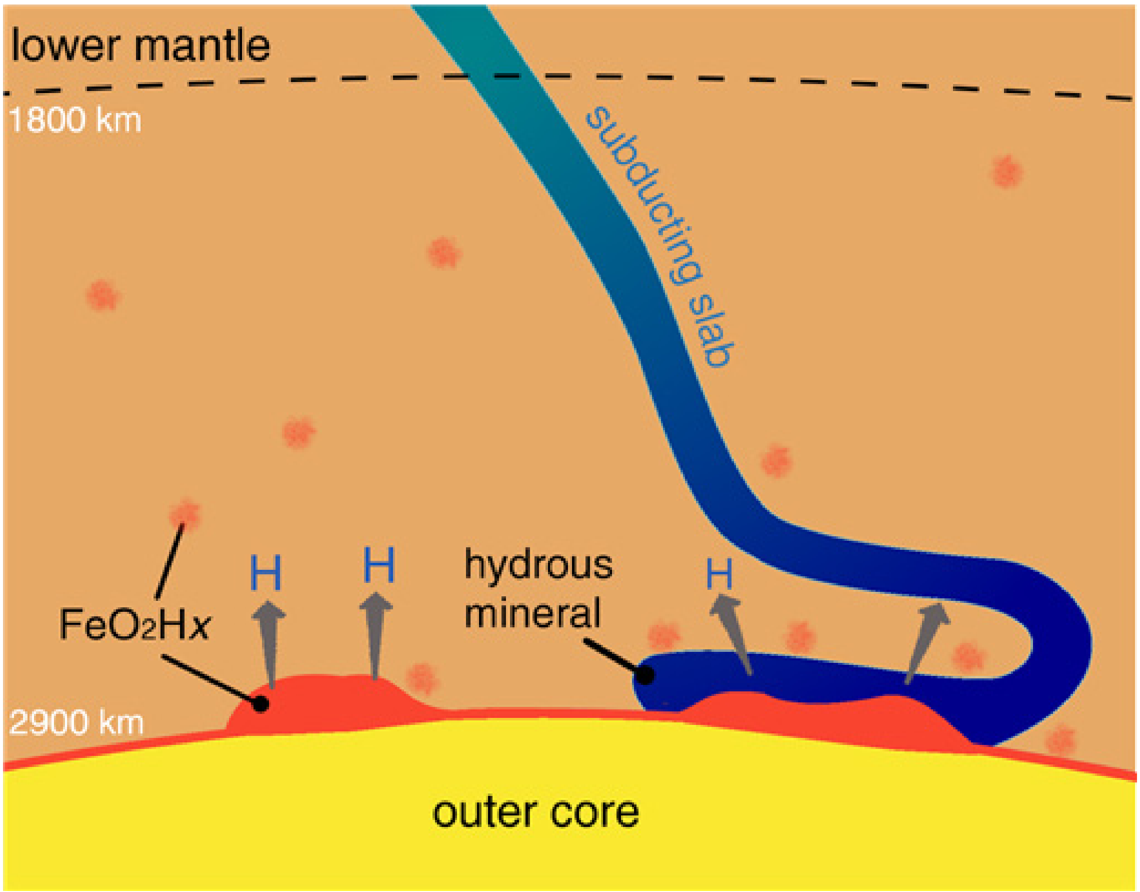
长久以来，由于水分子的化学结构相当稳定，地球内部的水循环与氢循环被认为是对等的。毛河光领导的研究小组发现，在下地幔条件下，含水矿物中的水分子的稳定性会下降，氢元素因此会独立于水，在高温高压下释放出来。通过 x 射线衍射和金刚石对顶压砧，小组将沼铁矿的主要成分 (FeOOH) 压缩至 72 万大气压以上，并通过激光加温，发现氢气会从样品中释放，这种脱氢速率与加热温度和时间息息相关。对地球化学家而言，下地幔一般认为是还原态的，而该工作表明在富含含水矿物的区域中，氢气会分离并向地幔上方迁移，而高度氧化的二氧化铁会留在地幔深处。这个新的发现将对地球内部化学环境的研究产生重要影响。

FEBURARY 04, 2017- In Earth interior, water (H_2O) plays an important role in rock physics but geoscientists rarely treat water in its decomposable forms, like hydrogen plus oxygen. However, new work from a team led by HPSTAR director, Dave Mao, has identified the hydrogen can escape from the water under lower mantle conditions. Their results were published in ***Proceeding of the National Academic Science, U.S.A.***

In the atmosphere, hydrogen is a colorless, transparent gas. It bonds with oxygen to form water which fuels the biosphere on the Earth surface. Deep in the rocky world beneath our feet, so-called hydrous minerals enriched with water mainly exist in the subduction slabs that are relatively colder than average geotherm. At ambient condition, the chemistry of water is so stable that it is considered as the unit of hydrogen carrier in the hydrosphere. For a long time, cycling of hydrogen is equivalent to the cycling of water in the Earth's solid crust and mantle.

"The stability of water in hydrous mineral might break at the lower mantle", said Dave. Using advanced diffraction tools, the team discovered hydrogen was freed from hydrous minerals in its elemental form.

Starting from a typical hydrous mineral – goethite and placing it under lower mantle pressure-temperature conditions (>720,000 atmosphere, and ~2,000 K), Dave's team was able to identify hydrogen released and the hydrogen loss closely related with the heating temperature and duration.



Caption: The hydrogen cycling in the deep Earth. Image courtesy Qingyang Hu.

“Oxygen and hydrogen cycles are separated above the Earth’s core.” suggested by Qingyang Hu, the lead author, “Hydrogen is not freezing, instead, freeing from rocks.”

The team’s results have led to a new paradigm change in the planetary science of lower mantle chemistry. The released hydrogen can directly source the liquid outer core, which is considered to have a substantial amount of hydrogen. Free hydrogen can also rise upwards to partially recover its loss from the subduction of hydrous minerals, and completes its journey in deep Earth.

Ref: Dr. Ho-Kwang Mao

Proceeding of the National Academic Science, U.S.A.

Helium chemistry under high pressure

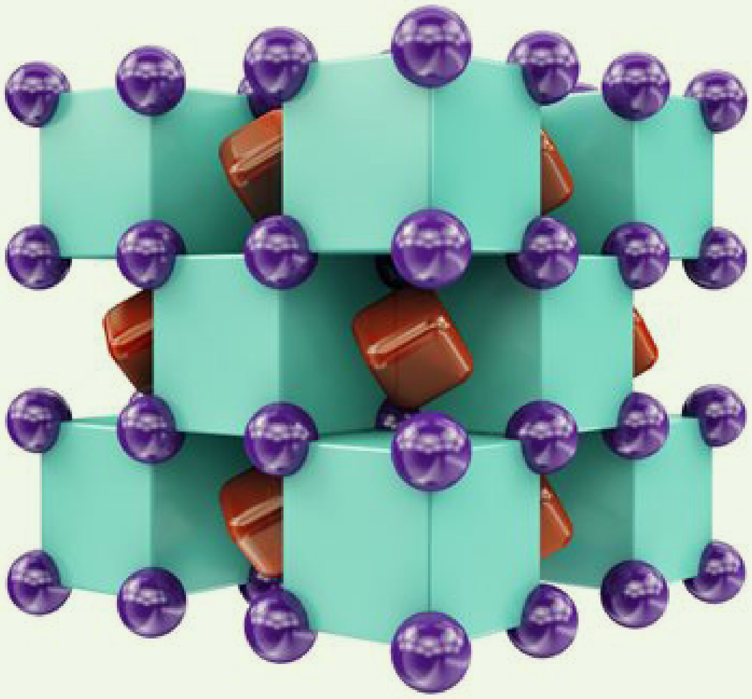
He 和 Ne 是世界上最惰性的两个元素。因为 1s2 满壳层结构，He 拥有最大的电离能和零亲和能，所以已知 He 仅有分子间化合物存在。通过理论预测和高压实验的方法证明 He 在高压下会和 Na 生成新的电子盐结构 Na_2He。亚晶格分析表明，He 的占位导致电子被局域到了原子缝隙中并在 Na 原子核的引力下形成多中心键，从而整个体系变成了电子盐体系。该过程中，孤立电子，Na 的内层电子与 He 的内层 1s 电子和外层的 2s，2p 轨道产生强烈的交叠。受泡利不相容原理的影响，He 的 1s 电子密度和外层电子轨道的分布被迫发生变化导致在 Na_2He 形成过程中 He 得到了 0.15 个电子。该工作证实了高压下 He 会具有弱的化学活性能够与在高压下还原性显著增强的 Na 形成化合物。

FEBRUARY 07, 2017-Although helium is the second (after hydrogen) most abundant element in the universe, it doesn't play well with others. Now, an international team of researchers, including HPSTAR scientist, Dr. Dongxiao has predicted two stable helium compounds — Na_2He and Na_2HeO. The scientists experimentally confirmed and theoretically explained the stability of Na_2He. This work published by ***Nature Chemistry*** (DOI:10.1038/nchem.2716), could hold clues about the chemistry occurring inside gas giant planets and possibly even stars, where helium is a major element.

Helium is a member of a family of seven elements called the noble gases because of their chemical inertness — they don't easily form compounds with other elements. Helium, widely believed to be the most inert element, has no stable compounds at normal conditions.

The authors of the new study used the first-principles evolutionary algorithm USPEX to conduct a systematic search for stable helium compounds. They predicted the existence of Na_2He, which was then successfully synthesized in a diamond anvil cell (DAC) experiment performed at the Geophysical Laboratory in Washington by Prof. Alexander F. Goncharov and his colleagues. The compound appeared at pressures of about 1.1 million times Earth's atmospheric pressure and is predicted to be stable at least up to 10 million times that.

"The compound that we discovered is very peculiar: helium atoms do not actually form any chemical bonds, yet their presence fundamentally changes chemical interactions between sodium atoms, forces electrons to localize inside cubic



Caption: Crystal structure of Na_2He, resembling a three-dimensional checkerboard. Purple spheres – sodium atoms, inside green cubes are helium atoms. Red regions inside voids of the structure show areas where localized electron pairs reside.

voids of the structure and makes this material insulating," said Dr. Xiao Dong, the first author of this work, also a research scientist of HPSTAR.

Na_2He is an electride, i.e., a special type of an ionic salt-like crystal. Its cation sublattice consists of sodium ions, while localized electron pairs make up the anion sublattice. Because electrons are strongly localized, this material is an insulator, meaning that it cannot conduct the free-flowing electrons that make up an electric current.

The other predicted helium compound, Na_2HeO, was found to be stable in the pressure range from 0.15 to 1.1 million atmospheres. It is also an ionic crystal with a structure similar to that of Na_2He. However, in place of electron pairs, it has oxygen anions (O^{2-}).

"This study shows how new surprising phenomena can be discovered by combination of powerful theoretical methods and state-of-the-art experiments. It shows that very weird chemical phenomena and compounds can emerge at extreme conditions, and the role of such phenomena inside planets needs to be explored" said Prof. Oganov.

Ref: Dr. Xiao Dong
Nature Chemistry
volume9, pages440–445 (2017)

Fe isotopic fractionation between mantle and metallic core

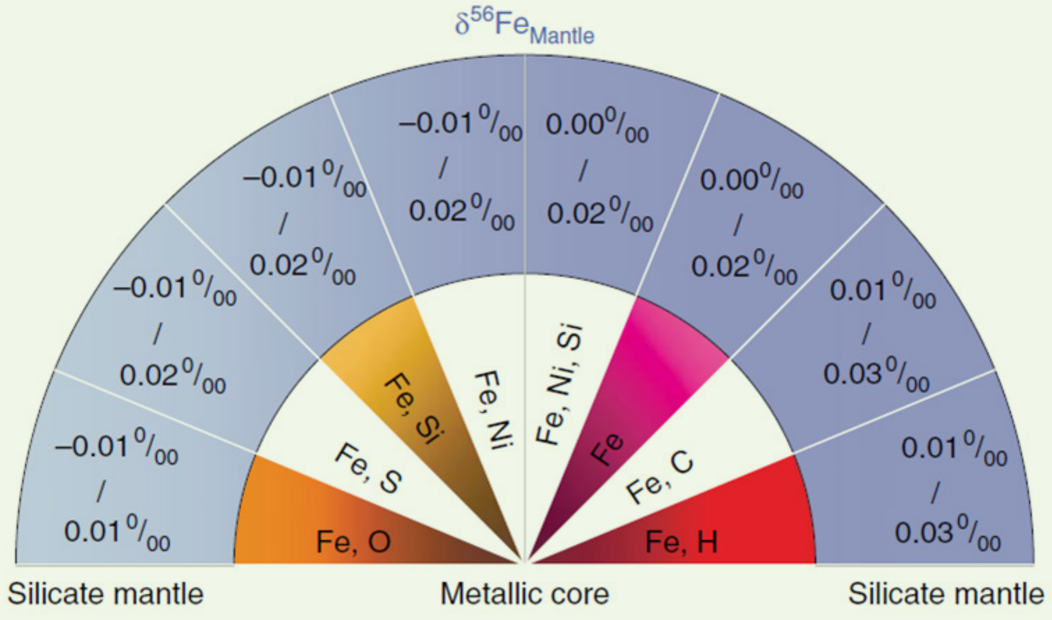
了解地球的化学成分对揭示地球起源至关重要。目前对地球铁同位素的观测表明地球表面的玄武岩比球粒陨石（地球的组成物质）稍稍偏重。这种细微的差别之前被认为可能来自地幔和地核间的铁同位素分馏，但是这种可能性还未被检验过。在本工作中，高科中心的林俊孚研究团队通过了高压下原位的铁原子的力常数测量，揭示了高压下硅酸盐和铁合金之间有限的铁同位素分馏。因此，核幔分异并不能够导致玄武岩中偏重的铁同位素特征。本工作关于各种铁合金的测量工作还揭示了硫、硅、镍的加入并不能显著改变铁的力常数，因此这些轻元素的合金效应对铁同位素分馏影响也是有限的。因此我们可以推断，行星体内部发生的核幔分异过程将不会对元素铁、铬、硅等产生显著的同位素分馏。

FEBRUARY 21, 2017-Equilibrium iron isotope fractionation is vital to understand the isotopic heterogeneity within the Earth, and therefore useful to reveal Earth's early history and its geodynamical evolution. New work led by HPSTAR scientists, Dr. Jung-Fu Lin and graduate student Hong Yang, and Dr. Nicolas Dauphas from the University of Chicago found that the equilibrium iron isotope fractionation between silicate and iron at conditions relevant to Earth's core formation is quite small relative to the observed heavy iron isotope enrichment in terrestrial basalts. This suggests that the interplanetary variability in iron isotopic composition cannot be ascribed to core formation. The work is published by ***Nature Communications*** (doi:10.1038/ncomms14377).

Iron, as one of the most abundant elements in the Earth, is shown to have differentiated in Earth's crust, mantle and core with different valence states — a core dominated by metallic Fe, a mantle that is rich in ferrous Fe^{2+}, and the surface characterized by oxidative environments where iron is found mostly as ferric Fe^{3+}. Geoscientists suggest that iron isotopes fractionation, a process that affects the relative abundance of isotopes, might be influenced by the redox state of iron and help understand how this layered structure was formed. All isotopes of iron behave the same way chemically but slightly differ in their masses. This tiny mass difference may cause some variations in iron isotope distribution in different layers of the earth.

"We need to know how iron isotopes are partitioned at equilibrium between core metal and mantle silicate in order to probe the core-mantle segregation and the core formation conditions," said Dr. Lin, a professor of the University of Texas and a staff scientist at HPSTAR.

Before now, the equilibrium iron isotopic fractionation between metallic iron and silicate post-perovskite at Earth's core-mantle



Caption: Schematics for δ^{56} Fe isotope signatures in the bulk silicate Earth with regard to varying compositional models of Earth's core.

boundary(CMB) conditions was considered sufficiently large to cause significant isotopic fractionation between the mantle and the core.

However, the team experimentally found that the equilibrium iron isotope fractionation between silicate and iron relevant to core formation in Earth is ~0–0.02 ‰, which is small relative to the measured iron isotope enrichment in terrestrial basalts of ~+0.1‰.

“This means that high-pressure mantle-core equilibration cannot be responsible for the heavy Fe isotopic composition measured in basalts. Therefore, the Fe isotopic composition of the mantle is representative of the bulk Earth”, Dr. Lin explained.

More importantly, they discovered that silicon and sulfur, two major light element candidates in the Earth’s core, and nickel alloyed with iron would also produce minimal isotopic fractionation in the silicate mantle relative to the bulk Earth.

“Our results support the notion that core formation of planetary bodies in the solar system is unlikely to fractionate significantly stable isotope ratios for elements like Si, Cr, and Fe. This study calls for a need to understand the isotope anomaly in basalts,” Dr. Lin added.

Ref: Dr. Jung-Fu Lin
Nature Communications
volume8, Article number: 14377 (2017)

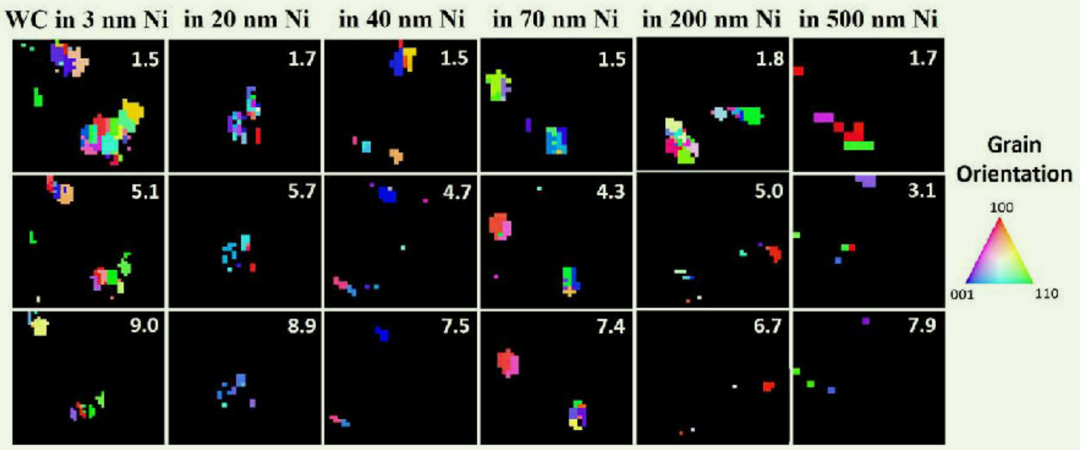
Smaller nanocrystals may not rotate more after all

观测微米以上大尺寸晶粒的转动技术上可行并已经实现。但原位探测超细纳米晶粒的转动目前仍然存在技术困难，因此延缓了纳米力学的进展。为了克服相关的技术障碍，陈斌研究员带领的团队运用了微区劳厄X射线衍射法探测埋在纳米镍粉里的晶粒转动标样。“在相同的应力条件下，同样粒径的碳化钨标样转动幅度应该大致一样。”陈斌研究员讲道，“但令人意外的是，我们发现埋在70纳米镍粉中的碳化钨标样转动比在任何其他尺寸镍粉中的标样转动幅度都大一些。”他们认为观察到的反转现象源于晶内位错机制到晶界位错机制的过渡。这个发现修订了纳米金属塑性形变的传统观点和理论，将会对理解和设计材料的结构和物性提供指导，从而促进纳米科技的进一步发展。

MARCH 2, 2017-For more than 60 years, the conventional belief has been that smaller grains of materials rotate more under stress due to the motion of grain boundary (GB) dislocations. Under the guidance of Dr. Bin Chen of the Center for High Pressure Science & Technology Advanced Research (HPSTAR), Xiaoling Zhou, a Ph.D. student of HPSTAR, and her co-workers observed that nanocrystals of a critical grain size rotate more than any other grain size. The results were published today in the journal ***Physical Review Letters***: “Reversal in the Size Dependence of Grain Rotation”.

Plastic deformation is a common physical process of solid materials that usually determines materials’ strength. General knowledge is well established for the plastic deformation of materials at a micrometer scale. However, the plastic deformation of nanomaterials has long been an outstanding challenge for the research and industrial communities. Grain boundary sliding and grain rotation are thought to be the dominant mechanisms of plastic deformations at the nanoscale. Grain rotation is significantly relevant in nano-mechanics. Classic theories developed in the 1950’s and later (e.g. the Read-Shockley model) stipulate that grain rotation can be accomplished primarily by grain boundary dislocations.

Although the observation of grain rotation in the deformation of micrometer-sized crystals is feasible [L. Margulies et al. Science 291, 2392 (2001)], in situ probing the grain rotation of ultrafine nanocrystals is difficult, precluding further investigation of nanoscale mechanics. To



Caption: 2D orientation maps of WC markers embedded in the nickel media. The vertical and horizontal axes correspond to the 2D scanning directions of sample stage. Different colors on the maps indicate different crystalline orientations, as referenced in the color triangle on the right. The numbers at the top right corners are pressure in units of GPa. Courtesy of Xiaoling Zhou.

overcome technical difficulties, Xiaoling Zhou and her co-workers used Laue x-ray micro-diffraction to monitor grain rotation markers in nickel media of various grain sizes. "Under the same stress conditions, the same sized tungsten carbide marker of grain rotation should rotate the same amount on average", said Dr. Bin Chen, the project team leader, "but surprisingly, we observed that the marker crystals in the 70 nm nickel media rotated more than in any other size of nickel media". They inferred that the reversal in the size dependence of the grain rotation arose from the crossover between the grain boundary dislocation-mediated and grain interior dislocation-mediated deformation mechanisms. This new finding could reshape our views and knowledge of nanometal plastic deformation, which provides guidance for understanding and designing the structural and physical properties of materials and potentially advances the development of nanotechnology.

The work was supported by support NSAF (Grant No. U1530402). X. Z. was partially supported by the ALS Doctoral Fellowship in Residence Program. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under Contract No. DE-AC02-05CH11231.

Ref: Dr. Bin Chen

Physical review letters 118, 096101

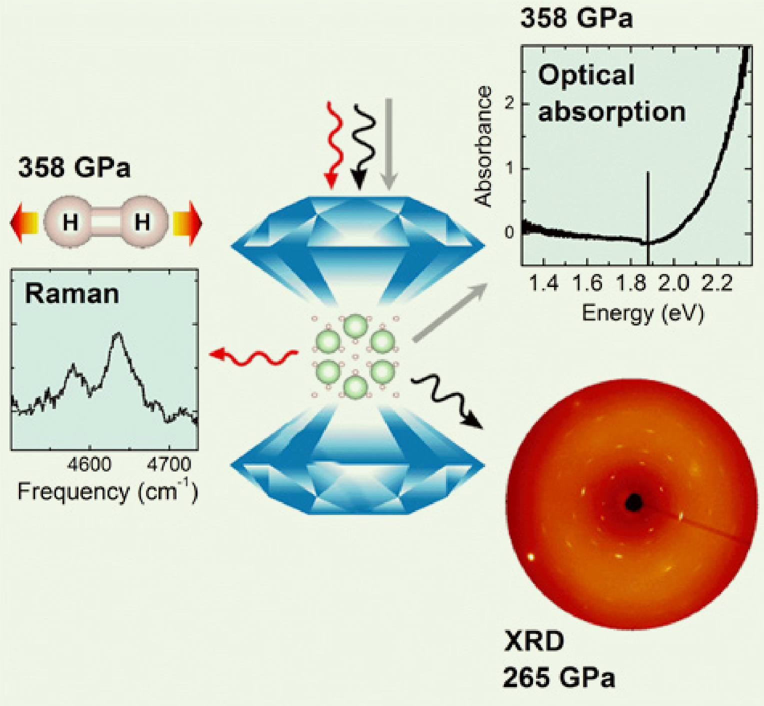
Record pressure squeezes stability of $Ar(H_2)_2$

在富氢化合物中，有一类新型的化合物是由氢分子与其他的原子或分子在高压下结合而成的范德瓦尔斯化合物，这种新的富氢材料在实验与理论上引起了人们的广泛关注与研究。一方面由于非氢元素的存在会对氢的子晶格产生化学预压作用，这些体系被认为有可能比纯氢更容易金属化。另一方面由于氢含量较多，富氢化合物可能具有像金属氢那样较高的超导转变温度，有望成为新型的超导体 - 氢基超导体。作为富氢材料的典型代表，$Ar(H_2)_2$ 在上世纪 90 年代被发现并且被认为可能促进氢的解离从而促成绝缘体 - 金属转变。随之引发了一系列的实验及理论工作研究其在高压下的结构及金属化现象。然而这些结果对与 $Ar(H_2)_2$ 在高压的晶体及电学性能一直存在争议。本研究中，吉诚等人借助金刚石对顶砧（DAC）将 $Ar(H_2)_2$ 的高压研究进一步推进到358万大气压的条件—目前研究富氢化合物的最高压力，来研究Ar的加入的氢分子作用力的影响。此团队发现在高达 358 万大气压的实验条件下，$Ar(H_2)_2$ 仍然保持原有的晶体结构，能带间隙的改变相对于纯氢也更小。这与之前研究发现的结构相变及高压下的金属化完全不符。

MARCH 15, 2017- Hydrogen-rich materials have been predicted to be promoters for the metallization of hydrogen. A group of scientists led by HPSTAR director, Dr. Ho-kwang Mao has studied $Ar(H_2)_2$, a hydrogen-rich material formed by Argon (Ar) and Hydrogen (H_2), to 358 gigapascals -almost the pressure in the inner core of the Earth, by combining experimental and theoretical methods. Contrary to the previous thought, it was observed that Ar damps the intermolecular interactions between H_2 molecules, an effect as 'negative' chemical pressure which postpones metallization. The results were published in ***Proceeding of the National Academic of Sciences, USA.***

Hydrogen molecule (H_2), the simplest molecule of the elements and the most abundant element in the universe, is an insulating gas at normal conditions. But under compressing to above 4 million atmosphere pressure-exceeds the pressure at the center of the earth, hydrogen was predicted to be metal and even room-temperature superconductor. Metallic hydrogen thus became a holy grail for materials science because it could be used for superconductors. However either probing the exotic structure of H_2 high pressure phase (H is the weakest scatter of X-ray) or transforming H_2 into metallic phase presents as extremely grand challenge.

Scientists have predicted that hydrogen-rich material may help the metallization of hydrogen through chemical pressure from the foreign atoms or molecules. $Ar(H_2)_2$ belongs to a typical hydrogen-rich material in form of Van der Waals compound. In $Ar(H_2)_2$, Ar atoms and H_2 molecules are 'glued' together by London dispersion force, so that H_2 units are preserved. It provides a unique opportunity to explore its crystal structure (due to the presence of heavier atom Ar), molecular properties (Raman), and electronic properties



Caption: XRD (Right bottom), Raman(left) and optical absorption spectroscopy (top right) of Ar$(H_2)_2$ at 265 and 358 gigapascals in diamond anvil cell (Middle). Image courtesy of Cheng Ji.

(optical absorption) at the same time to extremely high pressure.

The X-ray beam with high brilliance and sharp focus at beam lines 16-IDB and 13-IDD, APS, ANL, enables X-ray diffraction (XRD) data of Ar$(H_2)_2$ to be measured up to 265 GPa-a record pressure for studying hydrogen-rich materials by XRD.

This new study shows that the insulating Ar$(H_2)_2$ keeps the $MgZn_2$-type structure in the pressure range up to at least 358 GPa. A splitting of the H_2 vibron recorded above 216 GPa points to a molecular orientational ordering transition.

“Now, our work have clarified previous controversies in crystal structures of Ar$(H_2)_2$ at high pressures”, said Dr. Chen Ji, the first author on the study, leading the experimental work.

To explore the pressure affected electronic features on Ar$(H_2)_2$, the researchers measured the molecular vibrational properties and electronic properties by an advanced confocal micro-Raman system with 660 nm excitation to 358 GPa.

“Our results suggest that Ar does not facilitate the molecular dissociation and bandgap closure of H_2, moreover it works in the opposite direction,” explained Dr. Mao. “The results provide a solid basis for future searches of hydrogen-rich materials which facilitate metallization of hydrogen.”

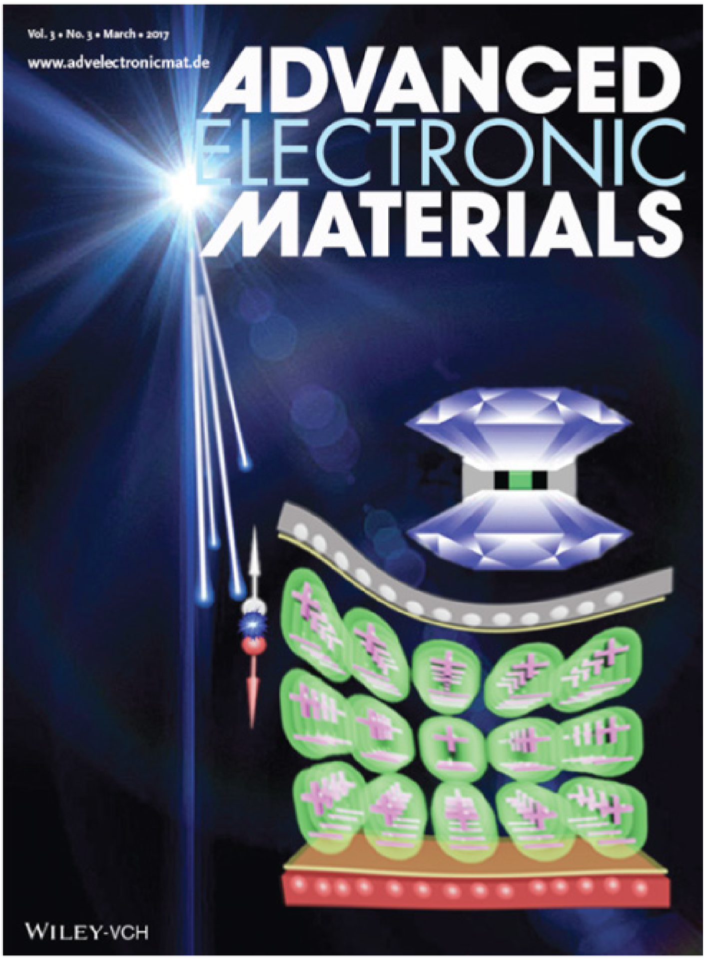
Ref: Dr. Cheng Ji

Proceeding of the National Academic of Sciences, USA.

Pages 3596-3600

Pressure-tuned multiferroic $KBiFe_2O_5$

对新型窄带隙铁电材料的探索和现有铁电材料光伏性能的优化研究已有很多途径和方法，但铁电材料光伏效率依然很低，这主要是由于缺乏有效手段来同时优化铁电材料的铁电性与导电性。研究表明：更大的剩余极化强度产生更高的光生电流和光电转换效率。然而，铁电材料的电阻率都较高、导电性较差，这就导致材料的载流子浓度和迁移率都很低，是阻碍铁电材料光电转换效率进一步提升的根本因素。北京高压科学研究中心张刚华博士带领的团队利用高压技术结合理论计算探究了一种新型铁电光伏材料 $KBiFe_2O_5$ 在压力条件下晶体结构、禁带宽度、铁电性能及光电性能的演变行为。他们发现通过高压诱导微结构相变的手段可以同时增强铁电材料 $KBiFe_2O_5$ 的铁电性能和光伏性能。此研究为设计和开发具有高性能的铁电光伏材料提供了一条简单有效的新途径。



MARCH 16, 2017-New study from a team of HPSTAR scientists, led by Drs. Ganghua Zhang and Wenge Yang, find that pressure can simultaneously enhance ferroelectric and photoelectric properties of multiferroic $KBiFe_2O_5$. These findings may open a new avenue to discovering and designing optimal ferroelectric compounds for solar energy applications. The work was highlighted on the ***Advanced Electronic Materials*** cover.

Multiferroic materials are highly promising for solar applications, and also potentially useful in devices like electronic sensors and flash memory drives because of absorbing solar radiation and possessing unique electrical and magnetic properties.

“Scientists have put a lot of efforts to improve the light absorption, optoelectronic properties of multiterroics from several ways,” said Dr. Ganghua Zhang, who led the research while he was a postdoc fellow in Dr. Wenge Yang’s group.

“We know that pressure is very significant technique in tuning physical properties of energy materials, eg. 2D materials, solar perovskites etc.” added Ganghua. “So we are expecting how pressure will change ferroelectric photovoltaics’ performance.”

The team utilized multiple high-pressure techniques and theoretical calculations to probe the crystal structure, bandgap, ferroelectric and optoelectronic properties of the multiferroic $KBiFe_2O_5$-a new multiferroics with optimal properties for solar applications.

Above about 7 gigapascals, the scientists observed a new phase with four times polarizations of the ambient phase. “This definitely means pressure enhanced ferroelectric polarization of $KBiFe_2O_5$,” said Dr. Wenge Yang, a staff scientist of HPSTAR and a senior author of the paper.

“The pressure–induced polarized new phase is promising ferroelectric photovoltaic material and great candidate for photosensitive switch applications,” added Dr. Wenge Yang.

This pressure induced phase transition also enhanced the electron transport, and visible light response in $KBiFe_2O_5$.

This study suggest that the hydrostatic pressure techniques have great potential as versatile tools to tune the structural, ferroelectric and optoelectronic properties of the ferroelectric materials toward better photovoltaic performances.

The other authors of the study are Fengliang Liu, Tingting Gu, Yongsheng Zhao, Nana Li of HPSTAR and Shouhua Feng of Jilin University.

Ref: Dr. Ganghua Zhang
Advanced Electronic Materials

Unexpected stoichiometry in Sn-Se system

压力作为一个新的维度，通过改变原子间距，电荷分布，从而改变物质的结构，形成具有新性质的高压相。近几年来的理论研究和实验表明，在高压条件下，压力还可以改变元素的化学配比，从而形成经典化学中不可能的化合物。比如 Na-Cl, Ca-C 等体系中新型化合物的发现，惰性气体化合物，Ar(H$_2$)$_2$， Na$_2$He 等等的发现突破了人们对原有化学知识的认知。这些在常压条件下不可能存在的化合物，在高压下都能被合成并稳定存在。在 Sn-Se 二元体系中，人们通常只观测到 SnSe 和 SnSe$_2$ 两种化合物。北京高压科学研究中心的李阔研究员及香港大学的陈粤教授通过理论预测及高压实验合成了此二元体系的另一新型化学组成的化合物—Sn$_3$Se$_4$。相关结果发表在 ***PRL***。

MARCH 30, 2017-Scientists from HPSTAR and The University of Hong Kong combined in situ synchrotron x-ray diffraction and density functional theory and evolutionary algorithms to examine the high-pressure structural behavior of Sn-Se system. The team observed a new compound with an unexpected stoichiometry in the Sn-Se binary system. The research is published in the March 28th edition of ***Physical Review Letters***.

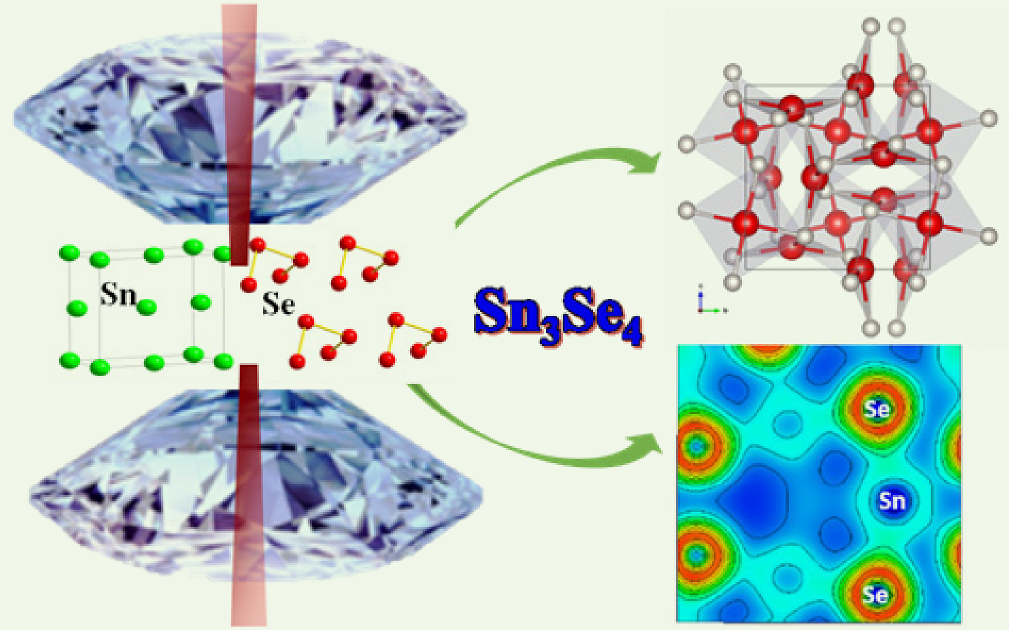
Under ambient conditions, Sn atoms exhibit oxidation states of +2 or +4, and Se atoms often have a -2 oxidation number, so the conventional binary compounds observed in the tin-selenium system are SnSe and SnSe$_2$, representing the typical stoichiometries in the IV-VI group.

While the team of scientists found that high pressure would change the conventional stoichiometry in the Sn-Se system just like what it did in the other binary systems, eg. Na-Cl, Ca-C and etc.

Extremely high pressure will completely alters elements' chemistry, and we will get more exotic compounds that we couldn't under ambient conditions. "So we could even say that pressure will make a new chemistry world compared to ambient pressure. This raises questions about chemistry and how elements behave beyond the world we know", said Dr. Kuo Li, a chemist of HPSTAR.

Sn-Se compounds attracted the group's interests because they are good semiconductors and widely applied in photovoltaic, thermoelectric and memory-switching devices. They are aiming to find other exotic compounds in the Sn-Se system because exotic compounds not only expand our understanding of chemistry but may find new practical applications in future.

First, the team used theoretical calculation to find stable compounds in the Sn-Se system up to 400 thousands atmosphere pressure and a new compound with an unexpected stoichiometry 3:4 was predicted to be stable at high pressure. "Unlike the layered crystal structures of SnSe



Caption: Novel pressure-stabilized superconducting tin selenide with unexpected stoichiometry.

and $SnSe_2$, Sn_3Se_4 has a more densely packed crystal structure with potential high hardness, good thermoelectricity, ferromagnetism or superconductivity.

“Fortunately, the large pressure range where Sn_3Se_4 is energetically preferable makes it possible to be synthesized. So inspired by theoretical predications, HPSTAR team managed to synthesized the predicted new compound Sn_3Se_4 at some 160 thousands atmosphere pressures and 900 oC using a laser-heated diamond anvil cell, and collected the corresponding X-ray diffraction data successfully.

“Our result is one more perfect collaboration between experimental and theoretical materials research," said Dr. Yue Chen of The University of Hong Kong, the co-led author. “Many novel materials were predicted everyday by the theoretical calculations but most of them are still need to be realized by experiment.”

From further electronic structure calculation, Sn_3Se_4 is predicted to be metallic and exhibit a superconducting transition at low temperature and low pressure, which is different from the conventional SnSe and $SnSe_2$ semiconductors. Moreover, Sn_3Se_4 shows a mixed nature of chemical bonds from electron density and Bader charge analysis. “The successful synthesis of Sn_3Se_4 paves the way for the discovery of other IV-VI compounds with non-conventional stoichiometries and novel properties,” added Dr. Lijuan Wang of HPSTAR, a co-author of the study who conducted the experimental work.

Ref: Dr. Kuo Li
Physical Review Letters

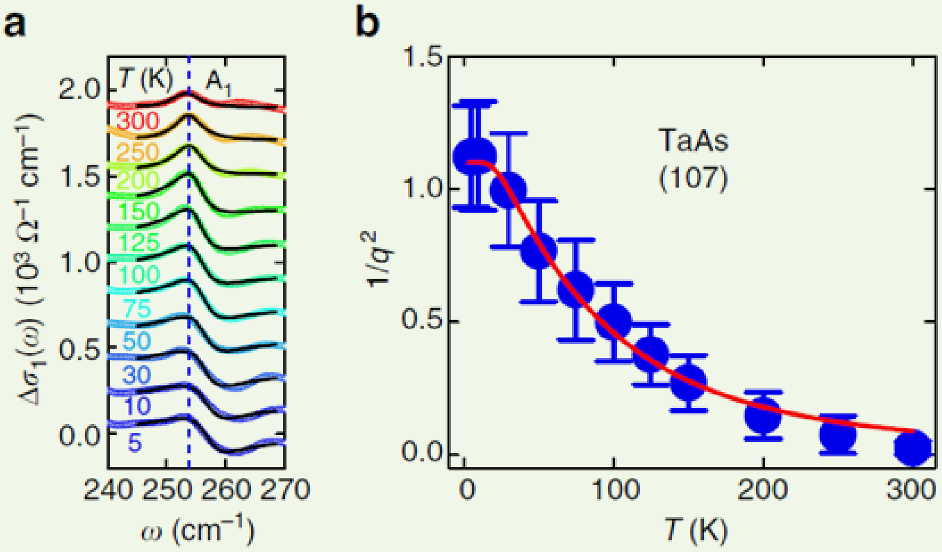
Strong coupling between Weyl fermions and phonons in TaAs

最近，伴随着外尔半金属体系在 TaAs 家族被理论预言并首次被实验证实，外尔半金属材料独特的拓扑特性以及其新奇的量子效应受到了广泛的关注和研究。这类材料具有表面态费米弧，手性反常导致的负磁阻特性，反常的量子霍尔效应以及极高的电子迁移率，在低能耗电子器件，量子计算等领域具有潜在的应用价值。来自北京高压科学研究中心，中科院物理所以及美国洛斯阿拉莫斯国家实验室的研究团队通过光谱手段研究了外尔半金属 TaAs 的电子和声子性质，首次发现了外尔费米子和声子之间存在的很强的耦合作用，而且这种耦合作用可以被温度有效的调控。此研究不仅揭示了外尔费米子和声子之间的耦合机制，也为研究外尔半金属的新奇量子特性提供了新的有效途径。相关结果发表在 ***Nature Communications***。

APRIL 5, 2017-Scientists from HPSTAR and IOP-CAS, in collaboration with Dr. Rohit Prasankumar's group at LANL, studied the temperature evolution of electronic and phonon properties of the Weyl semimetal TaAs using infrared spectroscopy. They found explicit evidence for strong coupling between an infrared-active A1 phonon and Weyl fermions in TaAs. The study is published in ***Nature Communications*** (DOI: 10.1038/ncomms14933).

Three-dimensional (3D) topological Weyl semimetals (WSMs) represent a novel state of quantum matter, which has an unusual band structure with two non-degenerate bands crossing at the Fermi level in 3D momentum space. At the band crossing points (Weyl points), the electronic dispersion is linear in all three directions, resembling a 3D version of graphene, and the low-energy excitations can be described by Weyl equations, producing a condensed-matter realization of Weyl fermions. Recently, such a Weyl semimetal state has been discovered in non-centrosymmetric transition-metal monoarsenides and monophosphides (TaAs, TaP, NbAs and NbP). In these materials, since the Weyl points are located in close proximity to the Fermi level, interband electronic transitions near the Weyl points occur at a very low energy. This energy scale overlaps optical phonon frequencies. Consequently, strong coupling between electronic transitions near the Weyl points (Weyl fermions) and phonons may arise.

The coupling between discrete phonon and continuous electron–hole pair excitations can induce a pronounced asymmetry in the phonon line shape, known as the Fano resonance. Such interesting phenomenon has been observed in bilayer or few-layer graphene, topological insulators, stripe-phase nickelates and high-Tc superconductors etc. However, the coupling revealed in all these



Caption: (a) Fano resonance shown by the infrared phonon lineshape at different temperatures. The black solid lines through the data denote the Fano fitting results. (b) Temperature dependence of the Fano parameter $1/q^2$. The red solid lines through the data represent the modelling results.

materials is associated with or has considerable contributions from coupling between phonons and conventional massive fermions.

In the present study, the scientists revealed an intrinsic, strong and temperature-tunable Fano resonance, which arises from quantum interference between phonons and massless Weyl fermions, in the recently discovered WSM TaAs. Using a model for strong electron-phonon coupling, they successfully elucidated the mechanism underlying the temperature-tunable phonon line shape.

“Our finding is the first observation of a temperature-tunable Fano resonance in TaAs.” Said Dr. Bing Xu, the co-first author of this work from HPSTAR, “More importantly, the Fano resonance is purely induced by the quantum interference between phonons and non-trivial massless Weyl fermions, which has great significance in studies of topologically non-trivial quantum phases.”

“These observations not only open a novel avenue for exploring exotic quantum phenomena in Weyl semimetals, but also set the stage for a variety of potential applications that take advantage of the ability to tune the Fano resonance using different parameters, for example,temperature, light or magnetic/electric fields.” added Dr. Yaomin Dai, the co-first author of this work from LANL.

Ref: Dr. Bing Xu

Nature Communications

volume8, Article number: 14933 (2017)

Hydration-reduced lattice thermal conductivity of olivine in Earth's upper mantle

在地球表面，当大洋板块与大陆板块相遇，大洋板块会被挤压俯冲到地球的深部形成富水的俯冲带。与地球内部的高温相比，俯冲带的温度较低，尽管随着俯冲带向地球内部下沉压力会不断升高，很多低压矿物会在俯冲带中维持亚稳状态。而当这些亚稳矿物最终发生相变时往往会有地震相伴。多年来，俯冲带中亚稳的橄榄石到底会下沉多深一直是国际上非常有争议的问题。起初科学家根据俯冲带的温度推断大量橄榄石会以亚稳状态的形式进入上地幔与下地幔间的过度带（410-660 公里深度范围），进而解释过度带中发生的深层地震。但后来科学家发现，橄榄石向高压相的相变速率会由于水的存在而大大加快，即便是在冲带的温度环境下，橄榄石也会很快发生相变而不会在过度带中以亚稳状态的形式存在。深层地震的解释再次陷入迷雾。北京高压科学研究中心陈久华研究员与台湾中央研究院谢文斌实验室合作，成功测试了高压下水对橄榄石热导率的影响，发现尽管常压下橄榄石热导率几乎不受水的影响，但在过度带的压力下（十三万大气压以上）橄榄石中的水会使其热导率下降一半。因此俯冲带中的温度会比原来科学家想象更低，橄榄石又可以在过度带生存了。该研究结果“Hydration-reduced lattice thermal conductivity of olivine in Earth's upper mantle”发表在 4 月 4 日的 ***PNAS***。

Earth's water cycle enables the incorporation of water (hydration) in mantle minerals that can influence the physical properties of the mantle. Lattice thermal conductivity of mantle minerals is critical for controlling the temperature profile and dynamics of the mantle and subducting slabs. However, the effect of hydration on lattice thermal conductivity remains poorly understood and has often been assumed to be negligible. Here we have precisely measured the lattice thermal conductivity of hydrous San Carlos olivine $(Mg_{0.9}Fe_{0.1})_2SiO_4$(Fo90) up to 15 gigapascals using an ultrafast optical pump−probe technique. The thermal conductivity of hydrous Fo90 with ~7,000 wt ppm water is significantly suppressed at pressures above ~5 gigapascals, and is approximately 2 times smaller than the nominally anhydrous Fo90 at mantle transition zone pressures, demonstrating the critical influence of hydration on the lattice thermal conductivity of olivine in this region. Modeling the thermal structure of a subducting slab with our results shows that the hydration-reduced thermal conductivity in hydrated oceanic crust further decreases the temperature at the cold, dry center of the subducting slab. Therefore, the olivine−wadsleyite transformation rate in the slab with hydrated oceanic crust is much slower than that with dry oceanic crust after the slab sinks into the transition zone, extending the metastable olivine to a greater depth. The hydration-reduced thermal conductivity could enable hydrous minerals to survive in deeper mantle and enhance water transportation to the transition zone.

Ref: Dr. Jiuhua Chen

Proceedings of the National Academy of Sciences of the United States of America

Pages 4078-4081

A Possible Route from C_2H_2 to Graphane

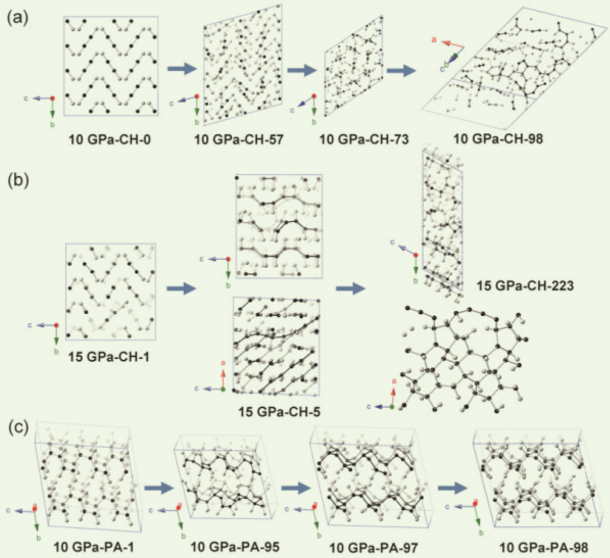
乙炔（C_2H_2）是最为简单的炔烃分子，众所周知，其在催化剂的作用下可以生成著名的导电高分子聚乙炔。压力也可以使乙炔发生聚合，常被作为高压反应的模型化合物，但是关于乙炔的聚合反应路径以及聚合产物，目前仍然知之甚少。北京高压科学研究中心的李阔和郑海燕研究员所带领的科研团队通过原位的中子衍射技术并结合分子动力学模拟系统的研究了极端条件下乙炔小分子的聚合反应过程，第一次获得了高压下聚合之前乙炔的精确晶体结构。在此基础上推断出了乙炔的聚合反应路径，第一次定量的解释了实验上所发现的顺式聚乙炔占优势的原因。并在此基础上，通过理论计算并结合红外光谱、固体核磁以及原子对分布函数证明了利用乙炔合成石墨烷的可能性。该研究为合成碳材料提供了新的思路，系统的证明了高压下的化学反应过程主要受分子取向及分子间距离的影响，并指出了利用低温结合高压技术合成晶态石墨烷的可能性。相关的研究成果“Pressure Induced Polymerization of Acetylene: Structure DirectedStereoselectivity and a Possible Route to Graphane”发表在 ***Angew. Chem. Int. Ed.*** (DOI:10.1002/anie.201702685)。

MAY 3, 2017-Scientists from HPSTAR, co-led by Drs. Kuo Li and Haiyan Zheng, have quantitatively explained the reaction route of polymerization of C_2H_2 under extreme condition by neutron diffraction and theoretical calculation. They discovered that under high pressure, acetylene molecules react along a specific crystallographic direction, which leads to the *cis*-polyacetylene. Following this route, the scientist discovered a potential method to synthesize graphane. By combing multiple methods, a layered polycyclic polymer was synthesized and identified as an intermediate between polyacetylene and graphane. This research provides a novel method of synthesizing carbon materialand the results are published in ***Angew. Chem. Int. Ed.***(DOI: 10.1002/anie.201702685).

Acetylene (C_2H_2) is the simplest alkyne and can be used as building blocks for synthesizing largermolecules or materials like benzene and polyacetylene. It can polymerize under high pressure without any catalyst and generate polyacetylene (PA); where *cis*-PA is the preferred product especially when synthesized under low temperature. However, until now, its reactionprocess under high pressure and different pressure/temperature conditions have not been well understood.

By using in *situ* and ex *situ* experimental methods as well as theoretical calculations, the team systematically investigated the pressure-induced polymerization of C_2H_2, explaining the domination of *cis*-polyacetylene in the process. More surprisingly, they predicted graphane as the final product of this route and experimentally identified a layered polycyclic polymer that is an intermediate between polyacetylene and graphane.

Compared with a traditional chemical reaction,



Caption: Selected structure models of metadynamic simulations. (a) 10 GPa, (b) 15 GPa, and (c) 10 GPa from *cis*-polyacetylene theoretically predicted by pressure induced polymerization.

which is controlled by the temperature or a catalyst, the reaction rule under extreme conditions is still unknown even for very simple systems like C_2H_2. “A pressure-inducedreaction usually happens in the solid phase. Unlike the reaction in the gas or solutionphases, it follows a completely different path and is controlled by the crystalstructure, the orientations, and the distances of the molecules,” said Dr. KuoLi.

Graphanewas predicted for a long time but not stoichiometrically synthesized. However, high pressure provides a new method that may lead to new materials. “Usually, we synthesize material by tuning the temperature, chemical composition orcatalyst but pressure, as a thermodynamic variable, can also determine the compound stability and reaction. By manipulating the pressure, novel materials which cannot be obtained under ambient conditions can be yielded, such as the sp^{3}carbon nanothread or Sn_3Se_4 *etc*.,” said Dr. Haiyan Zheng. This investigation is a critical example of how to study reactions under extreme conditions. In *situ* neutron diffraction is more sensitive to light elements, and is thus a crucial tool for determining crystal structures right before polymerization. The reaction possibility is based on the intermolecular distance and molecular orientation experimentally but theoretical predictions are also very important. “Molecular dynamic simulation based on the experimentally obtained structure can help us to understand the reaction route and predict the product under high pressure,” said Dr. XiaoDong, the HPSTAR postdoc who lead the calculations.

Ref: Drs. Kuo Li and Haiyan Zheng

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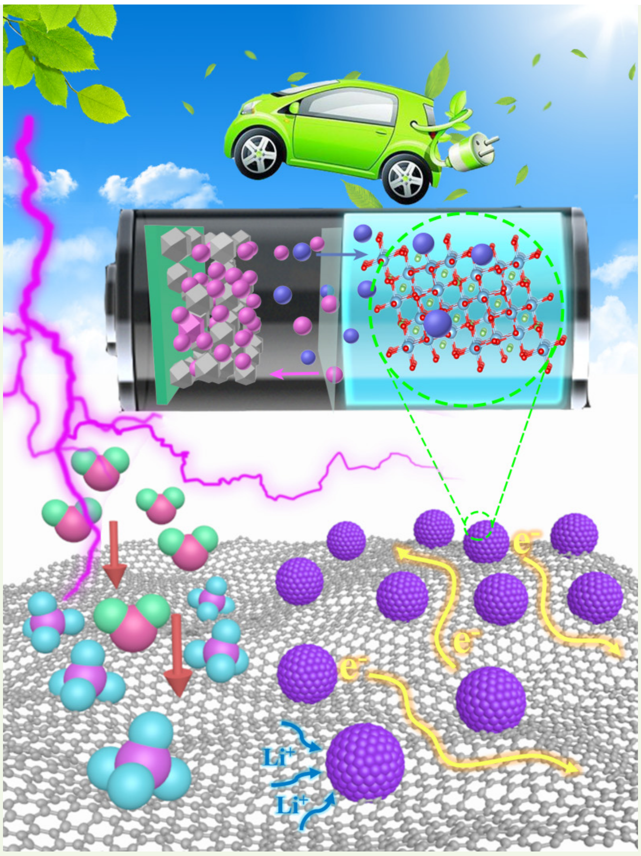
The composite material makes the ultrafast lithium ion capacitors

世界对能源及其新技术的需求持续增长，也对储能器件提出了更高的要求．锂离子混合超级电容器是一种基于锂离子电池和超级电容器双重储能机制的储能器件，由于具备高的能量密度和功率密度，长寿命以及高安全性，有望应用于纯电动和混合动力汽车领域。本研究首次利用原子层沉积育种技术制备钛酸锂 / 石墨烯复合电极材料，并利用第一性原理从理论上进行了计算分析。该材料独特的微观结构使其充电 25 秒即可实现 70% 的理论容量（即 100 C 电流密度时的放电容量高达 120.8 mAh/g）。此项技术为制备新型石墨烯复合电极材料开辟了新思路，以该复合材料为负极的锂离子混合电容器的功率密度甚至超越了双电层型超级电容器，具有重要的研究意义和实际应用价值。



Caption: A novel atomic layer deposition seeded $Li_4Ti_5O_{12}$/graphene anode for ultrafast lithium ion capacitors.

APRIL 14, 2017-The rapidly growing energy demand requires the development of advanced electrical energy storage technology. New work from a team including Dr. Huiyang Gou at HPSTAR and Dr. Gongkai Wang from Hebei University of Technology and Prof. Jie Lian from RPI published in ***Nano Energy*** show that the composite materials of nanosized $Li_4Ti_5O_{12}$ (LTO) and graphene nanosheets can have excellent reversible capacity, rate capability, and cyclic stability as anode materials for lithium ion capacitors.

The composite material showed the great performance for lithium ion capacitors, the reversible capacity of 120.8 mA h g^{-1} at an extremely high current rate of 100 C was achieved successfully, and the electrode can be charged/ discharged to about 70% of the theoretical capacity of LTO in 25s. Meanwhile, the composite exhibited excellent cyclic stability of 90% capacity retention at 20 C with nearly 100% Coulombic efficiency after 2500 cycles.

“We introduced ALD technique, for the first time, for the realization of high performance composites of nanosized LTO and graphenenanosheets as anode materials for LICs. TiO_2 nanoislands were seeded on graphene by ALD process in advance, ensuring the unique structure formation of subsequent LTO”, as the leading author of Dr. Gongkai Wang said.

The sintering treatment, the crystallinity, defect density, microstructure and electrochemical property of the composite have significant effects on its electrochemical performance, Huiyang said, this is also supported by theoretical calculations.

The results provides a foundation for a feasible design to incorporate energy storage materials onto conductive host materials, propelling the forefront and shedding new light of electrical energy storage devices with high power/energy densities.

Ref: Dr. Huiyang Gou
Nano Energy
Volume 36, June 2017, Pages 46-57

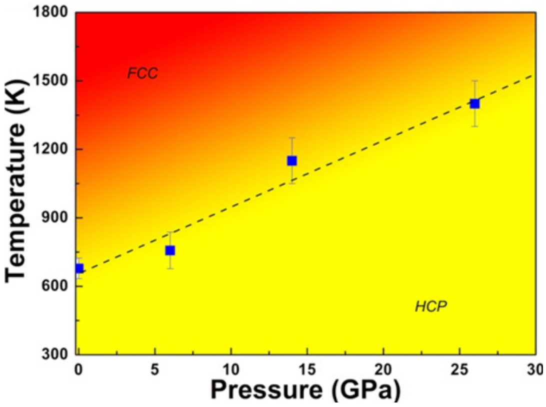
High-Entropy Alloy: changing faces under high pressure

含有五个基元的 CoCrFeMnNi 高熵合金是面心立方（fcc）结构高熵合金的代表体系，它具有极好的低温强度和断裂韧性、延展性和抗氢脆性。人们把这个合金作为高熵合金模型体系开展了大量的研究。然而，到目前为止，人们对其结构的认识还不是很清楚。理论计算认为该合金的密排六方结构（hcp）可能是常温下更稳定的结构，但是以往的实验从没有观察到该 hcp 结构的存在。从液氮温度到其熔点的大范围加热实验也表明 CoCrFeMnNi 高熵合金的 fcc 结构很稳定，不存在任何多形态相变，和其构成元素的丰富多形态现象形成鲜明反差。最近，北京高压科学研究中心的曾桥石研究员所领导的国际团队和北京科技大学吕昭平教授课题组合作，利用高压作为独特的调制参量，采用原位高压同步辐射 X 射线衍射技术对 CoCrFeMnNi 这一典型的 fcc 高熵合金的结构进行了系统研究，发现了该合金在加压过程中存在 fcc 到 hcp 的不可逆多形态相变现象。该研究团队又利用高压原位激光加热技术结合同步辐射 X 射线衍射技术，对 fcc 和 hcp 结构稳定性做了进一步研究。结果表明，fcc 其实是高温下的稳定相，而 hcp 才是低（室）温稳定相。该研究成果揭示了看似极度稳定的高熵合金中也能存在多形态相变现象，澄清了 CoCrFeMnNi 高熵合金中 fcc 和 hcp 结构相对稳定性的长期疑问，也为从原子结构层面调控和设计这类材料的性能提供了可能。而高压为解决这种挑战，提供了独特而有效的途径。

JUNE 2, 2017-A new class of solid solution alloys typically with five or more elements in equal or near-equal proportions-so called the high-entropy alloys (HEAs) are well known for their combination of the desirable properties including high strength, high ductility, high toughness, outstanding wear, fatigue, oxidation and corrosion resistance etc. Rather than the readily formation of multiphase microstructures in traditional multicomponent alloy systems, HEAs usually favor a single simple lattice, which was found to be very stable upon heating or cooling. New study co-led by a HPSTAR staff scientist, Dr. Qiaoshi "Charles" Zeng revealed irreversible polymorphic phase transitions between the fcc and hcp structures in a prototype high-entropy alloy CoCrFeMnNi using in situ high pressure and high temperature x-ray diffraction techniques. Their discovery was just published in ***Nature Communications*** (DOI:10.1038/ncomms15687) on June 1st. These results shed new light on the thermodynamics and kinetics of complex HEA systems and also opens a new avenue towards tuning HEAs' properties via polymorphic structural transitions for applications.

Conventional metallic materials are typically designed based on one or two principal elements, forming various alloys with compositions located at the corners or edges of phase diagrams. Different from this traditional design strategy, HEAs are developed near the center of multicomponent phase diagrams. Due to the high configurational entropy, the complex compositions of HEAs does not induce complex microstructures accompanied by brittleness as expected by traditional metallurgy, but surprisingly stabilize the system in a simple solid solution lattice, and impart attractive properties to these new alloys, forming a new frontier of metallic materials.

"It is generally believed that HEA lattices are severely distorted and atomic diffusion is extremely sluggish



Caption: The temperature and pressure metastability boundary (not the equilibrium phase boundary) of the polymorph hcp and fcc CoCrFeMnNi HEA.

due to the chemical complexity and configuration disorder", said Dr. Qiaoshi Zeng. "This make HEAs have exceptionally high structural stability.

Of all HEAs, the CoCrFeMnNi alloy termed as the Cantor's alloy, is the first reported HEA and a prototype fcc (face-centered-cubic)HEAs. CoCrFeMnNi can maintain its fcc structure over a large temperature range from cryogenic temperatures up to the melting temperature without any polymorphic phase transition.

"Although CoCrFeMnNi HEA is well known and has been extensively studied by experiments and simulations for more than a decade, a puzzle about its structure stability still remains unresolved. Simulations suggest that the hcp (hexagonal-close-packing) structure should be more stable than its fcc structure at room temperature. However, no hcp structure of the CoCrFeMnNi HEA has ever been observed in experiments. So far, high pressure as a dimension has rarely been explored in HEAs, we are therefore curious whether pressure-induced polymorphism also extensive exist in HEAs like what does in their typical constituent elements, said Qiaoshi.

A team led by Fei Zhang, a visititing Ph.D. student of HPSTAR in Qiaoshi's group, used a diamond-anvil cell to compress tiny CoCrFeMnNi samples to ~40 gigapascals. To their surprise, the initial fcc CoCrFeMnNi gradually transformed to a hcp structure monitored by in-situ synchrotron radiation x-ray diffractions (XRD).

"Acturally, the structural stability of the fcc CoCrFeMnNi HEA has been extensively studied in a wide temperature range at ambient pressure but no new structure was observed. Using high pressure as a tuning tool, we observed the first polymorphism in the CoCrFeMnNi HEA", Fei said.

Moreover, the hcp phase could be retained to ambient conditions after pressure release. While further heating experiments on the retained hcp sample at four different pressures indicate that the hcp CoCrFeMnNi HEA will return to the fcc structure at high temperatures, and the transition temperature for hcp-fcc transition increases with pressure

"This means that the well-known fcc phase actually is a stable polymorph at high temperatures, while the hcp structure is more thermodynamically favorable at lower temperatures", explained Dr. Hongbo Lou, a postdoctoral fellow at HPSTAR in Qiaoshi's group.

"Since the fcc-hcp polymorphic transition is irreversible and sluggish, it is easy for us to synthesize fcc-hcp dual phase composites with tunable volume fractions. Our results therefore open up a new avenue towards tailoring HEAs properties for novel applications via polymorphic transition-induced HEA composites" Qiaoshi said.

"The polymorphic transition discovered in this work is by nomeans limited to this specific CoCrFeMnNi HEA, and we expect that this behavior could be general in various HEAs at certain pressure and temperature conditions", Dr. Zeng added.

Ref: Dr. Qiaoshi Zeng
Nature Communications
volume8, Article number: 15687 (2017)

New form of carbon that's hard as a rock, yet elastic, like rubber

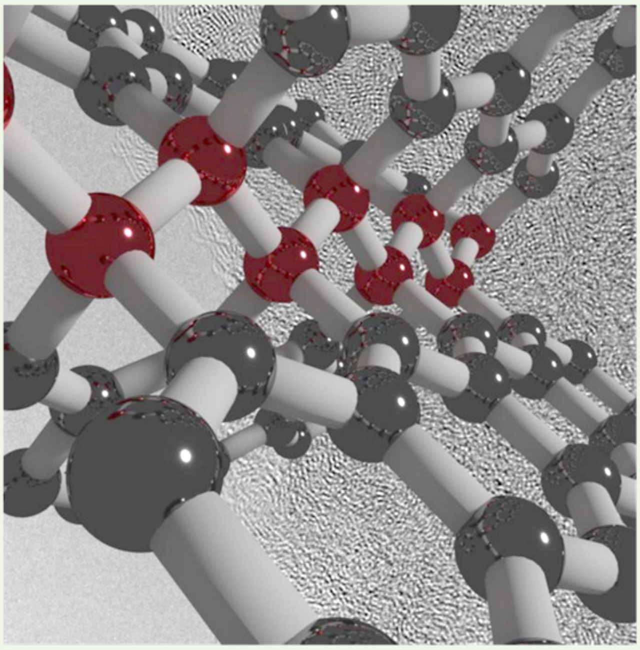
碳具有多种同素异形体，如石墨、金刚石 (钻石)、富勒烯、碳纳米管、石墨烯、玻璃碳等，其中石墨在压力下可以转变成超硬的金刚石。在此新研究中，科学家们以玻璃碳为原料，利用高压但比较温和的温度条件合成了新型碳同素异形体。它由玻璃碳压缩获得并保留了玻璃碳的一些特征，研究人员将其命名为“压缩玻璃碳”。在以前的玻璃碳在室温或高温下的高压转变研究中，制成的碳材料在卸压后又变回了玻璃碳；而在高压高温条件下，玻璃碳就直接转变成了金刚石。最新研究则在中等温度下对玻璃碳加高压，这样既能使玻璃碳发生相变形成新型碳材料，温度又不足以使它变成金刚石。压缩玻璃碳有以下特性：它是与石墨类似的轻质材料，单轴压缩强度是通常金属及合金材料的 5 倍以上，也远大于一般陶瓷材料；比强度（即强度—重量比）极高，是碳纤维、聚晶金刚石、碳化硅和碳化硼陶瓷的 2 倍以上；硬度极高，可轻松刻划高硬度的碳化硅单晶片；具有很高的弹性恢复性，明显高于普通金属和陶瓷，甚至高于高弹性的形状记忆合金及有机橡胶等 ; 此外还具有导电性。

JUNE 9, 2017-Carbon is an element of seemingly infinite possibilities. This is because the configuration of its electrons allows for numerous self-bonding combinations that give rise to a range of materials with varying properties. For example, transparent, superhard diamonds, and opaque graphite, which is used for both pencils and industrial lubricant, are comprised solely of carbon. A international team including HPSTAR scientists Drs. Jinfu Shu, and Ho-kwang “Dave” Mao, have developed a form of ultrastrong, lightweight carbon that is also elastic and electrically conductive. A material with such a unique combination of properties could serve a wide variety of applications from aerospace engineering to military armor.

The scientists pressurized and heated a structurally disordered form of carbon called glassy carbon. The glassy carbon starting material was brought to about 250,000 times normal atmospheric pressure and heated to approximately 1,800 degrees Fahrenheit to create the new strong and elastic carbon. Their findings are published by ***Science Advances***.

Scientists had previously tried subjecting glassy carbon to high pressures at both room temperature (referred to as cold compression) and extremely high temperatures. But the so-called cold-synthesized material could not maintain its structure when brought back to ambient pressure, and under the extremely hot conditions, nanocrystalline diamonds were formed.

The newly created carbon is comprised of both graphite-like and diamond-like bonding motifs,



Caption: Visualization of ultrastrong, hard and elastic compressed glassy carbon. The illustrated structure is overlaid on an electron microscope image of the material. Images are provided courtesy of Timothy Strobel.

which gives rise to the unique combination of properties. Under the high-pressure synthesis conditions, disordered layers within the glassy carbon buckle, merge, and connect in various ways. This process creates an overall structure that lacks a long-range spatial order, but has a short-range spatial organization on the nanometer scale.

"Light materials with high strength and robust elasticity like this are very desirable for applications where weight savings are of the utmost importance, even more than material cost," explained Zhisheng Zhao, one of the principal investigators on this project and also a professor of Yanshan University. "What's more, we believe that this synthesis method could be honed to create other extraordinary forms of carbon and entirely different classes of materials."

The other members of the team are: Meng Hu, Julong He, Wentao Hu, Dongli Yu, Hao Sun, Lingyu Liu, Zihe Li, Mengdong Ma, Jian Yu Huang, Zhongyuan Liu, Bo Xu, Yongjun Tian of the State Key Laboratory of Metastable Materials Science and Technology; Yanbin Wang of the University of Chicago; and Stephen J. Juhl of Penn State University.

Ref: Drs. Jinfu Shu, and Ho-Kwang "Dave" Mao
Science Advances
Vol. 3, no. 6, e1603213

Enhanced Superconductivity in Pressure Quench in In_2Se_3

实现高温、室温超导是超导学术界和工业界梦寐以求的圣杯。借助高压技术，创纪录的超导转变温度 165 K 和 203 K 先后在铜氧化物和硫化氢上实现。但遗憾的是，压力诱导的超导现象随着压力的卸除一起消失了。北京高压科学研究中心的柯峰博士及合作者最近观察到二维材料硒化铟压力诱导的超导行为在降压过程中反而增强了，超导温度比升压过程中的高了近一倍，并且维持到了很低的压力。这个鼓舞人心的结果表明合适地选择材料，高压诱导的高温超导现象可以保持至低压甚至室压条件下，使高压超导的应用成为可能。该结果于 7 月 10 日发表在著名国际材料学术期刊 ***Advanced Materials***。

JULY 11, 2017-Pressure induced superconductivity has been realized in several systems, while the superconductivity will disappear with pressure quench. So how to preserve the pressure-induced superconductivity remains a problem to be solved. New research from HPSTAR revealed that enhanced superconductivity happened in In_2Se_3 during pressure quench. This opens up a possible route to preserve the high-temperature superconductors induced by compression to low and even ambient pressure. Their work is published by ***Advanced Materials***.

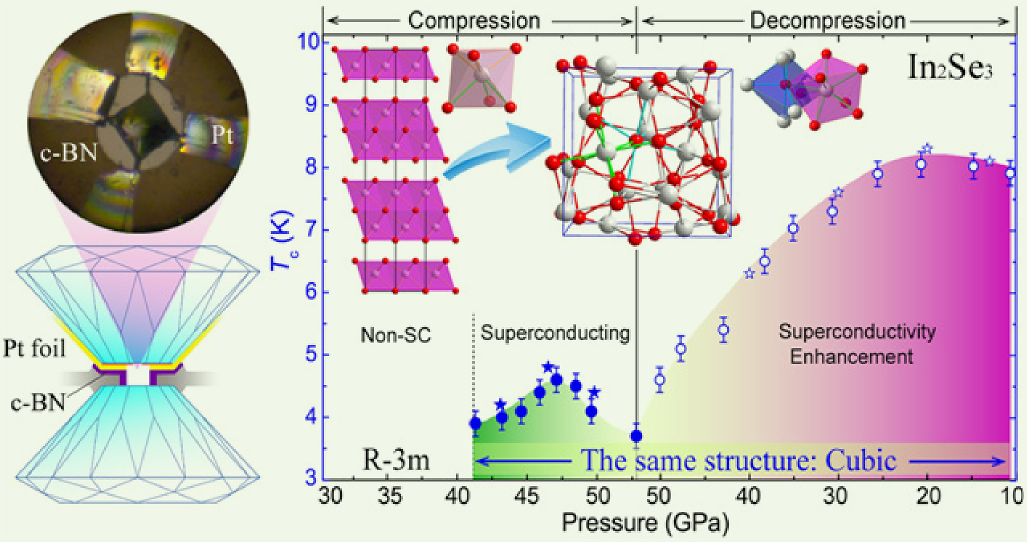
Since the first discovery of superconductivity in mercury in 1911, making new superconductor with higher superconducting transition temperature (Tc) has been the Holy Grail of the superconductor academia and industries.

“Pressure is a paramount significance for promoting superconducting transition temperature and making new types of superconductors, as exemplified by the superconducting transition of cuprate oxides and hydrogen sulphide system occurring at 165 and 203 kelven, respectively”, said Dr. Feng Ke who led the research.

“However, how to preserve the pressure-promoted superconductivity to low and even ambient pressure for practical applications is a long-term chanllenge” added Dr. Bin Chen, a staff scientist of HPSTAR and one corresponding author of this study.

The researchers from multiple institutions of China and the United States have conducted a step study toward this goal. They observed striking superconducting temperature evolution during compression.

“The most surprising is that the superconductivity of In_2Se_3 that occurs at ~43.1 gigapascalsduringcompression still remains



Caption: Left: The microphotography of the layered In_2Se_3 for high-pressure electrical transport measurements; Right: Tc of In_2Se_3 of different pressure cycles, courtesy of Dr. Feng Ke.

robust during pressure quenching, with a twofold increase at a lower decompression pressure", said Dr. Feng Ke.

"This much desired superconductivity enhancement in pressure quench can be attributed to the significant softening of phonon frequency in decompression and the irreversible layered or two-dimensional to three-dimensional structural transition of the high-pressure phases", explained Dr. Feng Ke.

Their findings provide guidance in search for pressure-quenchable superconductors: In_2Se_3-like low-dimensional layered materials which can keep relatively higher carrier concentration for electron-phonon coupling at lower decompression pressure may also demonstrate significant decompression-driven superconductivity enhancement.

"If quenchable pressure is sufficiently low, around a few gigapascals, some other approaches such as introducing chemical pressure may undertake the last-mile work of maintain high-pressure superconductivity in a practical condition, making possible the real application of pressure-induced superconductors", Dr. Bin Chen added, "More explorations are going on".

Ref: Dr. Feng Ke

Advanced Materials

LSO — Ideal optical pressure sensor

锡酸盐烧绿石 $La_2Sn_2O_7$ 是一种透明导电氧化物，是潜在的薄膜器件材料如发光二极管和电致发光平板显示器等。在室温常压条件下，$La_2Sn_2O_7$ 不具备电子跃迁导致的发光特性。北京高压科学研究中心的杨文革研究员与吉林大学的王欣教授合作的研究小组在锡酸盐烧绿石 $La_2Sn_2O_7$ 中观测到了强的室温常压近红外荧光光谱，在高压下发现了压致发光特性，而且这种压致发光是可逆的。他们提出烧绿石 $La_2Sn_2O_7$ 新颖的可逆压致发光特性、稳定的化学性质和强的抗辐射能力，将会成为在深海极端环境下工作的光压力传感器材料。

JULY 11, 2017-A material with good structural stability, chemical durability, and radiation tolerance under extreme conditions is necessary and long challenge for developing new pressure sensors. New work co-led by HPSTAR scientist, Dr. Wenge Yang found novel visble photoluminescence in pyrochlore $La_2Sn_2O_7$ induced bypressure. This unexpected reversible photoluminescence suggests that $La_2Sn_2O_7$ might be an ideal optical pressure-sensor under extreme conditions. The results are published on ***Advanced Materials***.

Pyrochlore $La_2Sn_2O_7$ (LSO) has potential applications in light emitting, disposing of high-level radioactive waste in safe geologic repositories under extreme condition due to its extraordinary chemical stability, and excellent radiation tolerance etc.

In addition, LSO is simultaneously transparent to visible light and well conducting electricity. There is very rare of this kind of materials.

Pyrochlore LSO shows a strong near-infrared fluorescence at ambient pressure. And the team's previous work has shown that pressure induced photoluminescence (PL) change in pyrochlore $Eu_2Sn_2O_7$.

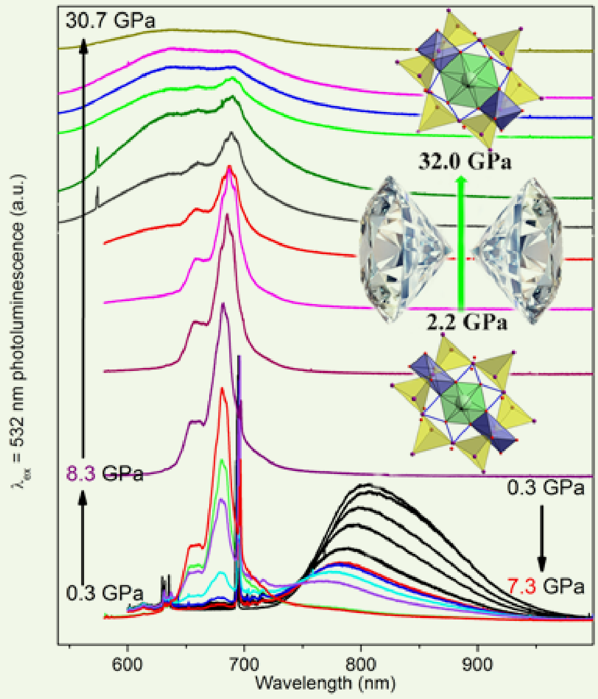
“Pressure has show powerful effect in tuning physical properties and discovering new phenomenon, which guides people for advanced materials discovery”, said Dr. Wenge Yang.

“These inspired us to further characterize the high-pressure PL phenomenon of pyrochlore LSO”, added Dr. Wenge Yang.

When subjects to compression, LSO shows visible PL above 2 gigapascals. PL spectrum intensity shows obvious change with pressure. What's more, the PL peak shifts with pressure.

“These are similar with what happens in Ruby, a pressure calibrate under extreme conditions”, said Yongsheng Zhao, a PhD student in Dr. Wenge Yang's group and who led the research.

More importantly, the pressure induced visible



Caption: Pressure-induced novel visible PL in LSO.

photoluminescence will disappear with pressure reduced to ambient conditions, which means the pressure induced PL is reversible.

“This reversible visible PL dependent on pressure suggests that LSO may provide a great calibration tool for pressure sense at extreme conditions”, Dr. Wenge Yang added.

With the aim of unraveling the mechanism behind the pressure induced PL effect, the researchers conducted detailed analyses of the high-pressure crystal/electronic structures of LSO.

In-situ high pressure X-ray diffraction and resistance measurements show that the anomalous PL behavior was associated with lattice distortion by phase decomposition and novel visible PL was associated with semiconductor-insulator transition.

“Pressure induced and enhanced visible PL would lead fundamental understanding and open up new applications of new PL materials under pressure. All these bring us a new sight for nuclear-waste host materials”, said Dr. Wenge Yang.

Ref: Dr. Wenge Yang
Advanced Materials

Zeolite Dehydration and Extra-Framework Cations

钠沸石 Natrolite (NAT) 是沸石族矿物的典型代表，具有小的、规则的椭圆形的空洞。根据钠沸石中骨架阳离子及空洞中水分子的位置分布的不同，钠沸石被分为两种：Li-,Na- and Ag-NAT 及 K-,NH4-, Rb-, and Cs-NAT。通过对钠沸石两种体系进行系统的高温结构及光谱学研究，该研究团队发现钠沸石的脱水温度与骨架阳离子的大小成反比并提出骨架阳离子的类型在钠沸石的结构稳定性方面起着比脱水程度更重要的作用。

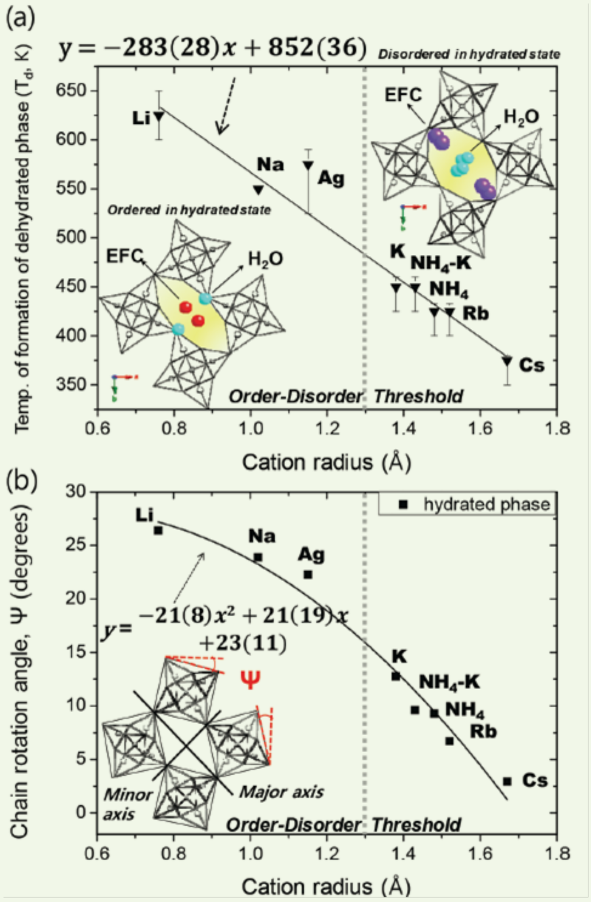
JULY 24, 2017-New work led by HPSTAR scientists, Dr. Yongmoon Lee and Prof. Yongjae Lee presents new results in Zeolite. They performed comprehensive high-temperature diffraction and spectroscopic experiments on natrolites, containing extra-framework cations (EFC) of various size and charge. They find systematic yet unusual structural and chemical behaviors. This work is published in the latest American Mineralogist, and is selected as "Editor's pick of notable papers" for this month in ***American Mineralogist***.

The team presents a comprehensive structural and spectroscopic study of the thermal behavior of monovalent cation exchanged natrolites as a model system of a small-pore zeolite.

Natrolite (NAT), one of the representative members in mineral zeolites, contain tiny, regularly spaced elliptical pores. There two types of NAT depending on the distribution pattern of extra-framework cations (EFC) and H_2O in the pores. In Li-, Na- and Ag-NAT, the EFC's are located in the middle of the pores and water molecules are closer to the amuminosilicate framework, whereas in K-, NH4, Rb-, and Cs-NAT, this distribution is reversed in a disordered fashion.

In this work, the team aimed to find out the influence of EFC on the temperature-induced structural and chemical changes. They found that the dehydration temperature is inversely proportional to the size of the EFC in such a way that Li-NAT shows the highest dehydration temperature while the dehydration temperature for Cs-NAT is the lowest in the NAT families. This can be understood given a possible Coulomb's Law effect on bonding strength.

What is special in this study is that those isostructural K-, Rb- and Cs-NATs with disordered EFC-H_2O distribution exhibit negative thermal expansion behaviors before dehydration. Their thermal expansion coefficients increase linearly from K-, Rb- to Cs-NATs, at which it becomes comparable to that of 'zero thermal expansion' alloys known to date. After dehydration, the EFC distribution of K-, Rb- and Cs-NATs becomes ordered, and their thermal expansion coefficients



Caption: Dependency of the (a) one set of dehydration temperature of NAT phases(Td),(b) Chain rotation angle.

become positive.

In contrast, in Li-, Na- and Ag-NATs with ordered EFC-H_2O distribution, thermal expansion coefficients are positive in Li- and Ag-NATs and negative in Na-NAT, which becomes reversed after dehydration.

To understand these phenomena, the team further probed the bonding interactions of EFC and H_2O molecules via X-ray absorption spectroscopy.

“Moreover, our structural work on NATs suggest that EFC type has a greater influence over the stability of zeolite structures than degree of dehydration, with stability increasing with decreasing EFC radius ”, Dr. Yongmoon Lee explained who is the leading author in the series of publications on natrolites in American Mineralogist.

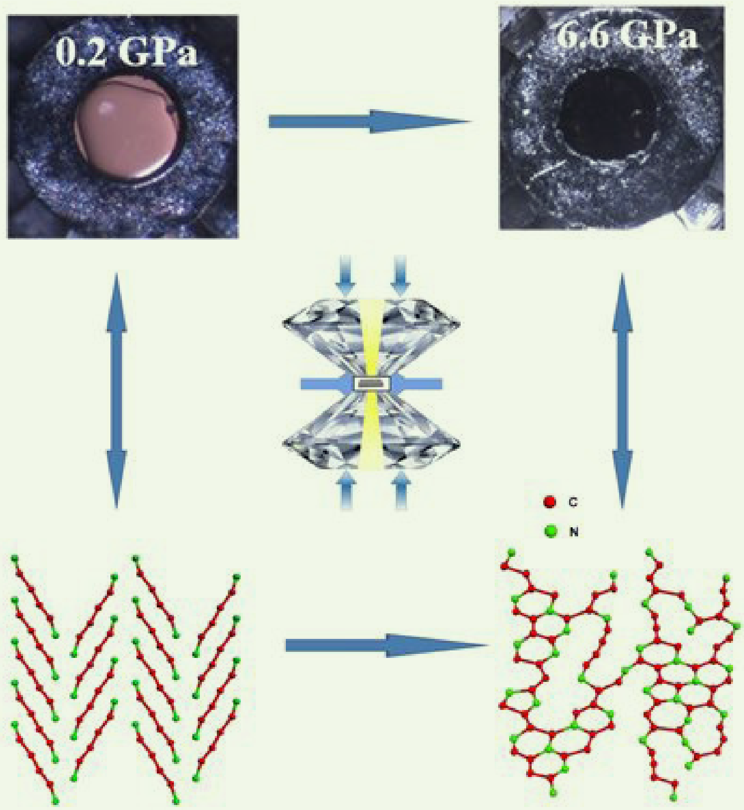
Ref: Dr. Yongjae Lee
American Mineralogist
2017, 102, pp 1462-1469

A new graphitic carbon nitride made under pressure

炭素材料以及富碳 - 碳氮材料具有独特的电子结构和优异的化学稳定性，广泛应用于光催化产氢、水氧化、有机物降解、光合成以及二氧化碳还原等，因此在能源和材料相关领域备受重视。碳氮相图中最稳定的是石墨相 g-C_3N_4，目前被认为是最有可能代替碳材料的新型应用功能材料之一。北京高压科学研究中心的缑慧阳研究员及其合作者利用金刚石对顶砧技术对具有线性分子链的二氰乙炔—C_4N_2 分子晶体进行了高压研究，首次澄清了其振动模式的研究中长期存在的争议。并且该研究团队发现 C_4N_2 分子晶体在较低的压力下就发生聚合反应，离散的线性分子链在压力驱动下逐渐形成无序的类石墨装的碳氮原子环状结构，并且仍然维持较高的 N 含量。研究结果发表在 ***Chemistry of Materials***。

AUGUST 14, 2017-Nitrogen-bearing, carbon-rich materials are known to have multiple functionalities and diverse applications. Graphitic carbon nitride (g-C_3N_4) is the most common C-N phase studied, but several other phases with varying compositions and properties have been predicted. A group of scientists led by Huiyang Gou of HPSTAR and Timothy Strobel of Geophysical lab performed high-pressure experiments on linear dicyanoacetylene (C_4N_2) using a diamond anvil cell, in which a pressure-induced reaction process of was uncovered. Discrete linear C_4N_2 molecules were found to polymerize into a disordered extended network without significant change to the bulk composition. The results were published in ***Chemistry of Materials***.

C_4N_2 is a linear molecule with alternating triple and single bonds (N≡C-C≡C-C≡N) that can burn with a flame temperature of more than 5000 K. This high-energy state represents a novel starting point for the synthesis of new carbon nitride extended networks with an interesting C:N stoichiometry in-between typical deposition-based syntheses (nitrogen doping) and systems like graphitic C_3N_4. The team found that C_4N_2 polymerizes into a disordered carbon/nitrogen network that can be recoverable at ambient conditions. Its local structure, composition and chemical bonding were established using a variety of optical and X-ray scattering methods. Simulations of the reaction process conducted by Li Zhu and Duck Young Kim indicate that the pressure-induced polymerization initiates between the shortest N•••C distances within a single two-dimensional “sheet” of molecules within the crystal. The polymerization proceeds within individual sheets through cycloaddition reactions producing predominantly 5- and 6-membered heterocyclic rings, giving the



Caption: C_4N_2 polymerizes into a disordered carbon/nitrogen network under compression.

overall structure a tendency to propagate in two dimensions.

The high-pressure behavior of C_4N_2 elucidates the nature of chemical bonding, reaction mechanisms, and the atomic structure of reaction products, which advances the general understanding of carbon nitride materials and provides fundamental contributions for realizing new diamond-like carbon nitride materials.

Other team members included Haw-Tyng Huang, Arani Biswas, Derek Keefer, Jordan Lerach and John Badding of The Pennsylvania State University; Brian Chaloux and Albert Epshteyn of the Naval Research Laboratory; Clemens Prescher of the University of Chicago; Liuxiang Yang and Matthew Ward of Carnegie; Shengnan Wang and Artem Oganov of Stony Brook University.

Ref: Dr. Huiyang Gou
Chemistry of Materials
2017, 29 (16), pp 6706–6718

High-Pressure Behavior of Hydrogen and Deuterium at Low Temperatures

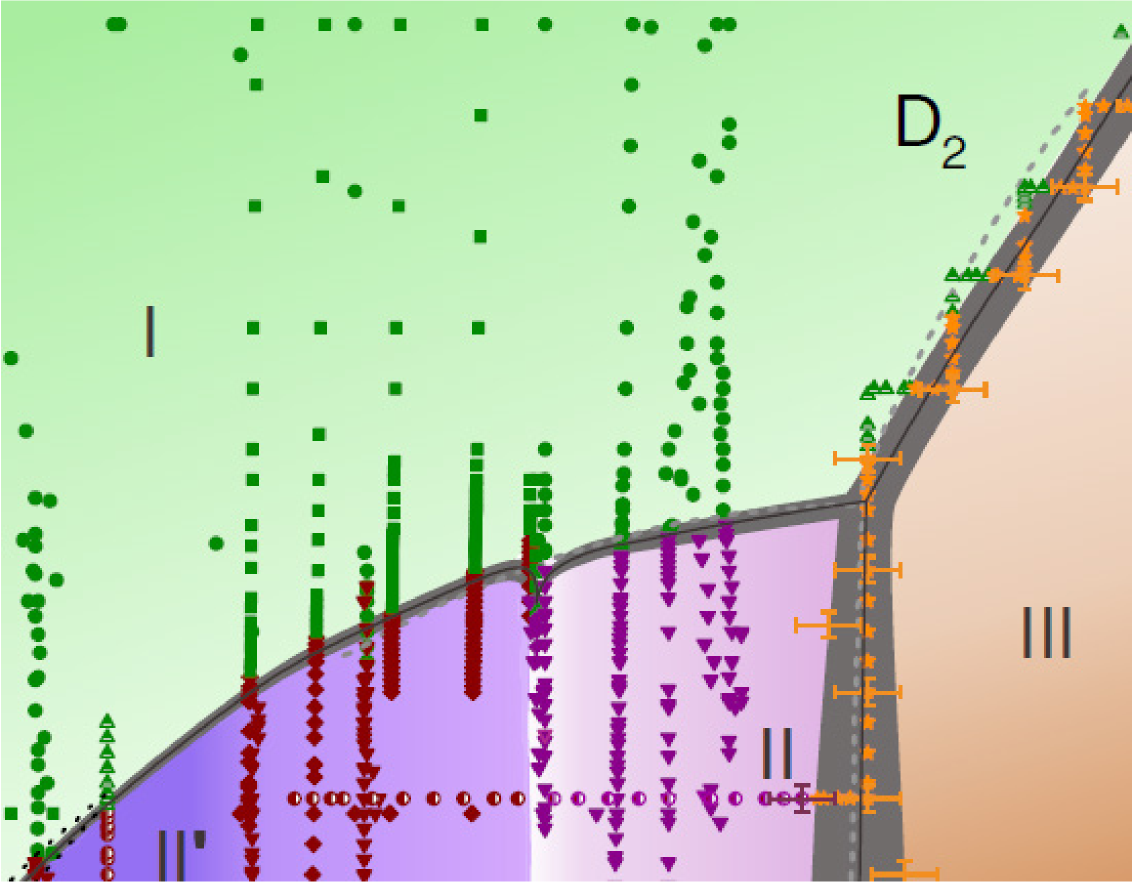
经过一个多世纪的研究，位于元素周期表中的第一个元素—氢的温度和压力相图本已基本确立。北京高压科学研究中心 Ross Howie、陈晓嘉、Eugene Gregoryanz 三位研究员与中国科学院固体物理研究所的研究人员一起，利用高压低温拉曼光谱系统，获得了氢和氘在压力（0-200 GPa）和温度（4-300 K）范围内的一系列等温变压和等压变温拉曼光谱。分析发现，氢的同位素氘的振动频率随温度变化中出现与早前熟知的第二相 (II) 不同的特征 , 这个新相存在于 25-110 GPa 之间低于 125 K 的低温区域，但在相同温度压力条件下在氢中并没有观察到此相，使得氘 II¢相成为目前唯一一个氢氘不共有的低温相。氘 II¢相的出现，推测是量子效应的结果，由于氘相对与氢较低的零点能以及分子间强的相互作用而导致复杂的转动运动。另外，研究还获得了氢和氘的相 I 到相 II 转变，相 II 到相 III 转变的证据，得到了精确的氢和氘相 I、II 和 III 的相边界，更新了氢和氘的高压低温相图。此研究是三十多年来氢氘在中压低温区研究的一大突破，对于理解氢的高压相图、相 II 中的量子效应等具有重要意义。

AUGUST 17, 2017-New work by HPSTAR's Ross Howie, Xiao-Jia Chen and Eugene Gregoryanz, in collaboration with the ISSP Chinese Academy of Sciences, presents the first high-pressure experimental study of hydrogen that was completely conducted within China. The authors present in situ high-pressure low-temperature high-quality Raman data for hydrogen and deuterium where they demonstrate the presence of a novel phase, phase II', unique to deuterium. This work is published ***Physical Review Letters*** (DOI: 10.1103/PhysRevLett.119.065301).

Elemental hydrogen under compression has been an alluring topic in the high-pressure sciences for several decades. Despite numerous theoretical and experimental studies, several outstanding problems remain. Despite the remarkable progress in our under- standing of the behavior of both isotopes at very high compressions, there has been no attention given to the P-T regimes where phase II exists.

Phase I of H_2 & D_2 is known to adopt a hexagonal close-packed structure with freely rotating molecules. The application of high pressures and low temperatures forces the molecules to adopt a broken symmetry phase, phase II, whereby the quantum-mechanical rotational motion is present, though hindered by the increased density.

Using a state-of-the art low-temperature Raman spectroscopic system at the Key Laboratory of



Caption: Proposed phase diagrams of hydrogen (a) and deuterium (b) in a low-temperature, medium-pressure range.

Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences based in Hefei as part of a collaborative effort, the authors systematically map out phase II of H_2 and D_2.

The changes in the Raman spectra of deuterium with pressure and/or temperature indicate the presence of a previously unknown solid phase existing between 20 and 110 GPa and below 130 K. The novel phase, called phase II', occupies the larger part of the P-T area that used to be known as phase II. If pressure is further increased at above 110 GPa, phase II' transforms into phase II. Remarkably, phase II' of deuterium is not observed in hydrogen, making it the only phase that does not exist in both isotopes.

"It really is remarkable that this is the first phase which is exhibited in deuterium but not in hydrogen. This is a clear demonstration of the role that quantum effects play in the isotopes" – Ross Howie

Ref: Drs. Ross Howie, Xiaojia Chen and Eugene Gregoryanz
Physical Review Letters
119, 065301

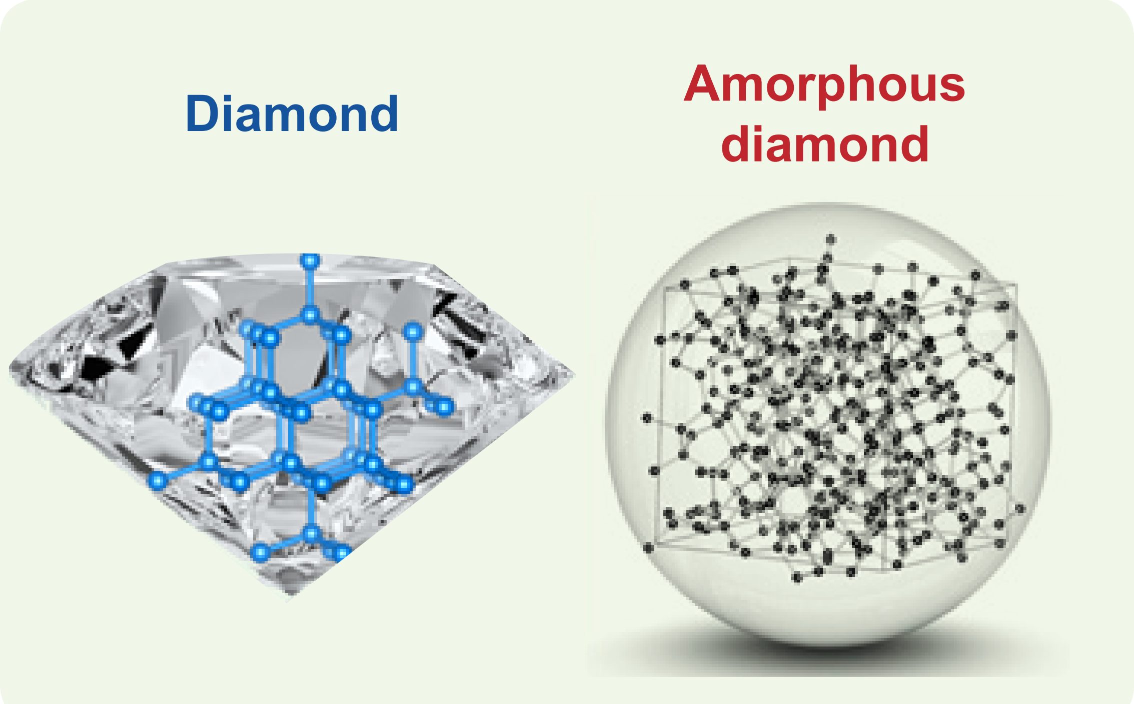
Diamond can be amorphous: from scenario to reality

金刚石是天然存在的硬度最高的材料，同时还具有最高的弹性模量（体模量），最高的原子密度、最高的热导率等优异性质。这些优异性能和其特殊结构有关。本研究采用玻璃碳（glassy carbon）作为起始材料，利用高压原位激光加温技术首次成功合成了块体状的 100% sp^3 共价键的新型非晶态碳材料。通过同步辐射 x 射线衍射、高分辨电子显微镜及电子能量损失谱等多种实验手段，一致证明这种新型碳材料具有典型非晶态结构，且材料内部所有碳原子间的共价键都是 sp^3 键，因而是真正的“非晶态金刚石”。非晶态金刚石的合成说明金刚石并不是唯一的全部碳原子都以 sp^3 键结合的碳材料，改变了我们对碳材料的传统认知。“非晶态金刚石”由于其无序的原子结构而具备非晶材料各向同性的特点，且材料内部不存在晶界、位错等传统晶体缺陷，又因高强度 sp^3 共价键的存在而很可能具备接近甚至超越单晶金刚石的优异性能（高压原位同步辐射 x 射线衍射实验已经证实其体模量高于金刚石），作为一种新型的超硬材料，可能在众多科学技术领域取得重要应用。

AUGUST 22, 2017-A team led by HPSTAR scientist, Dr. Zhidan Zeng synthesizes a new form of carbon—“amorphous diamond”—under high pressure and temperature (HPHT). This bulk amorphous diamond obtained under HPHT can be maintained to ambient conditions for potential applications, realizing possible the hardest amorphous (glass) material ever discovered. This work is recently published as an article by ***Nature Communications*** (Synthesis of quenchable amorphous diamond, doi:10.1038/s41467-017-00395-w).

Diamond is a famous allotrope of carbon with many unparalleled properties. In particular, diamond has the highest hardness and thermal conductivity of any ever known bulk materials, resulting in widespread industrial applications. Most of its unique properties originate fromits extremely strong sp^3 C-C bonding. The search for other bulk carbon allotrope with the same sp^3 C-C bonding has been a long-sought after yet elusive goal. In principle, any substance can be formed in an amorphous solid state. Is a fully sp^3 C-C bonded amorphous diamond also possible? By combining high pressure and high temperature, Z.D. Zeng and her colleagues successfully synthesized a completely sp^3-bonded tetrahedral amorphous carbon-- “amorphous diamond”, and recovered it to ambient conditions, for the first time.

Despite of the highest hardness, diamond as a crystalline material, is anisotropic and contains“weak planes” (cleavage planes) which make it easily to break along certain directions. “In contrast to diamond, the ‘amorphous diamond’ has a disordered three dimensional structure, therefore it is ideally isotropic and does not contain weak planes.” said Zhidan Zeng, “This structure with the strong three dimensional C-C bond network make amorphous diamond a super strong material. Our experiments confirm it has an ultrahigh bulk modulus exceeding any otherknown amorphous materials. And we expect that amorphous diamond may have many other unique properties complementary



Caption: Atomic structure of diamond (left) compared with amorphous diamond (right). Diamond is crystalline and anisotropic, the single crystalline diamond shown in the left picture contains lots of facets. In contrast, amorphous diamond is isotropic like glass, and it may be cut to any shape including ideal sphere.

to or even beyond diamond, which need further exploration."

The three important Group-14 elements C, Si and Ge all have sp^3-bonded crystalline phases with the same diamond-cubic structure. Si and Ge also have well-known sp^3-bonded tetrahedral amorphous forms which have broad applications. However, the amorphouscounterpart in C, an amorphous form of diamond, was conspicuously missing until now. This research finds this missing member of the carbon allotrope family, and demonstrates that it can be maintained at ambient conditions.

"Carbon-carbon bonding is very flexible, such as sp^1-, sp^2- and sp^3-hybridized bonds, resulting in numerous carbon allotropes. Among them, diamond is unique because it was the only bulk form of carbon with fully sp^3 C-C bonds. People have been looking for other bulk sp^3-bonded carbon materials over decades, but besides diamond, fully sp^3 bonded carbon allotrope seems impossible." Said QiaoshiZeng, "We combined high temperature and high pressure and carefully mapped the two dimensional temperature-pressure parameter space. Finally we obtained fully tetrahedrally bonded carbon in an amorphous form. These results enhance our fundamental understanding of carbon materials and will trigger intense follow-up study on the mechanical, thermal, optical, electrical, and chemical properties of amorphous diamond for potential applications."

Other co-authors in this team include HPSTAR's Liuxiang Yang, Hongbo Lou, Hongwei Sheng, Wenge Yang, and Ho-kwang Mao.

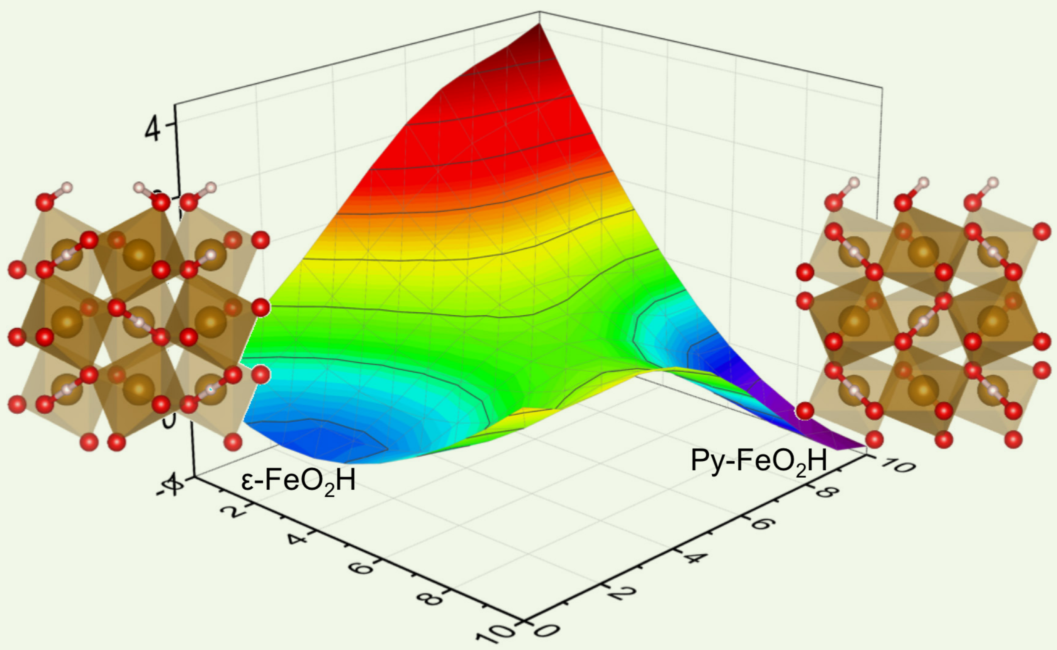
Ref: Dr. Zhidan Zeng
Nature Communications
volume 8, Article number: 322 (2017)

A degassing mechanism for deep hydrous mineral

氢的循环在地球化学中扮演着非常重要的角色。高压的条件下，非对称的 O-H•••O 键趋于对称化，即 H 原子处于两个 O 的中心位置。对称化后的 O-H-O 可以提高含水矿物的热稳定性，因此含水矿物可以深入下地幔而不发生分解。然而，H 是如何在地幔深部循环的，目前尚不清楚。我们的工作结合第一性原理计算和高温高压实验，来揭示一种代表性的含水矿物，即 FeO_2H 在深地幔的脱氢机理。实验发现大约有 50% 的 H 从 ε-FeO_2H 到 Pyrite 相的转变过程中释放出来；通过新的自由能抽样算法，在最低能垒通道中，我们的计算认为有一半的 O-H-O 键在 ε-FeO_2H 到更高压 Py-FeO_2H 相的相变的中断裂，因此导致了 O-H-O 的对称性破坏，致使大于一般的 H 释放。本研究将提高我们对具有对称 O-H-O 结构的含水矿物在相变过程中热力学稳定性的认识，同时也提供了一种含水矿物在深层地幔下具有普遍性的脱氢机理。

AUGUST 23, 2017-Water (H_2O) is one of the most common molecules on Earth and an indispensable ingredient for the existence of life. At ambient pressure, water is a transparent liquid that is generally stable between the freezing point (0 °C) and the boiling point (100 °C). By applying external pressure to a few thousands of atmospheres, water turns into ice even at room temperature. Underneath the earth's surface where the pressure and temperature is very high, most water molecules will be associated with rocks to form the so-called hydrous minerals. During the deep subduction containing hydrous minerals, a majority of them will dehydrate due to climbing temperature at the bottom of Earth lower mantle such that it completes its cycling in deep Earth.

Thanks to the symmetric O-H-O bonding, a certain class of hydrous minerals is recently discovered to survive in the high-pressure high-temperature condition that mimics the deep lower mantle. The composition FeO_2H, named goethite when they are found on Earth surface, is one of such hydrous minerals. It forms symmetric O-H-O framework at high-pressure hence features higher dehydration temperature. However, at even deeper depth scientists suggest new profound chemistry related to FeO_2H. New works from a team including HPSTAR's Shengcai Zhu, Qingyang Hu, Ho-kwang Mao, HongweiSheng and collaborator Wendy Mao from Stanford University has identified that such symmetric network will break above around 750,000 atmosphere and 1400 °C. Their results were published in the ***Journal of American Chemical Society*** (DOI: 10.1021/jacs.7b06528).



Caption: Free energy profile from e-FeO$_2$H to py-FeO$_2$H

“Due to the breakdown of symmetric hydrogen bond, hydrogen atoms will be liberated from water” said Qingyang Hu, whose team conducted computational simulation and suggests during the structural transition to its high-pressure form (py-FeO$_2$H), half of the O-H bonds in the mineral rupture. The theoretical simulation also supports our experiments that ~50% H are released. “This is also the first time that we address degassing at the atomic scale” Added Sheng-cai Zhu, the leading author in this work.

The dehydrogenation of FeO$_2$H sheds light on Earth’s hydrogen cycling, which will increase margins of mantle geochemistry for realizing novel reactions that introduces a new factor in Earth’s mantle.

Ref: Dr. Qingyang Hu

J. Am. Chem. Soc.,

2017, 139 (35), pages: 12129–12132

Pressure-induced irreversible conductivity enhancement in lithium acetylide

碳化锂 (Li_2C_2) 是一种重要的锂电极材料，但其低的电导率限制了碳化锂的进一步应用。在新的研究中，王丽娟等人使用高压的方法使碳化锂的电导率提高了 9 个数量级，并且增强后的电导率可以保留到常压。一系列原位测试表明碳化锂中的 C_2^{2-} 离子会在高压下发生聚合反应。因此碳化锂电导率的增加应该是由于在压缩下 C_2^{2-} 离子间间距缩短导致，而聚合反应帮助了增强的电导率可以被保留到常压。随着压力的卸载，高压下形成的聚合物会分解，表明碳骨架的电化学活性很高。

AUGUST 27, 2017-Lithium acetylide, as a widely used electrode material for Li-ion battery has the highest theoretical capacity while with low conductivity for applications. New work from a HPSTAR team increased the conductivity of Lithium acetylide by 9 orders of magnitude in the use of high pressure method. And this pressure-enhanced conductivity could be kept to ambient conditions. Their discoveries are published by the ***Journal of Physical Chemistry Letters*** (DOI: 10.1021/acs.jpclett.7b01779).

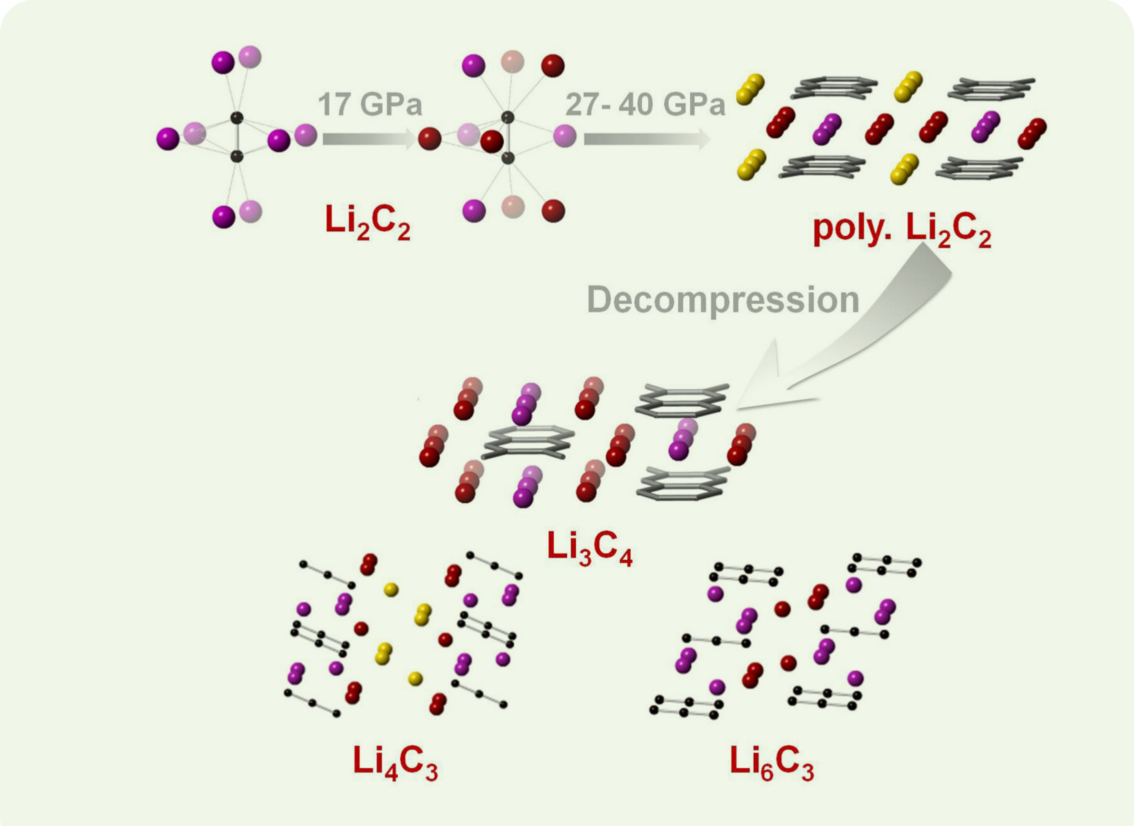
In polymer chemistry, polymerization is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks. There are many forms of stimulus of polymerization. Pressure is a straightforward and clean external stimulus for polymerization, which is always referred as pressure-induced polymerization. Except for chemical reactions, pressure may also tune other physical properties.

At ambient conditions, lithium acetylide (Li_2C_2) is electrode material which is mostly used for lithium extraction in lithium batteries. While the low conductivity at ambient conditions confine lithium acetylide's potential applications.

The HPSTAR team including Drs. Lijuan Wang, Xiao Dong, Yajie Wang, Haiyan Zheng, Kuo Li, Yufei Meng, and Ho-Kwang used high pressure to tune the electrical properties of lithium acetylide. They found that the conductivity was enhanced by nine orders compared to that uncompressed.

More importantly, the heavily enhanced conductivity could be kept to room pressure. This indicates its more practical applications in Li-ion batteries.

To find the behind reasons, the team performed the following high-pressure x-ray diffractions,



Capition: Pressure induced polymerization and disproportionation of Li_2C_2.

Raman, IR etc supportive measurements.

The C_2^{2-} anions in lithium acetylide approached to each other and polymerized to ribbon structure from chains upon compression. “So the compression of the distances between should be the main reason for the enhancement of the conductivity and the pressure induced C_2^{2-} anions polymerization is responsible for the irreversibility”, explained Dr. Lijuan Wang, the lead author.

The polymerization will disproportionate with pressure released to ambient conditions. “This disproportionation implies that the carbon skeletal is highly electrochemically active and potentially useful in designing electrode materials”, added Dr. Xiao Dong, the co-lead author.

This work demonstrated that applying pressure is an effective method to prepare novel Li−C frameworks, and hence shed light on the search for novel carbon-based electrode materials.

Ref: Drs. Lijuan Wang and Xiao Dong
Journal of Physical Chemistry Letters
2017, 8 (17), pp 4241–4245

Two superconducting domes in FeS

自被发现以来，超导一直是科学界研究的重要内容之一，随着科技的进步和发展，超导的研究也越发的多样化，而提高超导转变温度，寻找潜在的室温超导体是科技工作者一直以来梦寐以求的最高理想。北京高压科学研究中心的杨文革研究员小组和上海复旦大学的李世燕教授研究小组携手合作，通过金刚石对顶砧的实验方法模拟地球内部压力对四方 FeS 超导体的高压输运性质进行了一系列的研究。研究团队发现，四方 FeS 随压力表现出“超导—超导消失—超导再现—超导消失”的双超导相行为，且新超导相的超导转变温度提高了 30%，这一研究结果发表在 9 月 1 日的 ***NPJ Quantum Materials***。

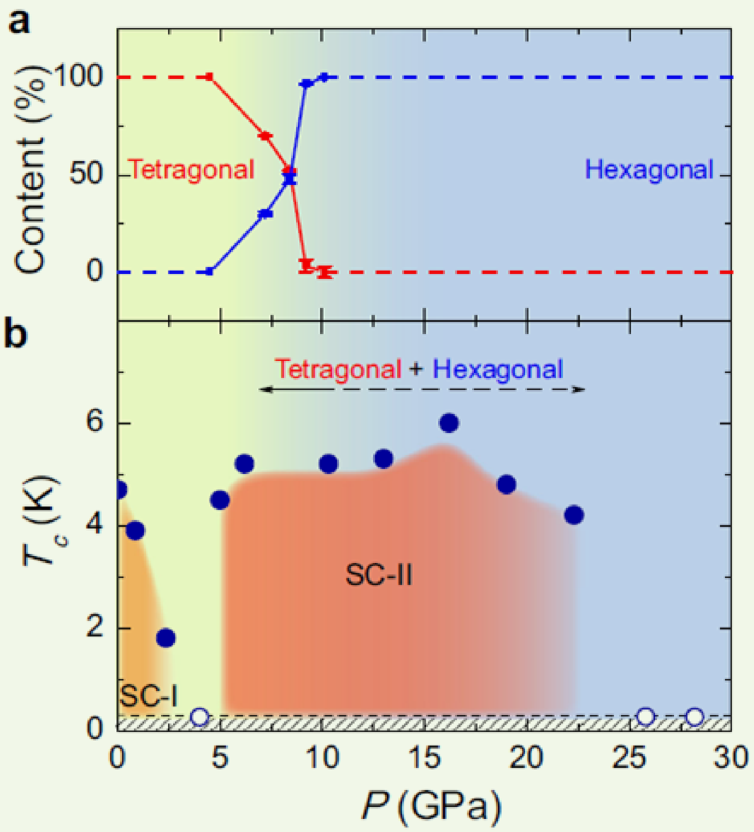
SEPTEMBER 1, 2017-A team co-led by HPSTAR PhD student Fengliang Liu, investigated the evolution of superconductivity and structure with pressure for the new superconductor FeS (Tc ≈ 4.5 K), a sulfide counterpart of FeSe. They observed two superconducting domes in FeS under compression with 30% enhancement in maximum Tc in the second dome. Their discoveries are published by ***NPJ Quantum Materials*** (DOI:10.1038/s41535-017-0050-7).

Iron-based superconductors are of great interest and fundamental importance due to their rich structural and physical properties.Isostructural to the FeSe superconductor, tetragonal FeS has attracted considerable attention due to its many similarities in crystal and electronic structures with FeSe. It provides us a new and simple platform as FeSe to realize high-temperature superconductors and to study the underlying mechanism of iron-based superconductivity.

“It is of fundamental importance to know whether pressure still affects FeS and how pressure tune the superconductivity of FeS, and how this relates to its structural properties at atomic level”, said Fengliang.

So the team applied in-situ high-pressure electrical transport and synchrotron X-ray diffraction (XRD) measurements on tetragonal FeS single crystals to find how pressure affects the physical properties of FeS.

Upon applying pressure, they observed that the Tc in the first superconducting dome continuously decrease with increasing pressure which vanishing superconductivity around 4GPa. The scond superconducting dome emerges from 5.0 GPa and lasts to 22.3 GPa, with an over 30% increasing in Tc (≈6.0 K) from the highest Tc in the first dome.



Caption: a: The pressure dependence of phase contents around the structure transition, which are obtained through refinements. b: Temperature–pressure phase diagram of FeS. There are apparently two superconducting domes, and the second dome is attributed to the remaining tetragonal phase.

“The two superconducting domes we observe here in FeS are quite different from that of other iron-based superconductors. For FeS, we thought that the second superconducting dome is from the residual deformed tetragonal phase” explained Fengliang.

Ref: Fengliang Liu
NPJ Quantum Materials
volume 2, Article number: 49(2017)

Pressure induced abnormal insulating state in Li_xCoO_2

自钴酸锂（Li_xCoO_2）被用作锂离子电池正极材料以来，由于其工作电压高，充放电结构稳定，循环寿命长，重量轻等特点被大量应用。研发更高性能的正极材料已经成为全球各国研究开发的重点。北京高压科学研究中心的杨文革研究员小组和北京大学深圳研究院的潘峰教授携手合作，通过金刚石对顶砧的实验方法以及理论计算，对钴酸锂的高压结构性质、电学性质等进行了一系列的研究，研究发现，在高压下钴酸锂的晶体结构十分稳定，但是其电学输运性质出现半导体到绝缘体转变的现象。他们进一步的讨论了该转变的机制，揭示了钴酸锂的晶体结构和其电子结构之间的联系，为寻找更高效的锂离子电池正极材料提供了重要途径。

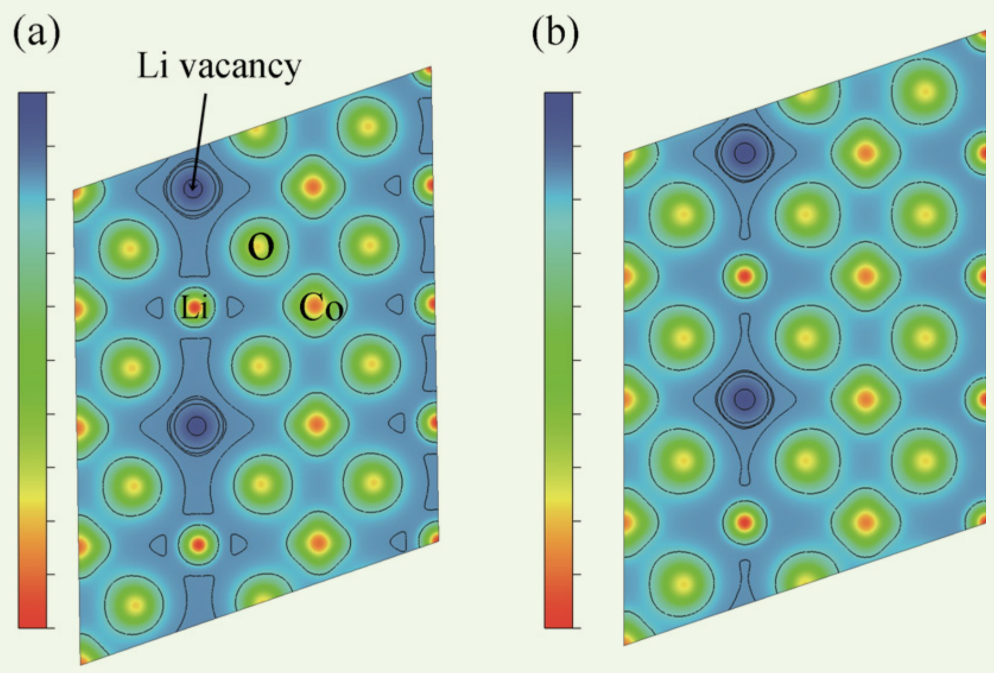
SEPTEMBER 8, 2017-New work led by HPSTAR graduate student, Cong Xu found abnormal semiconductor to insulator transition in cathode material, $Li_{0.9}CoO_2$ under pressure. The findings uncovered by the comprehensive high pressure investiations provide deep insights into the complex relationship of the crystal structure and electronic performance in this important cathode material, which may be used for guiding the future lithium metal oxides battery industry for better performane. The discoveries are published by the ***Journal of Materials Chemistry A*** (DOI: 10.1039/C7TA06084J).

Lithium cobaltite oxides (Li_xCoO_2) has been widely served as the cathode material for rechargeable lithium ion batteries (LIBs) due to its high voltage, high energy density and excellent cycling stability.

Li_xCoO_2 is a reference compound for a whole family of layered materials obtained by the substitution of other metals for cobalt. In order to improve battery performance, We need to understand the structural and electronic properties of Li_xCoO_2. In this work, the team utilized high-pressure technique, a very effective, clean tool, tuning the crystal and electronic structure of the layered compound $Li_{0.9}CoO_2$.

“Up to ~20 GPa, we didn’t observe any sign of crystal structural change in the sample, While surprisingly, we found its electric transport behavior changed from a semiconducting state to an insulating state”, said Cong, a former graduate student of HPSTAR, led the project while earning his master degree at Dr. Wenge Yang’s group.

“This semiconductor to insulating state transition in $Li_{0.9}CoO_2$ under high pressure is quite unusual. In most correlated oxides, pressure usually broadens the 3d bandwidth and thereby leads to a transition towards a more conducting state. The



phenomenon observed in this work is apparently connected with different physical mechanisms", added Dr. Yang.

Their multiple investigations, including X-ray diffraction (XRD), electric resistivity, UV-vis absorption spectroscopy, and DFT calculationsgive deep insights into the complex relationship of crystal structure and electronic performance in this important cathode material.

"This quite abnormal pressure effect, a transition from semiconducting state to an insulating state, is a consequence of the enhanced crystal field splitting in distorted CoO_6 octahedron with pressure increasing" explained Cong.

"The shrankage of Co-O bond length enhances the crystal field splitting, which leads to band gap opening and the decreasing Co-Co distance caused the electron holes to be localized."

Ref: Cong Xu
Journal of Materials Chemistry A
Citation:J. Mater. Chem. A, 2017,5, 19390-19397

Fate of water into the earth

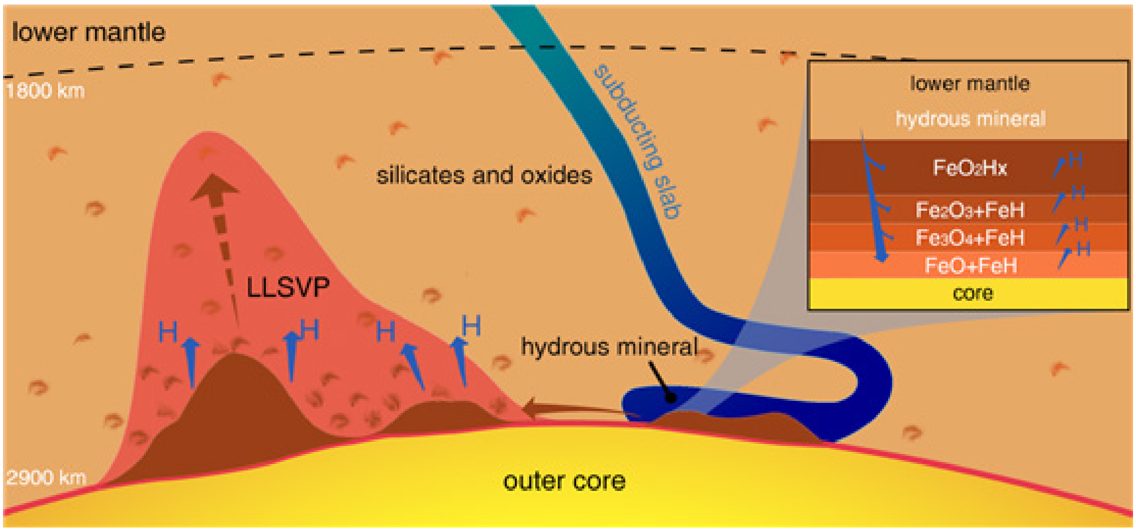
简单来说，地球自外而内分别由一层较薄的地壳、一层较厚的地幔和中心的大铁球地心所组成。地球表面的大洋大海中富集着大量的水，它们其中的一部分会与岩石反应生成所谓的含水矿物而进入地球内部，甚至深入地幔。当它们达到地幔底部进而遇到地心的时候，到底会发生什么样的变化？来自 HPSTAR 的毛河光院士带领的研究小组发现当水在地幔底部遇见铁，它们会发生化学反应生成一种高度氧化的矿物，甚至任意铁氧化物和水之间也存在类似的化学反应。由于地核可以提供接近于无限的铁，当水源源不断被输送到地幔深部，氧元素以 FeO_2H_x 的形式在地核上部慢慢积聚。同时他们发现当氧元素积聚的同时，氢元素则从水中分离出来并最终回到地球表面。高度氧化的 FeO_2H_x 在地幔中是不稳定的，当它到达一个临界点的时候，可能会爆发大面积的氧气爆发，最终导致地球表面的气候变化。

SEPTEMBER 11, 2017-From a geoscientist's view, the earth is made up of a giant iron core, covered by a thick layer of silicate mantle and a thin coating of crustal rocks. Water concentrates in oceans on Earth's surface. A portion of water reacts with rocks and forms the so-called hydrous minerals that can transport deep into the mantle. Once they reach the bottom of the mantle, naturally we'll ask the question: what will happen when water meets the iron core? A team led by Dr. Ho-Kwang Mao, director of HPSTAR published their answer to this question in the latest issue of ***National Science Review*** (DOI: 10.1093/nsr/nwx109).

"When water meets iron at the bottom of the mantle, it reacts with iron to form a highly oxidized phase", said Dr. Mao.

The team including collaborators from HPSTAR, Geophysical Laboratory of Carnegie Institution of Washington, Stanford University, HPCAT and Chicago University, subjected a piece of iron with water under lower mantle pressure-temperature conditions (about 960,000 times atmospheric pressure, and 1900 degrees Celsius). Using synchrotron x-ray diffraction and laser heating, they discovered the formation of an oxygen rich FeO_2H_x and iron hydride from the reaction.

The same phenomenon was soon observed in



Caption: The oxygen and hydrogen cycling in the deep Earth.

between the extended class of iron oxides and water. Since the earth core can provide almost inexhaustibly amount of iron, with the continuing transportation of water into the mantle, oxygen will accumulate in FeO_2H_x just above Earth's core.

The research team also finds oxygen tends to store in the form of FeO_2H_x, while hydrogen will separate from water and migrate upwards.

"The accumulation of highly oxidized FeO_2H_x introduces metastable domains in the mantle", explained Dr. Mao. "Once it reaches a critical point, it will incur a large scale of oxygen eruption to Earth's surface that possibly causes major climate change".

Ref: Dr. Ho-Kwang Mao
National Science Review
Volume 4, Issue 6, 1 November 2017, Pages 870–878,

How pressure change the world of perovskite solar cells

作为一种重要的钙钛矿材料，有机 - 无机杂化钙钛矿（organic-inorganic hybrid perovskite）由于其在光伏应用中高的能量转换效率和低的制备成本，在太阳能电池领域显示出巨大的应用潜力。在短短的几年时间内，有机 - 无机杂化钙钛矿太阳能电池的光电转化效率已经超过 22%，接近硅基太阳能电池的效率。然而，稳定性问题以及对其结构 - 性能关系理解的不足成为进一步发展的主要障碍。

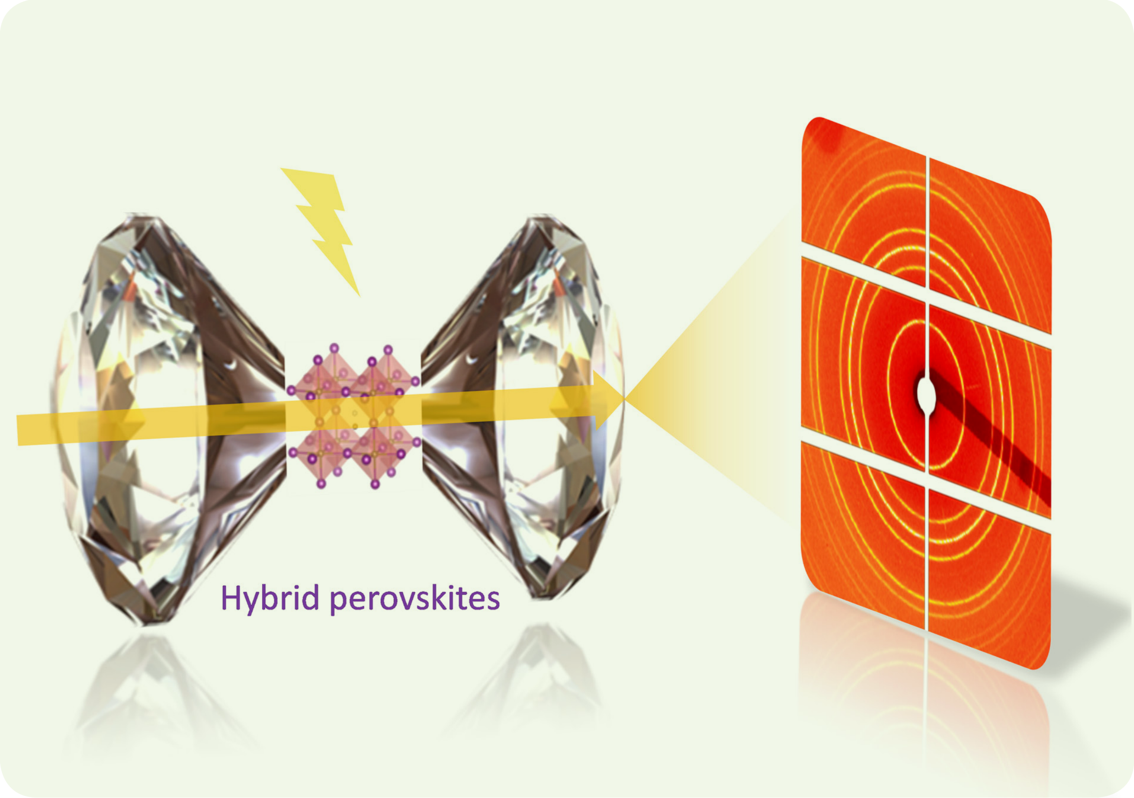
压力作为一种基础的热力学维度参数，是重要的材料调控手段。通过改变压力可以有效调节材料的电子和晶体结构从而调控材料的物理性质，进而影响其功能和应用。不同于化学掺杂，压力在对材料施加作用时不引入其他影响因素，因此被认为是一种“清洁”的调控手段，从而可以更好的揭示材料的结构性能关系。近几年的研究发现压力可以有效调控杂化钙钛矿材料的结构和性质。北京高压科学研究中心的杨文革和吕旭杰研究员等在 ***Chemical Science*** 上发表题为 “Pressure-induced dramatic changes in organic–inorganic halide perovskites”的综述。在这篇综述中，作者主要回顾了近五年来压力对有机无机杂化钙钛矿的结构，光电性能的改变，讨论了潜在的物理机制，并为高性能钙钛矿光电功能材料的发展提供新的视角。最后对压力及相关技术方法在未来有机无机杂化钙钛矿的研究发展中可能扮演的角色做了展望，例如通过引入化学压力和界面工程等方法来模拟外加高压电额效果，从而实现杂化钙钛矿的优化改性。

SEPTEMBER 29, 2017-Pressure, as a fundamental thermodynamic parameter that can tailor physical and chemical properties of functional materials, has recently been used in tuning structures and properties of organic-inorganic hybrid perovskites. In recent issue of ***Chemical Science***, a team of scientists led by Dr. Xujie Lü of HPSTAR gave a perspective of how pressure make changes in the hybrid perovskites.

Organic-inorganic hybrid perovskite - a new type of energy material which has recently been found to make highly efficient solar cells that could potentially be commercialized with low cost. In the past several years, their efficiency of converting solar energy into electricity has been improved over 22%.

Pressure has played a key role in alternating various properties of hybrid perovskites in the last a few years. Dr. Xujie Lü and co-workers including Dr. Wenge Yang from HPSTAR gave a comprehensive review on how pressure made changes in this field in their recent Chemical Science paper.

The authors reviewed the recent progress of



high-pressure research on hybrid perovskites, including pressure induced lattice and electronic structure changes, pressure induced optical and electrical property variations and summarized their common features and different behaviors, as well as possible reasons for the differences in structure and property changes caused by pressure treatment. Particularly, they described the pressure-induced novel phenomena and pressure-enhanced properties.

They also discussed the underling mechanisms of pressure effects on structure and property evolution. Finally, they gave an outlook on future high-pressure research on hybrid perovskites. The authors advise using chemical pressures and/or interfacial engineering to keep the pressure-induced enhanced properties for practical applications.

“Despite pressure has made intriguing findings in hybrid perovskite research, challenges still exist”, said by Dr. Lü. So a set of improved experimental methods and suitable calculations will be necessary.

Ref: Dr. Xujie Lü
Chemical Science
2017,8, pages: 6764-6776

First high pressure study on 2D hybrid perovskites

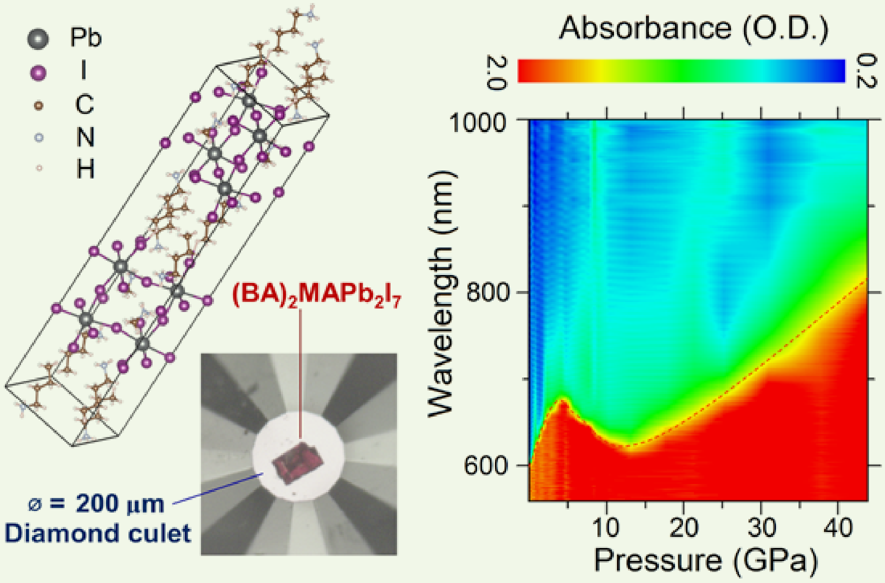
对于有机 - 无机杂化钙钛矿光伏材料而言，目前最重要的课题之一是如何同时实现高水平的光电转换效率和优异的环境稳定性。二维层状的杂化钙钛矿显现出较好的环境稳定性，但基于其的器件的光电转换效率仍较传统的杂化钙钛矿晶体有着较大的差距，其中一个关键的原因是其光学带隙较大，继而导致吸光性能下降。来自北京高压科学研究中心的刘罡博士研究小组利用静压力有效调控了二维杂化钙钛矿的晶体及电子结构，发现了压缩过程中的光学带隙的红移与再次红移现象。与施加压力前的样品相比，完全卸压后的样品更在保持其优良环境稳定性的基础上实现了光致发光增强和光学带隙减小等多个有利于吸光层器件应用的特性。

OCTOBER 19, 2017-New work led by HPSTAR researcher, Dr. Gang Liu experimentally convinced a first example of pressure-improved 2D hybrid perovskites and proposed that pressure treatments might offer a useful route to yield near-ideal single junction performance in the 2D hybrid perovskites. The discoveries are published by ***ACS Energy Letters***.

The power conversion efficiency of hybrid perovskites-based solar cell has been improved over 22%, whilst poor stability impedes its applications. This pushed researchers to investigate compositional and morphological variants. The recent developed two-dimensional layered perovskites show improved structure stability. However, the quantum confinement widens the band gap, which decreases the power conversion efficiency for low-cost, single junction devices.

The team including collaborators from HPSATR, Geophysical Laboratory of Carnegie Institution of Washington, Argonne National Laboratory, and Northwestern University gave a first in situ high pressure structural and optical study on 2D layered hybrid materials. They observed two regimes of compression, layer-to layer and interlayer in the layered perovskites.

“The two regimes of compression behavior correspond to the softer organic sub-lattice and



Caption：Ambient structure of 2D hybrid perovskites and their pressure-driven bandgap re-redshift behavior.

the less compressible inorganic sub-lattice", Dr. Liu explained. "And it's never found in 3D hybrid perovskites".

The research team also discovered two-step band-gap-redshift below 4 gigapascals and after 13 gigapascals from optical measurements.

"As both the two compressions will cause bandgap narrowing, the two-step bandgap shift can be attributed to the layer to layer and interlayer compressions, respectively", Dr. Liu further explained.

"We expect these results can be expanded into other 2D hybrid perovskites and suggest that pressure/strain processing could offer a new route to improved materials-by-design in applications", added Dr. Liu.

Ref: Dr. Gang Liu

ACS Energy Lett.,

2017, 2 (11), pages: 2518–2524

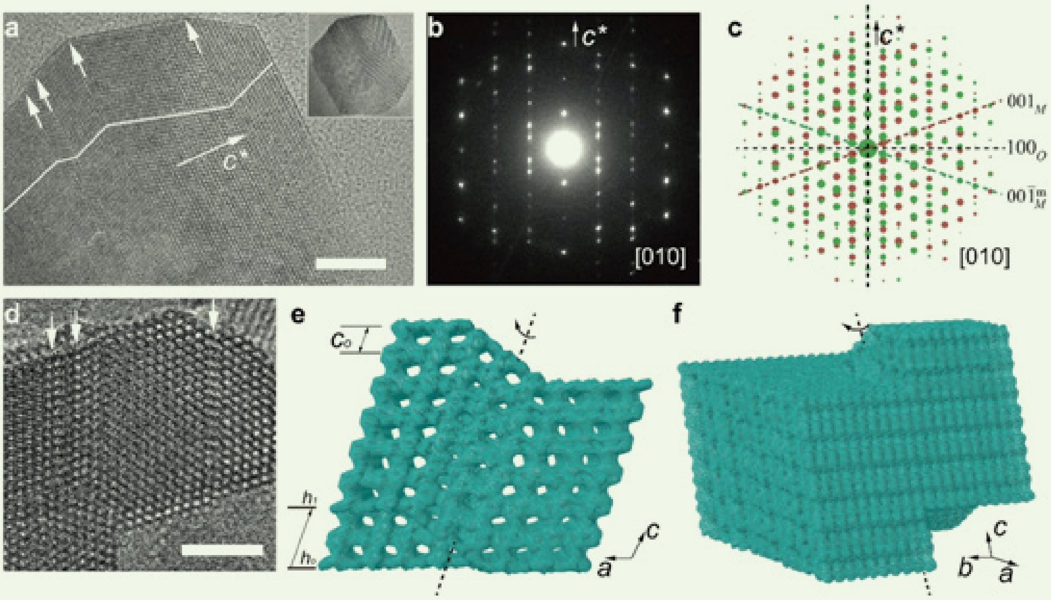
Complex screw dislocation core in zeolite MTW

螺旋位错核一直是物理、材料领域研究的的热点课题之一。在早前的报道中螺旋位错核一直是在致密相材料中被揭示，而在骨架材料（Zeolites,MOFs, COFs）中则鲜有报道。北京高压科学研究中心的博士后朱升财和上海复旦大学的唐颐教授研究小组携手合作，采用高分辨透射电镜及高分辨模拟精细结构对低对称性的 MTW 沸石进行了一系列的研究。该研究不仅从丰富的实验层面和晶体理论分析，对 MTW 沸石提出了新的空旷相螺旋位错核结构，更进一步结合文献结果，对不同相态的和不同空间对称性的沸石晶体材料的螺旋生长发展了较为统一的理论描述。这一研究结果发表在 ***Angewandte Chemie International Edition***。

OCTOBER 30, 2017-A group of scientists co-led by Dr. Shengcai Zhu of HPSTAR, investigated the evolution of hyper structure and screw dislocation for the framework material zeolite MTW, a useful industrial solid acid catalyst. They revealed that the complex screw dislocation core in zeolite MTW was composed by different crystal domains with different stacking vector. Their findings are published by recent issue of ***Angewandte Chemie International Edition*** (DOI:10.1002/anie.201704499).

Screw dislocation structures in crystals are an origin of symmetry breaking in a wide range of dense-phase crystals. Preparation of such analogous structures in framework-phase crystals is of great importance in zeolites but is still a challenge. On the basis of crystal-structure solving and model building, it was found that the two specific intergrowths in MTW zeolite produce this complex fractal and spiral structure. With the structurally determined parameters(spiral pitch h, screw angle θ, and spatial angle ψ) of Burgers circuit, the screw dislocation structure can be constructed by two different dimensional intergrowth sections. Thus, the reported complexity of various dimensions indiverse crystals can be unified.

“Such dislocation structures have been widely captured in dense-phase materials, such as metal oxides and alloy compounds, ceramics, carbon nanotubes, and even ice. Comparatively, in framework materials, the real nature of screw dislocation structure remains elusive”, said Lei Wang, one of the study’s two lead authors. “In



Caption: Stacking faults, screw dislocation and model of zeolite MTW.

the past, screw dislocation was considered in existence in the framework materials. However, via the high resolution TEM of this work, we renew the knowledge of screw growth on the framework materials".

"The diverse Si-O bonds on the framework materials make the screw dislocation extremely complex. Revealing the atomistic structure of screw dislocation in zeolite MTW will have a profound impact on the researches involving framework materials", said Dr. Sheng-Cai Zhu. "Via the 3D atomic level structure, composed by twin structure andscrew dislocation structures, which perfect interpret the observation ofexperiment".

Ref: Dr. Shengcai Zhu
Angewandte Chemie International Edition

Water modulation of photo- and piezochromism in viologen

紫罗精作为代表性的有机电致变色材料，具有良好的变色性能，通过选择合适的取代基，改变分子轨道能级和分子间电荷的迁移能来调节其电色效应。之前的研究提出晶格水不会作为紫罗晶中的电子供体而是通过改变电荷转移的动力学能。北京高压科学研究中心与华东师范大学合作，通过一系列的对比性实验发现紫罗晶晶格中的水含量越高，其对光及其压力的敏感性越低，因而导致紫罗晶越不容易变色，同时提出压力比光更容易实现电荷转移，因而更容易实现变色。

NOVEMBER 3, 2017-It is proposed that the lattice water does not act as an electron donor but serves to change the electro transfer energetic through its unique polarity and hydrogen bonding capability. New study led by Dr. Lin Wang of HPSTAR and Prof. Enqi Gao of East China Normal University found that the higher the water content in the lattice, the less sensitively the compounds respond to light and pressure in a series of different viologen pseudopolymorphic solids. The story is reported in the recent issue of ***JPCL***.

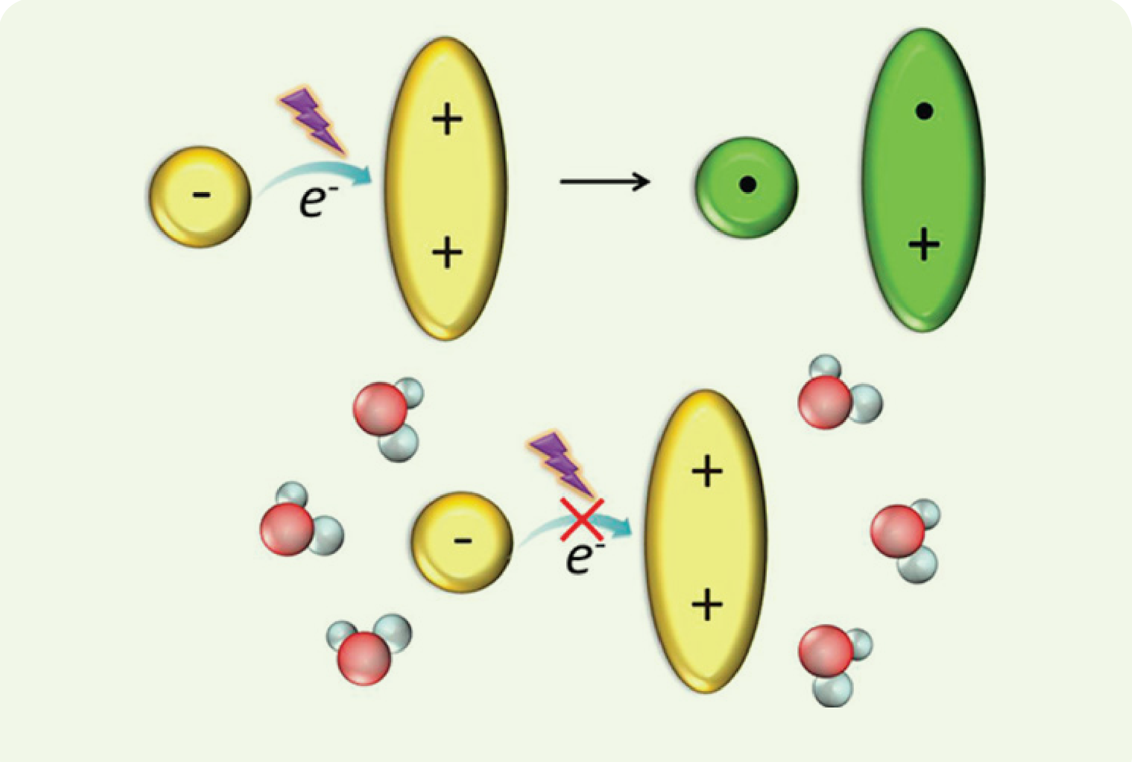
Viologen will change colors through forming radicals by electron transfer (ET) under various stimuli, such as light/photo or pressure, which are called photochromism and piezochromism, respectively.

Although the two phenomena are similar in associating with electro transfer and consequential radical formation, the stimuli are quite different in the way they operate on molecular materials.

So the team aims to find correlations and difference between piezochromism and photochromism in viologen. Drs. Qi Sui of East China Normal University and co-workers give a comparative study on a group of viologen compounds with different water contents.

They found that the viologens show different sensitivities to light, less lattice water facilitating electro transfer and racicals forming and thus inducing piezochromism at lower pressure.

It's interesting that photochromism can also be tuned by lattice water, less water stabilizing the radical-containing state and facilitating electro transfer.



Caption: Impact of lattice water on solid-state electron transfer in viologen pseudopolymorphs.

"In this way, we can say that piezochromism and photochromism show the same reaction to water, whilst the underling mechanism is different", said Dr. Lin Wang.

"Light can be directly absorbed by individual molecules, while has no direct intermolecular effect, it would not induce electro transfer if the donor and viologen were placed at unfavorable distances or in impedimental environments", explained Prof. Enqi Gao, the other lead-author of the study. "However, pressure forces molecules to move more closer, and the energy is absorbed by intermolecular interactions".

So for piezochromic viologen compounds, "pressure directly reduces the donor-acceptor distance to facilitate electro transfer, which in turn mitigates the intermolecular tension", added Enqi Gao.

Ref: Dr. Lin Wang
J. Phys. Chem. Lett.,
2017, 8 (21), Pages: 5450–5455

Synthesis and stability of hydrogen selenide compounds at high pressure

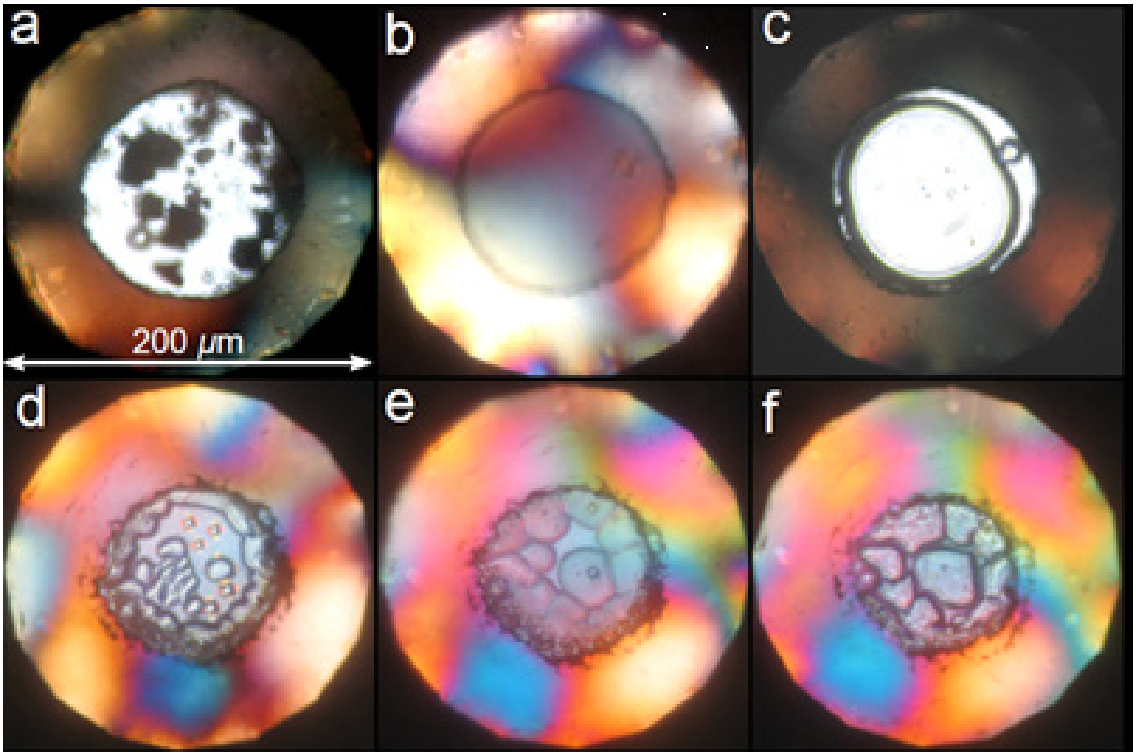
寻找高温超导材料一直是凝聚态物理研究领域的热点课题，H_2S 在高压下 ~200K 高温超导的发现刷新了高温超导的记录。与 H_2S 类似的氢基硫族化合物，H_2Se 的高压稳定性及超导性质等也引起了物理学家们的广泛关注。北京高压科学研究中心的 Howie 研究员领导的团队一直致力于氢及其化合物的高压研究。该团队使用高压原位 X 射线衍射，拉曼光谱研究了 H_2Se 的高压稳定性。他们发现 H_2Se 在高压下表现出与 H_2S 非常类似的结构稳定性，因此进一步研究或证实 H_2Se 的超导性很有必要，有望在 H_2Se 中也实现高温超导。

NOVEMBER 20, 2017-The observation of high-temperature superconductivity in hydride sulfide (H_2S) at high pressures has generated considerable interest in compressed hydrogen-rich compounds. The heavier hydrogen chalcogenides (i.e., H_2Se and H_2Te) are predicted to also exhibit high Tc superconductivity, however up until now remained experimentally unexplored. A new study led by Dr. Ross Howie of HPSTAR investigated the synthesis and stability of H_2Se at high pressure and finds remarkable similarities with H_2S. This study is published in ***J. Chem. Phys***.

Hydrogen selenide is synthesized in situ from elemental Se and molecular H_2 at pressures of 0.4 GPa and temperatures of 473 K. On compression at room temperature, the authors observe the high-pressure solid phase sequence (I-I'-IV) of H_2Se through Raman spectroscopy and x-ray diffraction measurements, before dissociation into its constituent elements.

Through the compression of H_2Se in H_2 media, the authors also observe the formation of a host-guest structure, $(H_2Se)_2H_2$, which is stable at the same conditions as H_2Se, with respect to decomposition.

Recent x-ray synchrotron measurements have suggested that high-Tc superconducting phase of H_2S could be due to the formation of H_3S, which reforms upon partial decomposition of H_2S at high pressure. This new study demonstrates that H_2Se and $H_2Se–H_2$ mixtures behave very similar to H_2S and $H_2S–H_2$ at high pressure and 300 K. Assuming the decomposition of H_2Se can be stabilized by low temperatures, it is very plausible that H_3Se could form at high pressures



Caption: Photomicrographs of the synthesis of H_2Se in a diamond-anvil cell sample chamber. The sample chamber is formed by a rhenium gasket. (a) H_2 and solid Se at 0.4 GPa and room temperature, (b) $H_2Se–H_2$ mixture at 0.4 GPa and 473 K, (c) liquid phase separation of H_2Se (central bubble) and H_2 (surrounding area) at 0.4 GPa and room temperature after heating, (d) H_2Se beginning to solidify, (e) slow coalescence of H_2Se regions, (f) completely solidified H_2Se at 1.5 GPa.

and exhibit superconductivity.

“Given that the behaviour of H_2S at high pressure is not completely understood, these experiments show that we can learn a lot from the other hydrogen chalcogenides. Future experiments on H_2Se at the conditions in which superconductivity is predicted could prove very insightful”, said Dr. Ross Howie.

This study involved Drs. Jack Binns, Philip Dalladay-Simpson, and Eugene Gregoryanz of HPSTAR and was in collaboration with Mr. Edward Pace and Dr. Miriam Peña Alvarez of the University of Edinburgh, both of whom were visitors at HPSTAR.

Ref: Dr. Ross Howie
The Journal of Chemical Physics
147, 184303 (2017);

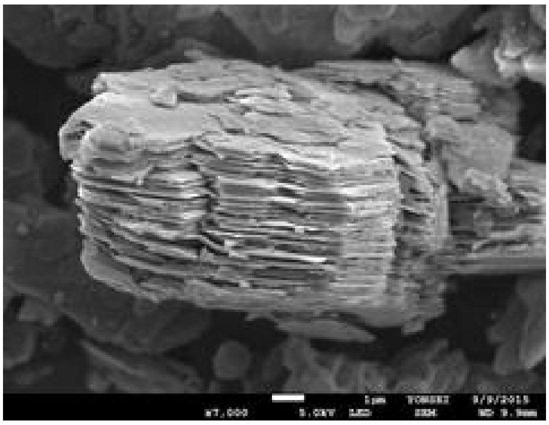
Clay mineral waters Earth's mantle from the inside

地震和火山活动的复杂过程皆发于地表以下难以直接观察，板块俯冲带中，较重的大洋板块与较轻的陆地板块碰撞并下潜移动至地幔中，矿物中的水随着海洋板块的移动进入到地壳内部，矿物经过百万年的缓慢沉积进入下地幔。通过在实验室环境中创造类似板块俯冲带的温压条件对其形成过程进行了研究，由北京高压科学研究中心 Yongjae Lee 研究员共同带领的研究小组在 2.7GPa-200°C温压条件下首次观测到了地幔矿物高岭石的超水合相，以全新的视角诠释了板块潜没产生的矿物水输运和释放引发激烈火山和地震活动的新机制并进一步明确了高岭石超水合物形成和分解的水循环过程对地幔俯冲带摩擦特性的影响和对该区域地震产生机制的改变。相关结果发表在 ***Nature Geoscience***。

NOVEMBER 21, 2017-The first observation of a super-hydrated phase of the clay mineral kaolinite could improve our understanding of processes that lead to volcanism and affect earthquakes. In high-pressure and high-temperature X-ray measurements that were jointly conducted at SSRF in China, SSRL and APS in USA, DESY in Germany, and PAL in Korea, scientists created conditions similar to those in so-called subduction zones where an oceanic plate dives under the continental crust. The transport and release of water during subduction causes strong volcanic activity. An international team led by Dr. Yongjae Lee, staff scientist at HPSTAR in China and professor at Yonsei University in the Republic of Korea and, presents the results in the scientific journal “***Nature Geoscience***”.

In a subduction zone, a heavy oceanic plate meets a second, lighter continental plate and moves under it and into the Earth’s mantle. With the oceanic plate, water enters the Earth as it is trapped in minerals of the oceanic crust or overlaying sediments. These minerals slowly sink deeper into the mantle over millions of years. With increasing depth, temperature and pressure in the subduction zone increase and the minerals become instable, break down and transform into new compounds. During the transformations, water is released and rises into the surrounding, hotter mantle where it decreases the melting temperature of the mantle rock. “When the mantle rocks melt, magma is generated. This can lead to volcanic activity when the magma rises to the surface.”, explains Yongyae Lee who led the study. “While we know that the water cycle in subduction zones influences volcanism and possibly seismicity, we don’t know much about the processes that form this cycle”.

Since these processes take place many kilometres under the Earth’s surface, it is impossible to observe them directly. One way to learn more about the transformations in subduction zones is to create similar conditions in the laboratory. High-pressure and high-temperature experiments allow scientists to take a close look at the structural changes in the different minerals that form the crust and sediments. One of these minerals is kaolinite, a clay mineral containing aluminium that is an important part of the oceanic sediments. The scientists were now able to observe the



Caption: Ordinary kaolinite under an electron microscope.

formation of a new phase of the mineral, so-called super-hydrated kaolinite. They examined a sample of kaolinite in the presence of water at pressures and temperatures corresponding to those at different depths in subduction zones. With synchrotron X-ray diffraction and infrared spectra measurements, structural and chemical changes were characterized.

At a pressure of 2.7 Giga-Pascal (GPa), more than 25,000 times the average pressure at sea level, and a temperature of 200 degrees Celsius, the super-hydrated phase was observed. These conditions are present at a depth of about 75 kilometres in subduction zones, which coincides with the boundary between shallow and intermediate earthquakes. In the new phase, water molecules are enclosed between the layers of the mineral. The super-hydrated kaolinite contains more water than any other known aluminosilicate mineral in the mantle. “During the formation of the super-hydrated kaolinite, significant amount of water will be removed at the interface between subducting and overriding slabs“ explains Dr. Ho-Kwang Mao, the Director of HPSTAR who supported this work as one of the co-authors. “This will affect the frictional properties of the slabs and hence the mechanism how earthquakes occur along the subduction zones will change”.

Lee’s team spent about 2 years to map the stability field of the super-hydrated kaolinite under various subduction zone conditions using five different synchrotron radiation facilities all around the world. This includes BL14B1 at SSRF in Shanghai, China. “We plan to develop a collaboration program to extend the pressure and temperature conditions further deep into the Earth“ says Dr. Wen Wen of SSRF who supported part of this high-pressure synchrotron experiments. The super-hydrated kaolinite broke down at 5 Giga-Pascal and 500 degrees, and two additional transformations happened at higher pressures and temperatures upto 19 Giga-Pascal and 800 degrees Celsius. During these transformations, the water that was intercalated in the kaolinite is released.

The observation of the formation and breakdown of the super-hydrated kaolinite bears important information about the processes that occur over a depth range of about 75 kilometres to 480 kilometres in subduction zones. Formation of the super-hydrated kaolinite could influence seismicity and mechanism of the earthquakes. Additionally, the release of water that happens when the super-hydrated kaolinite breaks down could be an important part of the water cycle that causes volcanism along subduction zones. The breakdown probably happens below a depth of about 200 kilometres, the released water could then contribute to the formation of magma. The scientists assume that other minerals in the sediment or crust could undergo similar transformations. Thus, the study could improve the understanding of the geochemical processes in subduction zones.

Ref: Dr. Yongjae Lee
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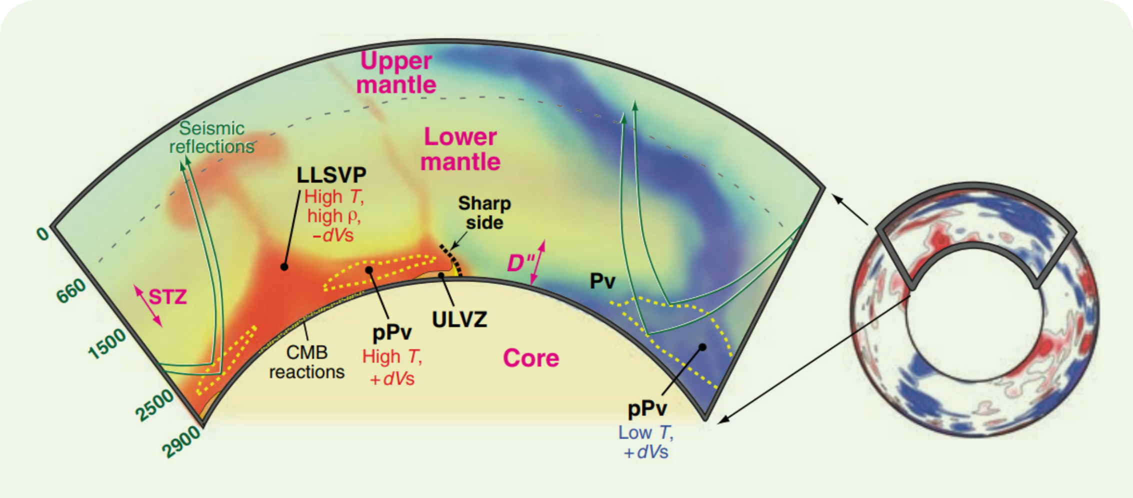
Giant oxygen reservoirs near the Earth's core – Seek and find

我们的生命倚赖于空气中的氧，但是空气中不是一开始就有氧的。地质学家们发现，在地球漫长的 46 亿年中，前一半古老历史的大气里并不含氧。直到 24 亿年前，地球发生了“大氧化事件”，空气中的自由氧突然飙升到百分之二十，维持至今，才会有人类的存在。北京高压科学研究中心（高科）主任毛河光院士带领国际科研团队，一年来系统化探索大氧化事件的根源，锁定在了高压下才存在的铁的新氧化物 ¾ 过氧化铁。该团队最新的研究更发现过氧化铁确实与核幔交界处超低速区的地震波速度符合。说明该区域可能有大量过氧化铁存在。当其所含氧爆发时，即能产生大氧化事件。此成果刊登在 11 月 23 日的 ***Nature***。

NOVEMBER 23, 2017-Free oxygen in the air that gives life to our living planet cannot be taken for granted. In fact, during the first half of the Earth's 4.6 billion year history, oxygen was absent in the atmosphere. Only 2.4 billion years ago at the Great Oxidation Event (GOE), oxygen appeared suddenly, thus enabling the aerobic life like us to thrive and evolve. In seeking for possible source of the oxygen rise, superoxidized iron from great depth is a potential candidate. Through direct experiments and theoretical calculations that mimic deep Earth environments, a group of scientists led Ho-kwang Mao, director of HPSTAR (the Center of High Pressure Science and Technology Advanced Research, China) found that the physical properties of iron peroxide match the seismic signatures of an enigmatic region, called ultralow velocity zone (ULVZ) at the boundary between the Earth's lower mantle and core 1800 miles beneath the surface, thus supporting ULVZ as a possible deep reservoir of oxygen. The findings are reported in the November 23 issue of ***Nature***.

Although oxygen is the most abundant element in the Earth, it bonds to other elements to form oxides, and does not yield free oxygen unless under highly oxidized condition. This is especially true in the Earth's deep interior when we approach the metallic core which is highly reducing, i.e., lack of oxygen. Therefore, during the late 20th century when ancient geological records firmly established the concept of sudden oxygen rise at GOE, an internal source of oxygen was not considered. Instead, the dominant theory assumed oxygen generation exclusively from cyanobacteria photosynthesis of surface carbon dioxide. Last year, a new pressure-induced chemical reaction to form superoxidized iron peroxide (FeO_2) was discovered (Hu, et al., Nature 2016). Further studies (Hu, et al., PNAS, 2017, Zhu, et al., JACS, 2017) indicated that this peroxide could be synthesized by reacting water with the iron at the Earth's core-mantle boundary (CMB) conditions. Considering the massive amount of water continuously carried down (Hwang et al., Nature Geosci. 2017) by subducting oceanic plate to meet the gigantic iron core, their reaction must form a giant oxygen reservoir that we ought to be able to find (Mao, et al., NSR, 2017).



Caption: The movement of seismic waves through the material of the mantle allows scientists to image Earth's interior, just as a medical ultrasound allows technicians to look inside a blood vessel. Image is courtesy of Edward Garnero and Allen McNamara's 2008 Science paper Structure and Dynamics of Earth's Lower Mantle, provided with Garnero's permission.

Earthquakes send seismic waves travelling through all regions of the Earth's deep interior to be recorded by the global network stations. They contain a wealth of information about the materials properties on their paths, and provide a clear visual image of these regions, analogous to the use of ultrasound to visualize the details and anomalies of human internal organs. Seismology has actually observed an abnormal region in the CMB region, called ULVZ, with 10% lower compressional-wave velocity and 30% lower shear-wave velocities than the average lower mantle.

Drs. Qingyang Hu of HPSTAR and Jing Liu from Standford University and co-workers conducted high pressure-temperature experiment using a diamond-anvil cell to study the corresponding wave velocities of the iron peroxide. Employing the high-energy synchrotron x-radiation and state-of-the art diffraction and spectroscopy probes at the High Pressure Collaborative Access Team facility at the Advanced Photon Source, Argonne National Laboratory, they found compressional and shear wave velocities of iron peroxide to be very low. A mixture of normal mantle rock with 40-50% iron peroxide would be sufficient to match the seismic signature of the ULVZ.

"Finding the existence of a giant internal oxygen reservoir has many far-reaching implications," said Mao. "Now we should reconsider the consequences of sporadic oxygen outbursts and their correlations to other major events in the Earth's history, such as the banded-iron formation, snowball Earth, mass extinctions, flood basalts, and supercontinent riftings."

Other team members including Jin Liu and Wendy L. Mao of Stanford University, Qingyang Hu and Duckyoung Kim of the Center of High Pressure Science and Technology Advanced Research, China, Zhongqing Wu and Wenzhong Wang of University of Science and Technology of China, Yuming Xiao, Paul Chow, and Yue Meng of High Pressure Collaborative Access Team, and Vitali B. Prakapenka of Center for Advanced Radiation Sources.

Ref: Dr. Ho-Kwang Mao

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