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DEVELOPMENT AND USE OF HIGH-ENTROPY MATERIALS

— ENTERING AN ERA OF NEW FUNCTIONAL MATERIALS COMPOSED OF MULTIPLE ELEMENTS —

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SUMMARY

- High-entropy materials that combine a larger number of elements are attracting interest, not just materials developed from a small number of elements. R&D in this area is being led by Taiwan, Japan, China and other countries in Asia.
- These efforts are expanding the potential for new material exploration by working with a large number of elements that have never been the subject of new material development. Machine learning and other advances in information processing technology are also enabling more efficient R&D.
- High-entropy materials are gaining attention due to global demand for the development of new materials that can improve the features or performance of existing technologies without the use of elements susceptible to geopolitical impacts such as rare metals or rare earths.

1. HIGH-ENTROPY MATERIALS

Just as the Iron Age followed the Bronze Age, the emerging Alloy Age can be considered the next step in human technological achievement. Alloys have traditionally been produced by adding just the right amount of cobalt (Co), nickel (Ni), manganese (Mn) or another metal to a base element such as iron (Fe) or aluminum (Al) to create materials such as extremely hard steel varieties or aluminum alloys of low weight and high durability. The 2000s saw the start of worldwide research and exploration into new materials that surpass existing materials in performance. This work has been made possible by faster supercomputer simulations, materials informatics and other advances in information processing technology. One example is a highly innovative material concept called high-entropy materials. It was proposed in 2004 independently by Professor Brian Cantor of the University of Sussex (UK)[1] and by Professor Jien-Wei Yeh of National Tsing Hua University (Taiwan).[2]

High-entropy materials are novel substances that emerged from a concept usurping the accepted wisdom of the time—investigating the types of materials that can be produced by just creating uniform mixtures of several elements without the use of methods that expand on conventional research or development. R&D on high-entropy materials is being led by Taiwan and other countries in Asia such as Japan and China. High-entropy materials can be seen as new elements (new materials) not existing in the periodic table. They are produced artificially by mixing multiple elements.

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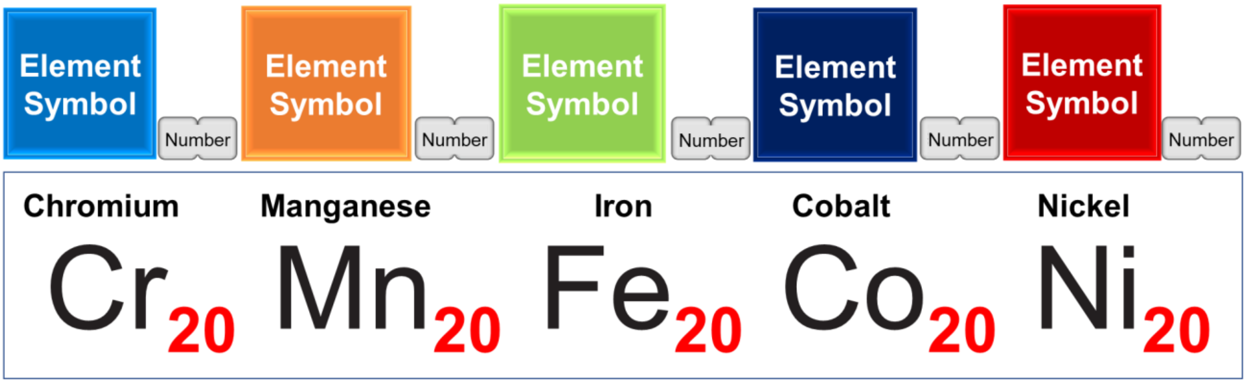
[1] Microstructural development in equiatomic multicomponent alloys: Materials Science and Engineering: A, Volumes 375–377, July 2004, Pages 213-218
[2] Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes: Advanced Engineering Materials, First published, 24 May 2004

1-1. Definition of high-entropy materials

Although no single definition is currently agreed on, high-entropy materials are usually defined as materials produced by creating a uniform mix of at least five elements in equal quantities (uniform equal-quantity mixing). This article defines them as materials composed of several elements not found together in nature, which have been mixed in various proportions. The components of high-entropy materials can be indicated using any of three different notation methods: (1) Hyphenating the component element symbols (such as 'Cr-Mn-Fe-Co-Ni'), (2) writing the component element symbols as a concatenated string ('CrMnFeCoNi'), or (3) adding numerical subscripts to the right of each component element symbol to indicate its mixing ratio (shown in Figure 1).

Figure 1: One notation used to indicate high-entropy material components (the material indicated by this example is a Cantor alloy)[3]



Source: Created by MGSSI

Before discussing the high-entropy materials covered by this article, it would be helpful to first describe the relationship between entropy and matter.

1-2. Relationship between entropy and matter

Entropy is most familiar as the concept used to express disorder (the second law of energy). Most of the materials encountered in everyday life are materials with a regular structure, meaning they are low-entropy materials (shown on the left in Figure 2).[4] For example, diamond is composed of carbon atoms in a regular and ordered array. The structural order of diamond is tightly preserved, providing very little room (degree of freedom) for the carbon atoms to move around freely. Aluminum alloys also have a regular structure despite containing a mixture of aluminum and other atoms. These materials preserve a high degree of order and remain stable. So low-entropy materials are composed of particles with frozen degrees of freedom, giving the material significantly low potential (for behaviors such as exhibiting unexpected features from processes such as fluctuations arising in the atomic order).

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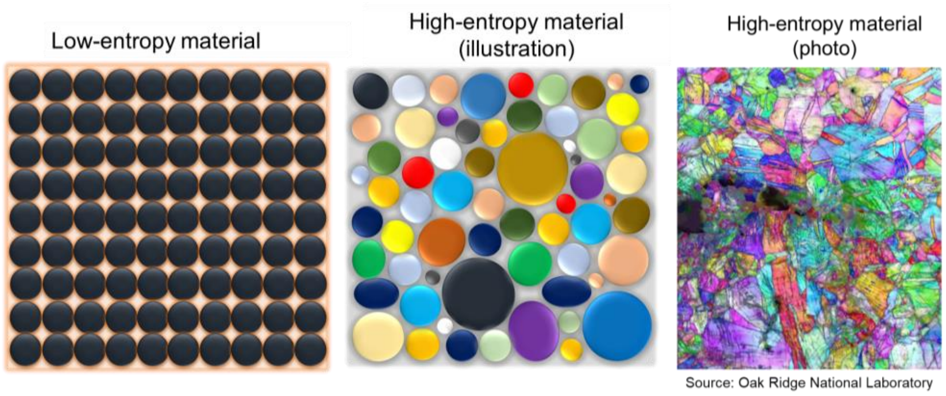
[3] Cantor alloys are the product of a study done in 1981 for a Bsc thesis submitted by Alain Vincent and supervised by Brian Cantor. High-entropy alloy is a term first used by Jien-Wei Yeh.

[4] In addition to high- and low-entropy materials, there are also medium-entropy materials (discussed later). As the name suggests, these materials have a medium amount of entropy. Medium-entropy materials have been commercialized since the 1980s in the form of medium-entropy alloys (MEAs). A groundbreaking advance in materials technology, MEAs are produced by selecting three of the five component elements of the original high-entropy material (the Cantor alloy shown in Figure 1).

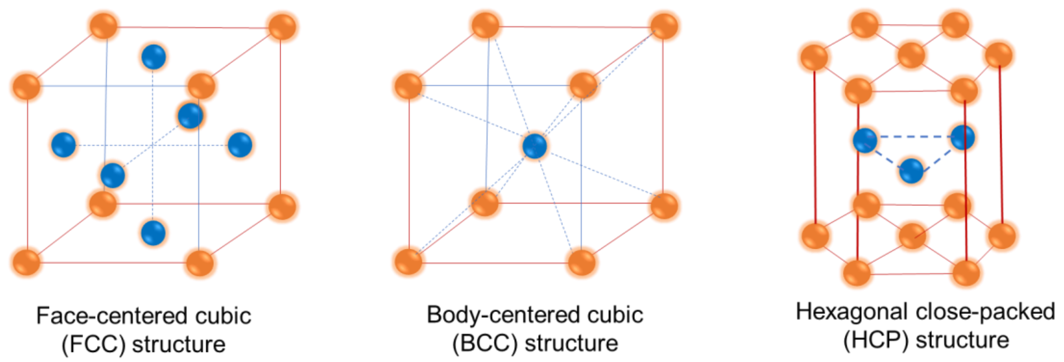
Figure 2: Low- and high-entropy materials (illustrations and photo)



Sources: Created by MGSSI (left and middle images); Oak Ridge National Laboratory (right image)[5]

In contrast, high-entropy materials have irregular and disordered atomic arrays even though their material structures are stable and their component atoms preserve a high degree of freedom. The governing principle that explains these characteristics is not understood, but they suggest that high-entropy materials could have high material potential (see the center illustration and photo on the right in Figure 2). High-entropy materials are made by creating a uniform equal-quantity mix of several elements, forming irregular internal structures (shown by the blue circles in Figure 3). High-entropy material research can be viewed as a field of technology that seeks to discover functions of new materials by intentionally increasing entropy (to high-entropy states).

Figure 3: High-entropy material internal structure examples[6]



Source: '*High-Entropy Gōkin: Cocktail Kōka ga Umidasu Tasai na Shinbussei*' ['High-Entropy Alloys: Various New Physical Properties Produced by the Cocktail Effect'][7]

1-3. High-entropy material synthesis methods

Arc melting, laser melting and other methods that simply mix and melt each element are often used to create a uniform mix of multiple elements. One recent example is a method called carbothermal shock (CTS) synthesis. It was developed to synthesize a high-entropy material (FeCoNiCuPdSnPtAu) using carbon nanofibers containing eight elements. The material is heated by passing an electric current through it. Another method called non-equilibrium chemical reduction provides a simple technique for synthesizing high-entropy

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5 https://www.ornl.gov/news/new-study-reveals-profound-properties-simple-metal-alloy

6 Typical examples of FCC structures include Cantor alloys ($Cr_{20}Mn_{20}Fe_{20}Co_{20}Ni_{20}$) and noble metal-based high-entropy alloys ($Ni_{20}Cu_{20}Pd_{20}Pt_{20}Au_{20}$). BCC alloys include fire-resistant high-entropy alloys ($V_{20}Nb_{20}Mo_{20}Ta_{20}W_{20}$). HCP alloys include titanium-based high-entropy alloys (Ti-Zr-Hf-Y-La).

7 Haruyuki Inui (Graduate School of Engineering, Kyoto University), http://www.rokakuho.co.jp/data/books/5137.html (Uchida Rokakuho Publishing)

materials. Developed by a research team led by Professor Hiroshi Kitagawa of Kyoto University, it provides a superior synthesis technique using a relatively easy procedure. The elements are mixed, and then a reducing agent is added before each element can coagulate together with its like. The elements are then solidified (fixed) while remaining separated. This method also enables automation of R&D processes, so it should dramatically increase the speed of high-entropy material discovery.

2. HIGH-ENTROPY MATERIAL APPLICATIONS

Research on high-entropy materials began with the development of the original Cantor alloy (CrMnFeCoNi), which was later followed by the development of other high-entropy alloys such as AuCuNiPdPt (a noble metal-based alloy)[8] and VNbMoTaW (a fire-resistant alloy). Materials now under development include alloys composed of over 10 elements and nanoparticle-based materials. Powdered high-entropy alloys are also sold as materials for use with laser 3D printers for additive manufacturing. These 3D printers are used to print artificial joints and other bone-substitute biomaterials. These biocompatible materials are difficult to develop due to their contradictory functional requirements.[9] Greater use of high-entropy alloys would be beneficial for these applications. High-entropy alloys are also known to provide superior performance as catalysts, and are used for catalytic reactions for ethanol, ammonia decomposition, hydrogen and other applications.

Figure 4: High-entropy material examples (highlighted symbols are rare metals)

Application	High-entropy material composition	Material form	Synthesis method
Ammonia oxidation	PtPdCoNiFeCuAuSn	Nanoparticle	Carbothermal shock
Ammonia decomposition	$Co_xMo_yFe_{10}Ni_{10}Cu_{10}$ (x + y = 70)	Nanoparticle	Carbothermal shock
Hydrogen evolution reaction	$Cr_{15}Fe_{20}Co_{35}Ni_{20}Mo_{10}$	Bulk	Arc-melling
Oxygen evolution reaction	AlMoCoIrMo	Nanoporous alloy	Dealloying
Oxidation-reduction reaction	Al-Cu-Ni-Pt-Mn	Nanoporous alloy	Selective dealloying
Carbon dioxide reduction reaction	AuAgPtPdCu	Nanocrystalline	Cast cum cryo-milling
Methanol oxidation reaction	AlMoCuPdAu	Nanoporous alloy	Dealloying
Ethanol oxidation reaction	RuRhPdOsIrPt	Nanoparticle	Wet-chemistry
Oxidation of aromatic alcohols	$(Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2})O$	Holey lamellar	Anchoring-merging process
Lithium-ion batteries	$(Mg_{0.2}Ti_{0.2}Zn_{0.2}Cu_{0.2}Fe_{0.2})_3O_4$	Powder	Solid-state sintered
Sodium-ion batteries	$NaNi_{0.12}Cu_{0.12}Mg_{0.12}Fe_{0.15}Co_{0.15}Mn_{0.1}Ti_{0.1}Sn_{0.1}Sb_{0.04}O_2$	Micro-powders	Solid-state sintered
Solid electrolytes	$(MgCoNiCuZn)_{1-x-y}Ga_yA_xO$ ($A = Li^+, Na^+, K^+$)	Bulk	Solid-state sintered
Semiconductors	$(Cr,Fe,Mg,Mn,Ni)_3O_4$	Bulk	Solid-state sintered
Hydrogen storage	TiZrHfMoNb	Micro-powders	Arc-melling & grinding
Supercapacitors	FeNiCoMnMg	Nanoparticle	Carbothermal shock
High-temperature fire resistance	$(Hf_{0.2}Zr_{0.2}Ta_{0.2}Mo_{0.2}Ti_{0.2})B_2$	Bulk	Spark plasma sintering

Source: Excerpted from 'High-entropy materials for energy-related applications' in *iScience*[10]

Alloy waste upcycling is another noteworthy application of high-entropy materials.[11] Upcycling is the process of recycling waste by adding value to it. A study from Ohio University has reported that discarded alloy scraps upcycled by vacuum arc melting has produced a high-entropy alloy (CrCuFeMnNi) with 50% higher strength than conventional alloys.[12] (The scraps were composed of (1) 304L stainless steel, (2) nichrome 80, and (3) copper cable.) With conflicts and other global geopolitical events generating large amounts of war waste, finding ways of repurposing the waste for peacetime applications has become a

8 Face Centred Cubic Multi-Component Equiatomic Solid Solutions in the Au-Cu-Ni-Pd-Pt System, Metals 2017, 7(4), 135

9 Artificial joints and other biomaterials need the same contradictory properties as bone—ultra-high strength combined with a low elastic modulus.

10 https://www.cell.com/action/showPdf?pii=S2589-0042%2821%2900145-0

11 Technologies to Watch in 2023: Upcycling Technology and Intellectual Report https://www.mitsui.com/mgssi/en/report/detail/__icsFiles/afieldfile/2023/03/20/2301report_e.pdf

12 Sustainable Low-Cost Method for Production of High-Entropy Alloys from Alloy Scraps | Journal of Sustainable Metallurgy (springer.com)

challenge.[13]

3. MARKET AND LEADING NAMES

The US market research firm Business Research estimates the global market for high-entropy materials at USD 54.7 million (2022), and forecasts growth to USD 202.97 million by 2028.[14] The high-entropy material market is seeing progressive growth from the rise of 3D printers and other additive manufacturing technologies. A medium-entropy alloy (MEA) market has also emerged. MEAs are related materials derived from the high-entropy Cantor alloy that was the world's first high-entropy material to be produced. US market research firm Research Nester estimates the MEA market at USD 1 billion (2023), forecasting growth to USD 2 billion in 2036.[15] MEAs are alloys produced by using arc melting or another method to create a uniform equal-quantity mix of three elements selected from among the five elements composing Cantor alloys (Cr, Mn, Fe, Co and Ni). Examples of MEAs include CrCoNi, FeCoNi and MnCoNi.

One of the leading names in the MEA and high-entropy material market is High Entropy Materials, a company founded by Jien-Wei Yeh himself. Other leading names in this market include companies in Japan, China and elsewhere in Asia, as well as companies and research institutes from Europe and the US. Along with developing and producing materials, these organizations are also researching tools and techniques designed to aid new material discovery. (See Figure 5.)

Figure 5: Leading names in MEA and high-entropy material market

Organization name	Role	Description, features
High Entropy Materials (Taiwan)	R&D Technology provider Research partnerships	A company specializing in high-entropy materials. Co-founder and technical advisor is NTHU Professor Jien-Wei Yeh. CEO is Professor Su-Jien Lin also of NTHU. Works with various high-entropy materials such as biomaterials, and materials providing resistance to heat, wear and corrosion.
MetalLab (Jiangsu Province, China)	Development/sales (Bulk alloys)	A metal material research organization launched by Panxingxin Hejin Cailiao (Changzhou). Provides bulk alloys (Cu, Cr, Ti, Fe and Ni) for high-entropy materials.
Beijing Yanbang Xincailiao Jishu (Beijing, China)	Production/sales (Alloys/powders)	Produces high-entropy materials and sells high-entropy alloys based on materials such as CoCrFeNiV, AlCrFeCuNi, CuFeAlNiCr, AlFeCuCoNi and AlCoNiCuFeNix.
Beijing Yijinxin Material Technology (Beijing, China)	Production/sales (Additive manufacturing powders)	Produces and sells high-entropy materials made using gas atomization and several other production methods. Works with high-entropy alloy powders compatible with overseas laser additive manufacturing brands such as 3D Systems and Stratasys, and with Chinese brands such as Xinjinghe, Longyuan, BLT, Huashu Hi-Tech, Binhu Electromechanical and Multi-energy Zhengguang.
MSE Supplies (US)	Production/sales (Alloy powders)	Mainstay products are iron (Fe)-, cobalt (Co)- and nickel (Ni)-based high-entropy alloy powders. Products include FeCoNiCrMn, FeCoNiCrTi and FeCoNiCrMn.
Duke University, US Naval Research Laboratory (US)	R&D (Ceramics) Tool development	Duke University and the US Naval Research Laboratory have partnered to develop high-entropy ceramic materials. The project has simultaneously developed a tool called DEED (disordered enthalpy–entropy descriptor), and a convolutional algorithm (cPOCC) to partition the immense number of material configurations in carbonitrides and other materials. High-entropy ceramics include materials such as (HfNbTiVZr)CN, (HfTaTiVZr)CN, (HfNbTaTiV)CN, (NbTaTiVZr)CN, (MoNbTaTiZr)CN and (HfMoNbTaZr)B2.
Proterial (US)	R&D (Alloys)	High-entropy materials and other composite metals are being developed by Proterial's in-house research lab, Global Research & Innovative Technology Center (GRIT).
Project Atlas (EU)	R&D (Additive manufacturing powders)	Project Atlas is an advanced design project for spacecraft propulsion created by the EU. It is developing high-entropy materials able to withstand use in space. The project's aims are to study ways of improving the heat resistance of materials used in spacecraft propulsion rockets and innovate material design structures. Two different additive manufacturing processes are being used.
Taniobis (UK)	Production/sales (Alloy powders)	Develops and produces metal products composed mainly of tantalum and niobium. Supplies a high-entropy alloy called Amtrinsic. Its high-entropy alloys based on the Group 6 elements (chromium, molybdenum and tungsten) are recently developed materials with superior high-temperature characteristics. But these metal elements are difficult to process and are produced with additive manufacturing technology for prealloyed powders.
Alloyed (UK)	R&D (High melting-point alloys) Licensing	Develops high-entropy materials with high melting points that enable use at ultrahigh temperatures that even nickel alloys are unable to support. Develops and produces additive manufacturing alloy powders, licensing technology to Aubert & Duval and other producers worldwide.
Fraunhofer Institute for Material and Beam Technology IWS (Germany)	R&D Research partnerships	Has devised methodologies for efficient synthesis and characteristic assessment of high-entropy materials. The applications of these methodologies extend beyond just high-entropy materials. They are also being used to develop sustainable, resource-efficient and high-performance metal materials. Is currently working on a project called M-ERA.NET (NovMat-AM).
Kyoto University	R&D Licensing Development partnerships	Kyoto University and Tohoku University are Japan's leading high-entropy material research institutions. KU has succeeded in synthesizing high-entropy alloy nanoparticles composed of platinum-group metals (PGM-HEAs). (The platinum-group metals (PGMs) are a group of six elements: platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os).) KU also works with the Japan Atomic Energy Agency on researching refractory high-entropy alloys (RHEAs).
Tosoh	Production/sales (Alloy powders)	US subsidiary Tosoh SMD produces high-entropy materials. Tosoh SMD's mainstay products are semiconductor thin film-forming materials. It also produces high-entropy alloy powders and titanium-based custom alloy powders such as Ti-Nb-Zr-Ta and Ti-Zr-Cu-Ni.
Hitachi Metals	R&D (Additive manufacturing powders) Research partnerships	Launched the Global Technology and Innovation Center in 2017. High-entropy materials are part of its work on developing advanced materials. Has partnered with Hitachi's R&D Group to develop a high-entropy alloy powder for additive manufacturing (HiPEACE).
JX Metals	R&D Production/sales (Medical alloys)	Has the world's largest global market share of tantalum powder for electronic materials. Develops tantalum- and niobium-based high-entropy materials such as TiTa and NbHfTi. Tantalum and niobium are non-allergenic and biocompatible, making them promising for use in artificial joints and other medical applications.
Tanaka Kikinzoku Kogyo	R&D (Noble metal alloys)	Develops high-entropy materials composed of five noble metal elements: Pt (platinum), Pd (palladium), Ru (ruthenium), Ir (iridium) and Rh (rhodium). Released the world's first high-entropy material composed solely of noble metals. Supplied as fine powders with particle diameters of up to 10 µm.

Source: Created by MGSSI

[13] War waste includes destroyed tanks, self-propelled artillery and other heavy weapons, along with metal artillery shell casings, landmines, cartridges and metal fragments.
[14] https://www.businessresearchinsights.com/market-reports/high-entropy-alloy-market-110243
[15] https://www.researchnester.jp/reports/medium-entropy-alloys-market/5321

4. SUMMARY

One final issue to note is the massive number of possible element combinations in high-entropy materials, which is the largest obstacle facing the technology. After excluding the noble gases and radioactive or other unusable elements, 75 of the 118 elements currently known could be used to synthesize high-entropy materials, resulting in about 219 million possible combinations.[16] The use of machine learning and other types of AI, along with traditional information processing technologies, is a key requirement for finding desired materials among the many possible combinations. For example, one recent project is using machine learning to discover hydrogen-absorbing high-entropy materials. The project paper describes the development of a hydrogen-absorbing alloy in 18 months after using machine learning to screen 600 promising hydrogen-absorbing materials.[17] Machine learning shortened development time and reduced costs while producing a result that the developers say would have otherwise taken several years. The emergence of machine learning is significantly altering the R&D landscape. The focus is moving away from metallic elements and increasingly into research areas such as ceramics. Research on high-entropy materials offering a wide range of functional characteristics is also gaining ground. Examples include shape memory, piezoelectric effects, thermoelectric effects and photoelectric conversion.

Machine learning and processor performance in CPUs, GPUs and other hardware have improved to a level enabling rapid development of materials composed of several elements. The technology is currently transitioning from the age of alloys to the age of multi-element compound materials. High-entropy material R&D and Japanese-led R&D on areas such as hypermaterials[18] should continue to produce real-world applications of new materials in the coming years. These materials should help solve a wide range of issues of public concern by providing better features or performance than existing technologies without the use of rare metals, rare earths or other elements susceptible to geopolitical impacts.

[16] High entropy alloys as a bold step forward in alloy development, Nature Communications volume 10, Article number: 1805 (2019)
[17] High-entropy nanoparticles: Synthesis-structure-property relationships and data-driven discovery https://www.science.org/doi/10.1126/science.abn3103
[18] Matter can be classified into crystals (with an ordered structure) or amorphous materials (with a disordered structure). The discovery of quasicrystal materials that are ordered (patterned) while appearing disordered was awarded the Nobel Prize in 2011. These materials are known as hypermaterials, and are the subject of research efforts in Japan. See the Tokyo University of Science website: https://www.rs.tus.ac.jp/hypermaterials/. The March 2023 discovery of einstein tiles should also aid the discovery of material internal structural patterns and functions in several ways (https://arxiv.org/abs/2303.10798). Einstein tiles create patterns that never repeat. Their discovery was a previously unsolved problem in mathematics.